PARAMAGNETISM IN ALTERNATING MAGNETIC FIELDS AT LOW TEMPERATURES

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INTRODUCTION

It is a well established fact that the great majority of salts containing ions of the metals of the transition groups (for instance the iron group or the rare earths) are paramagnetic. Without any doubt the paramagnetic properties are due to the presence of these ions, which are characterised by an incomplete electron shell (3d-shell for the iron group and 4f-shell for the rare earths). These ions possess an angular momentum and a magnetic moment.

A paramagnetic crystal therefore is characterised by an assembly of atomic magnetic moments, regularly distributed over the crystal lattice and interacting with each other and with the other constituents of the crystal. This assembly in many respects behaves as one single physical entity or, more precisely, as one large quantum mechanical system, which is often called 'spin-system'.

The purpose of this thesis is to study some properties of the spin-system in a number of paramagnetic salts, especially of metals of the iron group. Most of the experiments were carried out at low temperatures and they were pursued into two directions viz.

1) The study of the position of the lowest energy levels of the spin-system (experiments on paramagnetic resonance absorption, Part III).

2) The study of the establishment of thermodynamical equilibrium between the spin-system and the crystal lattice, more precisely the lattice vibrations (experiments on paramagnetic relaxation, Part II).

In Part I we propose to give a general theoretical introduction. Chapter 1 contains some considerations about the classical theory of magnetism, the thermodynamics of a magnetic body and the application of quantum theory and statistical mechanics. Chapter 2 contains a review of the theory of the energy levels of the spin-system. Chapter 3 contains some general considerations on the behaviour of a paramagnetic substance in alternating magnetic fields, while in Chapter 4 and 5 a review is given of the theory of paramagnetic relaxation and paramagnetic resonance absorption **respectively.**

Part II contains a detailed discussion of the experimental methods (Chapter 1), the results (Chapter 2) and the interpretation of the experiments on paramagnetic relaxation (Chapter 3).

Part III contains a similar treatment of the experiments on paramagnetic resonance absorption.

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PART I

THEORETICAL CONSIDERATIONS

Chapter I

GENERAL INTRODUCTION

1.1 Classical Theory.

In this section we propose to give a brief outline of the classical **macroscopic** theory of magnetism of non-conducting crystals to the extent required by our problems.

The macroscopic equations for the magnetic field in a space containing non-conducting magnetic matter can be written in the form using electromagnetic **cgs units** (cf. **C1**)

$$(a)\quad \mathit{curl}\,\mathbf{B} = 4\pi\,\mathit{curl}\,\mathbf{I} \quad (b)\quad \mathit{div}\,\mathbf{B} = 0. \tag{1}$$

A third vector **H** can be introduced with the equation

$$\mathbf{H} = \mathbf{B} - 4\pi\mathbf{I}; \tag{2}$$

equation (2) and (1) give $\mathit{curl}\,\mathbf{H} = 0$.

The formulation (1) is chosen, because it relates quantities, which have a distinct physical meaning. The magnetic induction **B** is the mean value of the 'microscopic' magnetic field taken over a small region containing many atoms. The current density of the 'Ampère' currents can be written in the form *curl* **I**, where **I** is called the magnetisation and (1a) expresses the proportionality between this current density and the *curl* of **B**.

It may be added that **I** is not uniquely defined, as a gradient may be added to it. Usually **I** is taken equal to the magnetic moment per unit volume. Then the component of **H** in a given direction is the field along the axis of a very narrow cylindrical cavity with its axis parallel to that direction. 'Very narrow' means, that the diameter of the cavity is small compared with the dimensions of the body and compared with the distance over which a change of **I** is noticeable. The component of **B** in a given direction is the field perpendicular to the plane sides of a thin disk-shaped cavity with the plane sides at right angle to that direction.

The magnetic properties of a body can be characterised by a relation between two of the three quantities **B**, **I**, **H**. Usually **H** and **I** are chosen.

Often the magnetisation is a linear function of the components of the magnetic field and we have $\mathbf{I} = \chi\mathbf{H}$, where χ is a tensor of the second rank, called the volume susceptibility. In this case we moreover have $\mathbf{B} = \mu\mathbf{H}$ with $\mu = 1+4\pi\chi$. If the substance under consideration is isotropic χ is isotropic as well.

Let us now consider a sample of an isotropic substance placed in a homogeneous field $\mathbf{H}_0$. Experimentally a relation between

$\mathbf{H}_0$ and the total magnetic moment $\mathbf{M} = \int \mathbf{I} dv$ can be found. The problem is to derive from this the relation between **H** and **I.** In the case of a homogeneous ellipsoid the eq.(1) have a simple solution, satisfying the required boundary conditions. (These boundary conditions are: at the surface of the body the tangential component of **H** and the normal component of **B** must be continuous.)

We only will describe this solution for details of the proof we refer to the existing litterature (Bl, Fl).

The vector **H** inside the body can be regarded as the gradient of a potential $\varphi (\mathbf{H} = -\nabla\varphi)$, where φ is the sum of a term φ_0 - the potential of $\mathbf{H}_0$ - and a term φ_1, which is the potential due to the presence of the magnetic matter. It can be shown that

$$\varphi_1 = \int (\mathbf{I}, \nabla\tfrac{1}{r})\ dv, \tag{3}$$

where r is the distance between the point where **H** has to be calculated and the volume element dv. The integral has to be taken over the volume of the magnetic matter. The physical meaning of (3) is, that every volume element of the substance acts as a dipole with dipole moment $\mathbf{I}dv$.

Now in an ellipsoid **I** is constant, so that we have

$$\varphi_1 = (\mathbf{I}, \nabla \int \frac{1}{r} dv) = (\mathbf{I}, \nabla\Psi). \tag{4}$$

Clearly **H** only can be homogenuous if Ψ is a quadratic function of x, y and z, which is only the case for an ellipsoid. If the equation of the ellipsoid is

$$x^2/a^2 + y^2/b^2 + z^2/c^2 = 1,$$

we have (Tl)

$$\Psi = -\tfrac{1}{2}(Ax^2 + By^2 + Cz^2) + D \tag{5}$$

with

$$\begin{aligned} A &= 2\pi abc \int_0^\infty dt/(a^2+t)T \qquad & B &= 2\pi abc \int_0^\infty dt/(b^2+t)T \\ C &= 2\pi abc \int_0^\infty dt/(c^2+t)T \qquad & D &= 2\pi abc \int_0^\infty dt/T \end{aligned} \tag{6}$$

$$T = [(a^2+t)(b^2+t)(c^2+t)]^{\frac{1}{2}}.$$

Consequently

$$\varphi_1 = I_x Ax + I_y By + I_z Cz,$$

so that

$$\begin{aligned} H_x &= H_{ox} - AI_x \\ H_y &= H_{oy} - BI_y \\ H_z &= H_{oz} - CI_z. \end{aligned} \tag{7}$$

If $\mathbf{H}_0$ is parallel to one of the axes of the ellipsoid we have

$$H_x = H_y = 0 \qquad H_z = H_{oz} - CI_z,$$

so that we can write

$$\mathbf{H} = \mathbf{H}_0 - \alpha\mathbf{I}. \tag{8}$$

Moreover we have

$$\mathbf{I} = \mathbf{M}/V. \tag{9}$$

α is called the demagnetisation coefficient, which is equal to A, B or C according as $\mathbf{H}$ is parallel to the x, y or z axis. The equations can be shown to fulfil the boundary conditions and therefore contain a complete solution of (1). Moreover they give the required relation between $\mathbf{H}$ and $\mathbf{I}$ if $\mathbf{H}_0$ and $\mathbf{M}$ are given in the special case of an homogeneous isotropic ellipsoid.

For a body of arbitrary shape we always can calculate a first approximation to the field by assuming a homogeneous magnetisation. In general it is impossible to calculate the rigorous solution.

The demagnetisation coefficients of an ellipsoid can be calculated with eq. (6). For a prolate ellipsoid with $a=b<c$ we have

$$\alpha_1 = C = 4\pi((1-e^2)/e^2)\,[(1/2e)\,\ln(1+e)/(1-e)-1],$$

if $\mathbf{I}$ is parallel to the axis of symmetry; and

$$\alpha_p = A = B = 4\pi[1/2e^2-((1-e^2)/4e^3)\,\ln(1+e)/(1-e)],$$

if $\mathbf{I}$ is perpendicular to this axis. In both formulae

$$e = (1 - a^2/c^2)^{1/2}.$$

For any ellipsoid $A+B+C = 4\pi$; for a sphere $A=B=C = 4\pi/3$ and for a 'infinitely long' specimen $A = B = 2\pi$, $C = 0$.

In the simple case $\mathbf{I} = \chi\mathbf{H}$, where χ is a constant, eq. (8) becomes

$$\mathbf{H} = \mathbf{H}_0/(1+\alpha\chi), \tag{8a}$$

so that if $\chi \ll 1$, $\mathbf{H} \simeq \mathbf{H}_0$ and we simply can take $\mathbf{H} = \mathbf{H}_0$.

1.11 The local field.

A macroscopic theory of magnetism, as has been outlined in the preceding section can not be satisfactory from a more fundamental microscopical point of view, even if we confine ourselves to a purely classical treatment. For an adequate theory we require the average magnetic field $\mathbf{H}_{loc}$ acting on the elementary magnets of the solid when an external field $\mathbf{H}_0$ is applied.

Now $\mathbf{H}_{loc}$ cannot simply be taken equal to $\mathbf{H}$, as can be concluded from the definition of $\mathbf{H}$. Therefore the problem arises how to calculate $\mathbf{H}_{loc}$ if $\mathbf{H}$ or $\mathbf{H}_0$ is known. The oldest theory is due to *Lorentz* (*L*1); many years later *Onsager* (*O*1) refined *Lorentz's* theory.

1) *Lorentz's* theory. The average field inside a molecule in a crystal can be resolved into two parts. First the field exerted by electrons inside the molecule itself, and secondly, the re-

mainder, which is due both to the applied field and to the magnetic moments of the other molecules in the crystal. The second part is called the 'local field' $\mathbf{H}_{loc}$ and is taken equal to the average field in a hypothetical cavity, which is formed by removal of the molecule, while the situation of the other molecules is supposed to be unchanged.

$\mathbf{H}_{loc}$ is then equal to the average sum of the contributions of all the molecules outside the cavity. In order to simplify the calculation *Lorentz* devided the molecules into two groups: those outside a sphere with its centre in the molecule and those inside the sphere. The radius of this sphere is chosen much larger than the dimensions of the molecules but is small compared with ordinary microscopic dimensions. Now outside the sphere the crystal is treated as a continuum and accordingly the field inside the sphere - which is equal to the average field excerted by the molecules of the first group - is given by

$$(\mathbf{H}_{loc})_1 = \mathbf{H} + (4\pi/3)\mathbf{I}.$$

The calculation of the field $(\mathbf{H}_{loc})_2$ exerted by the molecules of the second group is much more difficult. Under the assumptions that the field is caused by dipoles, having equal and parallel dipole moments, and which are placed on the lattice points of a simple cubic lattice, *Lorentz* showed that $(\mathbf{H}_{loc})_2 = 0$. In this case we have

$$\mathbf{H}_{loc} = \mathbf{H} + (4\pi/3)\mathbf{I}. \qquad (10)$$

Let us now introduce the susceptibility which would be found for independent ions χ^0. Then we have $\mathbf{I} = \chi^0\mathbf{H}_{loc}$ or

$$\chi = \chi^0\mathbf{H}_{loc}/\mathbf{H}. \qquad (11)$$

Elimination of $\mathbf{H}_{loc}$ from (10) and (11) gives

$$\chi = \chi^0/(1 - (4\pi/3)\chi^0). \qquad (12)$$

On the other hand we have in the case of an ellipsoid with demagnetisation coefficient α for the apparent susceptibility I/H_0

$$I/H_0 = \chi/(1 + \alpha\chi). \qquad (13)$$

Elimination of χ from (12) and (13) finally gives

$$I/H_0 = \chi^0/[1 - (4\pi/3 - \alpha)\chi^0], \qquad (14)$$

which can be expanded in the series

$$I/H_0 = \chi^0[1 + \Phi\chi^0 + \Phi^2\chi^{02} + \ldots], \qquad (15)$$

where $\Phi = 4\pi/3 - \alpha$.

This expression is useful for comparing *Lorentz's* result with the results of the more refined theories of *Onsager* and of *Van Vleck*.

2) *Onsager's* theory. Strictly speaking it is not possible to draw conclusions from *Lorentz's* theory for the case when the magnetisation of the medium is due to orientation of the constant magnetic moments. As *Onsager* remarked it is true that the average field of the molecules inside the sphere is zero. In

the calculation of this field we have to average over all possible directions of all the dipoles, that means also over all directions of the particular dipole at the position of which we want to know the average field. We are however interested into the orienting field exerted on the particular dipole, having a given orientation, by the other dipoles. The total field acting on this dipole is equal to the field $\mathbf{H}_{np}$, which would be there if this dipole were not present, plus an induced field $\mathbf{H}_{in}$ caused by the polarisation of the medium by the dipole. Only $\mathbf{H}_{np}$ is able to influence the orientation of the dipole; the induced field however changes its direction with the direction of the dipole, and therefore cannot influence the orientation. $\mathbf{H}_{in}$ gives rise only to an energy and consequently causes an additional specific heat. It may be remarked that the *Lorentz*'s field is the sum of $\mathbf{H}_{np}$ and the average value of $\mathbf{H}_{in}$.

The calculation of $\mathbf{H}_{np}$ by means of a direct calculation is rather difficult. *Onsager* obtained an approximation by replacing the substance by a continuum and by taking into account the absence of one molecule by a spherical cavity of properly chosen radius. According to ordinary magnetostatics the field inside such a cavity is given by

$$\mathbf{H}_{np} = \frac{3\mu}{2\mu+1}\mathbf{H} = \left[1 + \frac{\mu-1}{2\mu+1}\right]\mathbf{H},$$

where μ is the permeability of the medium. If $\mathbf{H}_{loc}$ is taken equal to $\mathbf{H}_{np}$, an entirely similar calculation as in the *Lorentz* theory yields

$$I/H_o = \chi^o[1 + \Phi\chi^o + \Phi^2\chi^{o2} - 2\,((4\pi/3)\chi^o)^2 + \ldots]. \quad (16)$$

The only difference with *Lorentz*'s formula in this approximation is the term $2((4\pi/3)\chi^o)^2$. For iron ammonium alum at one degree this amounts to 0.84×10^{-2}, at 0.2° K it amounts to 0.21. Although *Onsager*'s treatment cannot be rigorous, the order of magnitude of the correction to the *Lorentz* formula is correct, as is shown by the more rigorous theory of *Van Vleck* (section 2.3).

1.2 Fundamental thermodynamical relations.

In this section we shall give a summary of some thermodynamical relations, required especially in the discussion of paramagnetic relaxation.

The First Law of Thermodynamics of any rigid isotropic magnetic body placed in a homogeneous magnetic field, for instance produced by a coil, can be written in the form

$$dQ = dU - H_o dM, \quad (17)$$

where dQ is the heat supplied to the body, dU is the change in internal energy and $H_o dM$ is the external work done by the sources of the field. U is equal to the energy difference between the coil containing the magnetic substance and the empty coil carrying the same current. An alternative formulation can be found by introducing a function

$$E = U - H_oM, \tag{18}$$

where H_oM is equal to the potential energy of the body in the magnetic field. Then we have

$$dQ = dE + MdH_o. \tag{19}$$

From a thermodynamical point of view (17) and (19) are entirely equivalent, as the only difference is a different definition of the internal energy (E or U). It depends entirely on the particular problem under consideration which is the most useful formulation. Equation (18), however, corresponds better to the usual formulation of the statistical mechanics than (17) (compare 1.3), and therefore is preferred here.

Introduction of H_o and T as independent variables in (19) gives

$$dQ = \left(\frac{\partial E}{\partial T}\right)_{H_o} dT + \left[M + \left(\frac{\partial E}{\partial H_o}\right)_T\right] dH_o. \tag{20}$$

According to the Second Law of Thermodynamics

$$dQ = TdS. \tag{21}$$

Combination of (20) and (21) gives

$$\left(\frac{\partial E}{\partial H_o}\right)_T = T\left(\frac{\partial M}{\partial T}\right)_{H_o} - M. \tag{22}$$

Insertion of (22) in (20) yields

$$dQ = C_{H_o} dT + T\left(\frac{\partial M}{\partial T}\right)_{H_o} dH_o, \tag{23}$$

where

$$C_{H_o} = \left(\frac{\partial E}{\partial T}\right)_{H_o} \tag{24}$$

is the heat capacity of the body at constant magnetic field.

Introduction of T and M as independent variables in (23) gives

$$dQ = C_M\, dT + T\left(\frac{\partial M}{\partial T}\right)_{H_o} \left(\frac{\partial H_o}{\partial M}\right)_T dM, \tag{25}$$

where

$$C_M = C_{H_o} + T\left(\frac{\partial M}{\partial T}\right)_{H_o} \left(\frac{\partial H_o}{\partial T}\right)_M \tag{26}$$

is the heat capacity at constant magnetic moment.

If $M = f(H_o/T)$ we have

$$C_{H_o} = C_M + (f' H_o^2)/T^2, \tag{27}$$

where f' is the derivative of f to its argument; if *Curie's* law is satisfied we have $M = CH_o/T$ (where C is a constant) and accordingly

$$C_{H_o} = C_M + CH_o^2/T^2. \tag{27a}$$

Now (22), (23) and (26) give the *adiabatic change of temperature*

$$\left(\frac{\partial T}{\partial H_o}\right)_S = -\frac{T}{C_{H_o}} \left(\frac{\partial M}{\partial T}\right)_{H_o} = \frac{C_{H_o}-C_M}{C_{H_o}} \left(\frac{\partial T}{\partial H_o}\right)_M. \tag{28}$$

Introduction of M and H_o in (25) gives

$$dQ = C_M \left(\frac{\partial T}{\partial H_o}\right)_M dH_o + C_{H_o} \left(\frac{\partial T}{\partial M}\right)_{H_o} dM, \tag{29}$$

so that the *adiabatic susceptibility* becomes

$$\chi_{ad} = \left(\frac{\partial M}{\partial H}\right)_S = \frac{C_M}{C_{H_o}} \left(\frac{\partial M}{\partial H_o}\right)_T = \frac{C_M}{C_{H_o}} \chi_o. \tag{30}$$

Introducing the free energy $\Phi = E - TS$ we easily derive with the aid of (19) and (21)

$$d\Phi = -SdT - MdH_o, \tag{31}$$

so that

$$\left(\frac{\partial \Phi}{\partial T}\right)_{H_o} = -S, \quad \left(\frac{\partial \Phi}{\partial H_o}\right)_T = -M. \tag{32}$$

The equations (24), (26), (27) and (29) are important for the discussion of paramagnetic relaxation in I, Ch. 4.

It may be emphasized that the formulae in this section are quite general; they are valid for any non-conducting magnetic substance. The application is simplest in the case of magnetically 'dilute' substances, in which the difference between $\mathbf{H}$ and $\mathbf{H}_o$ is negligible. In other cases the relation between $\mathbf{H}$ and $\mathbf{H}_o$ (compare 1.1) has to be taken into account explicitly.

1.3 Application of quantum theory and statistics.

The aim of a rigorous theory of magnetism is to calculate rather than to relate only, as the macroscopic theory of 1.1 and 1.2 does, quantities like magnetisation, entropy etc. as a function of the magnetic field and the absolute temperature, starting from our present concepts of matter. This implies the use of quantum mechanics and statistics, and in principle is carried out along the following lines.

First we have to find the characteristic values of the Hamiltonian $\mathcal{H}$ of the system under consideration, or in other words the energy levels E_n of the system. In the case of a rigid magnetic body the Hamiltonian contains the magnetic field as a parameter. The second step is the calculation of the partition-function

$$Z = \Sigma_n \, exp(-E_n/kT), \tag{33}$$

where k is *Boltzmann's* constant and the summation has to be extended over all energy levels. Z is equal to the diagonal sum of $exp(-\mathcal{H}/kT)$.

Finally we have *(T2)*

$$\Phi = -\,kT\ ln\ Z.$$

With the aid of the formulae in 1.2 we easily derive

$$S = k\frac{\partial}{\partial T}\,(T\ ln\ Z)$$

$$E = kT^2\,\frac{\partial}{\partial T}\,(ln\ Z) \qquad (34)$$

$$C_{H_o} = kT\,\frac{\partial^2}{\partial T^2}(T\ ln\ Z) = k\,\frac{\partial}{\partial T}\,T^2\frac{\partial}{\partial T}\,ln\ Z.$$

Noting that $\mathbf{M}_{op} = -\partial\mathcal{H}/\partial\mathbf{H}_0$ (Compare *B2*, *V1*), we can write for the average moment

$$\mathbf{M} = \frac{Sp[(\partial\mathcal{H}/\partial\mathbf{H}_0)/exp(-\mathcal{H}/kT)]}{Sp[exp(-\mathcal{H}/kT)]},$$

where *Sp* denotes the diagonal sum of the matrix in square brackets. In the energy representation, in which $\mathcal{H}$ is a diagonal matrix, we find for the moment in the direction of the field

$$M = \frac{-\Sigma_n\ (\partial E_n/\partial H_o)\ exp(-E_n/kT)}{\Sigma_n\ exp(-\mathcal{H}/kT).}; \qquad \mathbf{(34a)}$$

this can be written in the form

$$M = k\,\frac{\partial}{\partial H_o}\,(T\ ln\ Z). \qquad \mathbf{(34b)}$$

It is important to note that the relation

$$TdS = dE + MdH_o$$

is identically fulfilled. Consequently the First Law of Thermodynamics becomes

$$dQ = dE + MdH_o\ ,$$

which is identical with (19). This is a consequence of the fact that the value of the Hamiltonian is not equal to *U*, but equal to *E*.

E may be called the spectroscopical energy (*G6*), as the change in energy caused by a transition between two energy levels corresponds to a change of *E*. For a proof of this statement and more details we refer to a paper of *Broer* (*B2*).

In the formulae (33) and (34) *Z* is the partition function of the whole crystal. We shall assume now - as is always done in the litterature - that we can write with a sufficient approximation

$$Z = Z_{sp}\ Z_l, \qquad (35)$$

where Z_{sp} contains $\mathbf{H}_0$ and is the partition function of the spin-system, while Z_l is independent of $\mathbf{H}_0$ and is the partition function of the system of lattice vibrations. The physical meaning of (35) is, that the relative positions of the energy levels of the spin-system are not influenced by the lattice vibrations. Or in other words, the spin-system and the lattice will be treated as independent if we are interested in the equilibrium properties of the substance. This assumption almost certainly is correct for low temperatures, but at higher temperatures this may be a too crude approximation (compare the results on paramagnetic resonance absorption in $NiSiF_6 . 6H_2O$ obtained by *Penrose* and *Stevens* (P1).

We henceforth shall assume the validity of (35) and we shall confine ourselves mainly to a closer consideration of the spin-system. The lattice vibrations do not enter at all in our considerations, except in the theory of paramagnetic relaxation and in the theory of the thermal broadening of resonance absorption lines.

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Chapter II

THE ENERGY LEVELS OF THE SPIN-SYSTEM

2.1 Introduction

As has been remarked already the spin system consists of the magnetic momenta of the paramagnetic ions in the crystal, which of course are immediately connected with the energy levels of the ions. Each magnetic ion is surrounded by other ions and often by water dipoles, and therefore one can anticipate that its states are not the same as the states of the free ion; this must be a consequence of interactions with the other constituents of the crystal. These interactions consist of three types.

First any ion is subjected to a strong inhomogeneous electric field - often called crystalline or Stark field - due to the other constituents of the crystal. This field has a definite symmetry, which is determined by the crystal structure, and is liable to split the levels of the free ion if these are degenerated. This will be discussed in detail in section 2.2.

Secondly there is exchange between the electrons of each ion and the other electrons of the crystal, and this as well is liable to have influence on the energy levels. In a first approximation only the exchange interaction between the electrons in incomplete shells of the different paramagnetic ions is taken into account, which will be discussed in section 2.3.

Thirdly there is a direct interaction between the paramagnetic ions, which will as well be discussed in section 2.3.

2.2 Highly 'dilute' salts

2.21 The Hamiltonian

To begin with we only shall consider the first interaction and neglect the other types. As the latter interactions decrease with increasing distance between the paramagnetic ions, this approximation is best in the case of magnetically very 'dilute' salts, or in other words, salts in which the distance between the paramagnetic ions is large. Consequently we will write the Hamiltonian of the spin system in the form

$$\mathcal{H} = \Sigma_i \mathcal{H}_i \,, \tag{36}$$

where ${}_i$ is the Hamiltonian of the *i*th magnetic ion, and the summation has to be extended over all magnetic ions. The influence of the crystalline field can be treated as a perturbation acting on the free ion. We will write $\mathcal{H}_i$ in the form

$$\mathcal{H}_i = \mathcal{H}_o + \lambda\,(\mathbf{L},\mathbf{S}) + V + \beta H(\mathbf{L} + 2\mathbf{S}) \tag{37}$$

where $\mathcal{H}_o$ is the Hamiltonian of the free ion without spin-orbit coupling, $\lambda(\mathbf{L},\mathbf{S})$ describes the spin-orbit interaction and V is the potential of the crystalline field. The last term describes the influence of an external magnetic field; β is the Bohr-magneton and $\hbar\mathbf{L}$ and $\hbar\mathbf{S}$ are the operators of the angular momenta of the orbital motion and the spins of the electrons respectively. This formulation is correct - apart from a very small term proportional to $(\mathbf{L},\mathbf{S})^2$ and terms proportional to $\mathbf{H}^2$ - for ions having *Russell-Saunders* coupling when free. In this case we can take $\mathbf{H} = \mathbf{H}_o$ and therefore we omitted the subscript o. An alternative formulation, where the energy levels - correct to the second order - are the eigenvalues of an observable involving only spin variables, has recently been given by *Pryce* (*P*4).

If we omit the last term in (37) we have to distinguish between three cases, depending on the magnitude of V:

(1) *Strong fields*. In this case the splitting due to the electric field is larger than the distance between the multiplets of the free ion. It is conceivable that the crystalline field is so strong that both the *ll*-coupling and the *ss*-coupling are removed, but this case is not likely to occur in practice. In less strong fields it is possible that the *ll*-coupling is removed, but the *ss*-coupling still exists, so that the spin quantum number still has a signification. A tendency towards this situation probably occurs in some ions of the iron group (V2).

(2) *Intermediate fields*. In this case the electric splitting is larger than the splitting of the multiplets, but is smaller than the distance between the multiplets of the free ion. Then the Hamiltonian (37) can be used; H_o is the zero order Hamiltonian, V - or at least some terms of V, see section 2.22 - is regarded as a first order perturbation and the remaining terms from (37) are regarded as a perturbation of the second order. Examples of this case are the bivalent and trivalent ions of the metals of the iron group, where the multiplet splittings are of the order 100-1000 cm^{-1} and the crystalline field splitting often is of the order 10^4 cm^{-1}.

(3) *Small fields*. The electric splitting is smaller than the distance between the levels of one multiplet. In this case the spin-orbit coupling best can be included in the zero order Hamiltonian, which therefore is taken equal to $H_o + \lambda(\mathbf{L},\mathbf{S})$; V again is regarded as a first order perturbation, and $\beta\mathbf{H}(\mathbf{L}+2\mathbf{S})$ can be regarded as a second order perturbation. Examples are the trivalent ions of the rare earths, for which the multiplet splitting is of the order 10^3 - 10^4 cm^{-1} and the electric splitting is of the order 10^2 - 10^3 cm^{-1}.

2.22 *The influence of the crystalline potential*

a) According to the previous section the energy levels of a paramagnetic ion in a crystal must be found by perturbation theory. Unfortunately V is never known exactly, because it is very difficult to determine the distribution of charges, the orientation of water dipoles and the overlapping of electron clouds. Often however the symmetry of the field is approximately known from X-ray analysis and this already can give important information.

Cubic or nearly cubic symmetry of the crystalline field occurs in the paramagnetic alums (chemical formula $M'M\,(SO_4)_2 \cdot 12H_2O$, where M' is a trivalent ion like Cr^{+++}, Fe^{+++} etc., and M is a monovalent ion like $K^+, NH_4^+, Rb^+, Cs^+, Tl^+$). X-ray analysis has revealed (L2) that every trivalent ion - often called 'central ion' - is placed in the centre of an octahedron having eight water molecules at the corners. This octahedron can be derived from a regular octahedron by a slight deformation along a trigonal axis, which makes the symmetry only trigonal. The elementary cell of the alums contains four such clusters $M'.6H_2O$, placed with their trigonal axes along the body diagonals of the elementary cell. The electric field acting on the central ion is trigonal, but deviates only slightly from a cubic field, and therefore can be called nearly or predominantly cubic. The more distant ions in the crystal probably give a small trigonal contribution - with the same trigonal axis - to the crystalline field. Similar crystalline fields are found in the fluosilicates of the iron group (with the possible exception of copper); the chemical formula is $M''SiF_6 \cdot 6H_2O$, where M'' is the divalent ion like Ni^{++}etc. M'' is surrounded by a slightly deformed octahedron of water molecules (S2) and the elementary cell contains one paramagnetic ion.

Nearly tetragonal symmetry probably is found in another group of double sulphates containing divalent ions of the iron group (Tutton salts). The chemical formula is $M''M(SO_4)_2 \cdot 6H_2O$; the divalent ion probably is surrounded by a tetragonal octahedron of water molecules (H1). The elementary cell contains two paramagnetic ions.

Summarising we can say that very often in hydrated salts the symmetry of the crystalline field is cubic in first approximation. It should be noted that this does not imply that the perturbation caused by the field is determined in the first place by the cubic part.

b) According to the group theoretical method of *Bethe (B3)* it is possible to obtain a review about the levels of the paramagnetic ion in a crystal if the symmetry of the crystalline field is known. This method has been reviewed by *Van den Handel* (*H2*) and *Mulliken* (*M1*). *Mulliken, Jahn* (*J2*) and *Opechowski* (*O2*) extended *Bethe's* results to a number of groups which *Bethe* did not consider.

The application of group theory is based on the remark that the *Schrödinger* equation of any system is invariant under certain transformations of the variables of the system. Examples are for instance certain rotations and reflections, which do not change the given field of force. Such transformations always constitute a group, often called the symmetry group of the system. It is easily seen that the *n* wave functions of a degenerated energy level are linearly transformed amongst each other under the transformations of the symmetry group. Or in other words, these wave functions transform according to a *n*-dimensional representation of the group. If the *n*-dimensional space, spanned by the wave functions, does not contain an invariant sub-space the representation is called irreducible.

An irreducible representation of the degree $(2F + 1)$, D_F, of the space rotation group (which contains all rotations of a three dimensional space around a fixed point) is induced by the $(2F + 1)$ wave functions of an atom having an angular momentum **F**. If such an atom is placed in a crystal, its symmetry group no longer is the space rotation group, but a group of lower symmetry, which however still is a sub-group of the original group. Of course the wave functions of the free atom transform according to a representation of the new group. In general, however, there are now invariant sub-spaces and the representation therefore is called reducible. In each of the invariant sub-spaces an irreducible representation of the new group is realised. It is essential, that there is no reason why the waves-functions belonging to different sub-spaces should have the same energy, except in the case of two complex conjugate representations which necessarily have the same energy (W1). Therefore in general the original level of the free atom will be split in a crystal in a number of other levels, which can be classified according to the irreducible representations of the new group contained by the original representation. The number of levels is equal to the number of irreducible representations of the new group found.

Bethe, Mulliken, Jahn and *Opechowski* calculated the irreducible representations of a considerable number of groups and with their results the reduction of a representation into the irreducible representations of a sub-group is easily found. We shall not give details of such calculations, but only summarise some results in the Tables I, II and III.

Table I

F	Cubic	*F*	Cubic
0 (1)	Γ_1	1/2 (2)	Γ_6
1 (3)	Γ_2	3/2 (4)	Γ_8
2 (5)	$\Gamma_3 + \Gamma_5$	5/2 (6)	$\Gamma_7 + \Gamma_8$
3 (7)	$\Gamma_2 + \Gamma_4 + \Gamma_5$	7/2 (8)	$\Gamma_6 + \Gamma_7 + \Gamma_8$
4 (9)	$\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$	9/2 (10)	$\Gamma_6 + 2\Gamma_8$

Table II

Cubic (O)		Tetragonal (D_4)		Trigonal (D_3)	
$\Gamma_1(1)$	$A_1(1)$	$\Gamma_1(1)$	$A_1(1)$	$\Gamma_1(1)$	$A_1(1)$
$\Gamma_2(1)$	$A_2(1)$	$\Gamma_3(1)$	$B_1(1)$	$\Gamma_2(1)$	$A_2(1)$
$\Gamma_3(2)$	$E\ (2)$	$\Gamma_1(1)+\Gamma_3(1)$	$A_1(1)+B_1(1)$	$\Gamma_3(2)$	$E(2)$
$\Gamma_4(3)$	$T_1(3)$	$\Gamma_3(1)+\Gamma_5(2)$	$A_2(1)+E(2)$	$\Gamma_2(1)+\Gamma_3(2)$	$A_2(1)+E(2)$
$\Gamma_5(3)$	$T_2(3)$	$\Gamma_4(1)+\Gamma_5(2)$	$B_2(1)+E(2)$	$\Gamma_1(1)+\Gamma_3(2)$	$A_1(1)+E(2)$
$\Gamma_6(2)$		$\Gamma_6(2)$		$\Gamma_5(2)$	
$\Gamma_7(2)$		$\Gamma_7(2)$		$\Gamma_5(2)$	
$\Gamma_8(4)$		$\Gamma_6(2)+\Gamma_7(2)$		$\Gamma_4(2)+\Gamma_5(2)$	

Cubic (O)		Rhombic (D_2)	
$\Gamma_1(1)$	$A_1(1)$	$\Gamma_1(1)$	$A_1(1)$
$\Gamma_2(1)$	$A_2(1)$	$\Gamma_1(1)$	$A_1(1)$
$\Gamma_3(2)$	$E\ (2)$	$2\Gamma_1(1)$	$2A_1(1)$
$\Gamma_4(3)$	$T_1(3)$	$\Gamma_2(1)+\Gamma_3(1)+\Gamma_4(1)$	$B_1(1)+B_2(2)+B_3(1)$
$\Gamma_5(3)$	$T_2(3)$	$\Gamma_2(1)+\Gamma_3(1)+\Gamma_4(1)$	$B_1(1)+B_2(1)+B_3(1)$
$\Gamma_6(2)$		$\Gamma_5(2)$	
$\Gamma_7(2)$		$\Gamma_5(2)$	
$\Gamma_8(4)$		$2\Gamma_5(2)$	

Table III

F	Free	Cubic (O)	Tetragonal(D_4)	Trigonal(D_3)	Rhombic (D_2)
0	(1)	(1)	(1)	(1)	(1)
1/2	(2)	(2)	(2)	(2)	(2)
1	(3)	(3)	(1)+(2)	(1)+(2)	3×(1)
3/2	(4)	(4)	2×(2)	2×(2)	2×(2)
2	(5)	(2)+(3)	3×(1)+(2)	(1)+2×(2)	5×(1)
5/2	(6)	(2)+(4)	3×(2)	3×(2)	3×(2)
3	(7)	(1)+2×(3)	3×(1)+2×(2)	3×(1)+2×(2)	7×(1)
7/2	(8)	2×(2)+(4)	4×(2)	4×(2)	4×(2)

Table I contains the reduction of the $(2F + 1)$ states of a free atom for different values of F under the influence of a cubic field. The notation is chosen according to *Bethe*. Table II contains the reduction of the irreducible representations of the cubic group under the influence of a tetragonal (D_4), trigonal (D_3) and rhombic (D_2) field. The results for each symmetry are given in two columns, the first colums is according to *Bethe's* notation, the second according to *Mullikens's* notation. The dimensions of the irreducible representations are given by the numbers in brackets behind the symbols of the irreducible representations. Table III finally contains a review of the splitting of the levels of a free ion in fields of a given symmetry; (n) again indicates a n-fold degenerated level.

If F is a half-integral number the representations are double-valued and accordingly the levels remain degenerated even under the lowest symmetry, which also is a consequence of a general theorem of *Kramers* (*K*1). This *Kramers*-degeneracy however can be removed by a homogeneous magnetic field.

The mentioned group theoretical arguments only indicate the type of levels which can occur, but nothing about their position. Only in the case, that each representation of the symmetry group occurs no more than once, it is possible to give the sequence and the ratio of the distances between the levels; then of course the splitting is determined by one parameter. Two examples are found in the Tables.

$F=3$. In a cubic field $(E_2-E_5):(E_5-E_4) = 5 : 4$.

$F=7/2$. In a cubic field now $(E_6-E_8):(E_8-E_7) = 5 : 3$.

c) Until now the signification of F has not been specified in detail. This depends on the magnitude of the spin-orbit coupling. In the rare earths the spin-orbit coupling is rather strong, and the influence of the crystalline field is rather weak. This is a consequence of the fact that the incomplete 4f electron shell is rather well screened of by the surrounding 5s and 5p shells. Consequently the spin-orbit coupling is not destroyed by the crystalline field and the energy levels in zero approximation correspond to the eigenvalues of $H_0 + \lambda(\mathbf{L},\mathbf{S})$, which can be labeled by the quantums numbers of the total angular momentum. In this case therefore $\mathbf{F}$ has to be taken equal to $\mathbf{J}$.

In the ions of the iron group the spin-orbit coupling is usually smaller, but the influence of the crystalline field is larger, because the incomplete 3d shell now is situated at the outside of the atom. Consequently the spin-orbit coupling is removed and $\mathbf{L}$ and $\mathbf{S}$ are indepently orientated relative to the crystal. In this case the zero-order levels correspond to the eigenvalues of H_0, which belong to wave functions not including spin factors. These eigenvalues can be labeled by the quantum numbers L of the orbital angular momentum $\mathbf{L}$ and we have to substitude $\mathbf{L}$ for $\mathbf{F}$. The corresponding energy levels may be called the 'orbital levels'. The wave functions of the actual free ion must include appropriate spin-factors and consequently the degeneracy of the actual energy levels in zero approximation is $(2S + 1)$ times the degeneracy of the corresponding orbital level. If the symmetry of the crystalline field is sufficiently low this degeneracy can be reduced both by the electric field and by the spin-orbit coupling. The decomposition caused by the spin-orbit coupling is found by reducing the direct products $\Gamma_i D_s$ (in *Bethe*'s notation). Examples can be found in the next section.

The magnitude of the splitting must be found by a perturbation calculus, which only is possible if V is known. The order of magnitude of the splitting by the (**L**,**S**) coupling however easily can be given. If the level under consideration is degenerated (as far as the orbital part is concerned), there is a first order splitting of the order $\lambda\,\mathrm{cm}^{-1}$; if the level is single there is only a higher order splitting of maximally the order $\lambda^2/\Delta\ \mathrm{cm}^{-1}$, where Δ is the distance to the nearest orbital level of the same symmetry type.

d) Before proceeding to a closer examination of the different ions of the iron group it may be useful to consider the crystalline potential in some detail.

According to *Bethe* (*B3*), *Kramers* (*K2*) and *Van Vleck* (*V1*) it is useful to expand the potential of the crystalline field U as a Taylor series about the centre of the paramagnetic ion

$$U = U_o + ax + \ldots + bx^2 + \ldots + cxy + \ldots + dx^3 + \ldots + ex^2y + \ldots + fx^4 + \ldots + \\ + gx^2y^2 + \ldots + hx^3y + \ldots \,. \qquad (38)$$

where U_o, a, b, c, ... are constants. Without loss of generality we can take $U_o = 0$; we neglect higher powers of x,y,z.

Equation (38) in many cases can be simplified considerably by taking into account the symmetry of U and moreover the fact that U must satisfy *Laplace*'s equation $\Delta U = 0$.

If the symmetry is cubic, with the cubic axis parallel to the x,y,z axis (38) reduces to

$$U = A\Sigma x^2 + B\Sigma x^2y^2 + C\Sigma x^4,$$

which becomes as $\Delta U = 0$

$$U = C\Sigma x^4 - 3C\Sigma x^2y^2.$$

This can be written in a more usual form by applying the relation $2\Sigma x^2y^2 = r^4 - \Sigma x^4$, where r is the distance from the origin. In this way we obtain

$$U = D\Sigma x^4 - (3/5)\,D\,r^4. \qquad (39)$$

Another important case is a trigonal field with inversion symmetry and with the trigonal axis in the [111] direction. Then the most general potential satisfying $\Delta u = 0$ can be written

$$U = A\Sigma xy + B\Sigma x^2yz - 6B\Sigma x^3y + D\Sigma x^4 - (3/5)D\,r^4. \qquad (40)$$

Similarly for a tetragonal field with inversion symmetry and with the tetragonal axis in the direction of the z-axis we have

$$U = A(x^2+y^2) - 2Az^2 + D\Sigma x^4 + E(z^4+6\,x^2y^2) + 6(E-D)r^4. \quad (41)$$

The terms in r are not essential if one only is interested in the splitting caused by U and they therefore usually are omitted. Then however U does not satisfy *Laplace*'s equation.

The potential energy in the Hamiltonian H_i corresponding to the potential U is

$$V = -eU.$$

The magnitude of the splittings of a given ion caused by (38) depends on the constants in the series expansion, which however only roughly can be estimated. It therefore is best to regard them as adjustable parameters which have to be chosen in order to give the best fit with experimental evidence, like results of susceptibility measurements.

As has been remarked already in section a) often the crystalline field deviates only slightly from cubic symmetry. This means that for instance in (40) and (41) the constants A,B and E are much smaller than D and consequently the splitting of the cubic levels is not always small compared with λ. Than the field of lower symmetry has to be taken together with the spin-orbit coupling in the perturbation calculus, which can make things much more complicated. Experimental data often only indicate that the symmetry slightly deviates from cubic symmetry, without giving any indication about the nature of the deviation. The perturbation than still can be trigonal, tetragonal or rhombic for instance. In order to avoid unnecessary complication of the calculations it is best to choose the field with the highest symmetry which can be reconciled with crystallografic and other experimental data.

Finally some remarks must be made about the *Jahn-Teller* effect. As we have seen the clusters $M'6H_2O$ have not an exactly cubic symmetry, but they are slightly distorted. This distortion is the consequence of the influence of the environment of the cluster, and of the *Jahn-Teller* effect inside the cluster. *Jahn* and *Teller* (*J1*) regarded a molecule in a state having a degenerated energy level as a consequence of a symmetry property. By grouptheoretical arguments they were able to show that such a state cannot be stable (except in the case of a linear molecule), and consequently a distortion will occur leading to a stable state with lower symmetry while the original degeneracy is removed. *Van Vleck* (*V3*) pointed out, that this theorem has to be applied to a magnetic ion and its immediate vicinity (usually a cluster of the type $M'6H_2O$). The result is such a deformation or the octahedron that all degeneracy (except the *Kramers* -degeneracy, *Jahn* (*J2*)) is removed. Usually this deformation is so small that it escapes detection by X-ray analysis.

2.23 *The ions of the metals of the iron group*

Starting from the theoretical background reviewed in the preceding sections 2.21 and 2.22 several authors contributed to the theory of the energy levels of the ions of the iron group in a crystal. In this section we will discuss these ions separately; it is not very well possible to discuss all the ions simultaneously in detail as the calculations differ too much in the various cases. Before proceeding to the discussion of the ions apart however some general remarks may be made.

In Table IV (see section 2.24) we listed the lowest configuration and the lowest level of the lowest multiplet- determined with *Hund's* rules - of the free ions of the iron group (the other columns of the table are discussed in section 2.24). It is seen that ions having 10–x 3d electrons have the same lowest orbital level as the ions having x 3d electrons; such ions may be called reciprocally related. *Van Vleck* (*V*4) has shown that the patterns of the orbital levels of reciprocally related ions, when placed in crystalline fields of the same symmetry, are inverse for a given sign of the constants in the series expansion of the crystalline potential. Moreover that the pattern of the ions of the lower half (cf. Table IV) having equal L (the pairs Ni^{++}, Co^{++}, and Fe^{++}, Cu^{++}) are inverted, and finally that if the lowest level of Ni^{++} is known (for instance Γ_2 in a cubic field), the lowest level of Cu^{++} is determined (Γ_3 in a cubic field). Consequently if for one ion the pattern is known the sequence of the levels in the patterns of all the other ions is determined. We will see below that in the case of Ti^{+++} the sequence of the cubic orbital levels can be found with a simple reasoning and hence the sequence of the cubic orbital levels in the other cases is easily determined.

Van Vleck pointed out that the patterns in a cubic field obtained in this way qualitatively explain the available data on the magnetic anisotropy and on the susceptibility of a large number of salts, if D-compare (39), (40), (41)-was supposed to be positive in all cases. According to *Gorter* (*G*7) D should be positive if the paramagnetic ion is surrounded by six negative ions or water molecules at the corners of an octahedron. X-ray analysis has revealed that this is the case in many hydrated salts.

We now shall discuss the ions of the iron group separately where we shall assume - except in the cases Fe^{+++} and Mn^{++} - that only the lowest multiplet of the free ion has to be considered. In each case we will quote the lowest level of the lowest multiplet of the free ion and the value of the constant of the spin-orbit coupling according to *Laporte* (*L*3).

1) Ti^{+++}. $3d\,{}^2D_{3/2}$; $\lambda = 154\ cm^{-1}$.

The only hydrated substance investigated is titanium caesium alum ($TiCs(SO_4)_2 \cdot 12\ H_2O$) and therefore the energy levels will be discussed for the case of a nearly cubic field with a small trigonal component. In a cubic field the D level is split according to $D_2 = \Gamma_3 + \Gamma_5$. The transformation properties of the two wave functions belonging to Γ_3 are given by the polynomials x^2-y^2, y^2-z^2; those of the three wave functions belonging to Γ_5

by *xy*, *yz*, *zx*. Now x^2-y^2 and xy have the same kind of density distribution, but these distributions are rotated relative to each other over an angle $\pi/4$ around the z-axis. In the alum the Ti^{+++} is surrounded by an octahedron of water molecules. These will turn their negative sides towards the central ion, and will be in the first case (x^2-y^2) opposite the place of highest density, in the second case (xy) however opposite places of lowest density. According to *Siegert* (S1) therefore the Γ_5 level must be supposed to be the lowest. We only will consider the Γ_5 level. In a trigonal field the Γ_5 level is split according to $\Gamma_5 = A_1 + E$, of which A_1 must be assumed to be the lowest (see above and ref. B4). The distance between these trigonal levels is Δ. Inclusion of the spin doubles the degeneracy of the three levels and, because $ED_{1/2} = \Gamma_4 + \Gamma_5$, the spin-orbit coupling splits the E-levels into twofold degenerated levels, while the A-levels remain degenerated $(A_2D_{1/2} = \Gamma_5)$. The resulting levels are all degenerated, as it should be according to *Kramers's* theorem. The distance of the higher levels above the lowest level is given by $\frac{1}{2}[S+\Delta-(3/2)\lambda]$ and S, where $S = [(\Delta+\lambda/2)^2 + 2\lambda^2]^{1/2}$ (*Bleaney* B4).

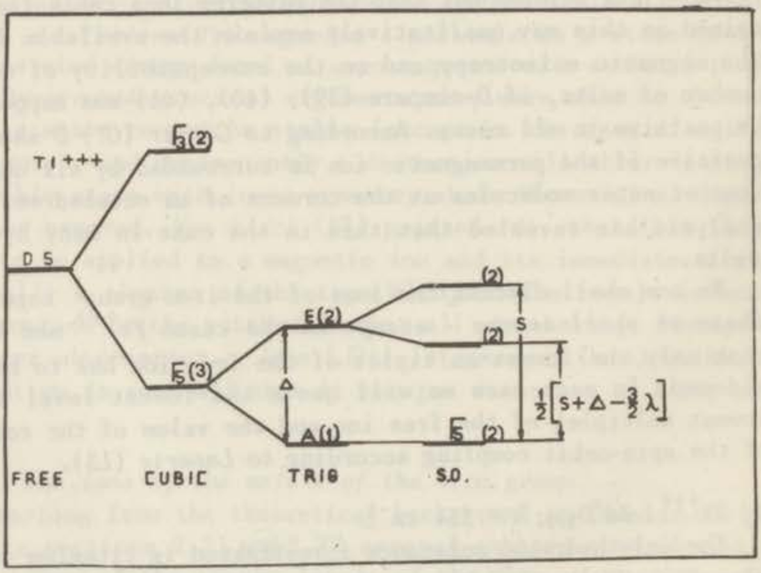

Fig. 1

If a magnetic field is applied the degeneracy of all the levels is removed. We shall confine ourselves to the cases that the magnetic field is either parallel or perpendicular to the trigonal axis, and to the splitting of the lowest cubic level.

In both cases the energy is a linear function of the magnetic field and the energy is given by $E = \pm \frac{1}{2} g_{\perp}\beta H$, where g, which may be called the effective *Landé*- factor, is different for the two cases. *Bleaney* finds

$$g_{//} = [3\ (\Delta + \lambda/2)]/S - 1 \quad g_{\perp} = [\Delta - 3\lambda/2]/S + 1. \qquad (42)$$

Van Vleck (V2) estimated the value of Δ and found $\Delta \simeq 10^3 cm^{-1}$. This value however is rather much higher than the value ($\Delta \simeq 10^4$ cm^{-1}) indicated by measurements on paramagnetic relaxation (V5) and the susceptibility (H2). -

Experiments on resonance absorption indicate $\Delta \simeq 400\ cm^{-1}$ (Cf. III, 2.2).

Finally we give in fig. 1 a review of the splittings mentioned in the absence of a magnetic field.

2) $V^{+++}.\ 3d^2\ {}^3F_2$; $\lambda = 150\ cm^{-1}$ *(H3)*.

The most interesting substance for us is vanadium ammonium alum ($VNH_4(SO_4)_2.12H_2O$). In a cubic field the orbital F level is split according to $D_3 = \Gamma_2 + \Gamma_5 + \Gamma_4$, of which Γ_5 lies between Γ_2 and Γ_4 (see p.22), and Γ_4 lies lowest. This can be seen in the following way (compare *Van Vleck (V4)*). Because the lowest cubic level of Ti^{+++} is Γ_5, the lowest cubic level of Cu^{++} is Γ_3. Then the lowest level of Ni^{++} is Γ_2 and consequently the lowest cubic level of V^{+++} is Γ_4. This Γ_4 level is split in a trigonal field according to $\Gamma_4 = E + A_2$. Of these levels the A_2 level lies lowest, which is not entirely trivial and therefore has been subject of special discussion in the litterature. This discussion only briefly will be summarised here. In both the titanium and the vanadium alum the potential of the crystalline field can be written in the form (40). *Siegert* (*S*1) already pointed out that only if the trigonal part of the potential (40) satisfies rather critical conditions, which we need not specify here, in both alums the lowest trigonal level can be single. Taking into account the direct influence of the SO_4-groups in the crystal and the influence of the distortion of the octahedron of watermolecules - caused by the *Jahn-Teller* effect in the $M'.6H_2O$ clusters and the action of distant ions - *Van Vleck* (*V*2) showed, that probably the crystalline field fulfils the requirement for making the single trigonal level lowest in both alums.

After inclusion of the spins the spin-orbit coupling can split the E and A_2 level according to

(sixfold) $ED_1 = 2E + A_1 + A_2$ (three fold) $A_2D_1 = E + A_1$.

The sixfold level splits in first approximation only into three twofold levels - as A_1 and A_2 still coincide, in second approximation the complete resolving is found. The threefold level only splits in second approximation. Then the single level A_1 lies lowest, at a adistance δ below the double level E. These levels

A_1 and E have the spin quantum numbers 0 and ± 1 resp. along the trigonal axis. If the cubic splitting is much larger than the trigonal splitting we have $\delta = \lambda^2/\Delta$, where Δ is the magnitude of the trigonal splitting. The final degeneracy must be completely removed by the *Jahn-Teller* effect, but this is not considered further here.

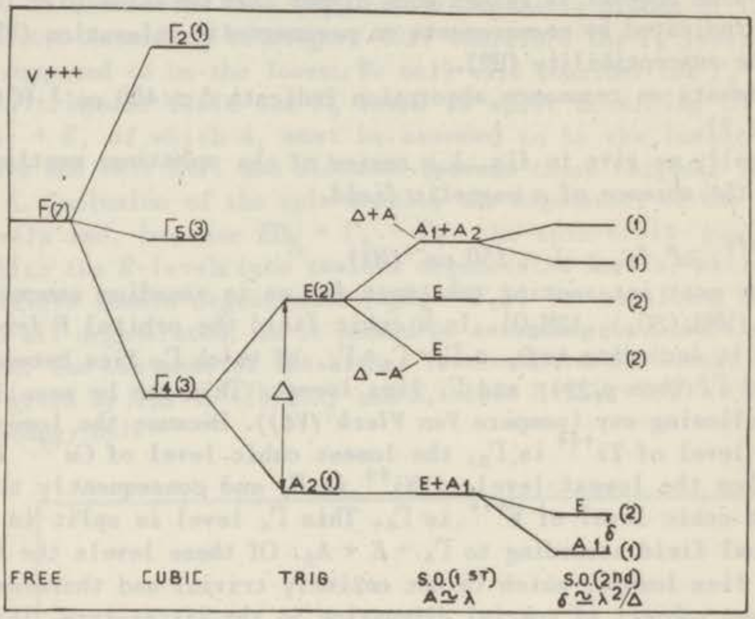

Fig. 2

The influence of a magnetic field on the two lowest levels has been considered by *Siegert* (*S*1). According to his results the energy in fields respectively parallel and perpendicular to the trigonal axis is given by

$$E_{/\!/} = \pm\, g_{/\!/}\, \beta H \qquad E_{\perp} = 0$$

$$E_{/\!/} = -\,\delta \qquad E_{\perp} = \tfrac{1}{2}[-\delta + (\delta + 4\beta^2 g_{\perp}^2\, H^2)^{1/2}] \quad (43)$$

where $g_{/\!/} = 2 - 3\,(\lambda/\Delta)^2$ and $g_{\perp} = 2 - 2\,(\lambda/\Delta)$, (44)

if the cubic splitting of the orbital levels is very much greater than the trigonal splitting.

According to *Van Vleck* (*V*2) $\Delta \simeq 1300$ cm^{-1}, while susceptibility experiments seem to indicate (H3), that $\Delta \simeq 800$ cm^{-1} and $\delta \simeq 5$ cm^{-1}; then $g_{/\!/} = 1{,}52$ and $g_{\perp} = 1{,}60$.

Finally we give a review of the level pattern in the different approximations in zero external field (fig.2).

3) Cr^{+++}. $3d^3\ {}^4F_{3/2}$; $\lambda = 87\ cm^{-1}$. (V^{++}; $\lambda = 55\ cm^{-1}$.)

In a cubic field the orbital F level splits according to $D_3 = \Gamma_2 + \Gamma_5 + \Gamma_4$ (compare V^{+++}), but now the Γ_2 term lies lowest *(Van Vleck (V4))*, so that already in a cubic field the lowest orbital level is single. Inclusion of the spins gives this level a fourfold degeneracy, which cannot be removed by the spin-orbit coupling, as $\Gamma_2 D_{3/2} = \Gamma_8$. There are, however, clear indications that in the chromium alums a small splitting of this fourfold level occurs, which implies that the symmetry of the field is lower than cubic. Assuming as usual an additional trigonal field the cubic Γ_8 level is split by the spin-orbit coupling according to $\Gamma_8 = \Gamma_4 + \Gamma_5$, where Γ_4 and Γ_5 are the double-valued representations of the trigonal group. A detailed perturbation theory shows, that this splitting is a higher order effect of the magnitude $(\lambda^2/\Delta_{cub})(\Delta/\Delta_{cub})$, where Δ is the trigonal splitting of the higher cubic orbital levels and Δ_{cub} is the cubic orbital splitting; this explains the smallness of the splitting actually found. For instance in the potassium alum $\delta = 0.12\ cm^{-1}$ at room temperature according to *Bleaney* (*B*6).

Simple group theoretical arguments easily snow that the Γ_4 and Γ_5 level respectively have the spin quantum numbers $\pm 3/2$ and $\pm 1/2$ along the trigonal axis. The splitting in a magnetic field has been calculated for arbitrary directions of **H** by *Broer* (*B*5) and for a special case(**H** parallel to a cube edge of the elementary cell of the alum, so that $\cos^2 \zeta = 1/3$, where ζ is the angle between the trigonal axis and the magnetic field) by *Kittel* and *Luttinger* (*K*3). The latter authors find

$$\varepsilon_{\pm 1/2} = \pm \tfrac{1}{2}\,[1+15x^2 - 6x(1+4x^2)^{\frac{1}{2}}]^{\frac{1}{2}}$$

$$\varepsilon_{\pm 3/2} = \pm \tfrac{1}{2}\,[1+15x^2 + 6x(1+4x^2)^{\frac{1}{2}}]^{\frac{1}{2}}, \qquad (45)$$

where we have labeled the energies with their appropriate *strong field* quantum numbers and where $\varepsilon = E/\delta$ and $x = g\beta H/\delta(3)^{\frac{1}{2}}$. In high fields ($x \gg 1$) we have $E_{\pm 3/2} = \pm 3/2 g\beta H$, $E = \pm \tfrac{1}{2} g\beta H$. If **H** is parallel to the trigonal axis we have *(Broer (B5))*

$$E_{\pm 1/2} = -\delta/2 \pm \tfrac{1}{2} g\beta H \qquad E_{\pm 3/2} = \delta/2 \pm 3/2 g\beta H \qquad (46)$$

The cubic splitting Δ_{cub} can be found from the deviation of the *Curie*-constant from the spin-only value (according to *Schlapp* and *Penney* (*S*3)) and is of the order $10^4\ cm^{-1}$(the deviation is small and the accuracy accordingly very low). With the mentioned values of δ and λ we find for the trigonal splitting Δ some hundred cm^{-1}, which seems reasonable. We finally review the splitting discussed (fig. 3).

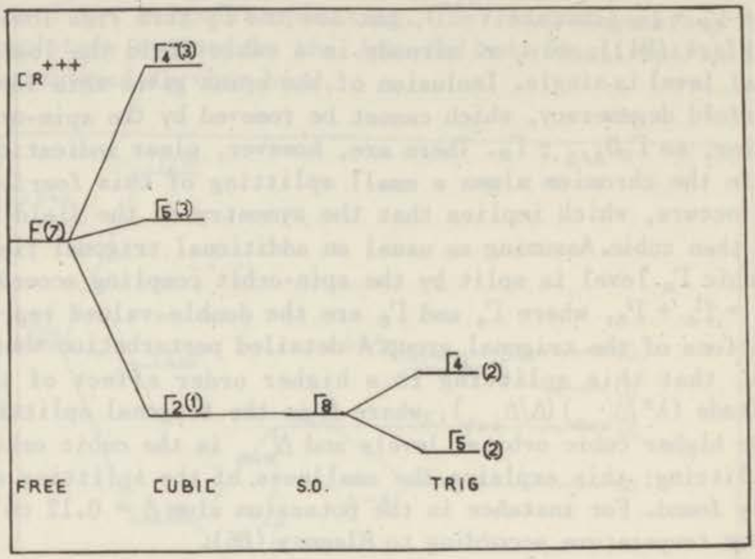

Fig. 3

4) $Cr^{++}.\ 3d^4\ {}^5D_0;\ \lambda = 57\ cm^{-1}\ (Mn^{+++})$.

Just as in the case of Ti the orbital level splits in a cubic field according to $D_2 = \Gamma_3 + \Gamma_5$, of which the 'non-magnetic' state Γ_3 lies lowest (compare *Siegert (S1))*. In an additional trigonal field the Γ_3 level is not split because $\Gamma_3 = E$. Introduction of the spin gives a tenfold degenerated level, which can be split by the spin-orbit coupling into three twofold levels and four single levels according to $ED_2 = 2A_1 + 2A_2 + 2E$, The remaining degeneracy can be removed by the *Jahn-Teller* effect and by a magnetic field.

In an additional rhombic field the Γ_3 level is split as $\Gamma_3 = 2A_1$. Introduction of the spins now gives a fivefold level which can be split by the spin-orbit interaction according to $A_1D_2 = 2A_1 + B_1 + B_2 + B_3$, so that five single levels result. As far as we are aware no calculation about the relative positions of the energy levels has been published.

5) $Fe^{+++}\ (Mn^{++}).\ 3d^5\ {}^6S_{5/2}$.

In these cases the lowest orbital level is single and therefore no splitting in the crystalline field can occur. In a first approximation the spins should be free and there should be no splitting of the spin levels. There is however abundant evidence showing that a small splitting of the spin levels occurs. According to *Van Vleck* and *Penney* (*V6*) this is a consequence of a small deviation from pure *Russell-Saunders* coupling in the free ion. It may be noted, that here we have two cases where the influence of other multiplets than the lowest one cannot be neglected. In a cubic field the spin levels are split in a fourfold and a twofold level according to $D_{5/2} = \Gamma_7 + \Gamma_8$, of which usually the twofold level (Γ_7) is supposed to be the lowest. The splitting in iron ammonium alum is roughly of the order 0.10 cm^{-1} (cf. Part III and (B7)).

The splitting in a magnetic field has been calculated for arbitrary directions of **H** by *Kronig* and *Bouwkamp* (*K4*) and for a special case (**H** parallel to one of the cubic axis) by *Debye* (*D1*). Writing $x = g\beta H/\delta$, $\varepsilon = E/\delta$, where 3δ is the splitting, we have, if **H** is parallel to a cubic axis

$$\begin{aligned} \varepsilon_{\pm 1/2} &= 1 \pm x/2 \\ \varepsilon_{\pm 3/2} &= -\tfrac{1}{2} \mp x/2 \pm 2[x^2 \mp x + (3/4)^2]^{\frac{1}{2}} \\ \varepsilon_{\pm 5/2} &= -\tfrac{1}{2} \pm x/2 \mp 2[x^2 \pm x + (3/4\ ^2]^{\frac{1}{2}} . \end{aligned} \tag{47}$$

In fig.4 we present ε as a function of x, calculated with (47). In high fields ($x \gg 1$) we have

$$\begin{aligned} \varepsilon_{\pm 1/2} &= 1 \pm x/2 \\ \varepsilon_{\pm 3/2} &= -3/2 \pm 3x/2 \\ \varepsilon_{\pm 5/2} &= \tfrac{1}{2} \pm 5x/2. \end{aligned} \tag{47a}$$

If **H** is parallel to a body diagonal we have

$$\begin{aligned} \varepsilon_{\pm 1/2} &= -\tfrac{1}{2} \mp x \pm 3/2\,[x^2 \mp 2x/9 + 1]^{\frac{1}{2}}/2 \\ \varepsilon_{\pm 3/2} &= 1 \pm 3x/2 \\ \varepsilon_{\pm 5/2} &= -\tfrac{1}{2} \pm x \pm 3/2\,[x^2 \pm 2x/9 + 1]^{\frac{1}{2}}/2, \end{aligned} \tag{48}$$

which becomes in high fields

$$\begin{aligned} \varepsilon_{\pm 1/2} &= -2/3 \pm x/2 \\ \varepsilon_{\pm 3/2} &= 1 \pm 3x/2 \\ \varepsilon_{\pm 5/2} &= -1/3 \pm 5x/2 \end{aligned} \tag{48a}$$

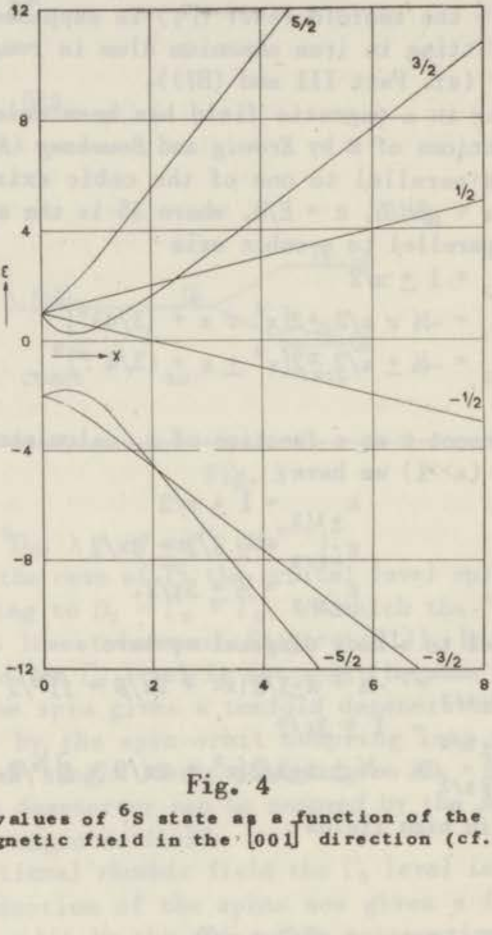

Fig. 4

Eigenvalues of ^6S state as a function of the constant magnetic field in the [001] direction (cf.(47))

All levels are labeled according to their high-field quantum numbers. It should be remembered however that the crystalline field in many alums (for instance of V and Cr) has a lower symmetry than cubic and probably is trigonal. It is therefore probable that in the iron alums (for instance in the ammonium alum) the crystalline field has a lower symmetry than cubic and possibly is trigonal as well. An adequate theory of the energy levels than only can be given by taking this lower symmetry into account. As far as we are aware such a theory has not yet been worked out. It is easily seen (compare Table III) that in case of lower symmetry than cubic there are in the absence of an external field three twofold spin levels. This of course applies as well to Mn^{++}. Divalent manganese does not form alums, but in the manganese Tutton salts the crystalline field highly probably has a tetragonal, possibly even lower, symmetry and the theory of *Kronig* and *Bouwkamp* therefore can not be adequate for this case.

6) Fe^{++}. $3d^6$ $^5D_4$; $\lambda = -100\ cm^{-1}$.

In a cubic field the orbital level is split according to $D_2 = \Gamma_3 + \Gamma_5$, of which Γ_5 lies lowest, contrary to the case of Cr^{++}. In a tetragonal field (Tutton salts) Γ_5 is spit according to $\Gamma_5 = \Gamma_4 + \Gamma_5$ of which the single level Γ_4 probably is lowest. Introduction of the spin gives a fivefold level, which can be split by the spin orbit coupling into one doublet and three singlets according to $\Gamma_4 D_2 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$. In a rhombic field the degeneracy of the cubic orbital levels is completely removed. A rhombic field also fully resolves the spin-multiplet, so that from the lowest cubic level five single levels result. No detailed calculation of the position of the energy levels seems to have been published. The splitting of the spin multiplet must be expected to be rather large; one of these splittings seems to be of the order 0.8 cm^{-1} (B7).

7) Co^{++}. $3d^7$ $^4F_{9/2}$; $\lambda = 180\ cm^{-1}$.

In a cubic field the orbital F level is split according to $D_3 = \Gamma_2 + \Gamma_4 + \Gamma_5$. The position of the cubic levels however is reversed compared with Cr^{+++} and now the Γ_4 level lies lowest. A further splitting occurs in fields of lower symmetry. *Schlapp* and *Penney* (S3) considered the case of a predominantly cubic field with a small rhombic component, in which the Γ_4 level splits according to $\Gamma_4 = B_1 + B_2 + B_3$ into three single levels. After introduction of the spins every level becomes fourfold degenerated; this degeneracy is partially lifted by the spin-orbit coupling, which splits each fourfold level into two *Kramers* doublets. The calculation of the energy levels is very complicated because probably the influence of the spin-orbit coupling and the influence of the presumed rhombic field are about of the same order of magnitude.

In different salts, however, the symmetry of the crystalline field must be supposed to be predominantly tetragonal instead of predominantly cubic, for instance in the Tutton salts. In a tetragonal field the lowest cubic level splits into a doublet and a singlet, according to $\Gamma_4 = \Gamma_3 + \Gamma_5$, of which probably the latter lies lowest. Introduction of the spins makes the degeneracy of the tetragonal levels four times as high. The spin-orbit coupling splits these levels in *Kramers* doublets according to

$A_2D_{3/2} = \Gamma_8 + \Gamma_7$ and $ED_{3/2} = 2\Gamma_8 + 2\Gamma_7$, so that again six doublets result. According to *Pryce* (P2) the tetragonal splitting is smaller than the splitting due to the spin-orbit coupling, which is a consequence of the almost complete cancellation of the effects of the second and fourth order terms in the series expansion of the potential. He estimates for the splitting between the two lowest doublets some 300 cm^{-1}. This is much larger than the value previously suggested by *Van Vleck* (*V*5), who estimated 10 cm^{-1}. *Pryce's* estimate seems to be more reliable, as it is corroborated by recent experiments on the hyperfine structure of the paramagnetic resonance spectrum of divalent cobalt (B8). The splitting between the two lowest doublets apparently is much larger for Co^{++} than for Cr^{+++}. This is partly due to the larger spin-orbit coupling and partly to the much smaller distance between the lowest orbital levels in a crystal in the case of cobalt.

8) $Ni^{++}.3d^8\ {}^3F_4;\ \lambda = -335\ cm^{-1}$.

In a cubic field the orbital F level is split as in Cr^{+++} ($D_3 = \Gamma_2 + \Gamma_4 + \Gamma_5$), so that the Γ_2 level is lowest (contrary to Co^{++}). In a rhombic field, as has been considered by *Schlapp* and *Penney* (*S*3), no further splitting occurs, because the Γ_2 level is single; we have $\Gamma_2 = A_1$. Introduction of the spin makes the lowest level three fold and the spin-orbit coupling resolves this level into three singlets according to $A_1D_1 = B_1 + B_2 + B_3$. On this basis it was possible to describe the magnetic anisotropy in the nickel ammonium Tutton salt, assuming for λ the value mentioned above and assuming one Ni^{++} per unit cell. The overall splitting of the three singlets was found to be about 3.4 cm^{-1} (B4). At present this nice result seems to be somewhat incidental, because the symmetry of the crystalline field must be expected to be tetragonal with cubic and tetragonal terms of the same order in the potential, and moreover the unit cell contains two Ni-ions with different magnetic axes. In therefore seems to be advisable to consider the tetragonal case as well, which can be done on the basis of the theory of *Schlapp* and *Penney* (*S*3), as tetragonal symmetry is only a special case of rhombic symmetry. This has not yet been carried out. It is easily seen that in a tetragonal field the cubic level gives rise to a doublet and a singlet because $\Gamma_2 = \Gamma_3$ and $\Gamma_3D_1 = \Gamma_1 + \Gamma_5$.

In the nickel fluosilicate the crystalline field is predominantly cubic with a smaller trigonal component (*Becquerel* and *Opechowski* (*B*10)). For a trigonal field we have $\Gamma_2 = A_2$ and after introduction of the spins the spin-orbit coupling gives a doublet and a singlet because $A_2D_1 = A_1 + E$. The situation is much the same as for V^{+++}, but now the doublet lies lowest. The splitting in a magnetic field, respectively parallel (B. and O.) and perpendicular (*Penrose* and *Stevens* (*P*1)) to the trigonal axis is given by

$$E_{\parallel} = \delta \qquad E_{\perp} = \tfrac{1}{2}\,[\delta \pm (\delta^2 + 4g_{\perp}^2\beta^2H^2)]^{1/2}$$
$$E_{\parallel} = \pm\, g_{\parallel}\beta H \qquad E_{\perp} = 0 \qquad (49)$$

where

$$g_{\parallel} = 2(1 - \lambda A) \qquad g_{\perp} = 2(1 - \lambda B)$$

and

$$\delta = (A - B)\,\lambda^2 \quad ;$$

A and *B* are parameters which depend in a complicated way on the crystalline field. The latter authors find $A \simeq 4.10^{-4}$ cm and $(A - B) \simeq 1.5\ .10^{-8}$ cm, so that pracically $g_{\parallel} = g_{\perp}$ The paramagnetic resonance is entirely consistent with the theory; δ is found to decrease with decreasing temperature. At 20 and 14 °K $\delta = 0.12$ cm^{-1}, in reasonable agreement with *Benzie* and *Cooke's* value of 0.16 cm^{-1} (B21). *Becquerel* and *Opechowski* (*B*10) find however 0.30 cm^{-1}, which seems to be in error. We finally review the splitting discussed (fig. 5).

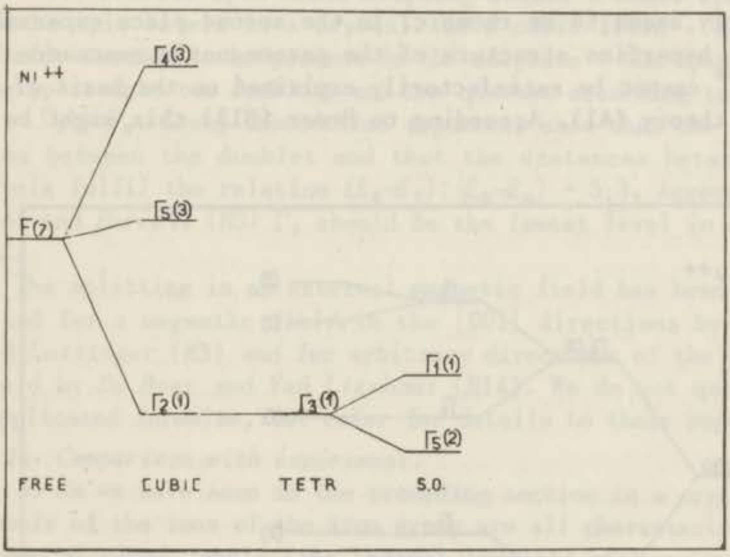

Fig. 5

9) Cu^{++}, $3d^9$ $^2D_{5/2}$; $\lambda = -852$ cm^{-1}.

In a cubic field the orbital D level is split into a triplet and a doublet according to $D_2 = \Gamma_3 + \Gamma_5$. The unmagnetic doublet Γ_3 lies lowest, as in the case of Mn^{+++} and Cr^{++}, but contrary to V^{+++}. In a tetragonal field Γ_3 splits into two singlets $(\Gamma_3 = \Gamma_1 + \Gamma_3)$ and the triplet into a singlet and a doublet $(\Gamma_5 = \Gamma_4 + \Gamma_5)$. Assuming a tetragonal field of the form (41) with cubic and tetragonal terms of the same order, *Polder* (*P*3) showed that the sequence of the levels, starting from the lowest one, must be $\Gamma_3, \Gamma_1, \Gamma_4$, and Γ_5. Introduction of the spin doubles all levels, but only the Γ_5 level is split (in two doublets). The splitting in a magnetic field resp. parallel and perpendicular to the trigonal axis of all the doublets is given by

$$E_{\parallel} = \pm \tfrac{1}{2} g_{\parallel}\beta H \qquad E_{\perp} = \pm \tfrac{1}{2} g_{\perp}\beta H\,, \tag{52}$$

where for the lowest doublet

$$g_{\parallel} = 2[1 - 4\lambda/E_4-E_3)] \quad g_{\perp} = 2[1 - \lambda/(E_5-E_3)]\,. \tag{53}$$

Here we have written E_i for the energy corresponding to the level Γ_i. On this basis fair agreement is found with susceptibility measurements on the copper potassium sulphate of *Miss Hupse* (*H*4), which give $g_{\parallel} = 2.44$ and $g_{\perp} = 2.05$, if it is assumed that $E_4 - E_3 = 15400$ cm^{-1} and $E_5 - E_3 = 26600$ cm^{-1}.

Recent evidence shows however that *Polder*'s theory does not account for all observed facts. In the first place experiments on resonance absorption in several copper Tutton salts show that deviations from the tetragonal symmetry occur, especially in the potassium and ammonium Tutton salts (B12), where the symmetry seems to be rhombic. In the second place experiments on the hyperfine structure of the paramagnetic resonance line of Cu^{++} cannot be satisfactorily explained on the basis of *Polder*'s theory (A1). According to *Broer* (*B*13) this might be explained by interaction between the lowest configuration $3d^9$ and the next lowest one $3d^8 4s$, which have the same parity. The effect of this interaction only can be found as a result of rather

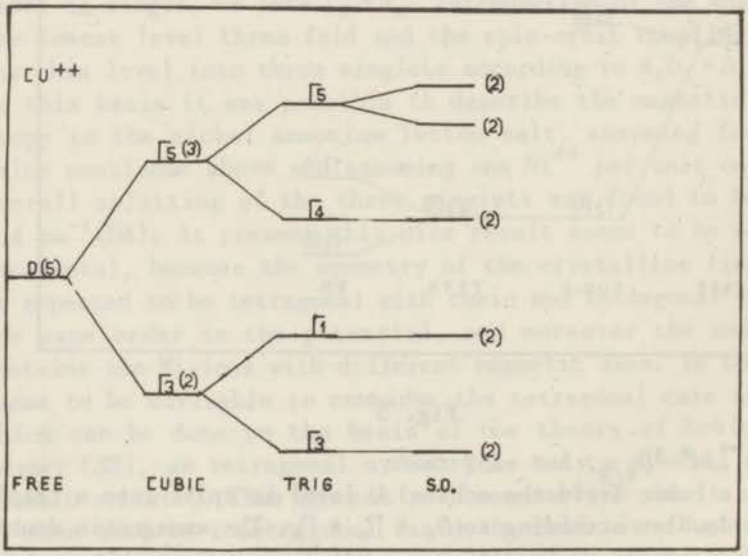

Fig. 6

complicated calculations, but it is entirely neglected in *Polder's* theory. According to *Pryce* a quadrupole moment of the nucleus should be responsible for the discrepancy mentioned.

It may be added that *Jordahl* (*J*3) gave the first theory about the Cu^{++}, assuming a predominantly cubic field with a small rhombic term. As *Polder's* theory accounts better for the known experimental facts we shall not discuss *Jordahl's* theory. We finally review the splittings discussed (fig. 6).

10) Gd^{+++}. $4f^7\ {}^8S_{7/2}$.

Although Gd belongs to the rare earths it is briefly discussed here because we carried out some experiments on gadolinium sulphate. The situation is much the same as for Fe^{+++} and Mn^{++}; as the lowest orbital level of the free Gd^{+++} is single, and there is only degeneracy due to the spins. Again as a consequence of small deviations of pure *Russell-Saunders* coupling in the free ion the spin-orbit coupling oauses a small splitting of the spin levels in a crystal. In a cubic field - which is usually assumed to be present in the sulphate - the spin levels are split into two doublets and one quartet according to $D_{7/2} = \Gamma_6 + \Gamma_7 + \Gamma_8$. Group theoretical arguments show that the quartet lies between the doublet and that the distances between the levels fulfil the relation $(E_8 - E_7):(E_6 - E_8) = 5:3$. According to *Hebb* and *Purcell* (*H*5) Γ_7 should be the lowest level in a crystal.

The splitting in an external magnetic field has been calculated for a magnetic field in the [001] directions by *Kittel* and *Luttinger* (*K*3) and for arbitrary directions of the magnetic field by *De Boer* and *Van Lieshout* (*B*14). We do not quote the complicated formulae, but refer for details to these papers.

2.24 Comparison with experiment.

a) As we have seen in the preceding section in a crystal the levels of the ions of the iron group are all characterised by a group of close levels (the 'normal levels') with a separation of maximally a few cm^{-1}, while all the other levels are at a distance of 1000 cm^{-1} (except for Co^{++}) or even much more above the lowest levels. At ordinary temparatures only the normal levels are occupied, which is easily seen because 1°K corresponds to 0.696 cm^{-1}. The higher levels have only influence on the properties of the paramagnetic substances in as much they influence the lowest levels. If we neglect the splitting of the normal levels the level pattern in a magnetic field corresponds to the levels of a system of free spins. This simple pattern is slightly modified by the influence of the spin-orbit coupling.

These results of the theory are all obtained in a natural way, but a definitive justification only can be given by a comparison with experimental evidence. Fortunately there is abundant evidence confirming the correctness of the sketched theoretical result in its main outline. We must confine ourselves to a brief summary, as a detailed discussion would fall outside the scope of this thesis; we refer to *Van Vleck* (V5), *Penney* and *Kynch* (P5) and *Freed* (F2).

The most direct - and ultimately the most complete - evidence about the normal levels is furnished by experiments on resonance absorption. We propose to discuss these later and therefore can omitt them here.

Less detailed information is given by measurements of the susceptibility and specific heat. In order to make possible a check of the level pattern mentioned, we have to discuss the theoretical expressions for the susceptibility and the specific heat.

b) We first have to calculate the partition function. In the case of a highly dilute salt - in which we can neglect the interactions between the paramagnetic ions - we can write at once

$$Z = Z_{ion}^{N}, \tag{54}$$

where Z_{ion} is the partition function of one ion and N is the number of paramagnetic ions. Z_{ion} is easily calculated in the case of free spins. A system of free spins with a spin quantum number S has in a magnetic field $(2S + 1)$ energy levels with the energies

$$E_m = g\, m\, \beta\, H, \tag{55}$$

where $m = S, S-1, ---, -S+1, -S$; the Landé-factor g is equal to 2 in the case of free spins. We shall write g in order to make the applicability of the formulae greater. It is easily shown that

$$Z = \sinh(S+\tfrac{1}{2})\, g\alpha / \sinh \tfrac{1}{2}\, g\alpha, \tag{56}$$

where $\alpha = \beta H/kT$. According to (34) we have

$$M = \beta[(S+\tfrac{1}{2})g \coth(S+\tfrac{1}{2})g\alpha - \coth \tfrac{1}{2}\, g\alpha]. \tag{57}$$

This expression becomes for small values of α

$$M = N\beta^2 g^2\, S(S+1)\, H/3kT, \tag{58}$$

so that *Curie's* law is satiesfied with the *Curie* constant

$$C = N\beta^2 g^2 S(S+1)/3k. \tag{58a}$$

This easily can be compared with experimental values of the susceptibility. The usual way of doing this is to compare the theoretical and experimental magnetonnumber p, defined by $p = (3\chi kT/N\beta^2)^{1/2}$. In Table IV we collected some results; the first column is trivial, the second column contains the configuration, the third column contains the lowest states of the free ions, determined with *Hund's* rules, the fourth column contains the values of p for the free ions. In this case $p = p_H = g[J(J+1)]^{1/2}$ - if the multiplet splitting is much larger than kT - and g is given by $g = 1+[J(J+1)+S(S+1)-L(L+1)]/2J(J+1)$. The fifth column contains the values of p calculated with (58), the 'spin-only'-values $(p_s = 2[S(S+1)]^{1/2})$. Inspection of the table shows that the experimental values p_{exp} agree nicely with the spin-only values, while on the other hand the agreement with the values for the free ions (except for Mn^{++} and Fe^{+++}) is very poor. Evidently the magnetism of the ions in a crystal differs considerably from that of the free ions and is to a fair approximation due to the spins alone. This justifies the level patterns given in section 2.23 in its general outline.

TABLE IV

Ion	Configuration	Lowest level	p_H	p_S	p_{exp}
Ti^{+++}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d$	$^2D_{3/2}$	1.55	1.73	1.75
V^{+++}	$3d^2$	$^3F_2$	1.63	2.83	2.8
Cr^{+++}, V^{++}	$3d^3$	$^4F_{3/2}$	0.77	3.87	3.9
Mn^{+++}, Cr^{++}	$3d^4$	$^5D_0$	0	4.90	4.9
Fe^{+++}, Mn^{++}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{++}	$3d^6$	$^5D_4$	6.70	4.90	5.5
Co^{++}	$3d^7$	$^4F_{9/2}$	6.54	3.87	4.4-5.3
Ni^{++}	$3d^8$	$^3F_4$	5.59	2.83	3.2
Cu^{++}	$3d^9$	$^2D_{5/2}$	3.55	1.73	1.9

The internal energy of a system of free spins is simply equal to

$$E = -(HM).$$

In low fields we have $E = -4\beta^2 H^2 S(S+1)/3kT = -CH^2/T$ (cf.(58a)), so that C_H is given by

$$C_H = CH^2/T^2 \tag{59}$$

this corresponds to (27) with $C_M = 0$. This result is independent of the value of g and remains correct as long as there is no splitting in zero field and moreover the interaction between the paramagnetic ions is neglected.

c) By considering the spins as free, however, we neglect the influence of the spin-orbit coupling, which appears to be essential for the explanation of some finer points, like the deviation from the spin only value of the magneton number, anisotropy of the susceptibility and the magnitude of the specific heat of the spin system.

The influence of the spin-orbit coupling on the energy levels has, according to the preceding section, three aspects. In the first place a small splitting of the spin multiplet occurs, except in the cases Ti^{+++} and Cu^{++}, in the second place the splitting in a magnetic field depends on the direction of the field relative to the axes of the crystalline field. And thirdly, in all cases where the energies are a linear function of the field, the *g*-values differ from those of free spins.

The influence of the spin-orbit coupling on the specific heat and the susceptibility can be discussed according to these three aspects. Let us consider the susceptibility first.

Clearly if the *g*-value differs from 2 deviations of the spin-only value of the magneton number must be found. This is the case with Ti^{+++} and Cu^{++}. Moreover in these cases the levels vary linearly with the magnetic field in all directions and the *g*-values depend on the direction of the magnetic field, so that the susceptibility must be anisotropic. This has been observed for instance in the case of copper salts and the theory satisfactorily explains the magnetic anisotropy in the copper Tutton salt. For details we refer to a paper of *Polder* (P3). In general a dependence of the level pattern on the direction of the magnetic field causes a magnetic anisotropy. Often the elementary cell contains more than one ion; then in general the direction of the crystalline field relative to the crystal axes is different for the different ions and consequently the anisotropy of the crystal can be very different from the anisotropy of an ion apart (see for instance *Polder* (P3)). Other examples can be found in a paper of *Schlapp* and *Penney* (S3).

The influence of a small splitting δ on the susceptibility only becomes noticeable if the temperature is so low that no-longer $\delta \ll kT$.

This is easily seen in the following way (compare *Casimir* (*C*1)). The splitting of the normal levels in a magnetic field can be found by solving the secular equation

$$|\mathcal{H}_{ij} - E_i \delta_{ij}| = 0.$$

In the case of an initial splitting we have to write

$$\mathcal{H}_{ij} = E^\circ_i - (\mathbf{HM})_{ij},$$

where E°_j are the energies of the normal levels in zero field. The partition function is the diagonal sum of $exp\ (-\mathcal{H}/kT)$ and, since this sum is invariant under unitary transformations, we can write in the energy representation

$$Z = \sum_j [(exp(-\mathcal{H}/kT)]_{jj}.$$

This however can be expanded in a series

$$Z = \sum_j [exp\ (-\mathbf{HM}/kT)]_{jj} + O(A/kT)\ f\ (\mathbf{HM}/kT), \qquad (60)$$

where A is a measure for the total separation of the E°_i 's, and $f(0) = 1$; $O(x)$ is a quantity of the order of magnitude x. To a first approximation the partition function therefore is the same as in the case when there are no splittings at all. This result is independent of the value of **HM**, which may be small or large compared with the initial separations.

The magnetic moment can be expanded in ascending powers of $1/T$

$$M = (CH/T)(1+B/T + \dots)$$

(if saturation is neglected), where C has the same value as if there were no splittings and B is of the order A/k, if not zero. The presence of small splittings does not influence the value of the *Curie*-constant but only adds higher powers of $1/T$ to the expression of M and the susceptibility $\chi = M/H$. Often for powders $B = 0$. (*Van Vleck* and *Penney* (*V6*), and *Gorter* (*G8*)), and only at very low temperatures the influence of the splittings becomes perceptible.

An example is the susceptibility of $NiSiF_6 \cdot 6H_2O$ in the direction of the hexagonal axis which coincides with the trigonal axis of the crystalline field. In this case we have

$$Z = 2[\tfrac{1}{2}\, exp(\delta/kT) + cosh\; g\alpha]$$

and

$$M = N\, g\beta sinh\; g\alpha/[cosh\; g\alpha + \tfrac{1}{2}\, exp(\delta/kT)]\,.$$

This formula fits the experimental results of *Becquerel* (*B15*) with a suitable choice of δ (δ = 0.30 cm^{-1}), which however is larger than the value obtained from resonance absorption (δ = 0.12 cm^{-1}, *Penrose* and *Stevens* (*P1*)). In low fields and at sufficiently high temperatures we have

$$M = (2N\, g^2\, \beta^2\, H/3kT)/(1 - 2\delta/3kT),$$

so that we have $B = -2\delta/3k$. Only at temperatures below about 4°K the influence of the splitting becomes noticeable.

According to (60) the specific heat in the absence of a magnetic field at temperatures for which $A \ll kT$ is given by

$$C_M = O(A^2/kT^2). \qquad (61)$$

It may be noted that for any system having lowest energy levels with a spacing much smaller than kT, while all other levels lie at distances much higher than kT, the specific heat is proportional to $1/T^2$. If M satisfies the *Curie*-law $M = CH/T$, we therefor can write (Cf. (27))

$$C_H = (b + CH^2)/T^2,$$

where b is a constant of the order A^2/k.

It it not difficult to calculate the complete expressions for C_M for different ions taking into account the splitting mentioned in 2.23. We only will summarize some results. For Cr^{+++} (in a trigonal field) we have

$$C_M = (Nk)\; \tfrac{1}{4}\; (\delta/kT)^2 + O\; (\delta/kT)^3 + \dots; \qquad (62)$$

for Fe^{+++} (in a field of lower symmetry than cubic) we have

$$C_M = (Nk)(2/9)(\delta_1^2 + \delta_2^2 - \delta_1\delta_2)/(kT)^2 + O(\delta/kT)^3 + \dots, \qquad (63)$$

where δ_1 and δ_2 are the distances of the two higher levels from the lowest level. In a purely cubic field $\delta_1 = \delta_2$ and the expression for C_M is simplified accordingly. Finally for Gd^{+++} we find

$$C_M = (Nk)(1/kT)^2 [¼ \sum_{i=1}^{3} \delta_i^2 - (1/16)(\sum_{i=1}^{3} \delta_i^2)] + O(\delta/kT)^3 + \ldots, \quad (64)$$

where δ_i are the distances to the lowest level. In the case of a cubic field this reduces to

$$C_M = (Nk)(33/256)(\delta_0/kT)^2 + O(\delta_0/kT)^3 + \ldots, \quad (65)$$

where δ_0 is the overall splitting. These formulae will be used in II, ch.II for calculating the splittings from data on the specific heat.

2.25 *Influence of the nuclear spin.*

In the considerations given so far the possible influence of a nuclear spin on the energy levels is neglected. The nuclei of many paramagnetic ions however possess a spin (compare Table V) and a brief discussion of its influence is necessary.

The interaction between the nucleus and the electron shell of a paramagnetic ion consists of two parts; a magnetic interaction between the nuclear magnetic moment and the magnetic field due to the spin of the electrons and the unquenched residual orbital momenta of the electrons, and an electric interaction between a nuclear quadrupole moment and the inhomogeneous electric field produced by the electronic charges of the ion and the other constituents of the crystal. These interactions cause a small splitting of the energy levels.

TABLE V

	Nuclear spin				
Z	Element	A	%	Spin	Column 1: 'Z' atomic number of element Column 2: 'Element' Chemical symbol Column 3: 'A' Mass number of isotope Column 4: '%' Percent abundance of isotope in naturally occurring element.
22	Ti	48	73.5		
23	V	51	100	7/2	
24	Cr	52	83.8		
25	Mn	55	100	5/2	
26	Fe	56	91.6		
27	Co	59	100	7/2	
28	Ni	58	67.4		
		60	26.7		
29	Cu	63	70.1	3/2	
		65	29.9	3/2	

The calculation of this hyperfine splitting is carried out along similar lines as in the case of free atoms. We have to add terms to the Hamiltonian (37) taking into account the interactions mentioned. In the case of ions of the iron group in a crystal **L** and **S** are decoupled and the Hamiltonian must contain terms allowing for the interaction of the nucleus with the orbital and spin magnetic moments separately. If μ_I **I** denotes the nuclear magnetic moment the magnetic interaction can be written in a first approximation

$$\mathcal{H}_{nucl} = \beta\mu_I\,(1/r^3)[(\mathbf{I},\mathbf{S}) - 3(\mathbf{Ir})(\mathbf{Sr})/r^2 - (\mathbf{I}\,\mathbf{L})]. \qquad (66)$$

An extra term, which is not given here, must be added if the nucleus has an electric quadrupole moment. The calculation of the matrix elements, which determine the splitting, is a difficult problem because a detailed knowledge of the orbital wave functions of the electrons is required. (If the symmetry of the crystalline field is known it is however possible to write (66) - after integration over the space coordinates - in a simpler form. For cylindrical symmetry we always can write

$$\mathcal{H}_{nucl} = A\,I_zS_z + B(I_x\,S_x + I_y\,S_y) + Q[I_z^2 - \tfrac{1}{3}\,I(I+1)]. \qquad (67)$$

where A, B and Q are constants, and the term with Q describes the influence of a quadrupole moment. This expression accounts for the observed hyperfine structure in different cases *(Bleaney* (B16)). The constants A, B and Q can then be determined directly by micro-wave observations.

The hyperfine splitting gives rise to an additional specific heat C_M, which for sufficiently high temperatures is given by

$$C_M T^2/R = (hc/k)^2[(1/9)(A^2+2B^2)S(S+1)I(I+1) +$$
$$+ (1/45)Q^2I(I+1)(2I-1)(2I+3)], \qquad (68)$$

where A, B and Q are in cm^{-1}. In different cases the agreement between the experimental values of the specific heat and the values calculated with (68)- using values of A,B and Q obtained from microwave experiments - is excellent. For details we refer to *Bleaney's* paper.

It can be shown that the hyperfine structure does not materially alter the term in $1/T$ in the expansion of the susceptibility and introduces no term in $(1/T^2)$ even for a single crystal.

2.3 Magnetic interaction.

2.31 *Introduction.*

In the previous considerations of this chapter we entirely neglected the possible influence of interaction between the paramagnetic ions. The question now arises in which cases this treatment can be justified. It will be remembered that the magnitude of the interactions mentioned in section 2.1, decreases with increasing distance between the magnetic ions. Therefore only for substances in which this distance in the average is sufficiently large it is allowed to neglect the interaction. In order to decide about this a measure indicating the strength of the interaction is required. A useful quantity is a field of magnitude H_i, if H_i^2 is the average of the square power of the magnitude of the field acting on a magnetic ion and caused by the other magnetic ions (cf. (83b)). In many rather strongly dilute salts like the alums and the Tutton salts, H_i is at least of the order of 100 Oersteds. From the considerations of this and following sections it will become clear, that in this case the influence of the interaction, for instance on the specific heat or resonance absorption lines, becomes perceptible.

Often however it is possible to reduce H_i by making mixed crystals, for instance of a paramagnetic alum with a suitable aluminium alum. As a matter of fact it is easily proved that in the mean $H_i \sim n$, where n is the number of magnetic ions per cm³. Therefore the preceding considerations are valid for paramagnetic alums or Tutton salts in which at least 90 % of the paramagnetic ions are replaced by diamagnetic ions.

In this section we propose to discuss some general aspects of the interaction between the magnetic ions. Some special points will be discussed in the chapters IV and V.

In order to take the interactions into account we have to supplement the Hamiltonian (36) with terms describing the interaction; we therefore shall write

$$\mathcal{H} = \sum_i \mathcal{H}_i + \sum_{i>i} W_{ij} , \tag{69}$$

where the second term indicates the interaction. The interaction can be written as the sum of two contributions, the coupling between the magnetic momenta of the ions - which is treated as a pure dipole-dipole coupling - and an exchange coupling between the ions, so that we have

$$W_{ij} = r_{ij}^{-3} \; [\mathbf{m}_i\mathbf{m}_j - 3(\mathbf{m}_i\mathbf{r}_{ij})(\mathbf{m}_j\mathbf{r}_{ij})/\mathbf{r}_{ij}^2] + V_{ij} , \tag{70}$$

where the first term denotes the magnetic interaction ($\mathbf{m}_i$ is the magnetic moment of the ion and $\mathbf{r}_{ij}$ is the radius vector between the ions i and j with the modulus r_{ij}) and the second term indicates the exchange interaction. We shall suppose that we can write for V_{ij}

$$V_{ij} = (A_{ij}/r_{ij}^3)(\mathbf{m}_i\mathbf{m}_j), \tag{71}$$

where (A_{ij}/r_{ij}^3) is a dimensionless scalar quantity proportional to the exchange integral between the ions. (This formulation allows the exchange interaction to be treated simultaneously with the magnetic interaction).

If for each of the N ions in a cubic centimetre we take into account n states, the Hamiltonian is a matrix of n^N rows and columns which is known in the representation corresponding to the case when the interaction is neglected. The calculation of the energy levels in the case of interaction involves the diagonalisation of this matrix. There can be little hope to carry this out. Fortunately, however, for finding the susceptibility and the specific heat this problem need not to be solved. We only require the partition function, which is the diagonal sum of $exp(-\mathcal{H}/kT)$. This diagonal sum does not depend on the system of wave-functions and therefore can be calculated in the original representation. We can now expand Z in a power series

$$Z = Sp\,[1 - \mathcal{H}/kT + \mathcal{H}^2/2(kT)^2 + \ldots], \tag{72}$$

so that

$$Z = n^N - (1/kT)\,Sp[\mathcal{H}] + (1/2(kT)^2)\,Sp[\mathcal{H}^2] + \ldots \tag{73}$$

In this way the problem is reduced to the calculation of the diagonal sum of powers of the Hamiltonian. This is comparatively simple for the lowest powers, but becomes very cumbersome for higher powers; this procedure therefore is only useful for sufficiently high temperatures where the series (72) converges rapidly.

2.32 Cases in which no electrical splitting occur.

1) Specific heat. The specific heat in the case when there is no applied field can be found by taking $H_0 = V_i = 0$, so that we can write for the Hamiltonian

$$\mathcal{H} = \Sigma\, W_{ij}\,.$$

The remaining terms in $\mathcal{H}$ only give rise to an additive constant in the energy and therefore can be omitted here. If only one multiplet component of the ions is active we can write for the magnetic moment

$$\mathbf{m} = g\beta\mathbf{J} \tag{74}$$

and consequently

$$W_{ij} = g^2\beta^2\, r_{ij}^{-3}\, [(1+A_{ij})(\mathbf{J}_i\mathbf{J}_j) - 3\,(\mathbf{J}_i\mathbf{r}_{ij})(\mathbf{J}_j\mathbf{r}_{ij})]. \tag{75}$$

Using the commutation rules of the components of the $\mathbf{J}_i$'s it can be shown that

$$Sp[\mathcal{H}] = 0 \tag{76}$$

and

$$Sp[\mathcal{H}^2] = (1/6)\, g^4\beta^4 J^2 (J+1)^2 N^3 Q, \tag{77}$$

where

$$Q = N^{-2}\, \Sigma_j\, r_{ij}^{-6}\, (A_{ij}^2 + 2). \tag{78}$$

Q can be calculated for cubic arrangements. Assuming that exchange interactions is confined to nearest neighbours, *Van Vleck* finds

$$\begin{array}{ll} \text{Simple cubic} & Q_{sc} = 12\,(1.40 + \tfrac{1}{2}A^2) \\ \text{Face centered cubic} & Q_{fc} = 12\,(1.20 + \tfrac{1}{2}A^2) \\ \text{Body centered cubic} & Q_{bc} = 256/27\,(1.53 + \tfrac{1}{2}A^2), \end{array} \tag{79}$$

where $A = A_{ij}$ for nearest neighbours.

In this approximation the partition function can be written

$$Z = n^N\,(1 + N\frac{\zeta^2}{T^2},\ \frac{Q}{12}), \tag{80}$$

where ζ is a quantity of the dimension of a temperature, defined by

$$\zeta = g^2 \beta^2 N J(J+1)/k. \tag{81}$$

The specific heat is given by

$$C_M = (Nk)\frac{Q}{6}\cdot\frac{\zeta^2}{T^2}. \tag{82}$$

The specific heat in a magnetic field now can be written if *Curie's* law is satisfied (cf. (27))

$$C_H = C(\tfrac{1}{2} H_i'^2 + H_o^2)/T^2 \tag{83}$$

where

$$H_i'^2 = 2g^2 \beta^2 J(J+1) \sum_{i>j} r_{ij}^{-6} (1+\tfrac{1}{2}A^2), \tag{83a}$$

and $C = \zeta/3$. H_i' can be interpreted as the effective magnetic field caused by the interactions between the magnetic ions.

It may be noted that exchange interaction increases the specific heat. The internal field H_i, introduced in section 2.31, is equal to the purely magnetic contributions to H_i', so that we have

$$H_i^2 = 2\, g^2\beta^2 J(J+1) \sum_{i>j} r_{ij}^{-6}\ . \tag{83b}$$

Van Vleck has also calculated the terms in the specific heat proportional to $(\zeta/T)^3$ and $(\zeta/T)^4$, which can be found in his paper. It is of some interest to note that the specific heat is independent of the shape of the body. This is a consequence of the fact that Q contains the distance between the ions to a high negative power, so that the influence of the ions at the boundary is entirely negligible. Moreover it may be noted that exchange interaction increases the specific heat.

With formula (82) it is not difficult to calculate the contribution of the dipole-dipole coupling to the specific heat. This can be done in the cases of Ti^{+++} and Cu^{++}, which ions do not have an electric splitting. According to *Hebb* and *Purcell* (H5) the calculated specific heat of titanium caesium alum agrees satisfactorily with the results of unpublished measurements of *Kurti* and *Simon*. In the case of copper, however, the specific heat calculated in this way is considerably smaller than the experimental values (cf. G 1). This must be due to the hyperfine structure, eventually combined with exchange interaction, or possibly to exchange interaction alone. This depends on the degree of dilution of the substance.

2) Susceptibility. The susceptibility can be found by including in the Hamiltonian the terms describing the influence of H. Now Z can be expanded in a power series in H

$$Z = Z^0\ (1+Z^{(2)}H^2 + \ldots). \tag{84}$$

For reasons of symmetry only even powers of H occur. *Van Vleck*, retainung terms until the fourth power in $1/T$ found for $Z^{(2)}$

$$Z^{(2)} = [\zeta/(6kT)^2][1+\tfrac{1}{3}\,\delta(\Phi-B)T^{-1} + (\tfrac{1}{3}\,\delta(\Phi-B))^2 - \gamma T^{-2}]\,. \qquad (85)$$

where ΦB and γ are constants. If H is directed along the z-axis Φ is given by

$$\Phi = -N^{-1}\sum_{i}\,[1-3\cos^2(z,r_{ij})]/r_{ij}^3\,. \qquad (86)$$

$M\Phi$ can be interpreted as the z-component of a magnetic field excerted on the i-th ion by a lattice carrying in every lattice point (except $i=j$) a dipole of the magnitude M/N directed parallel to the magnetic field. It is assumed that Φ is independent of the position of the ion i. This is correct for an ellipsoidal sample; $\Phi = 0$ for a spherical sample, because the mean value of $\cos^2(\mathbf{H},\mathbf{r}_{ij}) = 1/3$. We will see below that Φ is equal to the difference of the Lorentz factor and the demagnetisation coefficient.

B describes the influence of the exchange interaction; assuming that only exchange between nearest neighbours must to be taken into account and every ion has z nearest neighbours at a distance r, B is given by

$$B = Az/Nr^3\,. \qquad (87)$$

Finally γ is given by

$$\gamma = (Q\zeta^2/9\,[1+(3+3B/QZ)/8J(J+1)]\,. \qquad (88)$$

The magnetic moment is given by $I = 2kT\,Z^{(2)}H$ and consequently

$$I/H = \chi^0\,[1+(\Phi-B)\chi^0 + (\Phi-B)^2\chi^{0 2} - \gamma\,T^{-2}]\,, \qquad (89)$$

where we have written $\chi^0 = \zeta/3T$.

Comparison of (89) with the expressions (15) and (16) of the classical theory of magnetic interaction of *Lorentz* and *Onsager* respectively shows, that the classical expressions - apart from a possible 'exchange field', which adds an amount BI to the purely magnetic *Lorentz* field - agree with the rigourous expression up to the first power of Φ. Therefore the *Lorentz* formula describes the magnetic interaction correctly in the first approximation. In the second approximation however the *Lorentz* expression is no longer correct, and a term $-\gamma T^{-2}$ has to be added to the term $\Phi^2\chi^{0 2}$. The correction to the *Lorentz* formula given by *Onsager* $(-2(\frac{4\pi}{3}\chi^0)^2$ has to be replaced as well by the term $-\gamma T^{-2}$, which however is of the same order.

2.33 The influence of electrical splittings. The presence of electrical splittings complicates the situation considerably. Starting from a zero approximation in which the crystalline field and an external magnetic field was taken into account *Van Vleck* was able to calculate the partition function in the first approximation of the interaction. We shall not quote the complicated formulae of his paper, but only mention the most important results.

1) Specific heat. In the first approximation if there is no external field Z can be written in the form

$$Z = Z_o\,(1+N\Omega\zeta^2/T^2), \tag{90}$$

where Z_o is the partition function in the absence of the interaction. Ω is a complicated function, depending on the magnetic ions, crystal structure, the matrix elements of the magnetic moment in the crystalline field and A/kT, where A is a measure of the splitting. Ω has been calculated for several ions by *Hebb* and *Purcell* (*H*5). In the present approximation the specific heat is given by

$$C_M = (Nk)\,\frac{d}{dT}\,T^2\,\frac{d}{dT}\,\ln Z_o + (Nk)\zeta^2 T\,\frac{d^2}{dT^2}\,(\Omega/T), \tag{91}$$

where the first term denotes the specific heat if the interaction would be absent and the second term denotes the contribution of the interaction. At sufficiently high temperatures, where C_M is proportional to $1/T^2$, the second term of formula (91) approaches (82) ($\Omega\rightarrow Q/12$), so that in this case the specific heat is simply the sum of the electrical specific heat and the magnetic specific heat, calculated for ions without electrical splittings.

As an illustration we shall give the expressions for the specific heat in this case for some substances *neglecting the exchange*. Writing $C_M = b/T^2$ we get for Cr^{+++} in a chromium alum (compare (62) and (82))

$$b = (Nk)\,\tfrac{1}{4}\,(\delta/k)^2 + 2.40\,\zeta^2, \tag{92}$$

and for iron in iron ammonium alum (compare (63) and (82))

$$b = (Nk)\,\frac{2}{9}\,(\delta/k)^2 + 2.40\,\zeta^2, \tag{93}$$

where we have taken into account, that the magnetic ions are situated on a face centered cubic lattice (cf.(79)). Assuming the same situation for the Gd ions in gadolinium sulphate we find for this substance

$$b = (Nk)\,\frac{33}{256}\,(\delta_o/k)^2 + 2.40\,\zeta^2. \tag{94}$$

These formulae are useful for the calculation of the electrical splitting from specific heat data (see II, ch.II).

2) Susceptibility. Taking into account an external magnetic field *Van Vleck* calculated the magnetic moment. Again to a first approximation the influence of the magnetic interaction can be described with a *Lorentz* field; if exchange interaction is present an 'exchange field' has to be added to the *Lorentz* field. This result has been proved by *Van Vleck* in a very general way and remains correct also in the case of sa-

turation. The next approximation in general is extremely cumbersome to calculate. If therefore often is simpler to use the *Onsager* expression (16) which can be shown to be correct in the case when electrical splittings are present to the same degree of approximation as in the case when Stark splittings are absent. For a proof of this statement we refer to *Van Vleck's* paper.

It should be remembered that the theory reviewed in this section is only a reasonable approximation as long as the series expansions converge rapidly, or in other words at sufficiently high temperatures for substances in which the interaction between the magnetic ions is weak. The theory in other cases encounters great difficulties. The present theory however applies to the cases in which we are interested.

* * * *

Chapter III

THE MAGNETISATION IN AN ALTERNATING MAGNETIC FIELD

General remarks

3.1 Formal description.

A useful starting point for the treatment of the physical processes in which we are interested in this thesis is to consider a paramagnetic substance which is subjected to a magnetic field of the form:

$$\mathbf{H} = \mathbf{H}_c + \mathbf{h}\, \cos \omega t. \tag{95}$$

This is a superposition of a constant field $\mathbf{H}_c$ and an alternating field $\mathbf{h}$ with frequence $\omega/2\pi$; $\mathbf{h}$ and $\mathbf{H}_c$ may have different directions. It will be assumed henceforth that $h \ll H_c$ and moreover that h is so small that the induced magnetic moment varies harmonically as well. In this case we can write for the induced magnetic moment

$$\mathbf{M} = \mathbf{M}_c + \mathbf{m}' \cos \omega t + \mathbf{m}'' \sin \omega t. \tag{96}$$

In the general case of a magnetically anisotropic substance we have the relations (if we neglect saturation)

$$\begin{aligned} \mathbf{M}_c &= \chi_0\, \mathbf{H}_c \\ \mathbf{m}' &= \chi'\, \mathbf{h} \\ \mathbf{m}'' &= \chi''\, \mathbf{h}, \end{aligned} \tag{97}$$

where χ_0, χ' and χ'' are tensors of the second rank. χ' and χ'' are the tensors of the two components of the differential susceptibility. It should be noted that χ' and χ'' in general depend on the direction of $\mathbf{h}$ and $\mathbf{H}_c$, the magnitude of $\mathbf{H}_c$, the frequency and the absolute temperature. χ' is characteristic for the dispersion and χ'' is characteristic for the absorption in the alternating magnetic field.

It will be useful for the further considerations to split $\mathbf{h}$ into its components parallel and perpendicular to $\mathbf{H}_c$ and we therefore will write with obvious notation $\mathbf{h} = \mathbf{h}_{\parallel} + \mathbf{h}_{\perp}$. Then we have

$$\mathbf{M} = \mathbf{M}_c + (\mathbf{m}'_{\parallel} + \mathbf{m}'_{\perp}) \cos \omega t + (\mathbf{m}''_{\parallel} + \mathbf{m}''_{\perp}) \sin \omega t,$$

or

$$\mathbf{M} = \chi_0\, \mathbf{H}_c + (\chi'_{\parallel}\, \mathbf{h}_{\parallel} + \chi'_{\perp} \mathbf{h}_{\perp}) \cos \omega t + (\chi''_{\parallel}\, \mathbf{h}_{\parallel} + \chi''_{\perp}\, \mathbf{h}_{\perp}) \sin \omega t, \tag{98}$$

where $\chi'_{\parallel}$, $\chi'_{\perp}$, $\chi''_{\parallel}$ and $\chi''_{\perp}$ are again tensors in general.

Formula (98) is much simplified if $\mathbf{H}_c$ is directed along one of the principal axes of the magnetic polarisability. Then $\mathbf{m}'_{\parallel}$ is strictly parallel to $\mathbf{h}_{\parallel}$ (the same is valid for $\mathbf{m}''_{\parallel}$ and $\mathbf{h}_{\parallel}$), so that $\chi'_{\parallel}$ and $\chi''_{\parallel}$ can be treated as constants; in first approximation the same is valid for $\chi'_{\perp}$ and $\chi''_{\perp}$. In the case of a magnetically isotropic substance (or a powder) all χ's in (98) clearly can be treated as constants. We shall confine ourselves to these cases, and thus shall regard the χ's as scalars depending on H_c, T and the frequency.

It is sometimes advantageous to introduce the complex notations

$$\chi_{\parallel} = \chi'_{\parallel} - i\chi''_{\parallel} \qquad \chi_{\perp} = \chi'_{\perp} - i\chi''_{\perp}. \tag{99}$$

Then we can write instead of (95) and (96)

$$\mathbf{H} = \mathbf{H}_c + (\mathbf{h}_{\parallel} + \mathbf{h}_{\perp})e^{i\omega t} \tag{100}$$

and

$$\mathbf{M} = \mathbf{M}_c + (\chi_{\parallel}\mathbf{h}_{\parallel} + \chi_{\perp}\mathbf{h}_{\perp})e^{i\omega t}, \tag{101}$$

while the relation with (95) and (96) is given by

$$\mathbf{h} = \mathbf{h}_{\parallel} + \mathbf{h}_{\perp} = Re[\mathbf{h}\ exp(i\omega t)]. \tag{100a}$$

$$\mathbf{m} = \mathbf{m}_{\parallel} + \mathbf{m}_{\perp} = Re[\chi\ \mathbf{h}\ exp(i\omega t)]. \tag{101a}$$

In the remainder of this section we will omit the subscribts $_{\parallel}$ and $_{\perp}$. It should be understood that all formulae are valid for both $\chi_{\parallel}$ and $\chi_{\perp}$.

Without a detailed picture of the physical processes it is not possible to give a formulation of χ' and χ'' as a function of $\mathbf{H}$, T and $\nu = \omega/2\pi$. It is however obvious that at very low frequencies χ is equal to the static susceptibility χ_0 and that χ'' will be zero. Irrespective of the course of χ' and χ'' as a function of ν it can be shown that χ' and χ'' are mutually related by the *Kramers-Kronig* relations

$$\begin{aligned} \chi'(\nu_0) &= \frac{2}{\pi}\int_0^\infty \frac{\nu\,\chi''(\nu)}{\nu^2 - \nu_0^2}\,d\nu \\ \chi''(\nu_0) &= -\frac{2}{\pi}\int_0^\infty \frac{\nu_0\,\chi'(\nu)}{\nu^2 - \nu_0^2}\,d\nu, \end{aligned} \tag{102}$$

so that, if one of the components of the susceptibility is known as a function of frequency, the other is determined as well. Condition for the validity of these formulae is that $\chi(\nu)$ is an analytic function of ν which has no poles in the lower half of the complex ν-plane. They can be derived according to *Schouten* (cf. K10) from the plausible assumption that, if $\mathbf{H}$ is constant until a given moment and from then on has a slightly different value, the magnetic moment will have a constant value until the same moment.

The dependence of χ' and χ'' on the frequency can be very different. In different important cases χ'' has a well defined maximum at a certain frequency. Then χ' varies strongly at that frequency. A simple example is the *Debye*-function (cf. Chapter IV)

$$\chi = \frac{\chi_0}{1+i\rho\nu}, \tag{103}$$

which is equivalent to

$$\chi' = \frac{\chi_0}{1+\rho^2\nu^2}$$
$$\chi'' = \frac{\chi_0\rho\nu}{1+\rho^2\nu^2}. \qquad (104)$$

Another example is the friction damped magnetic oscillator

$$\chi = \chi_0 \frac{\nu_0^2}{\nu_0^2 - \nu^2 + i\nu_0^2\rho\nu}, \qquad (105)$$

which gives

$$\chi' = \chi_0 \frac{\nu_0^2(\nu_0^2 - \nu^2)}{(\nu_0^2 - \nu^2)^2 + \nu_0^4\rho^2\nu^2}$$

$$\chi'' = \chi_0 \frac{\nu_0^4\rho\nu}{(\nu_0^2 - \nu^2)^2 + \nu_0^2\rho^2\nu^2}; \qquad (106)$$

here ν_0 is the resonant frequency of the undamped oscillator.

A third example is the collision damped magnetic oscillator *(Fröhlich-Van Vleck-Weiskopff*'s formula, cf. Chapter V)

$$\chi = \chi_0 \frac{\rho^2\nu_0^2 + (1+i\rho\nu)}{\rho\,\nu_0^2 + (1+i\rho\nu)^2} \qquad (107)$$

which is equivalent to

$$\chi' = \frac{\chi_0}{2}\left[\frac{1 + \nu_0\,(\nu+\nu_0)\rho^2}{1 + (\nu+\nu_0)^2\rho^2} + \frac{1 - \nu_0(\nu-\nu_0)\rho^2}{1 + (\nu-\nu_0)^2\rho^2}\right] \qquad (108)$$

$$\chi'' = \frac{\chi_0}{2}\left[\frac{\rho\nu}{1 + (\nu+\nu_0)^2\rho^2} + \frac{\rho\nu}{1 + (\nu-\nu_0)^2\rho^2}\right].$$

It finally may be remarked that, if $m' \neq 0$ in (96) energy is absorbed; the amount of energy absorbed per second is given by

$$W = -\nu\oint M dH = \pi\nu\chi''\,h^2. \qquad (109)$$

3.2 Physical processes.

The considerations in the preceding section are purely formal or in other words the physical background of the phenomena discussed was not analysed. In this section we will consider this background from a general point of view.

To this end we will consider the spin system. This is composed of the atomic magnetic momenta - as they are established under the influence of the static interaction with the lattice - with their mutual interaction (dipole-dipole and if necessary exchange interaction). The spin system naturally has a very large number of degrees of freedom and its average properties best can be described by a properly chosen canonical ensemble. The temperature T_s characteristic for this ensemble usually is called the spin temperature. The spin-system is weakly coupled to the system of lattice vibrations. This coupling, although weak, will prove to be essential for different phenomena.

We now will assume that the substance is subjected to a magnetic field of the form (100). Then the processes leading to an absorption of energy can be devided into two groups.

3.21 Energy absorption governed by the non-diagonal elements of $\mathbf{M}$.

To begin with we shall neglect the coupling between the spin-system and the lattice. If the frequency of the alternating component of the magnetic field is very low, the system will be after a number of periods in the same state as before. Then the field varies adiabatically in *Ehrenfest's* sence. If, however, the frequency of the alternating field is higher there will be a finite probability that the system after a number of periods has made a transition from the original state *m* to a new state *n*. The probability for such a transition is proportional to $|M_{mn}|^2$, where M_{mn} is the non-diagonal element of the magnetic moment of the spin-system in the direction of the alternating field.

It is instructive to consider this absorption somewhat closer in the case of a system of pure spins without mutual interaction; for simplicity we shall assume that we have spins with $S = 1/2$. The Hamiltonian in a magnetic field is

$$\mathcal{H} = g\,\beta\,\mathbf{H}_c \sum_i \sigma_i ,$$

where $\hbar\,\sigma_i$ is the operator of the angular momentum of the i-th spin, and the energy levels are

$$E_n = ng\beta H_c ,$$

where $n = N^+ - N^-$ is the difference between the number of spins which are parallel or antiparallel to $\mathbf{H}_c$; the levels are equidistant with a spacing $g\beta H$, and the degeneracy of a level n is given by $N!/N^+!N^-!$, where N is the number of spins and $N = N^+ + N^-$.

We next have to consider the possible transitions between the levels. This is most conveniently done by taking $\mathbf{H}$ parallel to the z-axis. Then a wavefunction belonging to E_n may be given by

$$\psi_n = \prod_i \eta_i^{(s_i)}$$

where $\eta_i^{(s_i)}$ is the spin function of the i-th spin, which corresponds to an angular momentum in the direction of the z-axis of $\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$ if $s_i = +\frac{1}{2}$ resp. $-\frac{1}{2}$. In the expression N^+ of the indices s_i are $+\frac{1}{2}$ and N^- are $-\frac{1}{2}$. The operator of the magnetic moment is given by

$$\mathbf{M} = \beta \Sigma \sigma_i .$$

The straight forward calculation of the matrix elements components of **M** yields the result $(M_z)_{nn'} = 0$ for all values of n and n', except for $n' = n$ and both $(M_x)_{nn'}$ and $(M_y)_{nn'}$ are zero, except for $n' = n \pm 1$. Two important conclusions can be drawn from this result. First that only transitions between adjacent levels are allowed, so that, because the levels are equidistant, absorption only occurs at one frequency. The allowed transitions correspond to the 'turning over' of one spin. Secondly that only radiation can be absorbed which is polarised in the xy-plane, or, in other words, the alternating field must be perpendicular to the constant field. Therefore this kind of absorption and the corresponding dispersion can be described with $\chi'_\perp$ and $\chi''_\perp$ in the formulae of the preceding section, and is nothing else than the paramagnetic resonance absorption, which we will discuss in greater detail in Chapter V. In zero constant field - as long as we neglect the interaction between the spins - frequency of the absorption is zero. This can be expressed by saying that in zero field no work is required for turning over a spin.

Until now we neglected the interaction of the spin-system with the lattice, which is justified because the discussed absorption is independent of the interaction with the lattice. On the other hand it should be remembered, that some interaction of the spins with their surroundings is required for carrying away the absorbed energy, which otherwise would be stored up in the spin-system, causing an increase of the spin-temperatures. Although this interaction in general is weak, it is usually sufficient for making the rise of the spin-temperature negligible. If the rise of the spin-temperature is not negligible - which in principle always can be reached by increasing the intensity of the alternating field sufficiently - the difference in population of the levels between which the transitions take place decreases and therefore the intensity of the absorption decreases as well. This effect sometimes can be used for determining the spin-lattice relaxation time which is a useful measure for the strength of the spin-lattice interaction (cf. Part II, Chapter I).

If now the alternating field is parallel to the constant field, **M** has only diagonal elements and there will be no absorption if we neglect the interaction between the spins. If this spin-spin interaction is present non-diagonal elements of **M** occur and consequently absorption is found. This absorption is called spin-absorption, and is governed by a relaxation constant which is independent of T. As a consequence of the spin-spin interaction even in zero external field absorption occurs.

3.22 Energy absorption governed by the diagonal elements of **M**.

For the discussion of this effect we consider again the spin-system in a constant magnetic field. The probability to find the system in a stationary state is proportional to the *Boltzmann*-factor $exp(-E_n/kT)$, where we assume that the temperature of the spins is equal to the temperatures of the lattice.

If we apply an extra field **h** every energy level is shifted by $-M_{nn}[h]$, where $[h]$ is the increase in the magnitude of $\mathbf{H}_c$. Assuming that the spin-system is completely isolated and that the change of field is adiabatical in *Ehrenfest's* sense, we can conclude that the occupation of a level with the energy $E_n - M_{nn}[h]$ is the same as the occupation of the level E_n previously. This distribution not necessarily is again a *Boltzmann* distribution (cf. 4.22), which would allow to describe the new situation in terms of a different spin-temperature, but is certainly different from a *Boltzmann* distribution over the energy levels $E_n - M_{nn}[h]$ corresponding to the lattice temperature T. Establishment of this latter distribution only is possible if the spin-system can make transitions in which a change of energy is involved. Transitions of the spin-system are possible as a consequence of the interaction of the spin-system with the radiation field and with the lattice vibrations; the interaction with the lattice vibrations in mainly responsible for these transitions. During the process of redistribution energy is exchanged between the spin-system and the lattice. If the additional field varies harmonically with a very low frequency the total heat exchange per period is zero; this is no longer the case if the frequency is so high, that the occupation of the levels lags behind the alternating field as a consequence of the too slow exchange of energy. This process is called absorption by spin-lattice relaxation, and will be considered in more detail in Chapter IV.

It is important to note that the effect depends on the variation of the magnitude of the magnetic field for a given direction of the constant field. Therefore the effect is maximal if **h** is parallel to $\mathbf{H}_c$ and negligible if **h** is chosen perpendicular to $\mathbf{H}_c$. Consequently $\chi'_{\parallel}$ and $\chi''_{\parallel}$ in formula (98) account for the spin-lattice relaxation, apart from a usually small contribution of the spin-spin relaxation. From an experimental point of view these two effects nearly always can be separated.

* * * *

Chapter IV

THE THEORY OF SPIN-LATTICE RELAXATION

4.1 Introduction.

The program of a theory of spin-lattice relaxation can be devided in two parts. In the first place the dependence of χ' and χ'' on the frequency of the alternating field for given values of H_c and T should be explained. The relaxation constant or the relaxation constants in this stage occur as parameters, which have to be chosen in such a way that the theoretical values of χ' and χ'' agree with the experimental values. In the second place the values of the relaxation constant obtained for different values of H_c and T must be explained.

We propose to discuss in this chapter both parts of the theory of spin-lattice relaxation.

4.2 Thermodynamic theory.

In order to derive expressions for χ' and χ'' as a function of ν it is useful to start from the following picture. A paramagnetic substance which may be in heat contact with its environnement, for instance a liquified gas, can be regarded as a complex of weakly coupled systems. The spin-system is coupled to the - thermodynamic - system of the lattice vibrations; the latter system on its turn may be coupled with the liquid bath, which we shall suppose to have an infinitely large heat capacity. The temperature of the bath may be T_0. This picture is slightly more general than the picture of *Casimir* and *Du Pré* (C6) and than the more detailed picture of *Casimir* (C7); the results of both authors are contained in our more general formulae, as will be shown below.

The problem is now to calculate χ' and χ'' if the ions in the paramagnetic substance are subjected to a magnetic field $\mathbf{H}$ of the form

$$\mathbf{H} = \mathbf{H}_c + \mathbf{h}\, exp(i\omega t), \tag{110}$$

where we assume that $\mathbf{h}$ has the same direction as $\mathbf{H}_c$ and moreover that $h \ll H_c$. The basic assumptions of the thermodynamic theory now are

a) The spin-system is in thermodynamic equilibrium all the time. This condition shall be warranted if the time required for establishing the equilibrium in the spin-system is short compared with the time required for the establishment of the equilibrium between the spin-system and the lattice, and if the applied frequency is small enough so that the external conditions do not change appreciably during the time the spin-system establishes its equilibrium. This assumption has been introduced for the first time by *Casimir* and *Du Pré*; a discussion will be given in section 4.22.

b) The system of the lattice vibrations is in thermodynamic equilibrium all the time.

c) The substance is isotropic and homogeneous.

The assumptions a) and b) imply that there are all the time well defined temperatures of the spin-system and the lattice, and that thermodynamics can be applied. If there is a sufficiently small temperature difference between the spin-system and the lattice the amount of heat exchanged between these systems will be proportional to the temperature difference. Therefore the amount of heat absorbed by the spin-system in a short time dt is given by

$$dQ = \alpha_1\ (T_L - T_S)dt, \tag{111}$$

where T_S and T_L are the temperature of the spin-system and the lattice resp., and where the proportionality factor α_1 can be called the heat contact. The dimension of α_1 is cal sec^{-1} degree^{-1}vol^{-1}, which is different from a heatconductivity. Moreover we have for the spin-system (Cf. (28))

$$dQ = C_H\left(\frac{\partial T}{\partial M}\right)_H dM + C_M\left(\frac{\partial T}{\partial H}\right)_M dH. \tag{112}$$

Similarly the amount of heat absorbed by the lattice from the heat reservoir is proportional to the temperature difference between the heat reservoir and the lattice. Taking into account the heat exchange between the lattice and the spin-system we have

$$\alpha_1 (T_S - T_L)\ dt + \alpha_2\ (T_0 - T_L)dt = C_L dT_L. \tag{113}$$

Here α_2 is the heat contact between the lattice and the heat reservoir, and C_L is the specific heat of the lattice. We finally have the relation

$$T_S - T_0 = \left(\frac{\partial T}{\partial M}\right)_H dM + \left(\frac{\partial T}{\partial H}\right)_M dH. \tag{114}$$

We shall now assume a magnetic field of the form (110).
Writing $\Theta = T_S - T_L$ and $\Theta_L = T_L - T_0$ we can put

$$M = M_0 + m\ exp(i\omega t)$$
$$\Theta = \Theta_0\ exp(i\omega t)$$
$$\Theta_L = \Theta_{L_0}\ exp(i\omega t).$$

From (111), (112), (113) and (114) we easily derive the relations

$$-\alpha_1\Theta_0 = i\omega\left[C_H\left(\frac{\partial T}{\partial M}\right)_H m + C_M\left(\frac{\partial T}{\partial H}\right)_M h\right]$$

$$\Theta_0 = \left[\frac{\alpha_2}{\alpha_1} + \frac{i\omega C_L}{\alpha_1}\right]\Theta_{L_0}$$

$$\Theta_0 + \Theta_{L_0} = \left(\frac{\partial T}{\partial M}\right)_H m + \left(\frac{\partial T}{\partial H}\right)_M h.$$

Elimination of Θ_o and Θ_{L_o} yields after some calculation the following expression for χ

$$\chi = \chi_0 \frac{i\omega\left(1 + \frac{\alpha_2}{i\omega C_L}\right) C_M + \alpha_1 \left(1 + \frac{C_M}{C_L} + \frac{\alpha_2}{i\omega C_L}\right)}{i\omega\left(1 + \frac{\alpha_2}{i\omega C_L}\right) C_H + \alpha_1 \left(1 + \frac{C_H}{C_L} + \frac{\alpha_2}{i\omega C_L}\right)}\,, \tag{115}$$

where we have written $\chi_0=(\partial M/\partial H)_T$; χ_0 is the isothermal differential susceptibility which is equal to the static susceptibility if saturation can be neglected.

Of course it is possible to separate the right hand side of (115) in its real and imaginary part, and thus to obtain χ' and χ''. The resulting formulae however become very complicated and it is difficult to work with them. In this thesis however we only are interested into some limiting cases and we confine ourselves to a discussion of these aspects.

a) If the heat contact between the lattice and the heat reservoir is very good, so that the lattice virtually acts as a thermostat with the temperature of the heat reservoir, we can take $\alpha_2 = \infty$. Then we have

$$\chi = \chi_0 \frac{i\omega C_M + \alpha_1}{i\omega C_H + \alpha_1}\,. \tag{116}$$

If we split this expression into its real and imaginary part we obtain

$$\chi'/\chi_0 = (1-F) + \frac{F}{1+\rho^2\nu^2} \tag{117a}$$

$$\chi''/\chi_0 = F\frac{\rho\nu}{1+\rho^2\nu^2} \tag{117b}$$

with
$$F = (C_H - C_M)/C_H \tag{118}$$

and
$$\rho = 2\pi C_H/\alpha_1. \tag{119}$$

An alternative form of the formulae (117) is found by introducing $y = ln\rho\nu$; then we have

$$\chi'/\chi_0 = (1 - F) + \tfrac{1}{2} F\,(1 - tgh\ y) \tag{120a}$$
$$\chi''/\chi_0 = \tfrac{1}{2} F\ sech\ y. \tag{120b}$$

These formulae are illustrated by fig. 7b. These expressions for χ'/χ_0 and χ''/χ_0 will be called the *thermodynamic formulae.* According to these formulae χ'/χ_0 is represented by a constant term plus a simple *Debye* curve, and is one for $\nu = 0$ and decreases for increasing ν reaching a constant value $\chi_\infty/\chi_0 = (1-F)$ for very high frequencies; the curve has a point of inflexion for $\rho\nu = 1$, which is identical with the value of ν for which $\chi'/\chi_0 = 1-\tfrac{1}{2}(1-F)$. χ''/χ_0 is represented by a bell-shaped curve having a maximal value $\tfrac{1}{2}F$ for $\rho\nu = 1$. It is easily seen from (120a) that the slope for $y = 0$ in a χ'/χ_0 versus $ln\ \nu$ plot is $-F/2$ and in a χ'/χ_0 versus $log\ \nu$ plot is $-1.15F$. From (120b) it can be concluded that the width at half the maximum value of

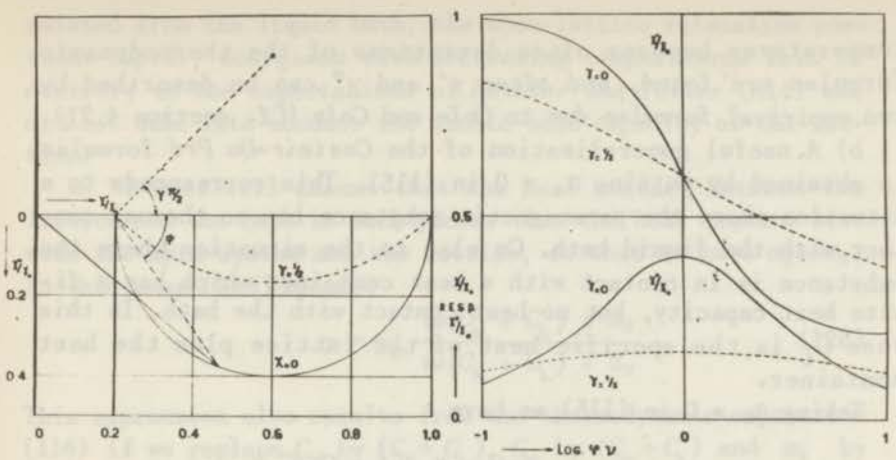

Fig. 7. The components of the susceptibility.
Thermodynamic formulae (117); F=0.8
Cole's formulae (129); F=0.8, γ=½.

the χ''/χ_0 versus *ln* ν plot is 2.64 and of the χ''/χ_0 versus *log* ν plot 1.14. (Here we have written *ln* for the natural and *log* for the briggian logarithm.)

It is easily seen that

$$\chi'_{\infty}/\chi_0 = (1-F) = C_M/C_H,$$

so that in tis case $\chi' = \chi'_{\infty} = \chi_{ad}$ (Cf. (30)); this result is obvious, because at high frequencies the heat contact is too weak and the process will be practically adiabatic. It is easily concluded from (117) that χ' and χ'', measured for the same H_c and T satisfy the relation

$$[\chi' - \tfrac{1}{2}(\chi_0 + \chi_{ad})]^2 + \chi''^2 = \tfrac{1}{4}(\chi_0 - \chi_{ad})^2, \qquad (121a)$$

so that the χ'' versus χ' plot is a semicircle with centre on the χ'-axis and passing through the points χ_0 and χ_{ad} on that axis (fig. 7a). Moreover we have

$$\mathrm{tg}\ \psi = \rho\nu. \qquad (121b)$$

In the case that $M = f(H/T)$ (Cf. 61a) we have

$$F = f' H^2/(b + f' H^2), \qquad (122)$$

which becomes

$$F = CH^2/(b + CH^2) \qquad (123)$$

if the magnetic moment satisfies *Curie*'s law $M = CH/T$. This formula has been derived the first time by *Casimir* and *Du Pré* and may be called the *Casimir-Du Pré* formula; it is very useful for determining b/C. It is sometimes useful to introduce a symbol for the fieldstrength H_h making $F = \tfrac{1}{2}$; according to (123) we have $H_h^2 = b/C$.

It finally may be noted that the formulae (117) often give a satisfactory description of the dependence of χ' and χ'' on the frequency at constant H_c and T, and then enable a determination of the relaxation constant for given H_c and T. At low temperatures however often deviations of the thermodynamic formulae are found, and often χ' and χ'' can be described by two empirical formulae due to *Cole* and *Cole* (Cf. section 4.21).

b) A useful generalisation of the *Casimir-Du Pré* formulae is obtained by putting $\alpha_2 = 0$ in (115). This corresponds to a situation where the paramagnetic substance has no thermal contact with the liquid bath. Or else to the situation where the substance is in contact with a heat container which has a finite heat capacity, but no heat contact with the bath. In this case C_L is the specific heat of the lattice plus the heat container.

Taking $\alpha_2 = 0$ in (115) we have

$$\chi = \chi_0 \frac{i\omega C_M + \alpha_1 \; (1 + C_M/C_L)}{i\omega C_H + \alpha_1 \; (1 + C_H/C_L)}, \tag{124}$$

which can be split into its real and imaginary part

$$\chi'/\chi_0 = (1-F) + (\frac{C_L}{C_H + C_L}) \frac{F}{1 + \rho_1^2 \, \nu^2} \tag{125a}$$

$$\chi''/\chi_0 = (\frac{C_L}{C_H + C_L}) \frac{F\rho_1 \nu}{1 + \rho_1{}^2 \nu^2}, \tag{125b}$$

where F is the same as before and ρ_1 is given by

$$\rho_1 = \frac{C_L}{C_H + C_L} \; \frac{2\omega C_H}{\alpha_1} = \frac{C_L}{C_H + C_L} \, \rho \, . \tag{126}$$

These formulae only differ from (117), (119) in that the relaxation constant is smaller by a factor $C_L/(C_H + C_L)$ and that the part of the magnetisation that is dependent on ν is smaller by the same factor.

As one should expect at high frequencies $\chi'/\chi_0 = 1-F$ as before, but at low frequencies ($\rho\nu \rightarrow 0$) we get

$$\chi'/\chi_0 = 1-F \, C_H/(C_H+C_L). \qquad \text{(127}$$

This formula could be applied to a determination of the specific heat of the lattice or the specific heat of a substance which is brought into good heat contact with the paramagnetic substance. We only need to measure χ'/χ_0 at very low frequency (for instance ballistically) for given value of the constant field, if we take a paramagnetic substance for which F and C_H are known. Experiments of this kind are in course of preparation at Leiden by *L.C.v.d.Marel*, phys. cand..

It may be added that *Casimir* (C7), who derived (126) for the first time, pointed out that in adiabatic demagnetisation experiments, where the paramagnetic substance is thermally insulated from the liquid bath, the spin-lattice relaxation constant rapidly decreases with decreasing temperature. This is contrary to the expectations of *Heitler* and *Teller* (H14) who did not take into account the finite heat capacity of the lattice.

b) We next will assume that the heat contact between the lattice and the bath is much poorer than the heat contact between the spin-system and the lattice, so that we have $\alpha_1 >> \alpha_2$. In this case (115) becomes

$$\chi = \chi_0 \frac{i\omega(C_M + C_L) + \alpha_2}{i\omega(C_H + C_L) + \alpha_2} . \tag{128}$$

This expression also results from the thermodynamic expression (116) if we replace C_H by $(C_H + C_L)$, C_M by $(C_M + C_L)$ and α_1 by α_2. The behaviour of χ' and χ'' as a function of the frequency is formally the same as in case a) and the formulae (117) apply if we replace F by $(C_H - C_M)/(C_H + C_L)$ and ρ by $\rho_2 = 2\pi(C_H + C_L)/\alpha_2$.

These considerations show that a poor heat contact between the substance and the bath can cause a relaxation effect, which however should be distinguished from paramagnetic relaxation. This spurious relaxation effect can be avoided by a good heat contact of the sample with the bath. This can accomplished by taking a sample of small crystals, which are immersed in the cooling liquid. *De Haas* and *Du Pré* (H11) proved the existence of the spurious relaxation effect by examining titanium caesium alum. This substance has a so short lattice relaxation time, that at liquid helium temperatures no relaxation is observed with the normal means (Cf. Part II) if the sample is immersed in the liquid. If the substance is sealed in a glass vessel containing a very small amount of helium gas as well, a relaxation effect was observed, which must be due to the much poorer heat contact in the second case. The heat contact in the first case apparently is so good that the lattice has virtually the same temperature as the bath. This probably will not be very different in other cases. From a theoretical point of view however the good heat contact between the salt and the bath is very puzzling *(Van Vleck* (V12)).

4.21 Deviations from the thermodynamic formulae.

In several cases however there is no satisfactory agreement between the experimental results and the formulae (117) or (120), as the experimental curves of both types are flatter than the theoretical curves. It is possible to use the difference between the slope of the observed χ'/χ_0 versus *log* ν curve in the point of inflexion and the value predicted by (117) or (120), or the difference between the observed and predicted width at half the maximum value of the χ''/χ_0 versus *log* ν curve, as a measure for the deviation from the formulae (117) or (120). In several cases an other description is possible, which presumably can be interpreted physically and therefore is preferred here. Often the χ'' versus χ' plot is still a circular arc passing through the points $\chi' = \chi_0$ and $\chi' = \chi_\infty$ on the χ'-axis, but now with its centre above the χ'-axis (compare fig. 7a).

According to *Cole* and *Cole* (C8) in this case (117a) and (117b) can be replaced by

$$\chi'/\chi_0 = (1-F) + \frac{F}{2}\left[1 - \frac{\sinh (1-\gamma)y}{\cosh (1-\gamma)y + \sin \tfrac{1}{2}\gamma\pi}\right] \qquad (129a)$$

$$\chi''/\chi_0 = \frac{F}{2}\,\frac{\cos \tfrac{1}{2}\gamma\pi}{\cosh (1-\gamma)y + \sin \tfrac{1}{2}\gamma\pi},$$

where $\frac{1}{2}\gamma\pi$ = the acute angle between the χ'-axis and the radius of the arc drawn to the point $\chi' = \chi_\infty$ (Cf. fig. 7b). For $\gamma = 0$ (129a) and (129b) are identical with (120a) and (120b) resp.; F of course is given by (118). Both $\frac{1}{2}\gamma\pi$ and γ are a measure of the deviation from the thermodynamic formulae (117) or (120).

An alternative way of formal description is found by assuming the existence of a continuous distribution of relaxation constants rather than one relaxation constant as occurs in the theory of *Casimir* and *Du Pré*. As *Fuoss* and *Kirkwood* (F5) have shown it is possible to calculate the required distribution for any observed χ''-frequency relation. In the present case the distribution function G is given by

$$G(s)ds = \frac{1}{2\pi}\,\frac{\sin \gamma\pi}{\cosh (1-\gamma)s - \cos \gamma\pi}\,ds, \qquad (130)$$

where $s = \log (\rho/\rho_{av})$. G has a maximum for $\rho = \rho_{av}$; ρ_{av} is the mean value of the relaxation constants, which can be calculated from the experimental results in the same way as ρ can be calculated (Cf. page 58). Compared with a Gaussian curve the curve (130) is sharper peaked near the maximum, but tails off slower.

The width of the distribution curve can be described with the ratio $\rho_{\frac{1}{2}}/\rho_{av}$ where $\rho_{\frac{1}{2}}$ is the highest value of ρ for which the value of G is half the maximum value; $\rho_{\frac{1}{2}}$ is determined by the equation

$$2 - \cos \gamma\pi = \cosh (1-\gamma)\, \ln (\rho_{\frac{1}{2}}/\rho_{av}). \qquad (131)$$

It seems to be reasonable to assume the existence of a distribution of relaxation times in the case of an imperfect crystal. Only a detailed theory, however, could explain the shape and the dependence on H_c and T - found experimentally - of this distribution.

It may be added that in all cases investigated χ'/χ_0 approaches a finite limiting value χ_∞ for high frequencies, irrespective of the details of the frequency dependence; χ''/χ_0 always approaches zero for high frequencies.

4.22 The assumption of thermodynamical equilibrium of the spin-system.

In this section we will discuss briefly the not altogether trivial first assumption (compare page 56) of the thermodynamic theory. It will be clear from the considerations given so far that χ_∞ is the differential susceptibility of the spin-system in a situation in which there is no interaction with the lattice vibrations; this statement is correct irrespective of the details of the dispersion and absorption.

According to the thermodynamic theory we have

$$\chi_\infty/\chi_0 = \chi_{ad}/\chi_0 = b/(b+CH_c^{\,2}).$$

This formulation implies that the spin-system is in thermodynamical equilibrium. An alternative point of view is to regard χ_∞ as the contribution to the susceptibility $\chi = (\partial M/\partial H_c)_T$, obtained upon differentiation of the magnetic moment, given by (34a) keeping the factors $exp(-E_n/kT)$ constant and differentiating only with respect to H_c. This implies that the occupation of the energy levels of the spin-system is independent of a variation of H_c. As we pointed out in section 3.22 this is the case if the spin-system is isolated from the lattice and therefore the susceptibility obtained here may be called the isolated susceptibility χ_{iso}.

The question at once arises wether χ_{ad} and χ_{iso} are equal. This would be the case if the thermodynamical equilibrium of the spin-system in a given state would not be affected by a changed of H_c. According to *Van Vleck* (mentioned by Miss *Wright* (W4)) however only under special circumstances χ_{ad} can be equal to χ_{iso}. This seems to invalidate *Broer's* considerations who aimed to show that the spin-system always remains virtually in a state of thermodynamical equilibrium after a small change of H_c (B16).

Miss *Wright* and *Broer* (Cf. (W4)) considered the simple case of a system of spinss with arbitrary S. In this case χ_{iso} in high fields, neglecting saturation and exchange, is given by

$$\chi_{iso}/\chi_0 = 0.80\; H_i^2/2H_c^2,$$

where H_i is given by (83b) with $J = S$. According to the thermodynamic theory we have (compare (83))

$$\chi_{ad}/\chi_0 = H_i^2/2H_c^2.$$

Obviously it is of great interest to examine the experimental values of χ_∞ as a function of H_c, as this may allow to conclude wether from an experimental point of view χ_∞ is equal to χ_{ad} or to χ_{iso}. This problem will be considered in Part II, 3.3. Here we can confine ourselves to the remark that at present there seems to be no convincing experimental reason for abandoning the interpretation of χ_∞ according to the thermodynamic theory and consequently the subsequent considerations are based on the assumption that thermodynamic equilibrium of the spin-system is maintained at all moments.

4.3 The theory of the relaxation constant.

4.31 The nature of ρ.

As we have seen in the thermodynamic theory the relaxation constant occurs as a quantity which has to be chosen in order to obtain the best fit of the theoretical results with the experimental data. Therefore within the scope of the thermodynamical theory no evaluation of ρ is possible. A more detailed consideration of the interaction between the spin-system and the lattice is required for this. Assuming that this interaction causes spontaneous transitions between the energy levels of the spin-system it is not difficult to express α_1 and hence ρ (Cf. (119)) in terms of the probabilities of these transitions (G1).

If we call A_{hk} the probability of a transition from level *h* to *k*, than we have in case of thermal equilibrium

$$N_h A_{hk} - N_k A_{kh} = 0, \qquad (132)$$

where N_h and N_k are the occupations of the levels; N_h and N_k must obey the *Boltzmann* distribution. Hence we have

$$N_h = \bar{N}_{hk}\ exp\ (\frac{E_h - E_k}{2kT}) \qquad N_k = \bar{N}_{hk}\ exp\ (\frac{E_k - E_h}{2kT})$$

and

$$A_{hk} = \bar{A}_{hk}\ exp\ (\frac{E_h - E_k}{2kT}) \qquad A_{kh} = \bar{A}_{hk}\ exp\ (\frac{E_k - E_h}{2kT}),$$

where we have written

$$\bar{N}_{hk} = \tfrac{1}{2}\,(N_h + N_k) \qquad \bar{A}_{hk} = \tfrac{1}{2}\,(A_{hk} + A_{kh}).$$

If the temperature of the *Boltzmann* distribution changes from T to $T + \Delta T$, the surplus per second of the process going from *h* to *k* is

$$N_h A_{hk} - N_k A_{kh} = \bar{N}_{hk}\ exp\ (\frac{E_h - E_k}{2k(T+\Delta T)})\ \bar{A}_{hk}\ exp\ (\frac{E_h - E_k}{2kT}) -$$

$$- \bar{N}_{hk}\ exp\ (\frac{E_k - E_h}{2k(T+\Delta T)})\ \bar{A}_{hk}\ exp\ (\frac{E_k - E_h}{2kT}).$$

Assuming $|E_h - E_k| << kT$ and $\Delta T << T$ we get

$$N_h A_{hk} - N_k A_{kh} = \bar{N}_{hk} \bar{A}_{hk}\, \Delta T (E_h - E_k)/2kT^2 .$$

The total energy (heat) transmitted per second to the lattice is found by multiplying this surplus with $(E_h - E_k)$ and summation over all values h and k. In this way we get

$$\frac{dQ}{dt} = \frac{\Delta T}{2kT^2} \sum_{hk} \bar{N}_{hk} \bar{A}_{hk} (E_h - E_k)^2, \tag{133}$$

so that

$$\alpha_1 = \frac{1}{2kT^2} \sum_{hk} \bar{N}_{hk} \bar{A}_{hk} (E_h - E_k)^2. \tag{134}$$

Since we can write

$$C_H = \frac{1}{2kT^2} \sum_{hk} \bar{N}_{hk} (E_h - E_k)^2 \tag{135}$$

and since N_{hk} is independent of the choice of h and k we finally obtain

$$\rho = \frac{2\pi \sum_{hk} (E_h - E_k)^2}{\sum_{hk} \bar{A}_{hk} (E_h - E_k)^2}. \tag{136}$$

In the case of free spins with $S = \frac{1}{2}$ we get the simple expression

$$\rho = 2\pi/(A_{12} + A_{21}),$$

which was obtained for the first time by *Gorter* and *Kronig* (G10).

In this way we have reduced the evaluation of ρ to an evaluation of the transition probabilities A_{hk}.

4.32 The calculation of the transition probabilities.

The calculation of ρ with formula (136) is very complicated, but can be simplified somewhat by regarding the ions as virtually independent - the interaction between the ions can be taken into account in first approximation by the internal magnetic field H_i, so that in (136) one can take for the levels E_h and E_k the levels of a free ion. The calculation of the A_{hk} however remains very difficult. Before proceeding to the discussion of the evaluation of the A_{hk} we shall make some remarks about the nature of the transition probabilities.

The energy required for the transition from E_h to E_k must be furnished by the lattice vibrations. This can happen in two essentially different ways, as has been pointed out by *Waller* (W3) already in 1932. In the first place an elastic quantum for which $h\nu = E_h - E_k$ can be absorbed or emitted. In the case of absorption the number of quanta of the lattice in the vibrational state ν diminishes from $n_\nu + 1$ to n_ν. The probability for this *direct process* is given by

$$A_{hk} = \left[\frac{\rho(\nu)}{\hbar^2} \left| \mathcal{H}_\nu (n_\nu + 1;\, n_\nu) \right|^2 \right]_{\text{average}}, \tag{138}$$

where $\rho(\nu)$ is the density of the states of the lattice with frequency ν; $\mathcal{H}_\nu(n_\nu + 1;\, n_\nu)$ is the matrix element of the transition. The average has to be taken over all directions of propagation and polarisation of the elastic vibration.

In the second place a lattice quantum $h\nu$ can be absorbed, while another quantum $h\nu'$ is emitted, so that $h(\nu-\nu') = E_h - E_k$. This process is equivalent to *Raman* scattering where the lattice vibration quanta replace the light quanta. The probability for this kind of transition (indirect or quasi-*Raman* process) is given by the expression

$$A_{hk} = \left[\frac{\rho(\nu)\rho(\nu')}{\hbar^2} \,|\, H(n_\nu + 1, n_{\nu'}; n_\nu, n_{\nu'} + 1)|^2\right]_{\text{average}} \quad (139)$$

which is similar to (138).

At first sight one might expect that the direct processes - which are a first order effect - are the more frequent ones. On the other hand however all lattice waves can participate in a certain transition by the quasi-*Raman* effect, while the direct processes require a lattice wave of the right frequency. According to *Fierz* (F6) and *Kronig* (K11) the number of quasi-*Raman* processes is proportional to T^2 for $T \gg \Theta$ and to T^7 for $T \ll \Theta$, where Θ is *Debye's* characteristic temperature of the lattice. The number of direct processes is proportional to T. Therefore only at very low temperatures (according to an evaluation those obtainable with liquid helium, see however Part II) the first order process can preponderate, while at higher temperatures the quasi-*Raman* processes will be more frequent.

The actual calculation of the matrix elements in (138) and (139) requires a detailed picture of the coupling between the spin-system and the lattice. Several mechanisms have been proposed in the litterature.

In first instance the lattice vibrations cause an alternating electric field at the position of a paramagnetic ion. This electric field however is unable to influence pure spins, since the matrix elements (138) and (139) vanish in this case. On the other hand the lattice vibrations cause variations in the magnetic field which the ions exert on each other and this effect can induce transitions of the spin-system. *Waller* (W3) who considered this mechanism for pure spins calculated that $\rho/2\pi = 10$ sec at liquid air and that $\rho/2\pi \simeq 10^{11}/H^2$ sec at liquid helium temperatures.

Heitler and *Teller* (H14) considered the case of substances having an electric splitting. The lattice vibrations cause variations of this splitting and accordingly transitions of the spin-system are induced. They only considered the direct process and arrived at the following formula for $T \ll \theta$

$$\rho \simeq 0.3 \times 10^{-8} 2\pi \, \frac{k^2 \Theta^3}{4\beta^2} \, \frac{1}{H_c^2 T} \qquad (140)$$

Taking $H_c = 2000$ Oersted, $T = 1^\circ$ K and $\Theta = 100^\circ$ K we find $\rho \simeq 100$ sec. *Fierz* (F6) considered the indirect process under the same assumptions as *Heitler* and *Teller* and arrived at the formula

$$\frac{1}{\rho} \simeq 5.10^{-10}\, T^7 \int_0^{\Theta/T} \frac{x^8 e^{x} dx}{(e^x - 1)^2}.$$

According to this formula we have if $T \gg \Theta$ $\rho \sim T^{-2}$ and if $T \ll \Theta$ $\rho \sim T^{-7}$. If $T \simeq \Theta$ the integral is of the order one and so we get for $T = 90^\circ$ K $\rho \simeq 10^{-4}$ sec. This value is considerably smaller than the value obtained by *Heitler* and *Teller's* formula for the same temperature ($\rho \simeq 1$ sec), so that apparently the indirect processes should be predominant.

If we compare these theoretical calculations with the values obtained from experiments we see that there is a wide discrepancy between the two. The experimental results for iron and chromium alum show that ρ is of the order of 10^{-2} sec. at liquid helium temperatures and 10^{-8} sec at liquid air temperatures. The discrepancy is even more striking in the case of titanium alum. As there is no electrical splitting *Waller's* theory should be applied and accordingly the relaxation constant should be much larger than for the other alums. No dispersion and absorption could be detected at the fréquencies ordinarily used in the experiments, which means that the relaxation constant must be much shorter than for the other alums. All these theories give a much too long relaxation constant and *Gorter* (G11) therefore concluded that apparently an other mechanism than those discussed must be active. According to *Kronig* (K11) this other mechanism is provided by the remains of the spin orbit coupling. The lattice vibrations influence the orbital moment of the paramagnetic ions and the spin orbit coupling in higher approximation gives non-vanishing matrix elements of the spin lattice transitions. *Kronig* illustrated this effect with a schematic model and arrived at an acceptable value of the relaxation constants, even in the case of titanium caesium alum. *Van Vleck* (V13) independently carried out similar calculations for the special cases of chromium and titanium alum. As these calculations are more detailed than *Kronig's* calculation we only will review *Van Vleck's* calculations.

We have to start from the Hamiltonian of the whole crystal, which is equal to the Hamiltonian of the spin-system (formula (37) if we neglect the interaction between the paramagnetic ions), plus the Hamiltonian of the lattice vibrations and a term describing the interaction between the orbital moments of the magnetic ions and the lattice vibrations. This can be written in the form

$$\mathcal{H}_{crystal} = \mathcal{H}_{Or} + \mathcal{H}_{L} - H_c M + \mathcal{H}_{OL} + \mathcal{H}_{SO}.$$

H_{Or} is the orbital energy, which arises from the terms $\mathcal{H}_0 + V$ in (37). The eigenvalues of $\mathcal{H}_{Or}$ are the orbital levels. $\mathcal{H}_L$ is the energy of the lattice vibrations, having the eigenvalues $\sum_{\nu} n_{\nu} h\nu$. The term $H_c M$ describes the energy in the magnetic field, where M in the total magnetic moment. $-H_c M$ can be taken diagonal as far as the spins are concerned, the orbital magnetic moment however causes non-diagonal elements between the different orbital levels. $\mathcal{H}_{so}$ is the spin orbit coupling. Finally $\mathcal{H}_{oL}$ is the interaction between the orbital moment and the lattice vibrations. The magnetic interaction between the magnetic ions is taken into account in first approximation by averaging the result, obtained for a certain value of H_c, according to a weight factor $exp[-(H_c-H_o)^2/H_i^2]$, where H_o is the applied field and H_c the field acting on one ion.

Van Vleck now regards in (142) H_{so}, H_{oL}, and the non-diagonal part of $-H_c M$ as perturbations and calculates the required matrix elements accordingly. The main difficulty is the calculation of the matrix elements of H_{oL}. For a rigorous calculation the interaction of the orbital moment with all the normal vibrations of the lattice would be required, which however is impracticable. *Van Vleck* simplifies the calculation by expressing H_{oL} in terms of the normal coordinates of the cluster $X.6H_2O$ formed by the magnetic ion X and the six water molecules which surround it. These normal coordinates in turn can be expressed as linear functions of the normal coordinates associated with the lattice waves, which are approximated by *Debye* waves. In this way expressions for the matrix elements of H_{oL} can be found.

The matrix elements for the direct and indirect transitions now can be found by higher order perturbation calculus. We shall not go into detail about these very complicated calculations, but we shall confine ourselves to a discussion of the results. It will be assumed throughout that the lattice acts as a thermostat (compare II, 3.2).

a) *Titanium alum.* In this case it is sufficient to consider only those states which belong to the lowest cubic orbital term. Assuming that $2\beta H_c \ll \Delta$, where Δ is the trigonal splitting (see p. 26), and that the wave length of the lattice vibrations is much larger than the cross section of the clusters, *Van Vleck* finds after a long calculation for the relaxation constant of the direct process

$$\rho_{dir} = \frac{2\pi\,(H_c^2 + \frac{1}{2}H_i^2)}{kTB\,[aH_c^6 + bH_c^4\,H_i^2 + cH_c^2\,H_i^2 + dH_i^6]}\,, \tag{143}$$

where a, b, c, d and B are constants; B is proportional to λ^2/Δ^4, where λ is the constant of the spin orbit coupling. H_i describes the influence of the magnetic interaction between the titanium ions and is given by (83). Taking $\Delta = 1000\ \text{cm}^{-1}$ and appropriate values for the other constants *Van Vleck* finds at $T = 1.2^\circ$ K for $\rho/2\pi$: 5×10^4, 1.7×10^2, and 1.8×10^{-2} for $H_c = 0, 10^3$

and 10^4 Oersted resp. The experimental results however indicate that $\rho/2\pi < 10^{-3}$ sec (H11), so that the discrepancy is large. It should be remarked however that *Van Vleck*'s choice for Δ is rather much higher than the value indicated by experiments on paramagnetic resonance absorption ($\Delta \simeq 400$ cm^{-1}) and this will reduce the values of ρ with a factor 40, which however leaves the theoretical values of ρ still at least a factor 10^4 too large.

For the quasi-*Raman* processes *Van Vleck* finds

$$\rho_{ind} \simeq 2.5 \times 10^{-11} . 2\pi \left(\frac{\Delta^8}{\lambda^2}\right) \frac{H_c^2 + \frac{1}{2} H_i^2}{H_c^2 + H_i^2} \cdot \frac{1}{T^9} \quad (T \ll \Theta), \qquad (144)$$

which can be written in a more useful form since $\frac{1}{2}H_i^2 = b/C$ (Cf. (83), (61a)). We then obtain

$$\rho_{ind} = \rho_0(T) \; (b + CH_c^2)/(b + \tfrac{1}{2}CH_c^2) \qquad (145)$$

$$\rho_0(T) \simeq 10^{-10} \; (\Delta^8/\lambda^2)\,(1/T^9) \qquad (145a)$$

This expression gives with $\Delta = 1000$ cm^{-1} and for values of $H_c \gg H_i$ $\rho_{ind} < 10^{-8}$ sec at liquid air temperatures, which explains the absence of paramagnetic relaxation effects in the experiments of *Gorter, Teunissen* and *Dijkstra* (G 12). This conclusion is not invalidated by the better choice $\Delta \simeq 400$ cm^{-1}. It is important to remark that consequently the effect of second order processes is not negligible at liquid helium temperatures, because $\rho_0 \simeq 10^{-3}$ sec at 2° K. The very short relaxation time at liquid helium temperatures therefore probably can be explained by second order processes.

From formula (144) it is seen that the relaxation constant is very sensitive to the value of the splitting Δ; large anisotropy which causes large values of Δ therefore is favorable for producing observable relaxation phenomena. This conclusion is correct for all ions having no electrical splitting, like the copper ion. In the case of ions having an electrical splitting the influence of larger anisotropy is different. Here larger anisotropy causes a larger electrical splitting so that b/C becomes larger. This can make the relaxation phenomenon unobservable with the ordinary means, because F may be too small (compare (117)). The value of ρ can be influenced in a different way. Often high values of b/C are accompagnied by low values of ρ, which should be expected in general, as a large value of b/C indicates a large anisotropy, and this causes a strong coupling between the spins and the lattice. Chromium salts for instance are an exception, because larger anisotropy only effects the b/C value; ρ depends only on the cubic splitting (see below).

b) *Chromium alum*. In this case the lowest cubic orbital level is single and consequently one has to take into account matrix elements of H_{OL} and H_{SO} between different cubic levels. As we have seen the lowest cubical term is split by a trigonal component of the crystalline field into two doublets. A consequence of the large distance between the cubic levels is a much larger theoretical value of the relaxation constant than in the case of titanium alum.

For the direct processes *Van Vleck* finds

$$\rho = 2\pi \frac{\frac{1}{4}h^2\delta^2 + 5(H_c^2 + \frac{1}{2}H_\perp^2)\beta^2}{\alpha T^2} \tag{146}$$

(where $\alpha \sim \lambda^2 H^2 / T\Delta_{\text{cub}}^4$; Δ_{cub} is the cubic splitting between the levels Γ_2 and Γ_5), which gives values of ρ which agree as to order of magnitude with the experimental values obtained at Leyden in the liquid helium region (see part II). *Van Vleck* expects for $T = 1.4°\text{K}$ $\rho/2\pi = 0.011$, 0.009, 0.0067 and 0.0030 sec in fields of resp. 0, 500, 1000 and 3000 Oersted. It should be remarked at once that according to theory $d\rho/dH_c < 0$ while according to experiment we have $d\rho/dH_c > 0$. Moreover from formula (146) we must conclude that $\rho \sim T^{-1}$ while the same experiments yield a higher negative power of T. This behaviour is very difficult to understand on the basis of the first order processes (see next paragraph), but is explained in a natural way by assuming that quasi-*Raman* processes still are important (see below). This point is discussed in detail in II, 3.

The negative value of $d\rho/dH_c$ for direct processes easily can be understood qualitatively. With increasing H_c the heat exchange between the spin-system and lattice is brought about by quanta of increasing magnitude, which are more effective for the heat exchange. Moreover the number of lattice vibrations, available for the transitions is proportional to ν^2, both in the adopted *Debye* theory of lattice waves and in the more general theory of *Blackman* (B33). Both effects make the energy exchange in high fields so much larger than in low fields, that although C_H increases proportional to H_c^2 (Cf. (61a)), $d\rho/dH_c < 0$.

For the indirect processes *Van Vleck* finds

$$\rho = \rho_0\ (T)\ \frac{b + CH_c^2}{b + pCH_c^2}, \tag{147}$$

where ρ_0 is about proportional to T^{-5} $(\Delta_{\text{cub}}^6/\lambda^4)$. ρ should be independent of the trigonal splitting, but depend on the cubic splitting; p should be independent of the temperature, having the value 0.50 for chromium alum; for iron alum it should be between 0.22 and 0.60. The formula (147) sometimes is called the *Brons-Van Vleck* formula. The relation of ρ and H_c therefore should be independent of T, so that we have $\rho = f(T)g(H)$. This is a consequence of the plausible assumptions that the modes of vibration of the lattice and the cluster do not depend on the temperature and that the wave length of the lattice waves is large compared with the dimensions of the cluster. The latter assumption is allowed if the experiments are carried out below the *Debye* temperature θ. Often however the experiments are carried out at about 100° K, which is of the order of θ. This might explain the dependence of ρ on T found for all substances investigated (except manganese ammonium sulphate (B26)).

According to formula (147) ρ will be independent of H_c if $H_c^2 \ll b/C$ and tends to a limiting value ρ_∞ for $H_c^2 \gg b/C$. This can be illustrated by a closer examination of (136). In this expression the transition probabilities A are weighted in proportion to the square of the energy differences, so that mainly transitions between levels with a relatively large energy difference are important. It may be expected that the transition probabilities are only slightly influenced by a field H_c if the corresponding shift of the levels is small compared with the original energy difference. This explains the constant value of ρ in small fields. In very strong fields all energy differences will be proportional to H_c; the A's will be independent of H_c, because the coupling between these levels depends only on the wave functions. These are essentially free spin wave functions which are independent of H_c. Therefore at high fieldstrength ρ tends to another constant value.

The experimental check of (147) for a number of chromium salts showed that (*Broer* (B26))

a) in all salts examined ρ decreases with increasing T. None of the salts however satisfies the predicted temperature dependence. For instance in the potassium alum the experimental decrease is stronger.

b) in many cases (147) is found to be satisfied with reasonable accuracy for constant T.

c) in none of the cases ρ is found to be independent of the temperatures but the order of magnitude agrees with the predicted value.

d) the order of magnitude of the predicted values of ρ is correct.

Summarising we can say that *Van Vleck*'s calculations, although they are not satisfactory as to the explanation of several details, explain the main properties of the relaxation constant of chromium reasonably well in the liquid air region of temperatures or, in other words, in the case that the indirect processes preponderate. The main features are consequences of sufficiently general assumptions for justifying a check for salts of other metals of the iron group.

4.33 Modifications of the theory.

The arguments for the negative sign of $d\rho/dH_c$ in the case of direct processes (see p.70) seem to be rather convincing. There is however the difficulty that in nearly all experiments it was found that $d\rho/dH_c > 0$. As it is not definite wether direct or quasi-*Raman* processes prevail in the liquid helium range, it is desirable to consider alterations in the theory of the direct processes which might lead to a positive sign of $d\rho/dH_c$.

Van Vleck advanced three possible explanations, which we will consider briefly. In the first place it is conceivable that the density of the lattice vibrations would be independent of ν^2 for low frequencies. This would make $d\rho/dH_c>0$ for the direct process, but for the quasi-*Raman* process $d\rho/dH_c<0$. Quite apart from the success of the *Debye* theory for the theory of the proporties of crystals, which justifies to a large extent the increase of density of the lattice vibrations proportional to ν for low frequencies, the qualitative agreement with experiment of *Van Vleck's* theory of the quasi-*Raman* processes indicates that the proposed explanation hardly can be correct.

Another possible explanation advanced by *Van Vleck* is that the assumption of thermodynamic equilibrium in the spin-system is not warranted. This assumption however seems to be contradicted by the very good agreement between the thermodynamical theory and experiment on the value of b/C. For a detailed discussion of this point we refer to sections I, 4.22 and II, 3.3.

A third possibility is that at low temperatures the heat contact is caused by conduction electrons rather than by lattice vibrations. Although this could make $d\rho/dH_c<0$, this possibility is highly improbable from a physical point of view, so that we will not discuss it further.

Summarising we can say that none of the suggestions made seems to lead to a positive value of $d\rho/dH_c$ for the direct processes. There is another possibility however which we did not yet discuss.

The theory given so far contains an inconsistency which may be the cause of the discrepancy between *Van Vleck's* theory and the experiments at low temperatures. The most fundamental assumption of the thermodynamical theory, which is justified in many cases by its success, is, that there is thermodynamic equilibrium in the spin-system. This necessarily implies a sufficiently strong interaction between the paramagnetic ions. But in *Van Vleck's* theory this interaction is discarded except for its average influence on the static magnetic field acting on the magnetic ions, and the ions are treated as virtually independent from each other. It will probably be very difficult to estimate the error introduced by this simplification, but, as the interaction seems to be an essential requirement for the validity of the thermodynamic theory, this interaction may play an important role in the relaxation process.

Temperley (T4) made the first attempt to account for the possible influence of the magnetic interaction on the relaxation constant by considering the possibility of having several atoms reversing their spins simultaneously. Transitions of this type, which correspond to $|\Delta m| > 1$, are possible in a system of spins having magnetic interaction (compare I, 5.43). The influence of the low transition probabilities - which are small of a higher order compared with those of the transitions $\Delta m = \pm 1$ - on the magnitude of ρ may be partially or entirely compensated by the larger energy quantum exchanged, and moreover because more lattice vibrations with higher energy are available. If this effect prevails at temperatures where the direct processes are predominant, ρ should first increase with increasing field, until at still higher fields the decrease according to *Van Vleck* could start. This might explain the increase of ρ with increasing H_c found in all substances except one (Cf. Part II), if the maximum field used was not large enough for causing the ultimate decrease predicted by *Van Vleck*, and if at liquid helium temperatures direct processes prevail.

It may be added that according to *Van Vleck* the probability of *Temperley*'s effect in first approximation is too small for influencing ρ to the required extent. It is feasible that higher approximations are important as the process of successive approximations is likely to converge slowly. This however has not yet been considered in detail.

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Chapter V

THE THEORY OF PARAMAGNETIC RESONANCE ABSORPTION

5.1 Introduction.

In this chapter we will give an outline of the theory of paramagnetic resonance absorption, or in other words, the theory of the spectrum of the possible transitions between the levels of the spin-system. To begin with we shall consider the spectrum of a highly dilute substance where we neglect the interaction with the lattice. Next we will discuss the influence of the interaction with the lattice on the spectrum and finally we shall consider the influence of magnetic and exchange interaction.

5.2 Resonance absorption in dilute substances.

5.21 Absorption of free spins.

In Chapter III we briefly discussed the allowed transitions between the levels of a system of free spins in a constant magnetic field H_c with $S = 1/2$. The essential features were that only transitions between adjacent levels in perpendicular constant and alternating field are possible. The allowed transitions correspond to a transition of one of the spins between its two energy levels and therefore the essential features of the absorption can be found by considering just one spin.

Clearly these transitions can be induced by applying electromagnetic radiation of the correct frequency. For experimental reasons one applies radiation of a given frequency ν and changes the value of the constant magnetic field until absorption occurs; then H_c satisfies the *resonance condition*

$$g\beta H_c = h\nu. \qquad (148)$$

Taking $g = 2$ - as is the case for pure electronic spins - and the well known values for h and β this relation can be written

$$H_c\lambda = 10710, \qquad (148a)$$

where the wave length λ is measured in cm and the magnetic field in Oersted. In a field of 3000 Oersted $\lambda = 3.5$ cm and $\nu = 8000$ Mc/sec; the absorption therefore lies in the micro wave region.

The situation is very similar in the case of free spins with $S > 1/2$. In a magnetic field we have the energy levels $g\beta m H_c$, where m has the values $S, S-1, \ldots -S$. When an alternating field at right angles to the constant field is applied transitions in m with $\Delta m = \pm 1$ are allowed and the resonance condition (148) applies.

5.22 Absorption in the absence of a magnetic field.

a) In Chapter II we mentioned that the energy levels of the ions of the iron group - both in absence or presence of a constant magnetic field - in general deviate from those of free spins. Consequently the resonance spectra in most cases are more complicated.

We shall consider first the case that $H_c = 0$. It was found that in many cases splittings of these levels of the order of 1 cm^{-1} or even smaller occur. Consequently, if there are allowed transitions between the normal levels, absorption lines in general allow a number of magnetic dipole transitions. Electric dipole transitions are forbidden by *Laporte*'s parity rule; the parity of the normal levels is the same since they originate from the same configuration of the free ion. Electric quadrupole transitions can be shown to have negligible intensity compared with the magnetic dipole transitions.

b) The selection rules can be found with a simple group theoretical argument. According to this theory magnetic dipole transitions are allowed between levels m and n only if $\Gamma_m \times \Gamma_n \times \Gamma_a$ contains the identical representation Γ_1; Γ_a is the representation of the magnetic moment operator which transforms under a rotation over an angle φ as an axial vector. *Kittel* and *Luttinger* (K3) made a list of the selection rules for a number of symmetries of the crystalline field. We shall not quote the results but we refer to their paper.

5.23 Absorption in the presence of a magnetic field.

In most cases the resonance spectrum to be expected deviates appreciably from the simple spectrum of free spins. Several reasons can be given for this. In the first place the energy levels of the actual paramagnetic ions deviate from those of free spins and often depend on the directions of the constant field (Cf. I, Ch.2). Secondly often the elementary cell contains a number of magnetic ions of the same kind, for which the direction of the symmetry axes of the crystalline field relative to the crystal axes is different. Therefore the spectrum observed in general is a superposition of the spectra of the different ions, corresponding to different directions of the magnetic field relative to the axes of the crystalline field. And thirdly the selection rules of the transitions often deviate from those of free spins as a consequence of the combined action of the crystalline field and the spin-orbit coupling. Examples can be found in *Kittel* and *Luttinger*'s paper (K3) and in Part III. In general therefore the resonance absorption spectra are rather complicated and often the interpretation is difficult.

It may be remembered that the level pictures given in chapter II are broadly speaking in agreement with the available data on the susceptibility and specific heat of many salts. There exist however inconsistencies as has been pointed out by

Van Vleck (V5), *Freed* (F2), and *Penney* and *Kynch* (P5). The study of the resonance spectra can provide us with more direct and more complete knowledge about the energy levels of magnetic ions in crystals and has already been fruitful in this respect. Examples of substances of which the observed spectra could be analysed, and which showed a fair agreement with the theoretical expectations of chapter II are: potassium chromium alum (B17, W2) and nickel fluosilicate (P1). The experiments carried out so far confirm the theory of Chapter II in its broad outline (B7), but on the other hand discrepancies have been found (Cf. Part III).

5.3 Thermal broadening of magnetic resonance lines.

5.31 Introduction.

Until so far in this chapter we neglected the possible influence of the interactions between the ions themselves and the interaction between the ions and the thermal motion of the lattice. An adequate theory of the line shape and line width of magnetic resonance lines should take into account both types of interactions. A general treatment on these lines has not been given, but only considerations, which are valid, either for the case that the interaction between the ions and the thermal motion of the lattice is much smaller than the interaction between the ions - so that the line shape practically is determined by the mutual interaction of the ions -; or for the case that the thermal interaction is much larger than the mutual interaction, so that the line shape practically is determined by the interaction between the ions and the lattice. The first case will be discussed in section 5.4 and the second case in this section.

5.32 The formulae of Fröhlich-Van Vleck-Weisskopf.

These formulae have been derived by *Fröhlich* for the shape of collision-broadened spectral lines in the special cases of rigid dipoles oscillating about an equilibrium position (F3) and of harmonic oscillators (F4). *Van Vleck* and *Weisskopf* (V8) critisised and revised *Lorentz's* theory of collision broadening (Cf. H6) and arrived at the same formula for the line shape, although their treatment differs from that of *Frohlich*. All three authors used a classical derivation; recently *Karplus* and *Schwinger* (K5) gave a quantum mechanical derivation, which we shall follow in its main outline.

To this end we consider a dilute paramagnetic substance in which the identical spins with $S = 1/2$ interact with the thermal motion of the lattice and which is subjected to a magnetic field of the form (95), while $\mathbf{H}_c \perp \mathbf{h}$. The problem is to calculate the optical absorption coefficient α in $I = I_0\, exp(-\alpha x)$, where

I is the intensity in a plane wave and x is the distance over which the wave has travelled, reckoned from a given point. α is given by the well known relation

$$\alpha = 8\pi^2\nu\chi''/c \text{ (nepers per cm)} \tag{149}$$

where c is the velocity of light.

The problem is therefore reduced to the calculation of χ'' as a function of the frequency of the alternating field. If we neglect the mutual interaction, this problem can be solved by introducing the density matrix of an ion ρ. Then the mean magnetic moment of an ion, $\bar{\mathbf{m}}_i$, is given by

$$\bar{\mathbf{m}}_i = Sp\,[\mathbf{m}_i\rho]. \tag{150}$$

If thermodynamical equilibrium would be maintained at all moments the density matrix would be given by

$$\rho_0 = C\,exp(-H/kT) \quad C = Sp[exp(-H/kT)], \tag{151}$$

where the Hamiltonian H can be written in the form

$$H = H_0 + V\cos\omega t; \tag{152}$$

the first term is the Hamiltonian of an ion without applied alternating field, the second term describes the influence of the alternating field. The change of the density matrix in the course of time is determined by

$$i\hbar\dot{\rho}_0 = H\rho_0 - \rho_0 H. \tag{153}$$

In the actual situation thermodynamical equilibrium is not maintained all the time, but there is a tendency - due to the interaction with the lattice vibrations - to reach equibrium. We will now suppose that the rate of change of ρ - the actual density matrix - is proportional to the instanteneous deviation from ρ_0 or, mathematically expressed, is equal to $-A(\rho-\rho_0)$. This assumption implies that there is one spin-lattice relaxation time. Adding this rate of change of ρ to the rate of change due to the 'motion' of the magnetic moments we get

$$\dot{\rho} = (-i/\hbar)\,(H\rho-\rho H) - A\,(\rho-\rho_0), \tag{154}$$

which is the equation we shall use for the evaluation of ρ and hence of χ''. It may be added that this equation is the exact quantum mechanical analogue of *Fröhlich*'s equation (7) (F4). It is more convenient to introduce the quantity $D = \rho-\rho_0$, which obeys

$$\dot{D} = (-i/\hbar)(H\,D - D\,H) - AD - \dot{\rho}_0. \tag{155}$$

This becomes in the representation in which the unperturbed Hamiltonian H_0 is diagonal

$$(\partial/\partial t + i\omega_0 + A)D_{kl} = -(\dot{\rho}_0)_{kl} - (i/\hbar)\sum_j(V_{kj}D_{jl} - D_{kj}V_{jl})\cos\omega t, \tag{156}$$

where

$$\hbar\omega_0 = g\beta H_c.$$

We have assumed that the radiation field is weak, which implies that the density matrix differs little from that of the system without applied alternating magnetic field at the same temperature (ρ^0). In the representation used we have

$$\rho^{o}_{kl} = \frac{[exp(-H_{o}/kT)]_{kl}}{Sp[exp(-H_{o}/kT)]} = \frac{exp(-E_{k}/kT)\,\delta_{kl}}{\Sigma exp(-E_{1}/kT)} = \rho^{o}_{k}\,\delta_{kl}.$$

We now can neglect the second term at the right hand side of (156). As the energy of the system in the radiation field will be small compared will kT, we can write in a sufficient approximation

$$(\rho_{O})_{kl} = \rho^{o}_{k}\,\delta_{kl} + (\rho^{o}_{k} - \rho^{o}_{1})\,(V_{kl}/\hbar\,\omega_{C})\ cos\ \omega\, t,$$

and we finally obtain for (156)

$$(\partial/\partial t + i\omega_{O} + A)D_{kl} = \omega(\rho^{o}_{k} - \rho^{o}_{1})\,(V_{kl}/\hbar\omega_{O})\ sin\ \omega\, y. \tag{157}$$

The steady state solution of this equation is

$$D_{kl}\ (t) = [\omega/(\omega-\omega_{O}+iA)](\rho^{o}_{k} - \rho^{o}_{1})\,(V_{kl}/\hbar\omega_{O})\,exp(-i\omega t) + \\ [\omega/(\omega-\omega_{O}-iA)]\,(\rho^{o}_{k}-\rho^{o}_{1})\,(V_{kl}/\hbar\omega_{O})\,exp(i\omega t).$$

Taking into account that $D = \rho - \rho_{O}$, the equations (100a), (101a), (148) and assuming that the temperature is sufficiently high for replacing the exponentials by the first terms of their series expansion, we finally obtain

$$\chi' = (\chi_{o}/2)\left[\frac{\Delta\nu^{2} - \nu_{O}(\nu-\nu_{O})}{(\nu-\nu_{O})^{2} + \Delta\nu^{2}} + \frac{\Delta\nu^{2} + \nu_{O}(\nu+\nu_{O})}{(\nu+\nu_{O})^{2} + \Delta\nu^{2}}\right]. \tag{158a}$$

$$\chi'' = (\chi_{o}/2)\left[\frac{\nu\Delta\nu}{(\nu-\nu_{O})^{2} + \Delta\nu^{2}} + \frac{\nu\Delta\nu}{(\nu+\nu_{O})^{2} + \Delta\nu^{2}}.\right] \tag{158b}$$

Here we have written $\Delta\nu = A/2\pi$ and $\chi_{o} = \Sigma|m_{kl}|^{2}/3kT$. These equations follow from (106) by the substitution $\rho = 1/\Delta\nu$ and may be called the *Fröhlich-Van Vleck-Weisskopf* formulae.

Discussion.

It will be clear from the given derivation of the formulae (158) that they are valid for any case in which the fundamental equation (154) is satiesfied, independent of whether we have electric or magnetic resonance absorption in solids, liquids or gases. The physical implications of the validity of (154) will be discussed in some special cases.

Let us consider first the case that $\nu_{o} \gg \Delta\nu$. Then for frequencies not too far from the resonance frequency ν_{O} the second term at the right hand side of (158b) can be neglected and the shape of the absorption line is determined by the structure factor

$$\Delta\nu/[(\nu-\nu_{O})^{2} + \Delta\nu^{2}].$$

This is exactly the expression *Lorentz* (L1, H6) derived for the line shape of a spectral line in the optical region - for which $\nu_{O} \gg \Delta\nu$ - in a gas, in which the collisions between the molecules cause a broadening. *Lorentz* assumed that the chance of a time t elapsing between the collisions is given by an exponential probability distribution of the form

$$(1/\tau)\,exp(-t/\tau),$$

where τ is the mean time between collisions. The 'line breadth constant' $\Delta\nu$ - which is equal to half the width at half intensity - is related to the mean time between collisions according to $\Delta\nu = 1/2\,\pi\tau$. If however $\nu_0 \simeq \Delta\nu$ *Lorentz's* expression is no longer valid and the complete expressions (158) have to be used.

In the limiting case of $\nu_0 = 0$ formulae (158) become equal to the corresponding *Debye* formulae (104). The 'non-resonant' *Debye* absorption and dispersion therefore are resonant absorption and dispersion with resonance frequency zero. We can conclude that the linebreadth constant is related to the relaxation time $\tau = \rho/2\pi$ according to $\Delta\nu = 1/2\,\pi\tau$ (In a gas the relaxation time is equal to the mean time between the collisions.). It is easily seen that the factor A in (154) is equal to $1/\tau$.

It is instructive to compare the collision damped oscillator, which we consider in this section, with the friction damped oscillator (Cf. (106)). To this end in fig. 8 have been plotted

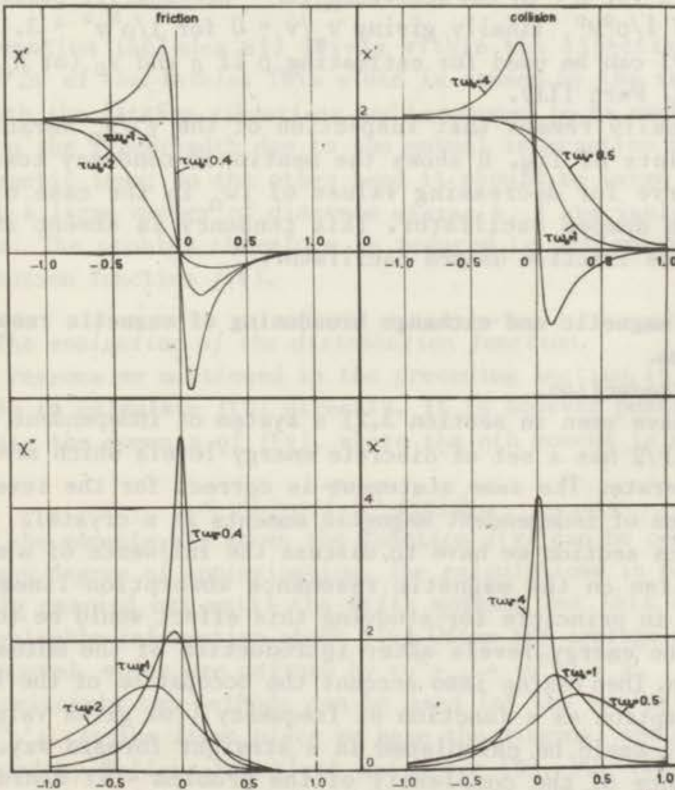

Fig. 8

a) Friction damped oscillator. b) Collision damped oscillator.

χ'/χ_0 and χ''/χ_0 for both types of oscillator as a function of $\log \omega/\omega_0 = \log \nu/\nu_0$, where ν_0 is the resonance frequency of the undamped oscillator, for different values of $\tau\omega_0 = \rho\nu_0$. From the χ''/χ_0 versus $\log \omega/\omega_0$ plots it is obvious that the maximum of χ''/χ_0 shifts for decreasing values of $\tau\omega_0$ to higher values of ω/ω_0 for the collision damped oscillator, but to lower values of ω/ω_0 for the friction damped oscillator.

In experiments on resonance absorption where the constant magnetic field - and consequently the resonance frequency - is varied the maximum of the absorption shifts to a lower value of H_c, say H_m, in the case of a collision damped oscillator, but to a higher value for a friction damped oscillator. If we define ν_m by the relation $h\nu_m = g\beta H_m$, the maximum absorption no longer is determined by $\nu = \nu_0 = \nu_m$, but for the collision damped oscillator by the relation

$$(\nu_m/\nu)^2 = -[(1/\rho^2\nu^2)+1] + 2[(1/\rho^2\nu^2)+1]^{1/2}, \quad (159)$$

which is readily derived from (108), assuming that $\rho = 2\pi\tau$ does not depend on H_c. It is easily seen that $\nu_m/\nu = 1$ only for $1/\rho^2\nu^2 = 0$ (or $\rho = \infty$) but decreases for - necessarily positive - values of $1/\rho^2\nu^2$, finally giving $\nu_m/\nu = 0$ for $1/\rho^2\nu^2 = 3$. Relation (159) can be used for estimating ρ if g and ν_0 (or H_m) are known (Cf. Part III).

We finally remark that inspection of the χ'/χ_0 versus $\log(\omega/\omega_0)$ plots of fig. 8 shows the mentioned tendency towards a *Debye* curve for decreasing values of $\tau\omega_0$ in the case of the collision damped oscillator. This tendency is absent in the case of the friction damped oscillator.

5.4 The magnetic and exchange broadening of magnetic resonance lines.

5.41 Introduction.

As we have seen in section 3.21 a system of independent spins with $S = 1/2$ has a set of discrete energy levels which are highly degenerate. The same statement is correct for the levels of any system of independent magnetic moments in a crystal.

In this section we have to discuss the influence of a mutual interaction on the magnetic resonance absorption lines. The best way in principle for studying this effect would be to calculate the energy levels after introduction of the mutual interaction. Then taking into account the occupation of the levels the absorption as a function of frequency (for given values of H_c and T) could be calculated in a straight forward way. As a consequence of the complexity of the problem - it would mean the solution of a secular problem of the order of about 10^{22} - this problem however is impracticable.

It is possible however to solve the problem at least partially along the following lines. First of all we may remark that the interaction spreads the discrete levels of the system without interaction practically over a continuum. This is a consequence of the large number of levels and makes an approximative treatment possible. Let us now consider the absorption in a magnetic field with given frequency ν. Then we have to deal with processes of absorption and stimulated emission. The surplus number of absorption processes is proportional to the differences in occupation between the levels participating in the process and is therefore proportional to $h\nu/kT$ (if $h\nu<<kT$, as is the case in all cases occuring in practice). The net absorption is proportional to $(h\nu)^2/kT$. Further, the absorption will be proportional to the average square of the non-diagonal elements M_{kl} of the magnetic moment corresponding to the frequency ν. If ν is varied the absorption will vary continuously and will be essentially determined by the distribution function $f(\nu)$ of the M_{kl}. According to *Broer* (B18) we have for the absorption per second per cm³

$$A_{sec} = (8\pi^3\nu^2/kT)\ f(\nu), \tag{160}$$

where

$$f(\nu) = \sum_{\Delta\nu} |M_{kl}|^2 . \tag{161}$$

The summation includes all levels within the effective line breadth $\Delta\nu$ of the levels. This width is caused by the interaction with the lattice vibrations and is assumed to be much smaller then the linebreadth due to the mutual interaction between the magnetic ions; on the other hand it should be large enough so that a large number of discrete states k, l are included in the sum. The problem therefore is reduced to determining the distribution function $f(\nu)$.

5.42 *The evaluation of the distribution function.*

For reasons we mentioned in the preceding section it is not feasible to calculate $f(\nu)$ directly. It is however possible to calculate the moments of $f(\nu)$, where the nth moment is defined by

$$< \nu^n > = \int_0^\infty \nu^n\ f(\nu)\,d\nu . \tag{162}$$

If all the moments are known the function $f(\nu)$ can be constructed in any degree of approximation. The calculations in practice are only carried out until the fifth moment, but this already gives valuable information about $f(\nu)$. Often the average moments are computed, which are defined by $<\nu^n>_{av} = <\nu^n>/<\nu^0>$.

In principle two methods can be used for the evaluation of the $<\nu^n>$'s. In the first place we have the diagonal sum method, developed by *Waller*, *Van Vleck* and *Broer* (W3, V9, V10, B18). They find the relations (neglecting terms in $h\nu/kT$)

$$\begin{aligned} <\nu^0> &= Sp\ [M^2] \\ <\nu^2> &= Sp\ [\dot{M}^2]/4\pi^2 \\ <\nu^4> &= Sp\ [\ddot{M}^2]/16\pi^4 . \end{aligned} \tag{163}$$

These moments can be evaluated using the general relation for the time derivative of a quantum mechanical operator

$$i\hbar\dot{M} = \mathcal{H}M - M\mathcal{H}\,, \tag{164}$$

and assuming that there is no crystalline splitting, but that magnetic and exchange coupling between the ions is present. Then the Hamiltonian is given by (69) and (70) with $\mathbf{m}_i = \beta\sigma_i$, while the first term of (69) is written $\Sigma\mathcal{H}_i = g\beta H_c\Sigma\sigma_{zi}$ This term describes the *Zeeman* energy (the energy due to the presence of the constant magnetic field directed along the *z*-axis). Unfortunately it is hardly feasible to calculate higher moments than the fourth, so that the information obtained in this way remains limited.

In the second place we have the perturbation method in which the interaction is treated as a perturbation. It is not altogether trivial that a perturbation calculus can be applied here, because the perturbation energy will be of the order $\beta N^{1/2}H_i$; the splitting of an energy level must be of the same order and certainly will be larger than the original distance between the levels for a system of many spins. *Broer* (B18) pointed out however that the matrix elements of the magnetic moment differ appreciably from zero only when the energy difference $h\nu$ between two states *k* and *l* satisfy the relation $h\nu \simeq \beta H_i$; or $h\nu \simeq \beta(H_c + H_i)$ or $h\nu \simeq \beta\,(2H_c \pm H_i)$. This theoretical justification is supported by the results of the perturbation theory, which are in agreement with the experimental facts.

The perturbation method has been used by *Broer* (B18) and in more detail by *Pryce* and *Stevens* (P6). *Broer* considered some general aspects of the influence of the mutual interaction, while the latter authors especially considered the influence on resonance absorption lines. The results will be quoted in the next section without details about the usually very complicated calculations. For details about this we refer to the papers mentioned.

5.43 *Review of the theoretical results.*

a) In order to obtain a general impression about the influence of interaction we shall consider the case of a system of identical spins or in other words ions having no electrical splitting. If we neglect the interaction, the distribution function $f(\nu)$ in the case $H_c = 0$ is very sharply peaked at $\nu = 0$, in the case of perpendicular constant and alternating fields sharply peaked around $\nu_H = g\beta H_c/h$ and is zero for all frequencies in the case of parallel fields. This follows from the considerations of section 3.21 for spins with $S = 1/2$, but the same is valid for spins with $S > 1/2$. As a consequence of the interaction of the spins with the lattice vibrations the peaks in the $f(\nu)$ versus ν curve have a finite, but, as we shall assume here, for our present purpose negligible width. This picture is changed in many ways if we introduce the mutual interaction. We shall assume here that the interaction is purely magnetic and neglect the influence of exchange interaction for the present. Then according to *Broer* (B18) - who discussed the first two moments of $f(\nu)$ -

a) if $H_c = 0$ the peak of $f(\nu)$ is broadened to a width of the order $\beta H_i/h$.

b) in perpendicular fields the peak around $\nu = \nu_H$ is broadened to the same width, while moreover much fainter peaks around $\nu = 0$ and $\nu = 2\nu_H$ occur; all peaks having a width of the order $\beta H_i/h$. (According to Miss *Wright* (W4) in still higher approximation faint peaks at higher multiples of ν_H must be expected too.) These transitions correspond to $\Delta m = \pm 2, \pm 3, \ldots$, which are forbidden for free spins. [In the case of spins with $S > ½$ two kinds of transition with $|\Delta m| > 1$ are possible. First one spin can make a transition with $|\Delta m| > 1$ and secondly two or more spins can make a transition simultaneously. In the case of $S = ½$ only the latter type of transition is possible.]

The area under the $f(\nu)$ curve is independent of H_c and the absorption of the lines at $\nu = 0$ and $\nu = 2\nu_H$ decreases in high fields ($H_c >> H_i$) proportional to $(H_i/H_c)^2$.

c) in parallel fields absorption occurs at frequencies $\nu \doteq 0$, $\nu = \nu_H$ and $\nu = 2\nu_H$. Now the area under the $f(\nu)$ curve decreases in high constant fields proportionally to $1/H_c^2$ and the adsorption at $\nu = 0$ vanishes proportionally to $(H_i/H_c)^4$; the other lines decrease in proportion to $(H_i/H_c)^2$. The width of all peaks is of the order $\beta H_i/h$.

In this thesis we are chiefly interested in the resonance absorption line. This special line will be discussed below in detail, where we shall consider both the effect of magnetic and exchange interaction on the line shape. Here we only mention the influence of exchange on the line shape of the other lines.

According to Miss *Wright* in the case $H_c = 0$ the line is narrowed by exchange. In perpendicular fields all lines, except the resonance line at $\nu = \nu_H$, are broadened, while in parallel fields all lines, including the line at $\nu = \nu_H$, are broadened.

The lines at $\nu = 2\nu_H$, $3\nu_H$ both in parallel and perpendicular fields hardly have been studied experimentally, but the low frequency side of the line at $\nu = 0$, which is responsible for the spin-spin relaxation, has been studied and still is being studied experimentally, both in the cases of electrical splittings and in the case of no electrical splittings. For details of the experimental results we refer to *Gorter's* book (G1) and for the theory to the papers of *Broer* (B18) and Miss *Wright* (W4).

5.44 The resonance absorption line.

a) *Identical spins*. The case of identical spins has been considered in detail by *Van Vleck* (V10) for high temperatures, where the formulae (163) are valid. *Van Vleck* derived expressions for the mean square and mean fourth power of the deviation of the resonance frequency. The first quantity is related to $\langle \nu^2 \rangle_{av}$ according to

$$\langle \Delta\nu^2 \rangle_{av} = \langle (\nu - g\beta H_c/h)^2 \rangle_{av} = \langle \nu^2 \rangle_{av} - g^2\beta^2 H_c^2/h^2 .$$

The corresponding expression for $\langle \Delta\nu^4 \rangle_{av}$ is easily found.

If the crystal has cubic symmetry *Van Vleck* finds

$$\langle \Delta\nu^2 \rangle_{av} = (3/8) g^4\beta^4 h^{-2} \, [a + b(\lambda_1^4 + \lambda_2^4 + \lambda_3^4] \, S(S+1), \qquad (165)$$

where λ_1, λ_2, λ_3 are the direction cosines of the applied field relative to the cubic axes. The constants a, b, are independent of the λ's, but depend on the type of cubic structure. For a powder of a substance having a simple cubic lattice *Van Vleck* finds

$$\langle \Delta\nu^2 \rangle_{av} = (3/5) g^4\beta^4 h^{-2} \, S(S+1) \sum_{i>j} r_{ij}^{-6} = (3/10) g^2\beta^2 h^{-2} H_i^2 . \qquad (166)$$

It may be noted that this expression is independent of exchange, which therefore does not contribute to $\langle \Delta\nu^2 \rangle_{av}$; exchange however contributes to $\langle \Delta\nu^4 \rangle_{av}$ (see below).
This expression has been derived with a Hamiltonian from which the terms which give rise to the absorption lines at $\nu = 0$ and $\nu = 2\nu_H$, ... have been dropped. This is necessary for obtaining a result which actually applies to the resonant line, because the subsidiary lines differ so much in frequency from the main line that, although they are much fainter, their contribution to $\langle \Delta\nu^2 \rangle_{av}$ would be of the same order as that of the main line.

Van Vleck also computed the mean fourth power of the frequency and found that exchange contributes to this moment. This necessarily means that the line tapers off less sharply in the wings than in the case of pure magnetic interaction, but at the same time is peaked more sharply near the centre of the line, so that the value of $\langle \Delta\ ^2 \rangle_{av}$ remains unaltered. This exchange narrowing is not likely to occur in nuclear resonance lines in crystals, but has been observed in several concentrated paramagnetic substances in which the resonance lines arise from electronic spins. An interesting example is copper sulphate which has been studied in detail at room temperature by *Bagguley* and *Griffiths* (B19).

It may be noted that in the case of pure magnetic interaction the line shape is about Gaussian. A Gaussian distribution having the correct value of $\langle \Delta\nu^2 \rangle_{av}$ is given by

$$f(\nu) = \left(\frac{1}{2\pi} \langle \nu^2 \rangle_{av}\right)^{1/2} exp[-(\nu - g\beta H_c/h)^2 / 2\langle \Delta\nu^2 \rangle_{av}]; \qquad (167)$$

the corresponding fourth moment is $3(\langle \Delta\nu^2 \rangle_{av})^2$. In the case of a simple cubic lattice and $S = 1/2$ the Gaussian distribution yields $(\langle\Delta\nu^4\rangle_{av})^{1/4} = 1.32\ (\langle\Delta\nu^2\rangle_{av})^{1/2}$, while in the case of pure magnetic interaction we have $(\langle\Delta\nu^4\rangle_{av})^{1/4} = 1.25\ (\langle\Delta\nu^2\rangle_{av})^{1/2}$. The deviation from a Gaussian distribution is therefore not great in this case; the actual curve is somewhat blunted compared with the Gaussian one.

It finally may be added, that *Pryce* and *Stevens* (P6) also considered the first moment, which is a measure for the mean displacement of the line. They found that in the present approximation of high temperature that the centre of the line is not displaced by the interaction.

b) *Two kinds of spins. Van Vleck* also considered the case of two kinds of spins, characterised by different g-values and possibly by different values of S. It is assumed that the g-values differ so much that the resonances of the two varieties of spins do not overlap. One must expect the normal resonance lines for the two types of spins and moreover quite a variety of subsidiary lines. *Van Vleck* calculated the second and fourth moment of the resonance line of one of the kinds of spins. We shall not quote the complicated expressions derived by *Van Vleck*, but we shall only mention the salient features of the result.

1) All other things being equal the magnetic coupling between dissimilar spins is less effective than between like ones in broadening the lines. The contribution of dissimilar spins to the average square width $\langle\Delta\nu^2\rangle_{av}$ is - apart from differences in the values of g and S - only 4/9 times the contribution of identical spins. This result easily can be interpreted as a consequence of 'resonance' between the spins. For seeing this let us consider two spins in a constant magnetic field. Classically they precess about the direction of H_c and the field they exert on each other is a superposition of a steady field and a rotating field. If the spins are identical the precessional frequencies are the same and the rotating field of one spin is able to turn over the other one. This effect reduces the lifetime of the spins in the given states and therefore makes the magnetic interaction more effective in the case of identical spins than otherwise. A detailed calculation gives the factor mentioned.

2) Exchange between dissimilar spins contributes to $\langle\Delta\nu^2\rangle_{av}$ and therefore tends to broaden the line, contrary to the effect for identical spins. *Pryce* and *Stevens* considered this effect in some detail for spins with $S = \frac{1}{2}$. For details we refer to their paper.

3) Both magnetic and exchange interaction between the spins of one type influence only the fourth - not the second - moment of the resonance line of the other type and consequently cause a narrowing of the line.

4) Exchange interaction between one type of spins contributes only to the fourth moment of the line of this type, even if the dipolar broadening is mainly caused by the interaction with the spins of the other type.

It may finally be added that the effects 1) and 2) both act on $\langle\Delta\nu^2\rangle_{av}$ and therefore do not necessarily imply that the Gaussian approximation is a bad one. The effects 3) and 4) on the other hand imply - if they are noticeable - that the deviation from a Gaussian shape is significant.

5.45 *The influence of temperature.*

In the considerations given so far on the magnetic and exchange broadening of resonance lines we confined ourselves to the case of high temperatures where terms in $1/kT$ in the expressions for $\langle\nu^n\rangle$ can be neglected (Cf. (163)). In the temperature region where this no longer is allowed in general the $\langle\nu^n\rangle$ are dependent on the temperature and moreover often on the shape of the sample. This is a consequence of the fact that the higher terms in the expansion of $\langle\nu^n\rangle$ to powers of $1/T$ involve summations over terms which depend on rather low powers of the distances between the magnetic ions (*Pryce* and *Stevens* (P6)).

We are especially interested into the possible displacement of the resonance line with decreasing temperature. This problem has been considered in some detail by *Dr K.W.H.Stevens* in a private communication to Professor *Gorter*, for the case of ions having a spin ½ and coupled only with magnetic coupling. Then the interaction between two ions is given by (70) and the mean displacement of the line to the order $1/kT$ is found to be equal to

$$(3/2)g\beta H_c\ (C/kT)\ \Phi,$$

where Φ is given by (86). Therefore a displacement in the first order of $1/kT$ has to be expected for all shapes which differ from a sphere.

In first approximation only exchange interaction between dissimilar ions can shift the line, the shift due to exchange interaction between like ions is zero in this approximation. As far as we are aware no calculations have been published about the case of strong magnetic and exchange interaction as for instance is present in ferromagnetic or anti-ferromagnetic substances. The theory in this case obviously will encounter many difficulties.

* * * *

PART II

EXPERIMENTS ON SPIN LATTICE RELAXATION

Chapter I

EXPERIMENTAL METHODS

1.1 Introduction.

An experimental check of the preceding considerations on spin-lattice relaxation involves the study of χ' and χ'' as a function of frequency ν, temperature T and constant magnetic field H_c, possible followed by a calculation of the relaxation constant as a function of H_c and T.

It may be noted that in principle a study of the adjustment of the magnetic moment to a new equilibrium value after a sudden change of H_c should give the same information. For practical reasons however a method using an alternating magnetic field has to be preferred and therefore the theory in I, Ch. 4 was developed for this case.

The technique actually required strongly depends on the frequency range in which considerable dispersion and absorption occurs and it is possible to classify the experimental techniques accordingly.

a) The methods used at frequencies between 0.1 and 78 Mc/sec are described in detail by *Gorter* in his monograph (G1), where many references to the existing litterature can be found. We therefore can refrain from a detailed discussion. χ' can be determined by placing the sample in the tank coil of an oscillator and by measuring the change of frequency of this oscillator, caused by changes of χ' due to variations of H_c and T. χ' can be measured by placing the sample in a sufficiently strong alternating field and by determining the rate of heating of the sample. It must be noted that χ' and χ'' are measured separately. This sometimes has the dis-advantage that the results of both types of measurement on samples of the same substance do not entirely agree, especially when they are not treated exactly the same as regards evacuating and sealing. A method of measuring χ' and χ'' simultaneously would remove this difficulty, but probably is difficult to develop in this frequency range.

b) At low frequencies (below 500 c/sec) two methods are feasible; as far as we are aware only one has been applied to spin lattice relaxation.

The first method consists in measuring the saturation of a resonance absorption line under increasing power input. This method for instance has been used by *Bloembergen*, *Torrey* and

Pound (B22) for the measurement of nuclear magnetic relaxation times and by *Bleaney* and *Penrose* (B23) for measuring the thermal relaxation time in ammonia gas at low pressures.

We will discuss briefly the case of paramagnetic substances, where we shall confine ourselves to the case of spins with $S = \frac{1}{2}$. Then the intensity of absorption depends on the difference in occupation of the two levels of the spins. In a steady condition this difference may be denoted by n_0 and when a radio-frequency field is applied by n. If now the probability of a transition by the radiation field is A then the rate of change of n due to this influence is given by $-2An$. The factor 2 accounts for the fact that for each transition n changes with 2. On the other hand there is an opposing tendency – due to the interaction between the spins and the lattice vibrations - which tends to reduce the difference $n - n_o$. The rate of change of n due to this effect is supposed to be proportional to $(n_o - n)$, or equal to $(1/\tau)(n_o - n)$, where $\tau = \rho/2\pi$ is the spin-lattice relaxation time. The total rate of change of n is given by

$$\frac{dn}{dt} = -2An + (1/\tau)(n_o - n).$$

In a steady state this is zero and we get

$$n/n_o = 1/(1 + 2A\tau). \qquad (168)$$

The ratio n/n_o is equal to the ratio between the actual absorption strength and the absorption strength at power level zero.

In the case of spins with $S = \frac{1}{2}$ it can be shown that

$$A = \tfrac{1}{2}\gamma^2 h^2 \tau' \varphi(\nu),$$

where h = the amplitude of the radiation field, γ is the magnetogyric ratio $(\gamma = g\beta/\hbar)$, τ' is the spin-spin relaxation time, which is a measure of the reciprocal width of the line; $\varphi(\nu)$ accounts for the finite width of the absorption line in the following way. As a consequence of the finite width of the line the surplus number n formally can be regarded as being distributed over a frequency range according to a function $\varphi(\nu)$ determined by

$$n(\nu) = n\varphi(\nu) \qquad \int_0^\infty \varphi(\nu)\, d\nu = 1.$$

It is further assumed that the frequency of the radiation field $h = \int h(\nu)d\nu$ is so well defined that $\varphi(\nu)$ can be taken constant over the frequency region where h is different from zero. It is not difficult to satisfy this condition in the micro wave range.

The absorption therefore is proportional to

$$n/n_o = \varphi(\nu)/(1 + \gamma^2 h^2 \tau\tau' \varphi(\nu)). \qquad (169)$$

In the case of a narrow absorption line $\varphi(\nu)$ at the resonance frequency is not very much different from one; then the intensity of absorption rapidly decreases if h becomes so large that $\gamma^2 h^2 \tau\tau' \simeq 1$.

In the case of a rather dilute substance like an alum we have $\tau' \simeq 10^{-8}$ sec and for electronic spins $\gamma = 1.76 \times 10^7$ Oersted^{-1}

$\sec^{-1}$, so that if $\tau = 10^{-3}$ sec the mean energy density required for making $\gamma^2 h^2 \tau\tau' = 1$ becomes $h^2/8\pi = 10^{-4}$ ergs/cm^3 [or $h \simeq 0.05$ Oersted], so that per sec per cm^3 $c \times h^2/8\pi = 3 \times 10^6$ ergs has to be applied. If therefore the volume of the crystal is 0.01 cm^3 the power required is 3×10^{-3} Watts. If $\tau = 1$ sec the power required is only 3×10^{-6} Watts. Power inputs of this order easily can be produced in the microwave range.

The application of (169) for determining τ requires the knowledge of γ, h and τ'. It is however possible to determine the ratio of the product $\tau\tau'$ at two temperatures by comparing the absorption as a function of the applied power (or h) for these temperatures. τ' can be calculated from the line width and, except at very low temperatures, is independent of T. It therefore is comparatively simple to determine the ratio of the spin lattice relaxation time for a given value of H_c at two temperatures.

Complications may arise in cases where several spin-lattice relaxation times come into play (in the case of spins with $S = \frac{1}{2}$ there can be only one relaxation time; cf. G2). We shall not discuss this point further.

It finally may be noted that this method in principle can be applied to cases where the relaxation time is too long ($\tau > 0.1$ sec) for being measured with the bridge method (see below).

An alternative method for investigating spin-lattice relaxation phenomena at low frequency is the study of χ' and χ'' with a suitable low frequency alternating current bridge. We will describe a very useful bridge in the next section (1.2). This method has the advantage that χ' and χ'' are determined simultaneously. Therefore the interpretation of the measurements no longer depends on the assumption that the relaxation phenomena can be interpreted with one relaxation constant. In the next chapter we will discuss cases where this assumption is not valid.

1.2 The bridge method.

1.21 Theory.

a) The basic idea underlying the use of an a.c. bridge for measurements on paramagnetic relaxation can be elucidated in the following way. Let us consider a mutual inductance with an alternating current flowing through the primary. In the case of an ideal mutual inductance the secondary voltage is exactly in quadrature with the primary current. This however is never the case in practice and the secondary voltage always has a - usually small - component in phase with the primary current.

If a paramagnetic substance, which may have a complex susceptibility due to relaxation, is placed inside the mutual inductance both the real and imaginary part of the coefficient of mutual inductance will change. These changes are a measure for the magnitude of the real and imaginary part of the susceptibility, and therefore the measurement of χ' and χ'' can be reduced to a determination of the two components of the coefficient of mutual inductance.

This can conveniently be carried out with an a.c. bridge. A bridge suitable for this purpose has to satisfy several requirements; the most important in our cases are

1) χ' and χ'' can be measured simultaneously and with sufficient accuracy. The second requirement implies that the detector is sufficiently sensitive and moreover that 'impurity' effects of the bridge elements (see below) are either negligible or can be taken into account.

2) The balance condition is rapidly attained. This condition is fulfilled if the bridge can be balanced by two independent adjustments of the bridge elements.

The bridge we actually used satisfied these requirements and is originally developed by *Hartshorn* (H7); it has previously been used by *De Haas* and *Du Pré* (H10). The circuit is drawn in fig. 9. M_1 is the mutual inductance containing the sample and is placed in the cryostat; M_2 is a variable mutual inductance and R is a resistance. The current through the detector D can be made zero by proper adjustment of M_2 and R.

In order to find the balance condition we write the relation between primary current I_p and the secondary voltage V_s of a mutual inductance in the form

$$V_s = [-i\,\omega(M + \zeta) + \sigma]I_p, \tag{170}$$

where ω is 2π times the frequency and M is the coefficient of

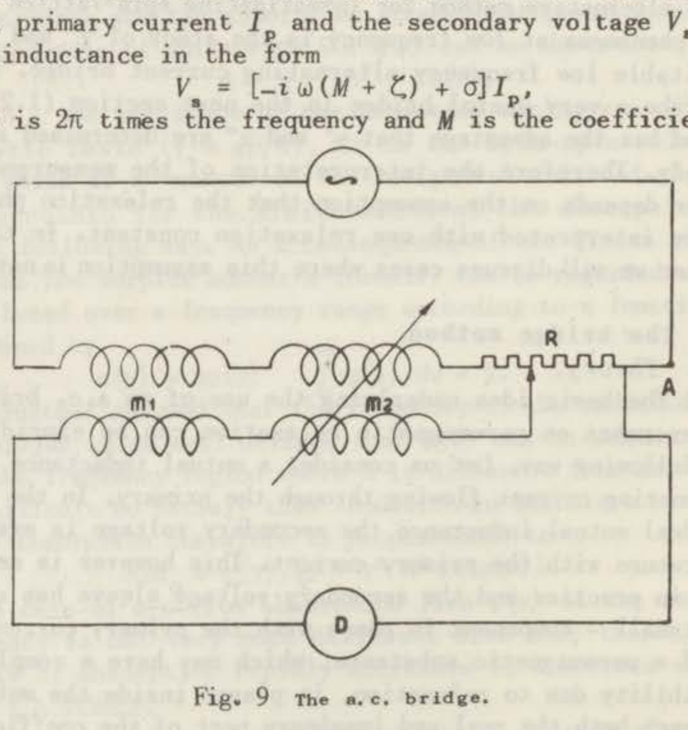

Fig. 9 The a.c. bridge.

mutual inductance for the limiting case of frequent zero; M therefore is real. The quantities ζ and σ in general depend on the frequency and describe the deviation of the actual mutual inductance from an ideal mutual inductance for which $\zeta = \sigma = 0$; σ describes the component of V_s which is in phase with I_p. The phase defect δ is given by $\mathrm{tg}\,\delta \simeq \sigma/\omega M$ (see fig. 10) and usually is small ($\delta \ll 0.01$).

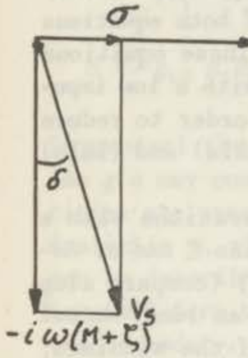

Fig. 10

If M_1 does not contain a sample - which is denoted by the suffix ^{o}- the ballance condition becomes

$$-i\omega M_1^o - i\omega M_2^o + R^o = 0 \tag{171}$$

or

$$[-i\omega(M_1^o+\zeta_1^o)+\sigma_1^o]+[-i\omega(M_2^o+\zeta_2^o)+\sigma_2^o]+R^o=0. \tag{172}$$

Separation into real and imaginary part gives the independent balance conditions

$$M_1^o + M_2^o + \zeta_1^o + \zeta_2^o = 0 \tag{173}$$

$$\sigma_1^o + \sigma_2^o + R^o = 0. \tag{174}$$

Balance of the bridge can be attained by two independent adjustments (M_2 and R) and the convergence towards balance therefore is rapid.

If now a sample is placed in M_1 the coefficient of mutual inductance becomes

$$M_1 = M_1^o\,(1 + f\chi), \tag{175}$$

where f is a factor depending on the geometry of the system and χ in general can be complex as a consequence of relaxation.

We will now introduce some important simplifications to be justified later. In the first place we shall assume that f is real and secondly that $\sigma_1^o \ll \omega M_1^o$. Consequently we can write

$$M_1 = M_1^o + (1/B)\chi, \tag{176}$$

where $1/B = f(M_1^o + \zeta_1^o)$, which is real.

Balance of course only can be obtained by renewed adjustment of M_2 and R, and we have the new balance condition

$$-i\omega M_1 - i\omega M_2 + R = 0, \tag{177}$$

or

$$-i\omega[M_1^o + \zeta_1^o + (1/B)\chi'] + [\sigma_1^o - (\omega/B)\chi''] + [-i\omega(M_2 + \zeta_2) + \sigma_2] + R = 0. \tag{178}$$

Application of (172) and separation into real and imaginary parts yields

$$\begin{aligned} \chi' &= B[(M_2^o - M_2) + (\zeta_2^o - \zeta_2)] \\ \chi'' &= (B/\omega)[(R - R^o) + (\sigma_2 - \sigma_2^o)]. \end{aligned} \tag{179}$$

In practice we neglected the terms $(\zeta_2^o - \zeta_2)$ and $(\sigma_2 - \sigma_2^o)$ (third simplification) and we always used the simple expressions

$$\chi' = B(M_2^o - M_2) \tag{180a}$$

$$\chi'' = (B/\omega)(R - R^o). \tag{180b}$$

It must be remembered that B depends on the frequency. This however has no effect on the ultimate results as we are only interested into the ratios χ'/χ_0 and χ''/χ_0. According to (180a) and (180b) χ' and χ'' can be derived from two independent bridge adjustments which is an important advantage of the *Hartshorn* bridge.

Finally it may be noted that the use of (175) instead of (176) leads to the expressions

$$\chi' = B[(M_2^0-M_2) + (\zeta_2^0-\zeta_2)] - (B/\omega)(R-R^0)(\sigma_1^0/\omega M_1^0) \quad (181a)$$

$$\chi'' = (B/\omega)[(R-R^0) + (\sigma_2-\sigma_2^0)] + B(M_2^0-M_2)(\sigma_1^0/\omega M_1^0), \quad (181b)$$

where the second terms at the right hand side of both equations describe the influence of the impurity of M_1^0. These equations clearly show the importance of measuring coils with a low impurity. Special care therefore has been taken in order to reduce the impurity so much that the second term in (181a) and (181b) is negligible.

b) It is desirable to extend these considerations with a discussion of the interpretation of the quantities ζ and σ. According to *Butterworth* (B24) and *Hartshorn* (H8) (compare also *Hague* (H9)) the factors causing deviations from an ideal mutual inductance are (1) self and intercapacities of the windings; (2) eddy current losses in the copper of the windings, terminals (in our case also the magnet coil producing the constant magnetic field); (3) leakage and dielectric losses; (4) resistance inadvertently included in common with both windings when these are connected at a common point. Each of these factors gives rise to quantities ζ and σ which are characterised by their dependence on ω. Usually a number of factors is acting simultaneously, which causes a more intricate dependence of ζ and σ on ω than if only one factor were acting. It is often still possible to find the sources of the imperfection of a given mutual inductance by analysing the dependence of ζ and σ on ω.

According to theory common resistance simply gives $\zeta = 0$; while σ is finite but independent from ω. Eddy currents give $\zeta = \omega^2\zeta^*$ and $\sigma = \omega^2\sigma^*$, where ζ^* and σ^* are constants depending on the geometry and the material of the conductors. Capacities and leakage can be taken into account simultaneously; according to *Butterworth* and *Hartshorn* as regards these effects a mutual inductance having a common point C is equivalent with the circuit drawn in fig. 11.

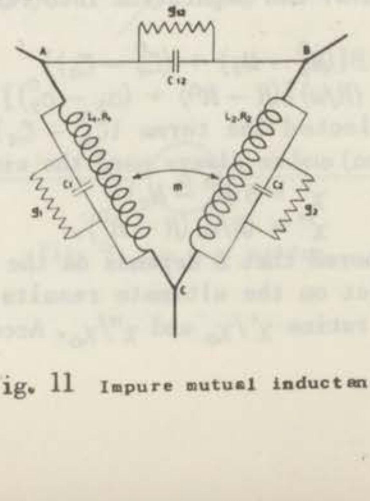

Fig. 11 Impure mutual inductance.

Here the intercapacitance is denoted by C_{12} and the self capacitances of the primary AC and the secondary BC by C_1 and C_2 respectively. The conductances g_{12}, g_1 and g_2 describe the leakage between the primary and secondary, and along the primary and secondary respectively. It can be shown by a long calculation that at low frequencies

$$\begin{aligned}\zeta &= -C_{12} R_1 R_2 - g_{12}[R_1(L_2+M) + R_2(L_1+M)] - (g_1R_1 + g_2R_2)M + \\ &\quad + \omega^2[(C_1L_1 + C_2L_2) + C_{12}(L_1+M)(L_2+M)] \\ \sigma &= -g_{12} R_1R_2 - \omega^2[(C_1R_1+C_2R_2)M + C_{12}\{R_1(L_2+M) + R_2(L_1+M)\} + \\ &\quad + g_{12}(L_1+M)(L_2+M) + (g_1L_1+g_2L_2)M]. \qquad (182)\end{aligned}$$

In general the dependence on ω is rather complicated because the g's may contain ω. If the g's can be neglected (only capacities are present) ζ contains a constant term and a term quadratic in ω, while σ only contains a quidratic term. Leakage can be described by constant g's and therefore only can add a constant term to σ if there is leakage between the primary and the secondary. Dielectric losses can be described with g's depending on ω (in a limited frequency range $g \sim \omega^{\alpha}$, $0<\alpha<1$). Therefore in this case ζ contains a constant term and a term proportional to ω^{α}, while ζ contains a term proportional to ω^{α} and a term proportional to $\omega^{2+\alpha}$. In general therefore both ζ and σ can be expected to be rather intricate functions of ω. From the magnitude of the coefficients of the different powers of ω is sometimes can be concluded which terms in ζ and σ are predominant in a given frequency region. This will be done in the next section for some coils used in our experiments. The results justify the use of the formulae (180) for frequencies below about 500 c/sec.

In the treatment given we neglected the influence of the earth capacitance. This can be justified by the remark that, if point A in fig. 9 is connected to earth, earth capacitances in first approximation merely shunt the self and inter capacities, and therefore are automatically included in the treatment given.

1.22 Apparatus.

In this section we propose to discuss the different bridge elements used in our experiments.

a) *The variable mutual inductance.* For our purpose we required a variable mutual inductance which could be adjusted continuously from zero to about 5 mH. This figure is determined by the desired accuracy in measuring χ and the sensitivity of the available detector.

The mutual inductance was made in the laboratory according to the following pattern. The primary simply was a long solenoid (length 70 cm, diameter 3 cm) of copper wire (diameter 0.06 cm) with varnish and silk insulation, wound on a glass tube. The secondary was wound on a wider glass tube and surrounded the primary in the middle; it was build up from groups of 100, 10 and 1 turns of a stranded rope of ten insulated thin copper wires. By stranding the wires the mutual inductance between all strands of one group and the primary is almost exactly the same and the total mutual inductance is proportional to the number of turns. On the other hand stranding introduces considerable capacitance between the strands. This is liable to give considerable impurity at higher audio frequencies, but did not cause troubles in our experiments.

By the use of three decimal dials any number of turns could be joined in series and their mutual inductance added, thus allowing to change the mutual inductance in steps of one turn. A subdivision in tenths of one turn was obtained by the following simple artifice (*De Klerk* (K6)). One extra turn of the rope of strands was placed at the middle and a second one near the end of the primary, in such a way that the flux through this turn was just nine tenths of the flux through the turn in the middle. Two decimal dials mounted on one shaft allowed to connect equal numbers of strands of both turns in series with mutual inductances opposed. In order to reduce the intercapacity between the primary and the secondary an earthed screen was placed between them.

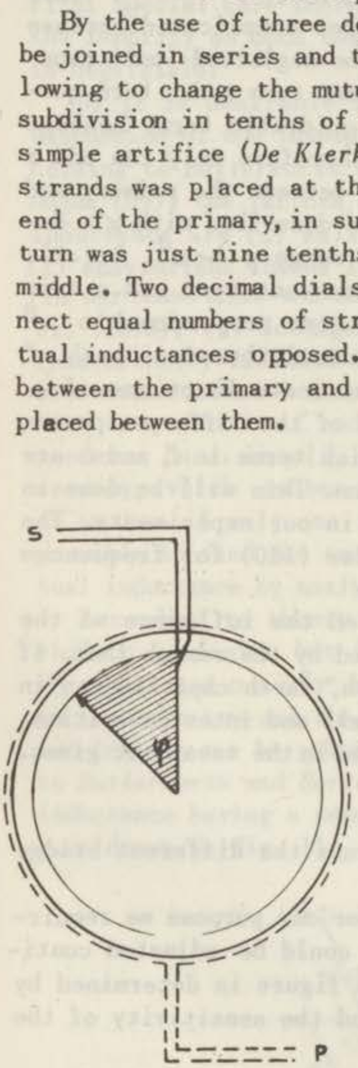

Fig. 12 The variometer

A simple variometer ranging from -0.1 to +0.1 turn allowed a continuous adjustment. It was made from a circular disk of ebonite which carried the primary windings P and the secondary S; S consisted of a single open turn, tapped in the middel (fig. 12). The other secondary lead passed through the centre of the disk and made contact with the secondary turn at the sliding contact C. In the case of proper construction the mutual inductance is proportional to the shaded area or to the angle φ. This was confirmed with a high degree of accuracy for the instrument used. A scale division allowed readings to 0.001 turn of the main mutual inductance which corresponds about to the mean accuracy of the detector.

Calibration. The calibration was carried out in two steps. In the first place the different groups of turns had to be compared in order to check the ratio of the mutual inductance of the different groups. This was done by comparing the maximum mutual inductance of one dial with one unit of the next higher dial, assuming that the strands of one dial had exactly the same mutual inductance. The very small deviations from the expected decimal rations ware taken into account in the calculations of χ' and χ''.

Secondly we studied ζ and σ by comparing M_2 with a *Tinsley* standard mutual inductance of 0.2 *mH*. The results are collected in Table VI where *M* and ζ are presented in units 4.53 *μH*, which is the mutual inductance of one turn of the secondary.

Table VI

<table>
<tr><th colspan="8">A.C. BRIDGE</th></tr>
<tr><th colspan="8">$M = 0.2\ mH = 42.415\ turns\ \ (1\ turn = 4.53\ \mu H)$</th></tr>
<tr><th>Frequency (c/sec)</th><th>175</th><th>225</th><th>275</th><th>325</th><th>375</th><th>425</th><th>475</th></tr>
<tr><td>ζ (in turns)</td><td>0.019</td><td>0.037</td><td>0.039</td><td>0.073</td><td>0.082</td><td>0.136</td><td>0.173</td></tr>
<tr><td>$\zeta/M \times 10^4$</td><td>4.5</td><td>8.7</td><td>9.2</td><td>17</td><td>19</td><td>32</td><td>41</td></tr>
<tr><td>σ (ohms) $\times 10^4$</td><td>0.39</td><td>0.53</td><td>0.65</td><td>0.91</td><td>1.21</td><td>1.65</td><td>2.13</td></tr>
<tr><td>$\sigma/\omega M \times 10^4$</td><td>1.8</td><td>2.0</td><td>2.1</td><td>2.3</td><td>2.7</td><td>3.2</td><td>3.8</td></tr>
</table>

It is assumed that both ζ and σ of the standard can be neglected. Of course objections may be raised against this procedure. We believe however that probably the order of magnitude of ζ and σ is correct. This is all we require for concluding that the terms $(\zeta_2-\zeta_2^0)$ and $(\sigma_2-\sigma_2^0)$ in (179) can be neglected. In the first place each of the ζ's and σ's is much smaller than χ' and χ'', and in the second place ζ and σ will be nearly independent of the setting of M_2. Consequently the third simplification (see page 91) is allowed even if χ' and χ'' are smaller than 0.1 turn.

We moreover found that (a) ζ is proportional to ω^2 and (b) σ varies more rapidly than ω^2. This must be due to dielectric losses, which are likely to occur because the coils were wound on glass and the wires had silk insulation. Both substances absorb moisture and this can give noticeable losses. Improvements easily could have been arranged but were not necessary for our measurements.

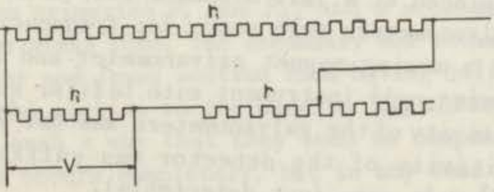

Fig. 13 The phase potentiometer.

b) The *phase potentiometer* (fig. 13) replaced the resistance R in fig. 9. We required values of R between 10^{-4} and 10^{-1} ohm, for which the potentiometer was more accurate than a slide wire. The fixed resistance r_1 carried the primary current and was shunted by another fixed resistance r_2 and a variable resistance r in series. The voltage required in the secondary was taken from the ends of r_2 and could be commuted. It is easily seen that

$$V = RI_p = r_1 r_2/(r_1+r_2+r)\, I_p, \tag{183}$$

where $R = r_1 r_2 \,/\, (r_1+r_2+r)$ is the resistance which an equivalent slide wire should have. The potentiometer is calibrated by measuring V, while I_p was a known direct current. We found $R \approx 0.586/(2.79+r)$, where R and r are expressed in ohms.

It may be noted that in principle it is possible to use the potentiometer by taking r constant and r_2 variable. This could be advantageous if $r_2 \ll (r_1+r)$; then the denominator in (183) would be practically constant and we would have $V \sim r_2$. Especially when r_2 is small the contact resistance of the variable resistance however enters critically and therefore we preferred the arrangement with variable r.

c) The *alternating current* I_p was provided by a *Philips* beat-frequency generator or a *Peekel RC* generator in series with a 5 watt amplifier. The *RC* generator was superior as to constancy of frequency and to distortion. It was possible to make I_p as high as 0.2 amps with sufficiently low distortion.

The frequency adjustment was made either by comparing the frequency with mains frequency by means of a cathode ray oscilloscope or by comparing higher harmonics with a tuning fork; the frequencies used were always different from the harmonics of the mains frequency in order to reduce the possible influence of pick up from the mains.

d) The *selective detector* consisted of a two stage battery-fed amplifier with resistance coupling and a tunable vibration galvanometer. The first valve was a Philips CF 50, which is characterised by a very low noise level and a high amplification factor. The second valve was a Philips EF 6 coupled to the galvanometer with a suitable transformer. In order to prevent oscillations the input had to be screened very carefully and each valve was given a separate anode battery. Moreover the amplifier was placed at a fair distance (4m) from the bridge.

Two galvanometers were used; for frequencies between 100 and 500 c/sec a moving magnet galvanometer and for lower frequencies a moving coil instrument with bifilar suspension. Although the sensitivity of the galvanometers was not very high the overall sensitivity of the detector was sufficient (voltages of about 10^{-7} volt were just detectable).

The detector allowed the measurement of M_2 with a sensitivity of about 0.001 turn for a primary current of 0.1 amp and for $\nu = 175$ c/sec; the sensitivity of the measurement of R was about 10^{-6} ohm. The sensitivity of the detector decreased at lower frequencies; the lowest frequency which could be used was 25 c/sec. At all frequencies the influence of noise was entirely negligible.

e) The *cryostat coils*. The mutual inductance M_1 originally used by *De Haas* and *Du Pré* (H10) simply consisted of two coaxial cylindrical coils. These coils however had a large impurity and accordingly the determination of χ'' was very inaccurate. It was found that the large impurity mainly was caused by eddy currents in the conductors, like the magnet coil and the silvering of the Dewar vessels surrounding the coils. It was therefore inticipated that coils having a smaller stray magnetic field would have a smaller impurity and would allow a more accurate determination of χ''.

Coils having a very small stray magnetic field have been designed and used by *Casimir, Bijl* and *Du Pré* (C2), and indeed had a much smaller impurity than the previous coils. The main improvement of the new coils was the primary, which now consisted of two coaxial coils giving opposite magnetic fields. The dimensions were chosen in such a way that the dipole moments compensated each other. Then each of the ends of the system acts as a magnetic quadrupole and at large distances the system acts as a magnetic octupole. Inside the coils however the resulting magnetic field is different from zero as is easily seen in the following way.

The magnitude of the dipole moment P and the magnetic field h in the centre of a cylindrical solenoid are resp. given by

$$P = 0.1\,\pi\, inlr^2 (\text{Ø cm}) \qquad h = 0.4\pi\, inl/(4r^2 + l^2)^{1/2}\ (\text{Ø}),$$

where i is the current in amps, l is the length, r is the radius and n is the number of turns per cm. Two coaxial coils of equal length have equal dipole moments if

$$n_1 r_1^2 = n_2 r_2{}^2 \qquad (184)$$

(with obvious notation), while on the other hand it is easily seen from the above formulae that the field strengths in the centre are not equal, except in the trivial case of identical coils.

The first system of coils constructed according to the principle just mentioned is drawn in fig. 14 and consisted of three coaxial coils, two primaries P_1 and P_2, and a secondary S; all coils are wound on glass tube. The secondary was wound in three sections, the upper and lower section each having half the number of turns of the section in the middle. The three sections are connected in such a way that they tend to compensate each other. This never occurs completely, but in any case the total mutual inductance is much smaller than the mutual inductance of one of the sections apart. In this way the possible influence of pick up from homogeneous stray fields (for instance from the mains) is very much reduced. Moreover the number of turns of M_2 required for compensation of S is much smaller than otherwise, which may improve the reproducibility of the bridge balance.

The sample to be investigated was placed in the spherical glass container C; C was connected to a long glass tube which was stuck at D with *Dekhotinsky* cément to the inside of the tube, which carried the whole system. At K the system was attached to the cap of the cryostat.

This set of coils was satisfactory in different respects. In the first place change of sample was reasonably easy, although it required cutting the glass above D and sealing after the replacement of the sample. In the second place tg δ was very small (see Table VII). Only in the limiting case that χ' is larger than 100 χ'' the extra terms at the right hand side of (181) become noticeable. Therefore in all our experiments the second simplification in the derivation of (180) (see page 91) is justified.

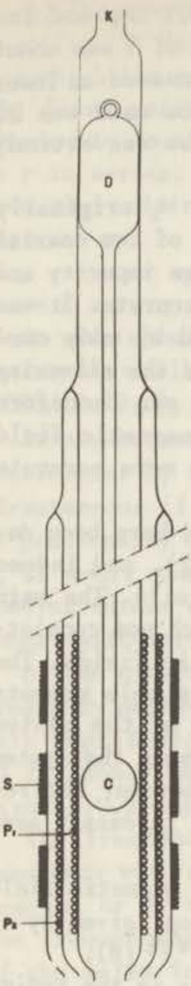

Fig. 14 The cryostat coils (first set).

TABLE VII

Cryostat coils (first set)									
T = 4.0 °K M = 39.230 turns *) (1 turn 2.77 μH)									
Frequency	16.7	25.0	37.5	64	85	102	128	170	256
ζ(in turns)	(0.026)	(0.017)	0.032	0.040	0.073	0.095	0.108	0.139	0.193
$\zeta/M_c \times 10^4$	(0.66)	(0.43)	0.81	1.00	1.86	2.42	2.75	3.53	4.90
σ(ohms)$\times 10^4$	0.086	0.20	0.49	1.24	2.00	2.77	3.89	5.79	9.96
$\sigma/\omega M \times 10^4$	7	12	19	30	34	39	44	50	57

From Table VII is furthermore can be concluded that for frequencies higher than 128 c/sec both ζ and σ vary with the square

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*) These measurements were carried out with Casimir and De Klerk's bridge (C4)

of the frequency; at lower frequencies however with a lower power of ν. This suggests that part of the impurity must be due to leakage. It is very unlikely that the cryostat coils - when at a temperature as low as 4 °K - would show other impurities than those due to capacitance and eddy currents. Consequently the leakage must have been outside the cryostat, presumably in the leads.

In an other respect however these coils were not entirely satisfactory, because after about 5 runs at liquid helium temperatures the impurity increased at least a factor 10 and it was impossible to obtain stable bridge settings; then the secondary had to be rewound. This trouble was a consequence of our imperfect technique of winding, which consisted in winding - without special precautions - many layers of thin copper wire (diameter 0.05 cm) with silk insulation.

We therefore decided to adopt another technique of winding which had been proved to be succesful in other experiments (B 25). All coils now were wound on tubes of fused quartz, which were connected to each other with thin quartz rods so as to give a system of coaxial tubes. The two other tubes carried the primary coils which were of the same design as the previous coils. A third tube inside these tubes carried the secondary and the sample was placed in a container of casein plastic which would be slipped with its top over the lower end of a fourth tube of quartz placed in the centre of the system. With this arrangement replacement of the sample was quite simple.

The secondary coils were wound of enameled copper wire (diameter 0.05 cm) under a microscope of low magnification in order to make sure that the turns would be as close to each other as possible. Each layer was varnished with shellack and was allowed to dry before the next layer was wound. The coils made in this way have been intensively used for more than two years without being rewound; the impurity only very slightly increased during this time.

The quality of the system can be judged from Table VIII and is found to be even better than the first set, as the values of δ are smaller now.

Table VIII

Cryostat coils (second set)								
T = 4.0 °K M = 404.830 turns (1 turn = 4.53 μH)								
Frequency	25	37	62	83	133	175	325	475
ζ (in turns)	(0.025)	(0.018)	0.035	0.057	0.137	0.233	0.84	1.81
$\zeta/M \times 10^4$	(0.062)	(0.044)	0.087	0.140	0.34	0.57	2.08	4.50
σ(ohms) $\times 10^4$	0.53	0.94	2.14	3.61	8.65	15	51.5	112
$\sigma/\omega M \times 10^4$	2	2	3	4	6	7	14	21

Both ζ and σ are proportional to ν^2 and therefore the impurity must be due entirely to capacitance and eddy currents, which is just what one must expect.

We safely can conclude that both systems of coils were very satisfactory for out purpose. Only in the case of very low susceptibility (for instance of very dilute salts) coils having more turns are required.

We still have to justify that f in equation (175) can be taken real. This can be done by considering the flux through the secondary coil (see fig. 15). The flux in the empty coil OF

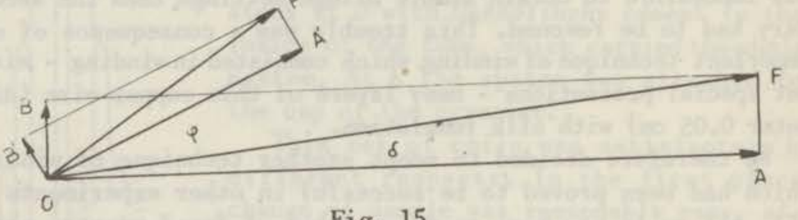

Fig. 15

contains a component OA at right angle with the primary current and a component OB in phase with the primary current. If now a paramagnetic sample showing relaxation is placed inside the coils an extra flux OF' passes through the secondary. This flux is the sum of contributions OA' and OB', both having the same phase difference φ with OA and OB resp. Assuming that OB is entirely due to eddy current losses in neighbouring conductors (magnet coil) and that the whole space is filled with paramagnetic substance, we would have

$$OA'/OA = OB'/OB,$$

or in other words OF' should have a phase difference φ with OF. Consequently f should be real. Of course the substance is only present inside the secondary and accordingly

$$OA'/OA > OB'/OB,$$

so that the phase difference between OF and OF' is not exactly equal to φ. This deviation certainly is smaller than δ - even in the case that OB were only due to eddy currents - and consequently f is complex with an argument smaller than δ. The maximum error in the argument of χ, caused by taking f real, is much smaller than δ and therefore can be neglected.

Summarising we can say that the bridge described and the measuring coils fulfil the requirements for making possible the use of the simple formulae (180).

f. The *constant magnetic field* was produced with an iron free solenoid constructed by Professor *Keesom*. The field obtained was 22.46 Oersted per amp. The water cooling was sufficient for permitting the use of 400 amps during 5 minutes, which corresponds to a magnetic field of about 9000 Oersted. The maximum current used in our experiments was 200 amps.

* * * *

Chapter II

EXPERIMENTAL RESULTS

2.1 Introduction.

In this chapter we will present the results of experiments on paramagnetic relaxation at very low temperatures obtained with the bridge method, discussed in Chapter I. Before proceeding to the review of the results themselves we briefly discuss the method of calculation.

It is easily seen that the computation of χ' and χ'' from the bridge settings with the formulae (180) requires the knowledge of B, M_2^0 and R^0. We arbitrarily chose $1/B$ equal to the mutual inductance between one turn of the secondary of M_2 and the primary; χ' and χ'' then are expressed in turn of M_2.

M_2^0 most easily is found by analysing the values of M_2 found at different temperatures in zero constant field. The susceptibility of the substance in which we are interested here always satisfies a *Curie-Weiss* law at the temperatures where the experiments are carried out. We than have $\chi = \chi_0 = C/(T-\Delta)$ (where C and Δ are constants) and consequently - if we neglect the impurity of M_2 -

$$M_2 = M_2^0 \, (1 + f\, C/(T-\Delta)). \tag{185}$$

By plotting M_2 as a function of $T-\Delta$, with properly chosen value of Δ, a straight line with slope $M_2^0\, fC = C/B$ is obtained and extrapolation to $T = \infty$ gives M_2^0. R^0 is equal to the value of R required for obtaining balance of the bridge in absence of a constant magnetic field and is at very low temperatures independent of T.

The first step in the interpretation of the measurements is a check of the thermodynamic formulae (117). This can be done by examining a χ'/χ_0 versus log ν plot, and a χ''/χ_0 versus log ν plot. Essential in the first plot is the slope of the tangent in the point for which $\chi' = \frac{1}{2}(\chi_0 - \chi_\infty)$ - determined by $\rho\nu = 1$ - and in the second plot the width at half the maximum value, determined by $\rho\nu = 1$ as well. In case of agreement with the theoretical values of the slope and the width (see p. 58) the values of ρ are readily found. An alternative method is to examine the χ'' versus χ' plot, which - as will be remembered - should be a circular arc with the centre on the χ' axis. This method however is less reliable than the other one, because it is usually not possible to draw the circles in an entirely unambiguous way. In general therefore the first method has to be preferred.

Only in case of agreement with the more flexible *Cole* formulae (129) the χ'' versus χ' plot is quite useful for determining the deviation from the thermodynamic formulae; these deviations readily can be expressed in the width $\rho_{1/2}/\rho_{av}$ of the distribution of relaxation constants. The average value of the relaxation constant ρ_{av} can be determined in the same way as above. It may be added that both in the case of the thermodynamic and the *Cole* formulae the χ'/χ_0 versus log ν and the χ''/χ_0 versus log ν curve, only differing by the value of ρ or ρ_{av} can be made to coincide by shifting them along the log ν axis.

The next step is a check of the *Casimir-Du Pré* formula (122). This can be done by plotting $1/(1 - F)$ as a function of H_c. If saturation is negligible the result is a straight line with slope C/b. From the value of b/C obtained in this way often the electrical splitting can be estimated.

Finally the values of ρ or ρ_{av} have to be compared with the theoretical expectations. Because our experiments are confined to very low temperatures the results should be compared in any case with the theories developed for this temperature region. It will be remembered that according to *Van Vleck* ρ should be proportional to $H^{-2}\,T^{-1}$ in the liquid helium range, while *Temperley* predicted that ρ should increase with increasing field before the decrease according to *Van Vleck* could start.

We will see below that the results suggest that it makes sense to compare the results obtained at very low temperatures with *Van Vleck's* calculations for higher temperatures as well. This involves a check of the *Brons-Van Vleck* formula (147), which can be done in two ways. First we can write (147) in the form

$$1/\rho = p/\rho_0 + (1-p)/\rho_0\,[1/(1+x^2)].\,^{*)} \qquad (186)$$

If therefore the $1/\rho$ versus $1/(1 + x^2)$ plot is a straight line (147) is satisfied, and p and ρ_0 easily can be calculated. An alternative way is to plot $(1 + x^2)/\rho$ - which is proportional to the heat contact α, between the spin-system and the lattice - versus x^2. In case of agreement with (147) a straight line is found. (It may be remembered that *Van Vleck* calculated α, and found for high temperatures $\alpha_1 = \beta + \gamma H_c^{\,2}$ (β, γ do not depend on H_c), which immediately leads to formula (147)). This method is a somewhat more direct check of *Van Vleck's* calculations and therefore is adopted in the next section.

2.2 Results.

2.21 *Review.*

In this section we represent the results of measurements on a number of substances. In order to save space most of the results are collected in tables. Some typical cases however are illustrated by diagrams as well.

We examined the following substances

Chromium potassium alum (3 samples)
Iron ammonium alum (3 samples)
Manganese ammonium sulphate

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*) Where $x = H/H_n$ (Cf. page 59).

Manganese sulphate
Copper potassium sulphate
Gadolinium sulphate
Dilute chromium potassium alum, (1:13)
Dilute iron ammonium alum, (1:16) and (1:60).

One sample of each substance was investigated unless otherwise stated; each substance will be discussed separately.

2.22 *Chromium potassium alum* $Cr\ K(SO_4)_2 \cdot 12H_2O$.

a) Sample A (C2) consisted of well grown crystals obtained by recrystallisation of a sample of chromium potassium alum Brocades puriss.. Dr *K.F.Waldkötter* kindly carried out an analysis and found for the chromium content 10.0 % (theoretical value 10.4 %). Aluminium, the most usual impurity, could not be detected. Probably the water content was slightly too high.

Both χ'/χ_0 and χ''/χ_0 satisfactorily agreed with the thermodynamic formulae and the values of χ_∞ found by extrapolation along the χ''/χ_0 versus χ'/χ_0 plot agreed satisfactory with the *Casimir-Du Pré* formula (123). We found $b/C = 0.81 \times 10^8$ Oersted^2; assuming, that only magnetic interaction between the ions is present, this corresponds according to (93) to $\delta = 0.181$ cm^{-1}.

The values of ρ, obtained from both the dispersion and absorption are included in Table XI (fifth row) and will be discussed together with the data of the second sample.

TABLE IX

ρ (sec) × 10^3				$Cr\ K(SO_4)_2 \cdot 12\ H_2O$				Sample A,B					
H(Ø) T(°K)	456	694	790	1040	1140	1390	1570	1735	2250	2430	2950	3370	3940
4.04	-	(2.1)	2.4^8	2.7^8	-	3.5^5	-	4.0^3	5.1^0	5.2^4	5.9^5	6.7^0	7.4^2
3.00	-	5.6^8	6.0^3	6.6^1	-	8.6^0	-	9.4^3	12.6	12.5	13.6	15.3	16.6
2.58	-	9.1^7	9.8	11.0	-	14.1	-	15.8	19.5	20.4	22.4	23.5	24.8
2.20	-	-	14.8	-	-	-	-	-	28.8	-	-	35.9	38.0
2.05$^{a)}$	15.0	-	17.6	-	21.2	-	27.4	-	$34.^7$	-	-	-	-
1.95	-	-	20.0	-	-	-	-	-	$36.^3$	-	-	44.1	48

a) values of sample A.

b) Sample B (K7) was prepared separately by recrystallising a sample of the same origin as sample A. Again χ'/χ_0 and χ''/χ_0 agreed well with the thermodynamic formulae. From the χ'/χ_0 data we calculated F and we found a satisfactory agreement with the formula (123); we found $b/C = 0.75 \times 10^8$ Oersted^2.

The values of ρ are collected in Table IX and fig. 16, together with those of sample A. There is very good agreement between the values of ρ of both samples and we found that between 1.9 and 4.1° K ρ is approximately proportional to T^{-3} for all

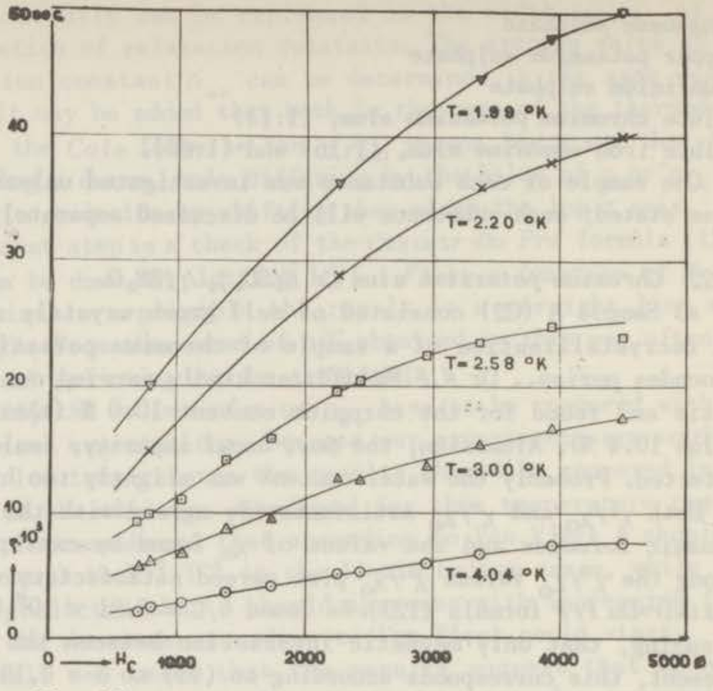

Fig. 16 Chromium alum (A, B). ρ as a function of H_c.

values of H_c. The dependence of ρ on H_c slightly deviates from the *Brons-Van Vleck* formula (147). This is easily seen from fig. 17, where we plotted $(1 + x^2)/10^3\ \rho$ as a function of x^2.

The curves obtained only slightly deviate from a straight line.

c) Sample C was available in the laboratory and probably was less pure than the samples A and B. This time χ'/χ_0 and χ''/χ_0 deviated from the thermodynamic formulae, but agreed satisfactorily with the *Cole* formulae (129). We collected ρ_{av} and $\rho_{½}/\rho_{av}$ for different values of H_c and T in Table X; the values of ρ_{av} are about one fifth of the values of ρ of the samples A and B. The dependence on H_c and T however are practically the same in all three cases. The value of $\rho_{½}/\rho_{av}$ slightly increases with increasing fieldstrength but

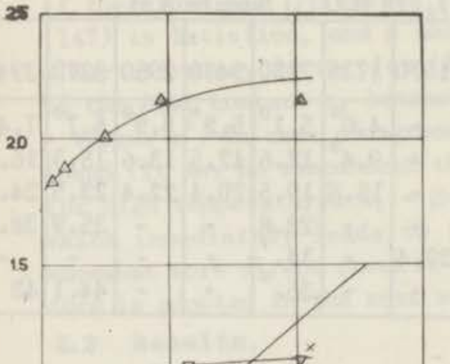

Fig. 17 $(1-x^2)/10^3\rho$ as a function of x^2. Iron alum Δ T 3.00 °K ∇ T 2.58 °K Chromium alum × T 3.00 °K + T 2.51 °K.

seems to be almost independent of the temperature. For b/C we found $b/C = 0.75 \times 10^6$ Oersted^2.

TABLE X

$CrK(SO_4)_2.12H_2O$		Sample C					
	$\frac{H(\text{Ø})}{T(°K)}$	355	710	1065	1775	2480	3100
$\rho \times 10^3$ sec	2.68	1.2	1.6	1.9	2.9	3.6	4.2
	2.20	-	2.3	3.6	5.5	7.1	8.0
	1.34	10	12.5	15	22	29	34
$\rho_{½}/\rho_{av}$	2.68	-	1.3^1	1.2^3	1.2^8	1.2^9	1.3^4
	2.20	-	1.1^7	1.1^9	1.3^1	1.2^8	1.3^1
	1.34	1.1	1.0	1.1^9	1.2^7	1.2^8	1.2^7

d) Summarising we can remark that

1) the less pure sample shows deviations from the thermodynamic formulae and has a much shorter relaxation constant than the purer samples,

2) the dependence of ρ and ρ_{av} on H_c and T is the same in all cases,

3) the value of b/C does not seem to be influenced by slight impurities or imperfections in the crystals. The most reliable value is

$$b/C = 0.75 \times 10^6 \text{ Oersted}^2,$$

which corresponds to a splitting ($\zeta = 0.0204°$ K (Cf.H5), $C = 1.88$)

$$\delta = 0.175 \text{ cm}^{-1} \text{ (Cf.(92))},$$

if only magnetic interaction between the chromium ions is present. *Broer* (B26) found at higher temperatures $b/C = 0.65 \times 10^6$ Oersted^2, or $\delta/k = 0.241°$ K, $\delta = 0.169$ cm^{-1}.

2.23 *Iron ammonium alum $FeNH_4(SO_4)_2.12H_2O$.*

This substance has been studied by *Du Pré* (P7) in the limiting case of high frequencies between 1 and 4° K. Our experiments aimed to examine the absorption and dispersion in greater detail by extending the ranges of frequency and constant magnetic field. Three different samples have been investigated (K7).

a) Sample A was prepared by recrystallisation from iron ammonium alum Kahlbaum puriss.. In low fields χ'/χ_0 and χ''/χ_0 closely agreed with the thermodynamic formulae, but at higher fields *Cole's* formulae gave a better description. This is illustrated by the values of $\rho_{½}/\rho_{av}$ in Table XI. There is an indication that $\rho_{½}/\rho_{av}$ increases with decreasing temperature. From the dispersion data we calculated $b/C = 0.25 \times 10^6$ Oersted^2, using formula (93).

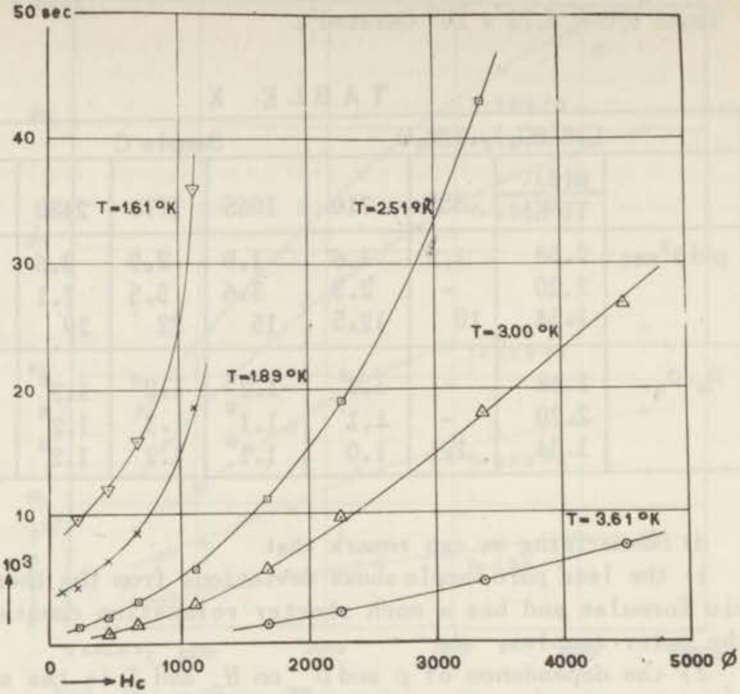

Fig. 18 Iron alum (A). ρ as a function of H_c.

TABLE XI

$Fe(NH_4)_2(SO_4)_2.12H_2O$				Sample A						
	H(Ø) / T(°K)	113	225	450	675	1120	1685	2250	3370	4500
$\rho \times 10^3$ sec	3.61	-	-	-	-	-	(1.4^5)	2.4^0	4.7^8	7.5^8
	3.00	-	-	(0.9^8)	(1.5^0)	3.0^1	5.7^4	9.9^0	$18.^0$	$26.^9$
	2.51	-	1.5^2	2.1^0	3.3^8	5.7^8	$11.^3$	(19.1)	$(42.^0)$	-
	1.89	4.2^6	4.4^6	6.5^8	8.7^0	$18.^7$	-	-	-	-
	1.61		9.0^8	$12.^2$	$15.^9$	(36)	-	-	-	-
$\rho_{½}/\rho_{av}$	3.61	-	-	-	-	-	(1.1^8)	1.2^4	1.2^7	1.3^3
	3.00	-	-	(1.0^0)	(1.1^1)	1.1^4	1.2^4	1.3^0	1.3^1	1.4^0
	2.51	-	-	1.2^1	1.1^1	-	1.2^7	-	-	-
	1.89	-	-	1.1^6	1.1^5	1.1^7	-	-	-	-

The values of ρ_{av} are collected in fig. 18 and Table XI and are much smaller than the values estimated by *Du Pré*. The deviations from the *Brons-Van Vleck* formula (147) are marked, as ρ_{av} continually increased with increasing field strength, rather than approaching a constant limit. This is corroborated by fig. 17.

Between 1.6 and 3.0 °K $\rho_{av} \sim T^{-4}$, while at higher temperatures ρ_{av} seems to vary even more rapidly with temperature.

b) We investigated two other samples (B and C), which were obtained by recrystallisation from Analar, analytical reagent. The deviations from the thermodynamic formulae are much larger than for sample A, but there is satisfactory agreement with the *Cole* formulae; this is illustrated by fig. 19.

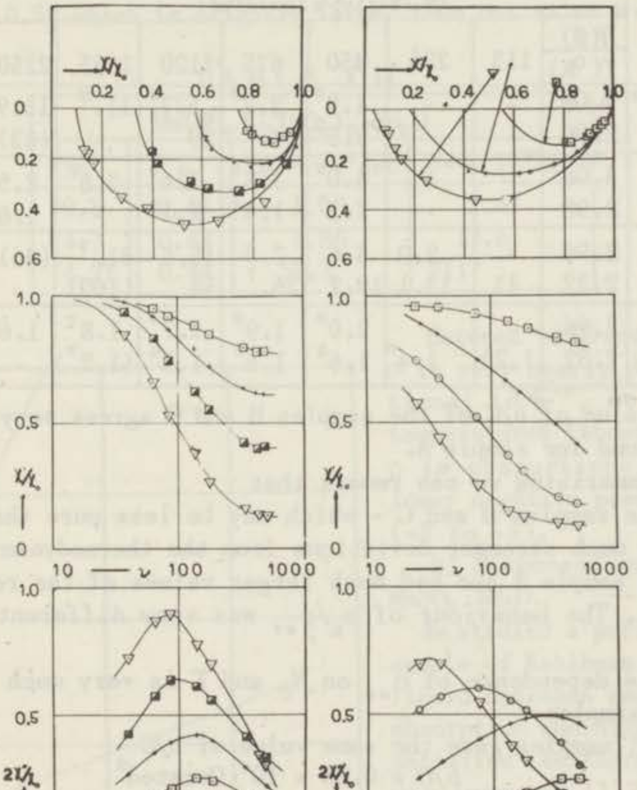

Fig. 19 Absorption and dispersion. Left: Manganese ammonium sulphate; T=14.3 °K. Curves according the thermodynamic formulae (117). Right: Iron alum (B); T=4.08 °K. Curves according to Cole's formulae (129).
For both substances: ⊡ 450 ø ▣ 1120 ø ▽ 3370 ø
\+ 670 ø ⊙ 2250 ø

The dependence on H_C and T of $\rho_{½}/\rho_{av}$ of both samples B and C markedly differs from the behaviour of sample A, but agree among each other. In high fields $\rho_{½}/\rho_{av}$ clearly decreases with increasing H_C, but in low fields this seems to be reversed, while $\rho_{½}/\rho_{av}$ has a maximum for intermediate fields. The field strength corresponding to this maximum possibly increases with increasing T (see Table XII).

The values of ρ_{av} in Table XII are all about three times as large as those of sample A, although the values of the samples B and C do not agree very well among each other. The dependence on H_c is much the same for all samples; ρ_{av} of the samples B and C is nearly proportional to T^{-5}.

TABLE XII

		Fe $NH_4(SO_4)_2.12H_2O$									
		H(0) / T(°K)	113	225	450	675	1120	1685	2250	3370	4500
Sample B	$\rho_{av} \times 10^3$ sec	4.08	-	-	1.8^2	2.2^9	5.7^2	$11.^8$	15.9	27	36
		2.98	-	-	8.5^0	$14.^9$	29	-	(83)	(133)	(180)
	$\rho_{½}/\rho_{av}$	4.08	-	-	4.0^2	3.5^3	3.4^9	2.8^3	2.5^0	2.3^2	1.6^8
		2.98	-	-	2.1^2	1.4^1	2.2^4	-	1.6^2	1.4^7)	(1.3^3)
Sample C	$\rho_{av} \times 10^3$ sec	2.96	-	2.9	4.6	7.5	15.5	$31.^7$	(46)	(71)	(100)
		2.32	11	13.1	19.2	$26.^7$	58	(100)	-	-	-
	$\rho_{½}/\rho_{av}$	2.96	-	-	2.0^8	1.9^8	1.7^4	1.8^1	1.6^7	(1.4^7)	(1.3^4)
		2.32	1.2)	1.4^8	1.6^3	1.6^3	1.5^3	(1.2^7)	-	-	-

The value of b/C of the samples B and C agrees very well the value found for sample A.

c) Summarising we can remark that

1) the samples B and C - which may be less pure than sample A - show much stronger deviations from the thermodynamic formulae than sample A and had much larger values of the relaxation constant. The behaviour of $\rho_{½}/\rho_{av}$ was very different in both cases.

2) the dependence of ρ_{av} on H_c and T is very much the same for all samples

3) all samples gave the same value of b/C

$$b/C = 0.25 \times 10^6 \text{ Oersted}^2,$$

which corresponds to a splitting. ($\zeta = 0.0472°$ K (Cf. H5), C = 4.33)

$$\delta/k = 0.185° \text{ K} \quad \delta = 0.126 \text{ cm}^{-1},$$

assuming that only magnetic interaction between the iron ions is present. Our value of b/C closely agrees with *Broer's* value at 77 and 90° K $b/C = 0.27 \times 10^6$ Oersted^2 (B26).

2.24 *Manganese salts* (B27).

a) *Manganese ammonium sulphate* $Mn(NH_4)_2(SO_4)_2.6H_2O$.

The sample investigated was prepared from $MnSO_4.4H_2O$ and $(NH_4)_2SO_4$ (both Analar analytical reagent) and was examined both at liquid helium and liquid hydrogen temperatures. The relaxation constants were so large that in the frequency range available absorption and dispersion only at liquid hydrogen temperatures could be measured in detail. We found excellent agreement with the thermodynamic formulae between 14 and 20° K as can be seen from fig. 19. Our value of b/C (b/C = 0.64 × 10^6 Oersted^2) agreed excellently with *Broer's* (B26) value obtained at higher temperatures.

The values of ρ agreed with the *Brons-Van Vleck* formula (147) with temperature independent p (Table XIII and fig. 20). *Broer* found p = 0.50 which is slightly larger than our value p = 0.43.

TABLE XIII

$Mn(NH_4)_2.(SO_4)_2.6H_2O$			
T°K	p	ρ_0 × 10^3sec	ρ_∞ × 10^3sec
20.3	0.43	1.06	2.47
14.3	0.43	5.86	13.6
4.21	0.44	50.3	117

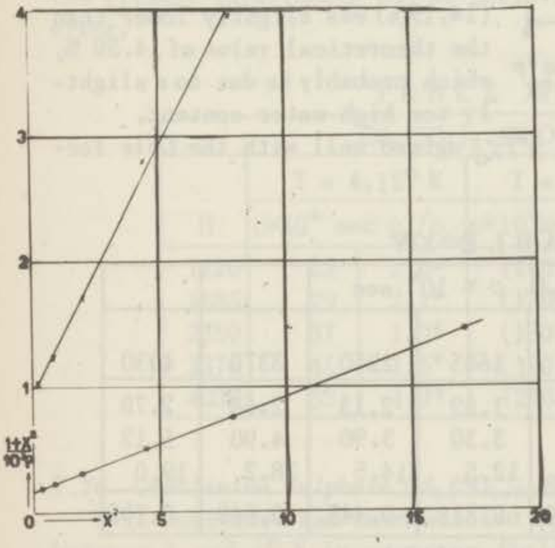

Fig. 20 Manganese ammonium sulphate. $(1+x^2)/10^3\rho$ as a function of x^2. ⊙ T=14.3 °K × T=20.3 °K

Between 14° K and 20° K ρ is very nearly proportional to T^{-5}, at lower temperatures (about 4° K) ρ is proportional to a lower negative power of T (-2 to -3).

b) *Manganese sulphate* $MnSO_4.4H_2O$.

We studied a purissimum sample of Kahlbaum in the liquid hydrogen range. The absorption and dispersion satisfied the thermodynamic formulae (117) very well. We calculated b/C = 6.2 × 10^6 Oersted^2, which agrees with *Gorter* and *Teunissen's* value obtained at higher temperatures (G3).

Contrary to manganese ammonium sulphate the values of ρ did not satisfy the *Brons-Van Vleck* formula (147) (compare fig. 21); they are collected in Table XIV. In the temperature range used ρ is nearly proportional to T^{-5}.

c) Summarising we can say that

1) both manganese salts behave similary as regards χ'/χ_0 and χ''/χ_0, showing excellent agreement with the thermodynamic formulae.

2) the b/C values in both cases agree with the values obtained at higher temperatures.

3) both substances have relaxaation constants of about the same magnitude, varying with T^{-5} at constant H_c in the liquid hydrogen region. The dependence on H_c at constant T however is different, as only the double salt agrees with the *Brons-Van Vleck* formula with constant value of p.

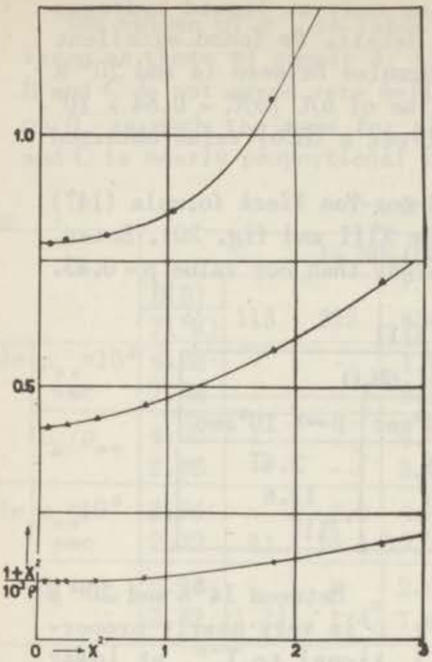

Fig. 21 Manganese sulphate, $(1+x^2)/10^3\rho$ as a function of x^2. × $T = 14.4$ °K △ $T = 18.4$ °K ⊙ $T = 20.3$ °K.

2.25 *Copper potassium sulphate $CuK_2(SO_4)_2 . 6H_2O$.*

The sample used was prepared from copper sulphate and potassium sulphate, both Kahlbaum 'for analysis'. The amount of copper (14.19%) was slightly lower than the theoretical value of 14.39 %, which probably is due to a slightly too high water content.

We found that χ'/χ_0 and χ''/χ_0 agreed well with the *Cole* formulae.

TABLE XIV

	$MnSO_4 . 4H_2O$ $\rho \times 10^3$ sec					
T°K \ H(Ø)	670	1120	1685	2250	3370	4030
20.5	1.37	1.52	1.82	2.13	2.64	2.78
18.4	2.56	2.82	3.30	3.90	4.90	5.12
14.4	9.3	10.5	12.5	14.5	18.2	19.0
F	0.070	0.165	0.315	0.445	0.640	0.705

TABLE XV

	$CuK_2(SO_4)_2 . 6H_2O$ $T = 4.015$ °K		
H	$\rho \times 10^3$ sec	$\rho_{1/2}/\rho_{av}$	F
113	(25)	-	0.125
225	30	1.6^3	0.340
340	40	1.5^4	0.540
450	45	1.4^3	0.670
675	60	1.3^1	0.810

From the *F*-values in Table XV we calculated $b/C = 0.10 \times 10^6$ Oersted^2, which agrees satisfactorily with *Broer* and *Kemperman's* value $b/C = 0.12 \times 10^6$ Oersted^2, obtained at higher temparatures (B28). It should be remembered that as a consequence of the low value of the *Curie*-constant of the substance the relative accuracy of the measurements is lower than of the measurements on the substances mentioned.before.

The values of the relaxation constant are so large that only at the highest temperature ($T = 4.015^\circ$ K) the values of ρ_{av} could be estimated by extrapolation with the *Cole* formulae. The results are collected in Table XV. It is seen that ρ_{av} increases with increasing field strength but a detailed analysis of this dependence cannot be made. We found clear indications that ρ_{av} increases rapidly with decreasing temperature; $\rho_{1/2}/\rho_{av}$ decreases with increasing field strength.

It must be added that older measurements (B29) indicated much shorter relaxation constants and moreover that b/C should depend on T. No such dependence of b/C on T has been found in the present experiments and we believe the old results to be in error.

TABLE XVI

$Gd_2(SO_4)_3.8H_2O$					
	$T = 4.15^\circ$ K		$T = 3.00^\circ$ K		
H	$\rho \times 10^3$ sec	$\rho_{1/2}/\rho_{av}$	$\rho \times 10^3$ sec	$\rho_{1/2}/\rho_{av}$	F
1120	25	2.0^6	(100)	-	0.170
1685	29	2.1^4	(120)	(1.8)	0.442
2250	37	1.9^4	(150)	(1.6)	0.575
3370	45	1.5^9	(190)	(1.5)	0.720
4030	55	1.3^9	(230)	(1.6)	0.800

2.26 *Gadolinium sulphate* $Gd_2(SO_4)_3.8H_2O$.

This substance has been studied by *De Haas* and *Du Pré* (H10) between 1 and 4° K in magnetic fields up to 2000 Oersted and with frequencies between 25 and 60 c sec. We examined a sample of the same batch of crystals in wider ranges of magnetic field and frequency.

We found that χ'/χ and χ''/χ_0 appreciably deviated from the thermodynamic formulae, but that the *Cole* formulae are reasonably well satisfied. From the values of *F* we calculated the overall splitting δ_0; this is slightly more complicated than in the other cases because, due to the relatively large value of δ_0, the next term in the series expansion (65) has to be taken into account, as has been noted by *Van Dijk* and *Auer* (D2). According to these authors we have to take instead of the first term of (65) for the specific due to the splittings

$$C_M = (Nk)(33/256)(\delta_0/kT)^2\,[1-(2/11)(\delta_0/kT)]. \qquad (187)$$

Instead of the simple *Casimir - Du Pré* formula (123) a somewhat more complicated expression has to be used. Taking for the magnetic specific heat (82) with $Q = 14.4$ (we neglect possible exchange), $\zeta = 0.189$°K (Cf. H5) and $C = 7.82$ we found

$$\delta/k = 1.36°\mathrm{K} \text{ or } \delta = 0.95 \text{ cm}^{-1},$$

which agrees with the value $\delta/k = 1.36$°K derived with (94) and (123) from experiments on relaxation at 77 and 90°K ($b/C = 3.9$ 10^6 Oersted^2, *De Vrijer, Volger* and *Gorter* (V11)) and from caloric measurements ($b/C = 3.8 \times 10^6$ Oersted^2, *Van Dijk* and *Auer* (D2); $b/C = 3.9 \times 10^6$ Oersted^2, *Giauque* and *MacDougall* (G5)). If the second term in (187) is neglected lower values of b/C are found in the liquid helium range. It is easily seen that this explains the low value $b/C = 3.0 \times 10^6$ Oersted^2 obtained by *De Haas* and *Du Pré* (H10) at 1.34° K, who used the *Casimir-Du Pré* formula (123).

We collected the values of ρ_{av} and $\rho_{½}/\rho_{av}$ for different values of H_c at two temperatures in Table XVI; the values of ρ_{av} at 3.00° K only could be obtained by extrapolation and therefore are rather uncertain. According to the results at 4.15° K $\rho_{½}/\rho_{av}$ decreases with increasing H_c; the dependence on T probably is small.

The relaxation constants ρ_{av} do not seem to agree with the *Brons-Van Vleck* formula; we estimated that $\rho_{av} \sim T^{-4}$ in the temperature range used. The previous values of ρ_{av} (H10) had only a provisonal character, and were much smaller (a factor of at least 10) than the present values. A more systematic study of the relaxation constants would have been desirable, but could not be carried out as a consequence of the large values of ρ_{av}.

2.27 *Dilute chromium potassium allum* (1:131)(B30).

The crystals used were obtained from a solution containing chromium potassium alum and aluminium potassium alum. Only small crystals were used in order to obtain a sample which was as homogeneous as possible. Dr *K.F.Waldkötter* kindly carried out an analysis and found for the ratio between the number of chromium and aluminium ions 1:13.

Taking into account that the susceptibility of the substance is so small the agreement of χ'/χ_0 and χ''/χ_0 with the thermodynamic formulae is very satisfactory. In fields up to about 800 Oersted the *Casimir-Du Pré* formula is satisfied very well, giving $b/C = 0.82 \times 10^6$ Oersted^2. Neglecting the interaction between the chromium ions we found for the splitting using formula (92)

$$\delta/k = 0.281^\circ K \quad \text{or} \quad \delta = 0.195\ \text{cm}^{-1},$$

which is somewhat larger than the value found for the undilute salt.

At higher fieldstrengths marked deviations from (123) occurred, especially at lower temperatures. In a previous publication (B30) these deviations were interpreted as an indication that thermodynamical equilibrium in the spin-system did no longer exist. A careful re-examination of the data however indicated that this conclusion probably was premature. This is a consequence of the fact that values of F in increasing magnetic field become gradually more sensitive to small uncertainties in the values of M_2^0 and C/B (compare (185)). As a matter of fact these uncertainties can account for the deviations of the *Casimir-Du Pré* formula found.

TABLE XVII

T°K \ H(Ø)	332	458	548	656	895	1110	1340	1575	1795	2290
	(Cr, AL) K $(SO_4)_2 \cdot 12H_2O$ (1:13) $\rho \times 10^3$ sec									
1.21	-	-	-	-	750	-	-	415	-	320
2.05	320	280	(290)	250	220	180	170	-	-	-
2.53	280	260	(260)	190	165	155	155	145	130	-
3.02	-	-	-	-	82	-	-	107	-	107
4.04	-	-	-	-	47	-	-	61	-	53

In Table XVII and fig. 22 we collected the values of ρ obtained, which are all much larger than the values of the undilute substance. In contrary to all other cases studied ρ decreases with increasing H_c except at 4.04 and 3.02° K. It must be added that the values at the two highest temperatures - obtained from complete dispersion and absorption curves - are more reliable than the other

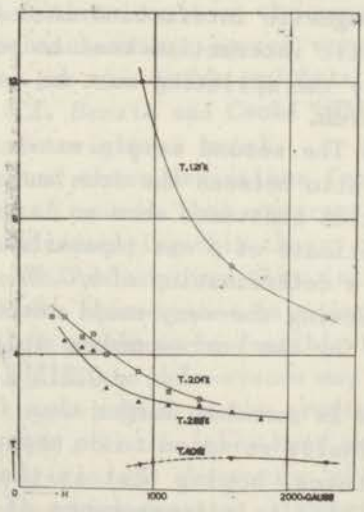

Fig. 22 Dilute chromium alum (1: 13). ρ as a function of H_c.

values which are only estimated. Although the latter values may be appreciable in error, we believe it to be unlikely that the dependence on H_c found is qualitatively incorrect and that the order of magnitude is wrong. On the other hand it would be premature to try to draw quantitative conclusions.

For the dependence of ρ on T we estimated $\rho \sim T^{-2}$.

2.28 Dilute iron ammonium alum.

Two samples of different degree of dilution haven been examined by *L.C.v.d.Marel*, phys. cand.; both samples were available in the laboratory.

a) The first sample was a mixed crystal between iron ammonium and aluminium ammonium alum in which the ratio between the number of iron and aluminium ions was 1:16.

In this case the relaxation constants were so large that they only at the highest temperature used (3.93° K) could be estimated. At lower temperatures determination of ρ was not possible. The results are collected in Table XVIII.

TABLE XVIII

Iron ammonium alum (1:16) $T = 3.93°$ K.					
$H(\emptyset)$	225	449	674	900	1125
$\rho \times 10^3$ sec	36	41	47	(53)	(77)

As usual ρ increases with increasing fieldstrength. For b/C we found $b/C = 0.26 \times 10^6$ Oersted^2, which is within the limits of accuracy the same as for the normal alum. A calculation of the splitting is difficult, because it hardly can be accounted for the magnetic interaction in a satisfactory way. Certainly the magnetic interaction must be weaker in the average and accordingly the splitting must be somewhat greater than in the normal alum.

b) The second sample was a similar mixed crystal in which the ratio between the iron and aluminium ions was 1:60. The relaxation constants were so large ($\rho > 0.1$ sec even at 4° K) that an estimate of ρ was impossible and we had to content ourselves with a determination of b/C. We found $b/C = 0.18 \times 10^6$ Oersted^2; neglecting the very small interaction between the iron ions we find for the corresponding splitting

$$\delta/k = 0.213°\mathrm{K} \quad \text{or} \quad \delta = 0.149\ \mathrm{cm}^{-1},$$

which is somewhat larger than for the undilute salt.

Finally we tried to do measurements at liquid hydrogen temperatures, hoping that in that region measurements would be possible. As a consequence of the high degree of dilution no dispersion and absorption could be measured.

* * * *

Chapter III

DISCUSSION OF THE RESULTS

3.1 Introduction.

In this chapter we propose to discuss the experimental results described in the preceding chapter. This will be carried out along the following lines. First we will discuss the thermodynamic formulae, then the *b/C* values and splittings derived from them. And finally the relaxation constants.

3.2 The thermodynamic formulae.

It will be clear from the preceding chapter that between 1 and 4° K χ'/χ_0 and χ''/χ_0 as a function of ν at constant H_c and T of most samples investigated showed marked deviations from the behaviour predicted by the thermodynamical theory (Cf. (117)). All substances we studied have been examined at temperatures above 77° K as well and at these temperatures a very satisfactory agreement with the thermodynamic theory was found (compare G1). Summarising we can say that - with the possible exception of the dilute alums, which have not yet been investigated in sufficient detail - the substances we investigated satisfy the qualitative rule:

'At liquid helium temperatures (1-4° K) the spin-lattice dispersion and absorption satisfies the thermodynamic theory less well than at higher temperatures. The degree of deviation depends on the substance and moreover can be different for different samples of the same substance.'

This formulation includes the measurements on the manganese salts between 14 and 20° K; both substances agreed very well with the thermodynamic formulae, but the double sulphate shows a slight deviation at 2.17° K (Cf. *Benzie* and *Cooke* (B31) who investigated a sample of the same origin as ours).

a) As regards an explanation of these deviations from the thermodynamic formulae we want to remark that apparently at least one of the basic assumptions underlying this theory is not satisfied. In the first place the assumption that internal thermodynamical equilibrium of the spin-system is maintained all the time may not be correct. It seems to be feasible that a lack of thermodynamical equilibrium of the spin-system may cause the dispersion and absorption to deviate from the predictions of the thermodynamic formulae (117). On the other hand we have seen in I, Ch. V, that the dispersion and absorption given by (117) is characterised by one relaxation constant, irrespective of thermodynamical equilibrium is maintained or not. It is not possible at present to check the above assumption of the thermodynamic theory by examining the dispersion and absorption. More useful is a consideration of χ_∞, which will be given in section 3.3.

It may be added that if lack of thermodynamic equilibrium causes the deviations from the formulae (117) our interpretation of these deviations in terms of a distribution of relaxation constants may be wrong.

b) In the second place the assumption that the sample is isotropic may not be satisfied. It will be remembered that our samples consisted of small crystals packed with random orientation in a glass container. If the relaxation constant depends on the direction of the magnetic field relative to the crystal axes a distribution of relaxation constants may be found. It is conceivable that an anisotropy of relaxation constants is much more pronounced in the case of direct processes than for quasi-*Raman* processes, which might explain the deviations from the formulae (117) found between 1 and 4° K. At 77 and 90° K, where the quasi-*Raman* processes are predominant, no anisotropy of the relaxation constant could be detected in iron and chromium alum (T3). Measurement of the relaxation constant of small (see below) single crystals for different directions of the constant magnetic field could test this suggestion. Substances having only one paramagnetic ion in the elementary cell (for instance the fluosilicates of the divalent metals of the iron group, see I,2.22) would be very suitable for this purpose. We must leave open the question to what extent anisotropy of the relaxation constant could explain the particular distribution of relaxation constants (130) suggested by the *Cole* formulae and the dependence of the distribution on H_c and T.

c) Thirdly the sample may not be homogeneous, or more precisely consists of crystals which are not perfectly homogeneous. The microscopic meaning of the word 'inhomogeneous' is, that the actual crystal lattice of the substance investigated is not the ideal lattice but that imperfections are present.

From an experimental point of view the strong influence of small differences in purity - it may be either in chemical or physical sense - is obvious. This influence however is of a rather complicated nature as will become clear from the following remarks about the two alums examined.

The first experiments in the liquid helium range indicated that pure samples had larger relaxation constants than the less pure ones. For instance after recrystallisation a sample showed a longer relaxation constant than before. Our present evidence however showed that the actual situation probably is more complicated.

In the case of iron alum the relaxation constants of the samples B and C are much larger than the relaxation constants of sample A. This might suggest that B and C are purer than A. On the other hand A showed a better agreement with the thermodynamical formulae than B and C and this might rather indicate that sample A would be the purest. No definite conclusion can be drawn therefore. In the case of chromium alum sample A and B have the largest relaxation constants and satisfy the thermodynamic formulae,(117), rather well. It should be added however that preliminary experiments with a fourth sample indicated strong deviations from the thermodynamic formulae but still larger values of the relaxation constant than sample A and B. Both the magnitude and the dependence of $\rho_{½}/\rho_{av}$ on H_c and T seem to be very sensitive to incidental imperfections. Compare for instance the discrepancy between the dependence of $\rho_{½}/\rho_{av}$ on H_c and T of the samples A and B or C of iron alum.

We can conclude that presumably very small impurities have a marked effect on the dispersion and absorption at very low temperatures, but we are not able to make any detailed deductions. A discussion of the possible influence of the different imperfections which are known to occur in crystals therefore seems to be premature. We will only mention that there are indications that crystals of the alums we investigated show imperfections, even if the crystals are well grown and are perfectly clear. Such crystals of iron alum are practically always strongly double refractive although this substance forms cubic crystals. Moreover according to a private communication of *Dr C.Kittel* to the author, the heat conductivity of chromium potassium alum (Cf. (B25)) suggests that there is a pronounced domain-like structure in this substance at low temperatures. The diameter of the domains, which act as scattering centers for the heat waves in the crystal, is at least 10^{-5} cm. It will be clear that only if many more experimental data are available one may hope to gain understanding of the influence of imperfections on the spin-lattice dispersion and absorption at very low temperatures.

d) We finally have to make a remark about the lattice temperature. As has been pointed out by *Van Vleck* (V12) from a theoretical point of view it is not certain that the lattice acts as a thermostat with the temperature of the bath, because the lattice temperature in the interior of a crystal may not be the same as near the surface which is in contact with the cooling liquid and moreover the heat contact between the crystal and the bath may be poor. These possiblities seem to be ruled out by *Du Pré's* experiments (P8) with samples of the same substance but with different - though small - size of crystals; no influence of the size of the crystals on the dispersion was found. It should be remarked however that these experiments only can be regarded as preliminary and that the present experimental means would allow a more accurate test of *Van Vleck's* theoretical conclusions about the lattice 'thermostat'. It therefore seems worth while to repeate *Du Pré's* experiments.

e) Summarising we can say that in our opinion at present no simple and general explanation can be given of the deviations from the thermodynamic formulae (117). Possibly future research can throw light upon this problem, and perhaps is most promising along the following lines.

In the first place investigation of the possible anisotropy of the relaxation constant may be fruitful at very low temperatures where the first order processes can be expected to be predominant. Possibly a method has to be devised which allows the measurement of longer relaxation times than with our set up, because lower temperatures probably are required for this (see below).

In the second place a systematic study of many samples with known impurities may reveal the details of the influence of these impurities on the relaxation phenomena at very low temperatures. The problem probably will be to know the amount and kind of impurities present in a given sample. Chemical impurities probably are easiest to deal with, but possibly physical methods like X-ray analysis may help to determine certain physical imperfections in the crystals. In order to reduce the amount of auxiliary research it will be advisable to use small samples. This may require an appreciable refinement of the experimental technique used hitherto.

In the third place a systematic investigation of the possible influence of the size of the crystals of the sample may allow a check of *Van Vleck's* conclusions about the lattice 'thermostat'.

In general it will be advisable to investigate in the first place substances in which the splittings in a magnetic field (for instance found by resonance experiments) can be explained by the theory from I, Ch. II; $NiSiF_6.6H_2O$ may be a useful substance (compare I, 2.23, 2.24).

3.3 The adiabatic susceptibility.

a) In the preceding chapter we have seen that the different samples of one substance had the same value of b/C calculated with the formula (123) or in other words the same value of χ_∞ for given H_c and T. Apparently χ_∞ is not nearly as sensitive to small impurities as the dispersion and absorption, and the magnitude of the relaxation constants. This allows the conclusion that apparently the splittings and the static part of the interaction between the paramagnetic ions - which determine χ_∞ - are not very sensitive to impurities. Impurities therefore in the first place influence the processes governing the energy exchange between the spin-system and the lattice and an independent discussion of χ_∞ is possible.

b) As has been pointed out in I, Ch. IV and the preceding section the interpretation of χ_∞ depends on wether one assumes thermodynamical equilibrium or not. It is not a priori clear which assumption is correct and therefore we will consider in how far other experimental evidence allows us to draw a conclusion about this point. This in principle can be carried out along the following lines.

In the first place it is possible to check the *Casimir-Du Pré* formula (123), or the more general formula (122) if a demagnetisation factor and saturation have to be taken into account. According to our own experience these formulae are satisfied very well in fields up to at least a few times H_h. At higher fields deviations often occur but these are always within the limits of accuracy of the measurement. It must be remarked that the determination of small values of χ_∞ becomes increasingly sensitive to the uncertainty in M_2^0 (compare (185)) and the measurements of χ_∞ in high fields therefore are very inaccurate.

Table XIX

$b/C \times 10^{-8}$ Oersted^2

Substance	Relaxation		Cal.	Ref.
	$1/4^\circ$ K	77° K		
Chromium potassium alum	0.75	0.65	0.86	C3
			0.69	V13
Iron ammonium alum	0.25	0.27	0.24	C4
Manganese ammonium sulphate	0.64	0.64	-	-
Manganese sulphate	6.2	6.2	-	-
Copper potassium sulphate	0.10	0.12	0.12	K9
Gadolinium sulphate	3.9	3.9	3.8	D2
			3.9	G5

The next step is to calculate *b/C*, assuming the validity of (123) and to compare the result with *b/C* values obtained from caloric measurements. This can be done for the substances we investigated with the aid of Table XIX were we collected the values of *b/C*, obtained from relaxation experiments between 1 and 4° K, and at 77° K - which were mentioned in the preceding chapter - together with the *b/C* values obtained from adiabatic demagnetisation and specific heat measurements; the last column contains the references of the results of the previous column.

Except for chromium alum the agreement is excellent. The agreement found rather suggest the validity of the formulae (122) and (123), and consequently the correctness of the assumption that thermodynamical equilibrium in the spin-system is established all the time. Chromium potassium alum is not a very suitable substance for the present purpose because according to *Bleaney* (B32) not all chromium ions have the same electrical splitting at low temperatures, which seems to be connected with a transition point at about 80°K. (The splittings found are however difficult to reconcile with the data on *b/C*). This is not the case with chromium caesium alum and with chromium methylamine alum. It seems to be worth while to carry out the measurements with these alums.

A further possibility for checking the values of *b/C* is to compare the splittings calculated from them with splittings found from resonance experiments. This procedure is made more difficult by the fact that *b/C* contains contributions from the electrical splittings, the interactions between the paramagnetic ions and possibly from hyperfine splittings. Only in the cases that all these extra contributions can be either accurately calculated or neglected, this procedure may be expected to have success. Consequently this procedure seems to be promising in the first place for highly dilute salts, where the interactions can be neglected. As far as we are aware for no dilute salt sufficiently data are available for carrying out the comparison. Not even in the case of the very dilute iron ammonium alum of which we examined both the relaxation (Cf. preceding chapter) and the resonance absorption (Cf. III, Ch. II). The reason is that from the resonance experiments we carried out the electrical splitting cannot be derived, as will be discussed in III, Ch. II.

In cases where the interactions between the paramagnetic ions are not negligible one has the difficulty that at most the magnetic interaction can be accounted for with a reasonable degree of accuracy on a purely theoretical basis. If both the electrical and hyperfine splitting are known from experiments on resonance absorption, direct measurements of the specific heat may allow to calculate the contribution due to exchange. Then a calculation of the electrical splitting from the *b/C* values-obtained from relaxation measurements - is possible. We do not know cases where this could be carried out at present.

Summarising we can say that the available data on *b/C* values determined by relaxation and direct measurements agree, and that consequently the first assumption underlying the thermodynamic theory seems to be valid. The other possibility for checking the *b/C* values cannot be carried out at present, but seems to be possible in future.

3.4 The relaxation constant.

a) In the preceding chapter we have seen that - for the undilute alums studied - the relaxation constants are strongly affected by impurities in the sample. A more detailed analysis shows that in the first place the magnitude is affected, but that the dependence of ρ or ρ_{av} on H_c and T is nearly the same for different samples of one substance or in other words is not sensitive to small impurities. One therefore must expect that it makes sense to compare the experimental data of ρ_{av} with the theoretical expectations even if the deviations from the thermodynamic formulae are considerable.

b) According to *Van Vleck*'s calculations the relation between ρ and H_c - both for the direct and quasi-*Raman* processes - is independent of T. In a temperature region where one of these processes prevails we can write $\rho = f(T)g(H_c)$, where f and g only depend on the argument in brackets. This condition will be satisfied for temperatures well below the *Debye* temperature. For temperatures above 77° K the above relation between ρ and H_c and T is only approximately fulfilled (compare for instance *Broer* (B26)), except for manganese ammonium sulphate where it is satisfied very well. The same is valid for temperatures in the liquid helium range, but there the relation $\rho = f(T)g(H_c)$ is better fulfilled. The deviations from this relation at higher temperatures possibly can be explained by the fact that in that case the temperature is no longer very small compared with the *Debye* temperature; if this explanation is correct the better agreement at very low temperatures is easily understood.

c) As we have seen in I, Ch. IV according to *Van Vleck*'s calculations ρ (at constant H_c) should be proportional to T^{-1} at temperatures, where direct absorption and emission processes prevail; at temperatures where the quasi-*Raman* processes prevail ρ should be proportional to T^{-7} if $T \ll \theta$, and proportional to T^{-2} if $T \gg \theta$, where θ is the *Debye* temperature. *Van Vleck*'s calculations only indicate that for chromium alum $\rho \sim T^{-5}$ for temperatures of the order of θ.

TABLE XX

Exponent of T of variation of ρ for $H_c = H_h$		
	1-4° K	14-20° K
Chromium potassium alum	-3	-
Iron ammonium alum	-5	-
Manganese ammonium sulphate	-2.5	-5
Manganese sulphate	-	-5

In order to check these expectations we collected in Table XX the exponents of the power of T describing the variation of ρ as a function of T at constant $H_c = H_h$ derived from our experiments for a few substances. Although the powers of T vary rather much among each other for all temperatures, at higher temperatures ρ increases with decreasing T, with the one puzzling exception of gadolinium sulphate, of which ρ decreases for decreasing T between 90 and 77° K. Except for this substance, in all cases listed here and for all other cases investigated by other authors (Cf. G1) the increase of ρ with decreasing temperature qualitatively agrees with the expectations of all the theories quoted in I, Ch. IV.

In the liquid helium range however ρ varies much quicker with T than predicted by *Van Vleck* for direct processes, which where expected to be predominant at these temperatures. As to the higher temperatures we refer to the discussion given by *Broer* (B26) who points out that *Van Vleck's* theory does not give a satisfactory description of the dependence of ρ on T. The deviation at very low temperatures probably can be explained by the two possibilities: (1) contrary *Van Vleck's* expectations quasi-*Raman* processes still contribute appreciably to the relaxation process at liquid helium temperatures, (2) the predicted negative first power of T is in error. From fig.23 it can be concluded that at very low temperatures the variation of ρ with T becomes less rapid. This possibly means that with decreasing temperature the direct processes become relatively more important. For a check of this idea still lower temperatures would be required.

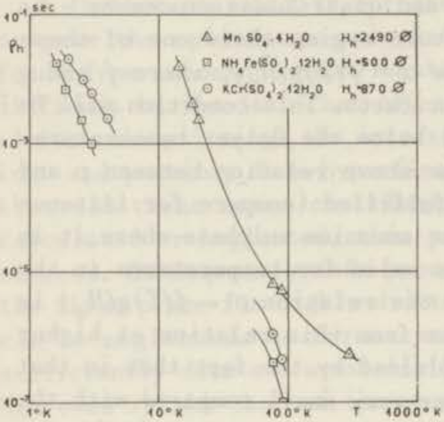

Fig. 23

ρ as a function of T at constant H_c for different substances.

c) The idea that even at liquid helium temperatures quasi-*Raman*-processes are important is corroborated by the dependence of ρ on H_c at constant T. In the liquid hydrogen range the *Van Vleck-Brons* formula (147) is satisfied very well for manganese ammonium sulphate. This rather suggests that in this temperature range the quasi-*Raman* processes still are predominant in this substance, which probably is the case as well for other substances. The dependence of ρ on T of this salt at about 4° K is still so near the dependence between 14 and 20° K, that probably even here the quasi-*Raman* processes are important. Moreover the dependence of ρ on H_c for chromium potassium alum so nearly satisfies the *Brons-Van Vleck* formula (147) that one must conclude that in this case as well quasi-*Raman* processes are important in the liquid helium region. Also for the other substances listed in Table XX (iron ammonium alum and manganese sulphate) this conclusion is likely to be correct, as is suggested by the dependence of ρ on T. In these cases marked deviations from the *Brons-Van Vleck* formula were found, but in our opinion this probably does not affect our conclusion about the quasi-*Raman* processes, as the interaction between the paramagnetic ions may have a strong influence on the relaxation constants and especially on the dependence on H_c. It must be noted that if quasi-*Raman* processes are important at liquid helium temperatures a natural explanation is available for explaining the increase of ρ with increasing H_c, which from *Van Vleck's* point of view would be very puzzling, if only direct processes would be important.

The dependence of ρ on H_c for direct processes only can be studies at still lower temperatures than we used. This would require a modified experimental technique allowing the measurement of very long relaxation constants. Measurement of the saturation of a paramagnetic resonance line with increasing power input may be a solution of this problem (compare II, 1.1).

d) We finally have to discuss the experiments on the dilute salts. Unfortunately these measurements are not as complete as would be desirable. This is mainly a consequence of the large values of the relaxation constants, which in most cases were too long for being determined with a reasonable accuracy. It is however possible to draw the conclusion that the relaxation constants increase with increasing dilution. This increase at first sight may be a consequence of changes in the crystalline field and moreover of the smaller magnetic interaction. The first possibility seems to be ruled out by the results on the dilute chromium alum. As a matter of fact the larger b/C value of the dilute substance indicates that the symmetry of the crystalline field is lower in the dilute than in the normal alum. We have seen however in I, 4.32 that ρ is determined mainly by the *cubic* orbital splitting which hardly can be very different in both alums. We therefore are inclined to believe that the increase of ρ with increasing dilution, is mainly a consequence of the decreasing magnetic interaction.

According to *Van Vleck* increasing dilution should make ρ larger if direct processes prevail, but smaller if quasi-*Raman* processes prevail (compare I, 4.32), since dilution diminishes H_i. Therefore the effect of dilution found experimentally rather would suggest the predominance of the direct processes. This seems to be corroborated by the dependence of ρ on H_c of the dilute chromium alum. On the other hand the experiments with the dilute chromium alum are not very accurate and we believe it to be premature to attach to much importance to them. Only measurement of the dependence of ρ on H_c for other dilute substances would allow us to conclude wether direct processes prevail or not. Therefore such experiments are very much needed.

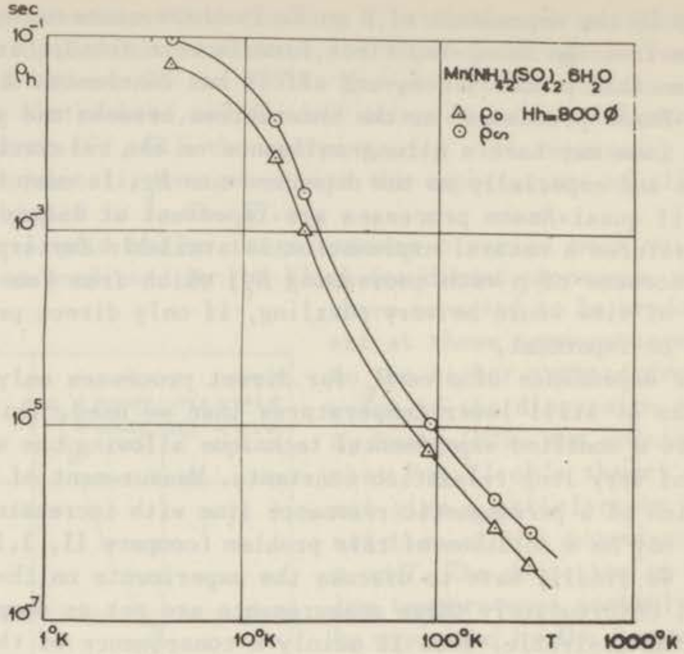

Fig. 24 Manganese ammonium sulphate. ρ as a function of T at constant H_c.

As has been remarked already these measurements could not be carried out with our apparatus.

As a matter of fact we believe that the arguments leading to the conclusion that the quasi-*Raman* processes are important at liquid helium temperatures, are more convincing than the arguments suggesting that direct processes prevail. Therefore we adopt the (provisional) opinion that quasi-*Raman* processes are still important in the liquid helium range. If this conclusion is correct - which can be checked by studying the dependence of ρ on H_c for the dilute substances - there remains the problem that increasing dilution increases the relaxation constant. This may imply that the description of the influence of the magnetic interaction on the relaxation constant with a (static) internal magnetic field is not correct.

According to the adopted point of view still lower temperatures would be required for checking *Van Vleck*'s and *Temperley*'s calculations for the direct processes. It will be inevitable to develop a new experimental technique allowing the measurement of longer relaxation constants (see p. 97) both for being able to work at lower temperatures and for measuring the dependence of ρ on H_c for the dilute substances.

* * * *

PART III

EXPERIMENTS ON PARAMAGNETIC RESONANCE ABSORPTION

Chapter I

EXPERIMENTAL METHOD

1.1 Introduction.

In section I,5.2 we pointed out that for the direct measurement of the absorption spectra of paramagnetic ions in a crystal, which is subjected to a magnetic field of some thousand Oersted, electromagnetic radiation of a wave length of the order of some cm is required. In this Part we will describe a few experiments on this subject and especially in this chapter we will consider the experimental aspects of the problem.

The experimental technique used in this region of the gamut of electromagnetic waves differs in several respects from the technique used in the optical region, where usually continuous radiation is applied to the substance investigated and the absorption lines are determined with some form of spectroscope; three reasons can be given for this.

In the first place the wave length is macroscopic rather than microscopic. This means that gratings, mirrors etc. which could be used for this wave length region must have rather unwieldy sizes. On the other hand wave lengths of this order allow the use of the much more elegant and convenient wave guide techniques, which we shall briefly discuss below. As a matter of fact most experiments on absorption in the microwave region have been carried out using wave guide methods; an exception are for instance the pioneer experiments of *Cleeton* and *Williams* (C5) on the inversion spectrum of ammonia.

In the second place there are sources of radiation available (especially the reflex klystron) which give a virtually monochromatic radiation. No instrument of the nature of a spectroscope therefore is required to separate the different wave lengths.

In the third place the absorption coefficients - defined in section I,5.32 - are very small as the absorption is proportional to the square of the frequency of the transition (compare (160)). It is not difficult to estimate α for a paramagnetic resonance line in an average case.

According to the *Kramers-Krönig* relations (102), taking $\nu_0 = 0$, we have for the static susceptibility

$$\chi'(0) = (2/\pi) \int_0^\infty \frac{\chi''(\nu)}{\nu} d\nu.$$

If we assume that there is one absorption line at a frequency $\bar{\nu}$ with a halfwidth $\Delta\nu$ this becomes roughly

$$\chi'(0) \simeq [\chi''(\bar{\nu})/\bar{\nu}]\Delta\nu$$

or

$$\chi''(\bar{\nu}) \simeq \chi'(0)(\bar{\nu}/\Delta\nu). \qquad (188)$$

The susceptibility in a resonance absorption line therefore will be roughly $\nu/\Delta\nu = H/\Delta H$ times the static susceptibility. This relation is very useful for estimating χ'' in the calculation of α (Cf. G9).

The static volume susceptibility of a paramagnetic alum is of the order 10^{-5} at room temperature; the line width which is assumed to be due to the magnetic interaction is of the order 500 Oersted. At a wavelength of 3 cm the resonance value of the constant magnetic field is about 3000 Oersted, so that we have $\nu/\Delta\nu \simeq 6$ and $\chi'' \simeq 6.10^{-5}$. Then it is easily seen that $\alpha \simeq 1.5 \times 10^{-3}$ nepers cm^{-1} or 1.3×10^{-2} db cm^{-1}. Therefore the absorption per cm path is some tenths of a percent and a path length of several meters would be required for an absorption of 50%; even at 3 °K several cm would be required, as the absorption is inversely proportional to the temperature.

It will be obvious that the measurement of these very small absorption coefficients in the ordinary way will involve many difficulties as a consequence of the large path length required, even at low temperatures. A much better method is to use a resonant cavity as will be discussed below.

A detailed discussion of micro wave techniques lies outside the scope of this thesis. Moreover several books about this subject are available. For details we refer to the books of *Huxley* (H12), *Ramo* and *Whinnery* (R1), *Sarbacher* and *Edson* (S5) and to the 'Proceedings of the Radiolocation Convention', March -May 1946 (P9). We shall confine ourselves to a very brief discussion of the main points.

1.2 The micro wave apparatus.

1.21 Wave Guides. The most useful means for transporting micro waves are waveguides. They are characterised by a low attenuation and moreover the waves are entirely confined to the interior of the guide, so that no losses by radiation occur. For these reasons they are extensively used in micro-wave work. Coaxial lines have much the same properties, but especially at the smaller wave lengths (3 and 1 cm) the losses in a coaxial cable are much larger than in a wave guide. A wave guide is a single hollow conductor in which electromagnetic waves can travel. In a wave guide of given dimensions propagation of many waves with different modes of propagation and different wave length is possible. Each mode is characterised by its own particular configuration of electric and magnetic field. Characteristic for a given wave guide is that for each mode a critical wave length - determined entirely by the dimensions of the wave guide and the special mode - exists, above which no transmission of waves of this mode takes place, or more precisely the wave is subject to a very rapid exponential decay. There is always a mode - called principal mode - having a larger critical wave length than all the others and accordingly there is for a given wave guide a wave length region in which only the principal mode can be propagated. This situation is usually preferred for practical reasons. If for instance a discontinuity causes the excitation of other modes they cannot be propagated as a consequence of their rapid decay.

The most convenient shape is rectangular with the narrow dimension smaller than half the wave length and the wide dimension between one-half and one wavelength. Then only the principal mode can be propagated, which is characterised by an electric field parallel to the narrow side, while the magnetic field forms closed loops in planes parallel to the wide side; the electric field in this type of wave is transverse, but the magnetic field has a longitudinal component. Waves of this types are called TE (Transverse Electric) or H waves. The wave guide we used for our experiments with waves of 3 cm wave length was of this type and had the internal dimensions 1 × ½ in. or 2.54 × 1.27 cm.

Owing to the finite conductivity of the walls the wave inside the guide is attenuated in a rate which depends on the dimensions and the material of the wave guide, the mode of propagation and on the wave length. In the copper wave guide we used the theoretical value of the attenuation was about 0.1 decibels per metre; the value in practice may have been somewhat higher. Often waveguides are silverplated in order to reduce the resistive losses in the walls.

Another transmission line we used was a coaxial line which consisted of two coaxial cylindrical conductors. The principal mode is characterised by a radial electric field, while the magnetic lines of force form concentric circles around the axis of the line; none of the fields has a component in the direction of propagation. This mode therefore is called a purely Transverse Electro Magnetic or T.E.M. mode. It is important to note that the critical wave length of the principal mode in this case is infinite, and it is easily possible to choose the dimensions of the line in such a way that only the principal mode of the desired wave length can be propagated. The requirement for this is that the mean circumference of the inner and outer conductor is smaller than the wave length used. The coaxial lines we used fulfilled this requirement.

An important advantage of the coaxial line excited in the principal mode is the much smaller cross section than a wave guide - able to propagate waves of the same wave length - would have, and this is the main reason why we used this type of transmission line in our low temperature experiments. An disadvantage is the much larger attenuation than a wave guide would give. This is mainly a consequence of the presence of the dielectric required for the support of the inner conductor. At very low temperature however this disadvantage is much reduced.

The waves can be launched in a wave guide by means of coupling probes or coupling loops in the same way as will be discussed below for cavity resonators.

1.22 Oscillator tubes. The most useful oscillator tube for our purpose is a reflex klystron, because the generated waves are virtually monochromatic. The wave output is continuous and the high frequency power given off is of the order of 100 milliwatts for the klystrons we used. The tuning range of these tubes is about 5% and the constancy of the frequency especially when they are run on batteries can be sufficient for our purpose.

For our experiments at 10 cm wave length we used a British CV87 tube, which was tunable between about 9.5 and 10.0 cm. The required anode voltage is only 250 volts and the output was about 100 milliwatts. The anode voltage was supplied by a stabilised power pack.

For our experiments at 3 cm wave length we used a British CV272 tube. The required anode voltage in this case was about 1600 volts and the output was sufficient. This tube was run entirely on batteries and the frequency stability was ample for our purpose.

1.23 The detector. We used a silicon - tungsten crystal rectifier coupled to a sensitive galvanometer as detector. This type of detector is more sensitive than other types used so far like thermionic detectors and bolometers. Crystal rectifiers are available in the form of capsules; a suitable contact has been found in the manufacture and is stabilized so that it is not disturbed by normal handling. The rectified current is about a few microamperes of rectified current per milliwatt of radio frequency power and is about proportional to the r.f. power applied, or to the square of the r.f. voltage applied. It is preferable to use a low resistance galvanometer as the rectified current is more nearly proportional to the applied r.f. power when it is working into a low impedance load.

It must be remarked that the crystal characteristic usually not accurately satisfies the 'square law' mentioned, and moreover that the characteristic is not constant in the course of time. Calibration of a rectifying crystal - which ought to be carried out at frequent intervals - can only be carried out if some means of producing a known variation in the r.f. power is available. We had no such means at our disposal and therefore provisionally assumed the validity of the square law. The values of the constant field corresponding to maximal absorption, which we observed, are practically independent of small deviations of the square law of the rectifying crystal and therefore are reliable. Accurate determinations of line widths however only are possible in cases where the characteristic of the rectifying crystal is known and therefore were not possible with our apparatus.

1.24 Cavity resonators. A resonance cavity can be regarded as a length of wave guide closed at each end with a reflecting wall, in which standing waves can be excited in much the same way as hollow gas-filled vessels can be excited into accoustical resonance. A given cavity will resonate at a number of discrete frequencies, each corresponding to a particular mode of oscillation with its own characteristic electromagnetic field pattern. In practice a given cavity resonator usually is excited in the principal mode which is the mode of oscillation with the longest possible wave length. The field pattern of this mode is simply a superposition of forwards and backwards traveling waves of the principal mode of a wave guide, having the same cross section, and which are reflected at the ends of the cavity.

Since the resistivity of the walls usually is kept small the radiation traverses the cavity many times before its final decay. This implies that a large effective multiplication of path length is obtained and that a resonance cavity must be a suitable device for measuring small absorptions. An alternative way for understanding the advantage of the resonant cavity for measuring small absorptions is regarding the cavity as a resonating system with a very small damping. A small extra damping caused by absorption for instance in a paramagnetic substance then easily can be detected.

The amount of damping can be judged from the quality or magnification factor Q of the resonator which is defined by $Q = 2\pi$ (energy stored / energy dissipated per cycle). If W is the energy stored than the energy dissipated per cycle is $(dW/dt)T$, where T is the period, and we have - as $\omega = 2\pi/T$ -

$$Q = \omega \frac{W}{(dW/dt)} ,$$

so that

$$W = W_o exp(-\omega t/Q); \qquad (189)$$

W_0 is the stored energy at $t = 0$. If therefore the resonator is shock excited and left to oscillate freely the stored energy is reduced to $1/e$ of its original value after a time Q/ω.

The accurate value of Q depends on the material of the cavity and on the mode of oscillation (compare for instance ref. (S5), p. 396). The order of magnitude of Q is given by the simple expression

$$Q = \frac{Volume\ of\ cavity}{\delta \times surface\ of\ cavity},$$

where δ is the skin depth of the wall currents. It may be added that values of Q as large as 10^4 are easily achieved.

In our experiments we used cavity resonators of different type for the 3 and 10 cm wave length work, which we will describe in some detail.

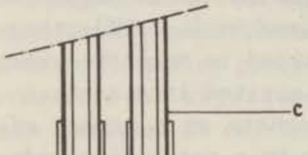

Fig. 25
The 10 cm wavelength resonator

a) The resonator for 10 cm wave length. This resonator essentially consisted of a piece of coaxial cable of length $\frac{1}{4}\lambda$, which was short circuited at one end and open at the other end. The actual resonator is sketched in fig. 25.

The resonator consisted of two brass parts, an upper part T and a silver plated bottom B carrying a stub S. Both parts were connected with a nut N, while a greased rubber washer W_1 and a brass washer W_2 allowed T and B to be connected vacuum tight. The r.f. power was transported downwards along a coaxial line C consisting of two concentric thin walled german silver tubes of diameters of about 2 and 4 mm, which were insulated from each other by polythene spacers placed at regular distances from each other (not shown in the figur). The calculated attenuation was about 1.5 db/m at room temperature, but was smaller at low temperatures. The lower end of C was connected to a length of pyrotenax coaxial cable - which consists of copper conductors with MgO as insulator - and which ended in a coupling probe P. P excited the standing wave which was largely confined to the lower part of the resonator. A similar system of coaxials and probe allowed to feed a small amount of power to the detector. In this way changes in energy density easily could be detected. The whole resonator was placed in the desorption apparatus to be described in the next section. It may be added that german silver was taken for the coaxial lines in order to reduce the heat influx to the resonator.

The coaxial resonator was excited in the principal mode. Then the electrical field has a node at the bottom and is maximal near the end of the stub; the electric lines of forces are practically radial near the bottom but have a vertical component near the end of the stub. In order to obtain a sufficiently strong coupling the probes are placed parallel with the electrical lines of force. The magnetic field has a node near the end of the stub and is maximal at the bottom. The sample to be investigated is placed at the bottom. Then the magnetic absorption measured is maximal and possible electric absorption is reduced very much.

The resonant wave length is practically determined by the length and diameter of the stub. The relation between the resonant wave length and the dimensions of the stub is given by the formula (cf. (Rl), section 10.09).

$$Z_o \, tg(2\pi/\lambda)l = 1/\omega C_o \, , \tag{190}$$

where Z_0 is the characteristic impedance of the coaxial line. Z_0 depends only on the radii a and b of the outer and inner conductor resp., and is given by $Z_0 = 138 \; {}^{10}\log b/a$ ohms,

l is the length of the stub

C_0 is capacity of a circular disk with the same cross section as the stub.

In this formula C_0 approximately accounts for the end effects of the stub. In our case we have $Z_0 = 117$ ohms and $C_0 = 0.7 \; \mu\mu F$. The required resonance wave length was taken equal to 9.8 cm. With the figures given we found $l = 2.16$ cm. The actual resonance wave length was found to be 9.78 cm.

The quality factor Q was estimated to be at least 1000 but could not be determined.

It finally may be added that if we neglect the end effects we have $C_0 = 0$, so that resonance occurs if l satisfies the condition $l = (2n + 1)\lambda/4$. In our case we have $n = 1$ and therefore this type of resonator usually is called a quarter wave length coaxial resonator. The length of the stub is about $\frac{1}{4}\lambda$ as it should be.

b) *The resonator for 3 cm wave length.* This resonator simply consisted of a length of a cylindrical wave guide closed at both ends and is sketched in fig. 26a. The bottom part B was soldered with *Wood's* metal S at the upper part T. This time the coupling with the coaxial lines of pyrotenax p was attained with coupling loops L. The resonator could be evacuated through the pumping tube P. The whole resonator was made of silver plated brass.

This resonator was excited in the H_{111} mode, which is the principal mode of a cylindrical cavity. The magnetic lines of

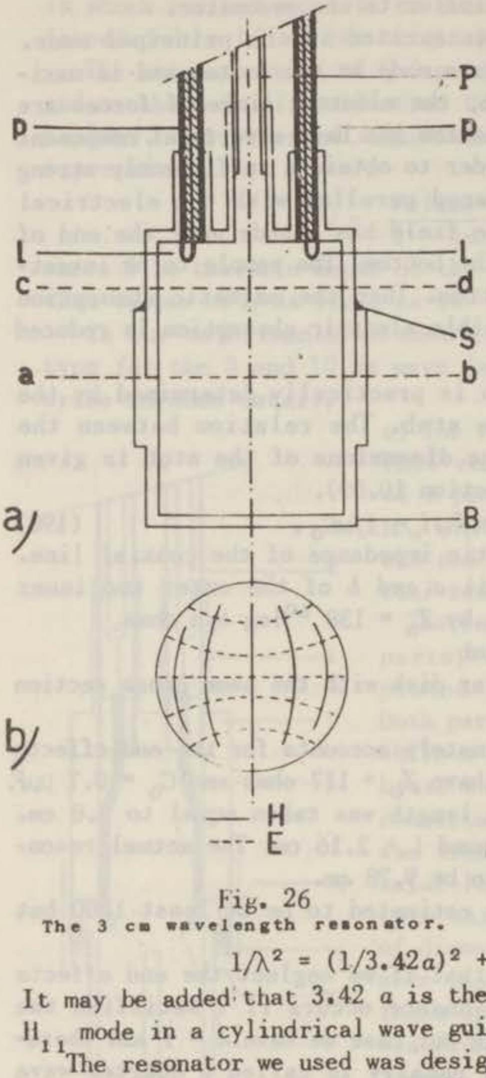

Fig. 26

The 3 cm wavelength resonator.

force of this mode form vertical closed loops with the same axis ab; the magnetic field is maximal at the top and the bottom of the resonator, and has a node at the half height. The electric lines of force of course are at right angles to the magnetic lines of force and are approximately situated in planes perpendicular to the axis of the cavity. The field pattern in a cross section may be illustrated by fig. 26b. The sample was placed on the bottom.

The resonant wave lengths of a cylindrical cavity are related to the dimensions of the cavities in a more complicated way than in the case of the coaxial resonator discussed above and depend on the roots of *Bessel* functions.

From *Huxley* (H12) we quote the following formula for the free space resonant wave length λ of the H_{111} mode of a cylindrical cavity of length d and with radius a

$$1/\lambda^2 = (1/3.42a)^2 + (1/2d)^2 \qquad (191)$$

It may be added that 3.42 a is the critical wave length for the H_{11} mode in a cylindrical wave guide with radius a.

The resonator we used was designed for a wave length of 3.15 cm. The length was chosen equal to 3.00 cm; then according to (191) the radius must be 1.08 cm. The resonance wave length of the actual resonator was 3.14 cm at low temperature. The Q-value was about 3500 at 90°K. This value is rather low for a H_{111} resonator; this probably is a consequence of a small overcoupling.

1.25 The measurement of absorption. It is not difficult to derive a relation between the absorption coefficient of a sample placed inside a cavity resonator and the Q-values of the empty and the filled resonator respectively. This is most simply done assuming that the standing wave in the resonator is simply a superposition of waves travelling into opposite directions and reflecting at the ends of the resonator, as is allowed for the principal mode of oscillation of a cylindrical cavity. We shall assume that the absorbing substance fills the whole resonator.

If now the resonator is shock-excited at $t = 0$ the wave started at that moment with carry an energy W, which decays by the presence of the sample according to

$$W = W_0 \, exp(-\alpha c t), \tag{192}$$

where α is the absorption coefficient of the substance (Cf p.76) and c is the velocity of the wave in free space. On the other hand we have according to (189)

$$W = W_0 \, exp(-\omega t/Q_s), \tag{193}$$

assuming that the only losses in the cavity are due to the substance; this is denoted by the subscript $_s$. Comparison of (192) and (193) yields

$$\alpha c = \omega/Q_s. \tag{194}$$

It now is easily shown that we have the relation

$$1/Q = 1/Q_0 + 1/Q_s, \tag{195}$$

where Q_0 is the quality factor of the empty resonator and Q is the quality factor of the resonator containing the absorbing matter.

Combination of (194) and (195) gives

$$\alpha = (2\pi/\lambda)\,[1/Q - 1/Q_0]. \tag{196}$$

In the case that the absorbing substance does not fill the resonator entirely, as is usually the case in experiments on paramagnetic resonance, this becomes

$$\alpha = a[1/Q - 1/Q_0], \tag{197}$$

where a is a constant depending on the mode of oscillation, the shape of the crystal, and the resonant wave length. It is in general difficult to calculate a accurately, but this is not necessary if we are only interested in relative values of the absorption.

It now can be shown that the power reaching the detector is proportional to Q^2 if the resonator is in resonance and is excited in one mode (Cf. ref. (H12), § 7.18).(It is essential that the direct coupling between the coupling loops or probes is negligible.) Assuming that the current given by the rectifying crystal is proportional to the power applied we have the relation for the empty cavity

$$\delta_0 \backsim I_0 \backsim Q_0^2 \, ,$$

and similarly for the cavity containing the sample

$$\delta \backsim I \backsim Q^2 \, ,$$

where δ_0 and δ are the deflections of the galvanometer respectively in the absence and presence of the sample ($\delta_0 \geqslant \delta$). Then it is easily shown that we have the relation

$$\alpha \backsim [(\delta_0/\delta)^{1/2} - 1], \tag{198}$$

which relates the absorption expressed in arbitrary units with the galvanometer deflections δ_0 and δ. Clearly this relation is only valid if the rectified current is proportional to the power reaching the detector. It is instructive to estimate δ_0/δ for an average case. Taking for the absorption coefficient $\alpha = 1.5 \times 10^{-3}$ (see p. 126) we find that for $\lambda = 3$ cm $Q_s \simeq 1000$ for a entirely filled resonator (compare (194)). In practice only a small part of the cavity is filled. We therefore shall take for the 'effective' value of $Q_s \simeq 10^4$. Assuming that Q_0 is 3000, it is easily shown using the relations (197) and (198) that $\delta_0/\delta = 1.4$ or $\delta/\delta_0 = 0.7$. This is easily detectable, unless δ_0 is very small and therefore justifies our statement that a cavity resonator is a suitable device for measuring small absorptions.

1.26 The measurement of wave length. For the measurement of the wave length we used a very simple wave meter consisting of a long cylindrical cavity in which from one side a rod could be intruded, so that the rod and the cavity form a coaxial resonator. It is easily concluded from (190) that resonance occurs if the length of the rod in the cavity satisfies the relation $l = l_0 + n\lambda/2$, where l_0 is the shortest resonant length. This relation is correct as long as the end capacity of the rod remains independent of the position of the rod, which implies that the end of the rod does not reach the end of the cylindrical cavity too closely. The wave length is measured by determining the distance between two positions of the rod giving resonance.

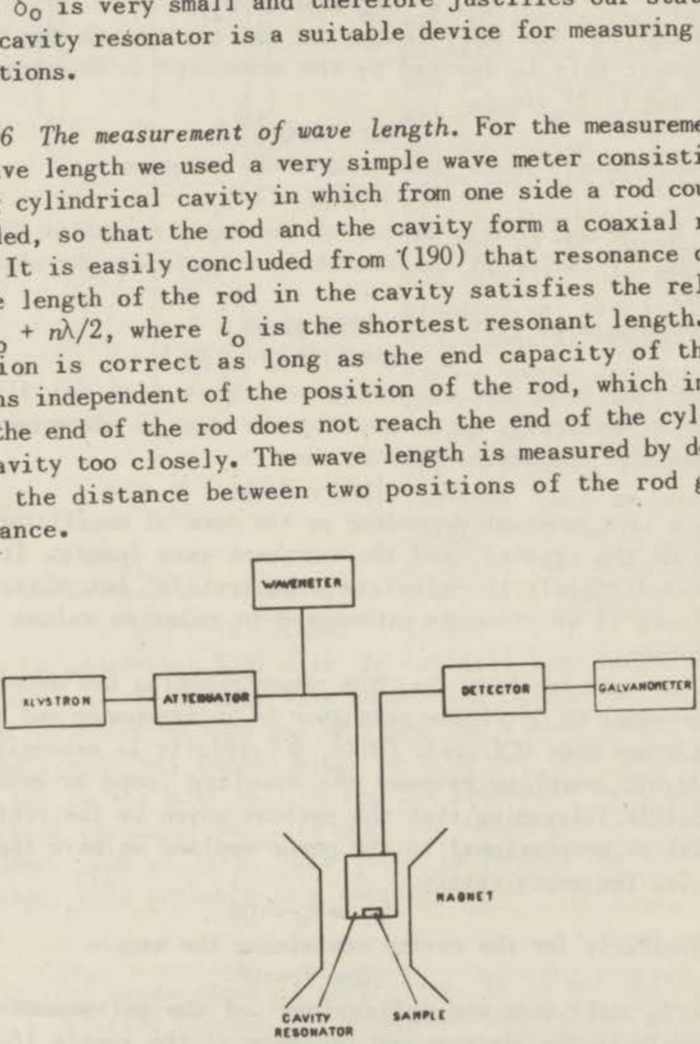

Fig. 27
Block diagram of the apparatus.

1.27 The method of measurement. This most easily can be described with the aid of the block diagram of the apparatus (see fig. 27), which does not need a special explanation.

A crystal of the paramagnetic substance is placed in the resonator, which is brought into resonance by adjusting the frequency of the klystron. Then an external magnetic field is applied and the deflection of the galvanometer is measured as a function of the magnetic field. In the case that the rectifying crystal satisfies a square law the absorption as a function of applied field is found with the relation (198). At each setting of the magnetic field the oscillator was adjusted to give maximal galvanometer deflection. This was done in order to avoid errors due to detuning of the cavity by the anomalous dispersion in the paramagnetic salt and to drift of the oscillator frequency.

2.3 The low temperature equipment.

The cavity resonators described in the preceding section have been used at low temperatures and it is desirable to discuss the low temperature parts of the apparatus in some detail.

2.31 The three centimetre apparatus. The 3 cm apparatus was placed in an ordinary cryostat. The resonator was suspended on the pumping line which was soldered to the cap of the cryostat. The pyrotenax leads were connected to coaxial leads, made of thin walled brass tube with paraffine wax as insulator. We used brass in order to reduce the heat influx along the coaxial lines. At room temperatures the attenuation in these leads was so large that no measurements could be carried out, but at low temperatures the performance was satisfactory. The lower part of the cryostat was placed between the pole pieces of a *Weiss* magnet.

2.32 The ten centimetre apparatus. a) The low temperatures in the experiments with 10 cm wave length were obtained with a *Simon* desorption apparatus (see for instance (S6)); the actual design followed the design of *De Haas* and *Van den Berg* (H13) in different respects. A sketch of the apparatus is given in fig.28.

D was a *Dewar* vessel with a narrow tail, connected with a rubber sleeve Sl to the brass cap C; D was supported by a ring Ri. The desorption space was a wide glass tube T - sealed in a brass tube on top of C - with a silvered double walled lowest part E. The space E could be evacuated through a pumping line p. T was connected with a conical ground joint j to a glass T-piece Tp and could be evacuated through a wide tube P; Tp was clamped to a metal stand, not shown in the figure, and carried on top a brass plate Pl which was waxed to the ground flange F.

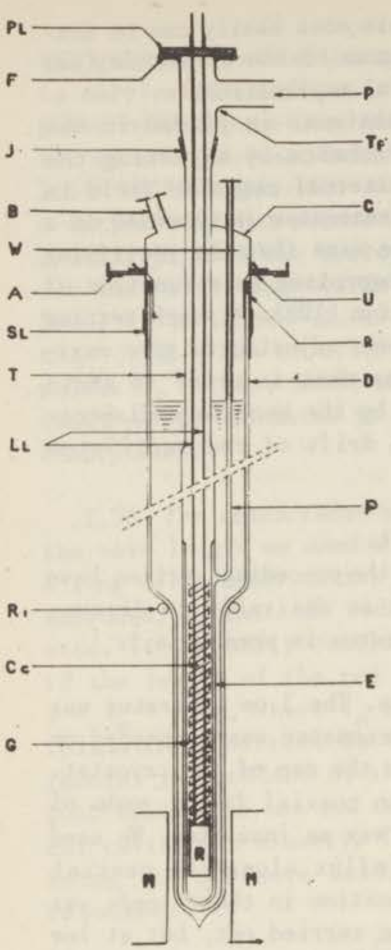

Fig. 28
The desorption apparatus

Two coaxial lines of german silver (compare 1.24) were soldered to Tp and carried the cavity resonator R. On top of R was placed a cylinder of copper gauze G, which contained the charcoal Cc. The temperature of R was measured with a simple gas thermometer (not shown in the figure).

The cap C was supported by two wings W, which were resting on a U-shaped plate U; U could slide along to strips of angle iron A which were connected to the metal stand. The apparatus easily could be opened by first sliding U backwards and then slipping the cap with T downwards; the interior of T remained hanging on the coaxial lines and it was easily to open the resonator R.

Usually D was filled with liquid hydrogen, of which the temperature could be lowered by pumping off the hydrogen vapour through tube B. The magnet was wheeled on after the complete apparatus was assembled.

b) The course of an experiment was as follows. After the sample had been brought in R, activated charcoal was quickly put in G. Then T was slipped over and the charcoal was pumped for several hours. (It was not possible to activate the charcoal while it was in G because this would have destroyed the sample in the resonator.) Finally helium gas was admitted to T and E and the whole cryostat was cooled down. In the meantime helium gas was allowed to be absorbed by the charcoal until the charcoal was saturated at the desired starting temperature for the desorption; this temperature usually was about 11 $^{\circ}$K.

Then E was carefully evacuated in order to break the heat contact between the charcoal and the hydrogen bath, and the helium gas in T was quickly pumped off. Consequently the temperature of the charcoal and the resonator dropped and after some time the temperature passed through a minimum. The temperature near the minimum was constant during at least 15 minutes within the limits of accuracy of the thermometer ($\simeq$ 0.05 degree). The minimum temperature reached usually was about 6 °K.

During the period of approximate constancy of the temperature the resonance experiment was carried out. As soon as the temperature started to rise again some helium gas was admitted to the charcoal, which gave of course a rise of temperature. (E was pumped all the time.) Then the helium gas was pumped off again. The lowest temperature reached this time was somewhat higher than the first time. This process of letting in some helium gas and pumping off afterwards could be repeted several times and allowed us to carry out a number of resonance measurements at increasing temperatures.

The performance of this desorption apparatus was not quite as good as for instance of the apparatus of *De Haas* and *Van den Berg*, with which temperatures as low as 4 °K have been reached. This is possibly a consequence of the small amount of charcoal we could use as the dimensions of the apparatus were largely determined by the dimensions of the available *Dewar* vessel. Moreover the capacity of the pump available for pumping the helium from the charcoal was not very large and it is suspected that a more powerful pump would have allowed us to reach lower temperatures.

* * * *

Chapter II

EXPERIMENTAL RESULTS AND DISCUSSION

2.1 Introduction.

In this chapter we represent some results of experiments on resonance absorption. These experiments as a whole are less complete than the experiments on paramagnetic relaxation and have a preliminary character. Several reasons can be given for this.

In the first place some special topics, which are especially of interest at low temperatures, are chosen. This choice has been largely influenced by the preliminary results obtained for many substances by *Bagguley* et al. (B7).

In the second place the rather primitive micro-wave equipment at our disponal only permitted reliable determination of splittings and g-values. For accurate measurements of line shapes and line widths a more elaborate set-up would be required.

In the third place lack of time prevented us from carrying out more experiments. This applies especially to the work with the desorption apparatus, which had to be carried out during a stay of ten months at Oxford.

Summarising we can say that in our opinion the work on resonance absorption.is rather a start for further study than a completed research.

In the remainder of this chapter we will discuss some results obtained for three substances:

a) *Titanium caesium alum.* This substance only profitably can be studied at very low temperatures, because at higher temperatures thermal broadening makes the absorption line too broad for being observable.

b) *A dilute iron ammonium alum.* This substance was so highly diluted that only at low temperatures the absorption could be measured.

c) *Anhydrous chromium chloride.* This 'concentrated' substance is interesting at low temperatures because it has a transition point at about 17 ^{o}K, which has in some respects resembles the *Curie*-point of ferromagnetic substances.

We do not attempt a discussion of the line widths as we believe this to be premature for reasons mentioned above.

2.2 Titanium caesium alum.

2.21 *Introduction.*

According to I, Ch. II the two lowest energy levels of the titanium ion in a crystal which is placed in a magnetic field are given by $E = \pm \frac{1}{2} g\beta H_c$, where the value of g depends on the direction of the magnetic field relative to the crystal axes. Consequently one resonance absorption line should be expected. *Bagguley* et al. (B7) examined titanium caesium alum but could not find any absorption, even at a temperature as low as 20 °K. As these authors pointed out this implies that the line is too broad, and therefore cannot be observed with the available means. This abnormal width can be explained in a natural way by an exceedingly short spin lattice relaxation constant. As we have seen in I, Ch. IV both direct experimental and theoretical evidence indicate that the spin lattice relaxation constant of Ti^{+++} is exceptionally short. At sufficiently low temperatures, however, τ should become long enough for making the line detectable. It seemed therefore worth while to investigate the titanium alum at still lower temperatures. This research was carried out with the apparatus described in section III, 2.32; the sample consisted of small crystals (B20).

2.22 *Results and discussion.* Only below 8 °K one absorption line was observed and we found that the intensity of the absorption increased at lower temperatures. This confirms the correctness of the explanation given in the preceding section for the unobserved absorption at higher temperatures.

TABLE XXI

T °K	6.33	6.58	6.72	6.76	7.04	7.35	7.46	7.88
H_m	1540	1510	1490	1490	1450	1410	1410	1360
g_{eff}	1.35	1.38	1.40	1.40	1.43	1.48	1.48	1.53
$r \times 10^{10}$ sec	0.96	0.73	0.66	0.66	0.58	0.52	0.54	0.49

In Table XXI we collected the values of the fieldstrength giving maximum absorption H_m and the corresponding 'effective' g-values, calculated with the relation $h\nu = g\beta H_m$, at different temperatures.

It will be noted at once that g_{eff} depends on the temperature. Now titanium caesium alum is a rather dilute substance and moreover the titanium ion has a small magnetic moment (one spin). Although the temperature is low it seems to be very unlikely that the behaviour of g_{eff} can be explained by the magnetic interaction between the titanium ions. In our opinion a much more natural explanation is given by the assumption that τ is sufficiently short for the line shape to be strongly influenced, if not determined, by τ. According to section I, 5.32 the line shape for a given direction of the magnetic field should be given by (158b), if the spin lattice relaxation is determined by one relaxation constant which we will assume. Then moreover the maximum absorption should shift to lower values of the constant field for smaller values of τ, or in other words, for higher temperatures. This agrees with the experimental result.

A further discussion requires the knowledge of g. The present experiments however do not allow us to determine the value of g for a powder - which is the average over the g-values for different directions of the magnetic field -, as lower temperatures would have been required for this. Unfortunately *Van den Handel*'s measurements on the susceptibility of a powder give very different g-values (between 1.2 and 2.0) for different samples, so that no reliable value of g can be obtained from them (H2). We shall assume that for our sample $g = 1.34$; possibly the correct value would be somewhat lower.

According to *Bleaney* (B4) this result can be interpreted in the following way. The fraction of ions whose trigonal axis make an angle θ with H_c is $\frac{1}{2}\sin\theta d\theta$ and they have a g-value determined by $g^2 = g_{\shortparallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$; resonance should occur at $H_c = h\nu/g\beta$. Using the relations between H_c and g, g and θ one finds that the intensity distribution as a function of the field for constant frequency should be

$$dI/I = g^2 \sec\theta dH_c/2\,(g_{\shortparallel}^2 - g_{\perp}^2)H_0.$$

For not too large anisotropy the absorption in the vicinity of the maximum absorption is mainly determined by sec θ and consequently the absorption is sharply peaked at the resonant field for the ions having the trigonal axis at right angle to the magnetic field. The finite width of the resonance line will round off the peak but not obliterate it if the width due to the magnetic interaction is small compared with the spread in a powder due to the anisotropic g-values.

We therefore shall assume that our value $g = 1.34$ corresponds approximately to $g_{\perp}$; then inserting this in equation (42) gives $\Delta = 410$ cm^{-1} and $g_{\shortparallel} = 1.75$. At 10 cm wavelength therefore the absorption line in a powder would be spread some hundreds Oersted owing to the anisotropic g-values and at shorter wave length this would be even more. The line width due to magnetic interaction should be only about 50 Oersted.

Taking $\Delta = 410$ cm^{-1} and $\lambda = 154$ cm^{-1} we find for the distances of the next two levels above the lowest level resp. 360 and 540 cm^{-1}.

From the values of H_m we estimated the values of the spin lattice relaxation time given in Table XXI. Insertion of the value at 7.9 ^{o}K in (145a) gives $\Delta \simeq 250$ cm^{-1}, which is about half the value obtained from the g-value. In view of the uncertainty of all our estimates the agreement hardly can be expected to be better. It may be noted that the dependence of τ on T is much smaller ($\backsim T^{-1}$) than *Van Vleck* predicts ($\backsim T^{-9}$).

We finally checked the line shape by comparing it with the line shape predicted by (158), assuming constant τ. A qualitative agreement was found but systematic deviations occur; several reasons can be given for this. First the anisotropy of the g-values must cause deviations, secondly τ may depend on the magnetic field and thirdly the low chemical stability of the substance may cause imhomogeneities resulting in different g-values for different regions of the crystal. In conclusion we want to remark that in our opinion the described experiments demonstrate some essential features of the thermal broadening of paramagnetic resonance lines. The experiments are far from complete however, and experiments on more stable substances (for instance on Fe^{++} salts) are highly desirable.

2.3 Iron ammonium alum.

2.31 General remarks. In I, Ch. II we discussed the energy levels of the Fe^{+++} in a cubic crystalline field and the splitting of these levels in a magnetic field of a given direction. We shall consider now the resonance spectrum which must be expected if the magnetic field is parallel to one of the cubic axes (for instance the [100] axis) of the crystalline field. This corresponds to a magnetic field having the direction of a cubic crystallografic axis of iron ammonium alum.

For our purpose it is sufficient to consider only the case of high fields ($x >> 1$; Cf. (47a)). The spins are practically free and one must anticipate that the selection rule for free spins $\Delta m = \pm 1$ will be approximately fulfilled, or in other words, that the transitions allowed by this selection rule are much stronger than all other conceivable transitions. We shall consider these strong transitions first. In Table XXII we collected the values of the energy differences ΔE corresponding to the selection rule $\Delta m = \pm 1$, calculated with the equations (47a). Resonance absorption lines should occur for values of H_c determined by

$$h\nu = g\beta H_c + a\delta , \qquad (199)$$

where ν is the frequency of the applied radiation and the values of a can be read from Table XXII. It may be noted that the spacing of these lines is independent of H_c.

It is easily possible to derive ΔE for transitions corresponding to $|\Delta m| > 1$ using the equations (47) or (47a). We shall not quote the expressions for ΔE in these cases, but mention only that groups of absorption lines symmetrically grouped around half, one third, one fourth and one fifth of the field strength determined by (199) are expected to exist, corresponding to $\Delta m = \pm 2, \pm 3, \pm 4, \pm 5$ respectively.

TABLE XXII

Transitions $\Delta m = \pm 1$		
m	m'	ΔE
5/2	3/2	$g\beta H_c + 2\delta$
3/2	1/2	$g\beta H_c - \frac{5}{2}\delta$
1/2	−1/2	$g\beta H_c$
−1/2	−3/2	$g\beta H_c + \frac{5}{2}\delta$
−3/2	−5/2	$g\beta H_c - 2\delta$

Kittel and *Luttinger* (K3) calculated the relative intensities of many of these transitions for various values of x and showed that in high fields the transitions with $|\Delta m| = \pm 1$ are very much stronger than all the others, while at lower fields the transitions with $|\Delta m| > 1$ become relatively more important. At low fields ($x \ll 1$) they even can be stronger than those with $|\Delta m| = 1$. Moreover some of the transitions with $|\Delta m| > 1$ are allowed in the case of parallel constant and alternating field. These subsidiary lines are a consequence of the remains of the spin-orbit coupling.

All the absorption lines mentioned will be broadened by the interaction between the iron ions and moreover the interaction can cause weak absorption lines at about one half, one third etc. of the field strength giving resonance with the transitions with $|\Delta m| = 1$. In general it therefore will be not possible to interprete the weak subsidiary lines without ambiguity, but on the other hand the subsidiary lines due to the magnetic interaction will become relatively weaker if the crystal is diluted, or in other words, a number of the paramagnetic ions is replaced by non-magnetic ones. In this way it should be possible to separate the contributions of the magnetic interaction and the spin-orbit interaction to the subsidiary lines. There are experiments under way in the Kamerlingh Onnes Laboratory to do this.

2.32 Results and discussion. We examined two specimen at 20 °K with the constant field along the [100] axis and the alternating field at right angle to it, using the second apparatus and a wavelength $\lambda = 3.17$ cm. The first specimen was a crystal of the undilute alum and the second specimen was diluted in the ratio 1:80 with aluminium ammonium alum. The absorption A, expressed in arbitrary units (Cf. (198)), is plotted as a function of the constant field in fig. 29. The dotted line represents the absorption of the undilute alum and the full drawn line the absorption of the dilute salt; the units of the ordinate are chosen in such a way that the maximum values of the absorption in the two cases are the same.

In the case of the undilute salt only one broad absorption line is found instead of the five lines predicted, while the shape of the line suggest the presence of a large central peak and two weaker side peaks. This is confirmed by the curve of the dilute salt which indeed shows the peaks suggested. Apparently the lines in the undilute salt are broadened so much by the interaction between the iron ions that the lines are fused. Each line should have a width of the order H_i = 435 Oersted (Cf. (83)).

In the case of the dilute salt we found two weak and three strong absorption lines.

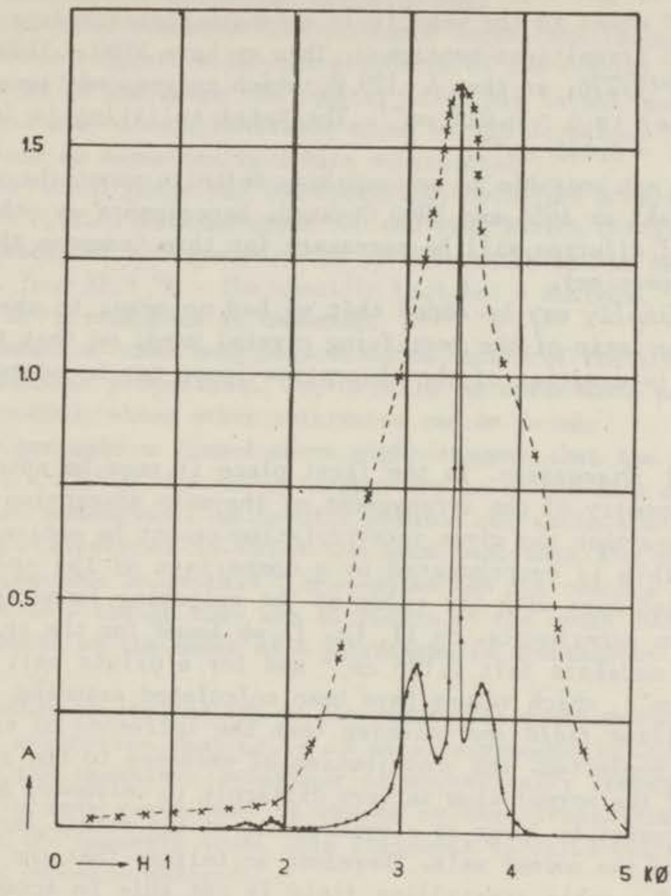

Fig. 29
Resonance absorption in iron ammonium alum.
The absorption in arbitrary units as a function of H_c;
$\lambda=3.17$ cm, $T=20\,^{\circ}$K, H_c in the [001] direction.
x undilute salt •dilute salt (1:80)

TABLE XXIII

H_m	1655	1900	3130	3470	3700
A	0.016	0.018	0.37	1.64	0.32

In Table XXIII we collected the field strengths corresponding to the maxima of absorption together with the values of A. It is seen at once that the peaks at 3130 and 3700 Oersted are not symmetrically arranged relative to the central peak at 3470 Oersted. If we forget about this for the moment we can try to interprete the strong lines on the basis of the theory given in the preceding section. Assuming that lines at 3130 and 3700 Oersted are in fact the fused lines corresponding to the pairs of transitions (–1/2, –3/2), (5/2, 3/2), and (1/2, 3/2), (–5/2,

-3/2) respectively, it is reasonable to take the fields 3130 and 3700 equal to the mean field strength corresponding to the pairs of transitions mentioned. Then we have 3700 - 3130 = 570 Oersted $=(9/2)\delta$, so that $\delta = 129$ Ø, which corresponds according to (148a) to $\delta = 0.012$ cm^{-1}. The total splitting is in this case $3\delta = 0.036$ cm^{-1}.

It is not possible to say anything definite about the subsidiary peaks at 1655 and 1900 Oersted. Experiments at other degrees of dilution will be necessary for this (compare the preceding section).

It finally may be added that we had no means to check the characteristic of the rectifying crystal used, so that the relative intensities of the absorption lines may be somewhat in error.

2.33 Discussion. In the first place it must be noted that the asymmetry of the arrangement of the main absorption lines indicates that the given interpretation cannot be entirely correct. This is corroborated by a comparison of the splitting suggested here with the value of the splitting found from relaxation experiments. In II, Ch. II we found for the splitting in the undilute salt 0.126 cm^{-1} and for a dilute salt (1:60) 0.145 cm^{-1}, which values have been calculated assuming a cubic crystalline field and assuming that the influence of exchange can be neglected. The contribution of exchange to the specific heat of the normal alum is very difficult to estimate, but probably cannot be large as a consequence of the rather large dilution of the normal salt. Therefore we believe that the assumption of a cubic crystalline field is not able to account for the suggested splittings. As has been discussed in I, Ch. II the properties of other alums - especially chromium alum - rather suggest that in iron ammonium alum the symmetry of the crystalline field must be lower than cubic, presumably trigonal. Then in the absence of an external field we should have three twofold levels. This is consistent with the results of very accurate measurements of the specific heat of the spin-system by *Benzie* and *Cooke* (B21), which rather suggest that there are three about equally spaced doublets. In this case however the overall splitting should be 0.16 cm^{-1}. At present it is not possible to calculate the splitting of the dilute alum from the resonance absorption, assuming a trigonal field. Therefore we must leave open the question, whether a trigonal field can account for the observed facts. Apart from the theory of the splitting of the Fe^{+++} in a trigonal crystalline field, more experimental results - for instance obtained at other wave lengths, temperatures and directions of the magnetic field relative to the crystal axes - probably will be required before this question can be answered.

2.4 Anhydrous chromium trichloride.

2.41 *General remarks*. This substance forms thin laminar crystals which suggests a laminar structure of the crystal lattice. As far as we are aware the crystal structure is not known. The magnetic and caloric behaviour shows marked devations from the behaviour of magnetically dilute substances.

In the first place the susceptibility satisfies a *Curie-Weiss* law $\chi = C/(T-\theta)$ between about 300 and 100 °K with $\theta = 32.5$ °K.

Secondly at a temperature of 17 °K - which is not very different from 32.5 °K - the specific heat has a maximum. Thirdly below 17° K remanence is observed.

A number of other anhydrous salts of metals of the iron group show similar properties. For details we refer to a paper of *Schultz* (S4), where other references can be found.

The properties listed above might suggest that the temperature $T = 17$ °K is a *Curie* temperature as in the case of ferromagnetic substances. As *Schultz* pointed out there are however marked differences of which the most important are that the magnetisations below this '*Curie*-point' do not reach a saturation value - though they are in fields of the order 20000 Oersted almost of the order of a ferromagnetic spontaneous magnetisation -.

Possibly an explanation of the properties mentioned is given by the assumption that $CrCl_3$ is anti-ferromagnetic (Cf. N1). Anyway the anomalous behaviour of magnetically concentrated salts in many cases must be caused by the strong interaction between the magnetic ions. This statement is valid for the anhydrous chromium chloride.

For this reason we presumed that $CrCl_3$ might be an interesting substance for investigation.

2.42 *Results and discussion*. We investigated three different samples. Sample I was obtained from British Drughouse Ltd. and was investigated with the 10 cm apparatus. The shape of the sample deviated not very much from a sphere. Samples II and III both were obtained from the stock from which *Woltjer* (W5) obtained his sample for his measurements on the susceptibility. The shape of sample II deviated not much from a sphere, but we took great care to give sample III a shape as nearly spherical as possible.

In all cases one absorption line was found and we calculated effective g-values with the relation $h\nu = g_{eff}\beta H_c$. The results for all samples are collected in Table XXIV and fig. 30.

TABLE XXIV

CrCl$_3$					
Sample I		Sample II		Sample III	
λ = 9.60 cm		λ = 3.17 cm		λ = 3.17 cm	
T °K	g_{eff}	T °K	g_{eff}	T °K	g_{eff}
290	2.00	79	2.00	79	2.00
90	2.00	20.0	2.03	20.0	2.02
20.3	2.18	18.5	2.10	18.5	2.04
11.4	2.80	17.4	2.17	17.1	2.08
7.52	2.80	16.5	2.19	16.5	2.22
6.80	2.80	15.6	2.24	15.6	2.27
6.25	2.80	14.3	2.29	-	-
5.75	2.80	-	-	-	-

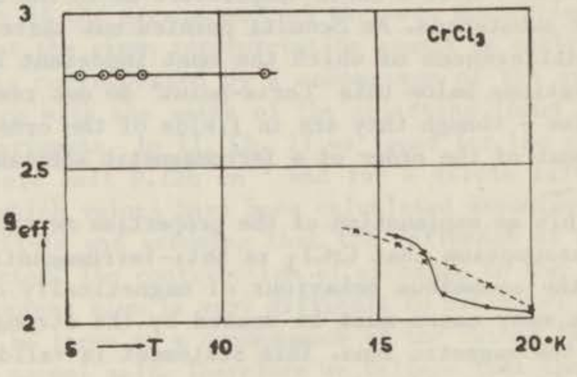

Fig. 30
CrCl$_3$. g_{eff} as a function of T.
⊙Sample I. Nearly spherical. λ=9.60 cm.
×Sample II. Nearly spherical. λ=3.17 cm.
•Sample III. Spherical. λ=3.17 cm.

Several comments about these results must be made.

a) The fact that only one line is found may be due to exchange forces large enough to overcome the effect of the crystalline electric field. As a matter of fact the large majority of salts of metals of the iron group have a number of non-equivalent ions in the elementary cell and each of these ions in a dilute salt will give its own resonance spectrum in general. Exchange forces however may be cause all the lines to fuse, as is for instance the case in copper sulphate. This presumably is the case in CrCl$_3$, where exchange forces must be considerable as a consequence of the high concentration of the chromium ions.

b) The next thing to note is the small but distinct difference between the results for a non-spherical and a spherical sample. Moreover the curves of fig. 30 seem to have about the same shape as curves susceptibility versus temperature for a fieldstrength of the order of 1000 to 3000 Oersted, which are steepest for a temperature of 17 °K and become horizontal for temperatures below about 14 °K (Cf. S4). It therefore seems feasible that the shift of g-value as function of T and H_c can be described with an effective field of the form $H_{eff} = H + \kappa I$ (so that $h\nu = g\beta H_{eff}$) where κ is a constant independent of H_c and T, but dependent on the shape of the sample. This constant κ cannot be equal to the constant of the 'internal' field of the *Weiss* theory of ferromagnetism, but must be smaller. According to *Weiss* $H_{eff} \sim (\theta/C)I$ where θ is the *Curie* temperature and C is the *Curie* constant. In our case we have $\theta \simeq 17$ °K and $C = 1.63$ so that we find for an external field of 2600 Oersted $H_{eff} \simeq 19000$ Oersted. Such a high value of H_{eff} cannot be reconciled with a 'true' g-value of 2.00 - as is found at high temperatures - and the fact that at 10 cm and 3 cm wavelength absorption at low temperatures has been observed. Possibly the randomly orientated internal field which is assumed to be present in anti-ferromagnetic materials can be reconciled with our results.

As is well known both types of internal field must be attributed to exchange forces, which on the other hand may not give a satisfactory explanation of the variation of the g-values in which we are interested here. This is perhaps not surprising from the point of view of *Pryce* and *Stevens* (P6), worked out by *Stevens* in a private communication to Professor *Gorter* (compare I, Ch. V), who showed that in first approximation displacement of the line only can be caused by the magnetic interaction or by exchange between dissimilar ions. A definite statement cannot be made because the approximation of *Pryce* and *Stevens* is valid for temperatures well above the *Curie* temperature and hardly can be a good one near the *Curie* point. Possibly the conclusion that in the first place the magnetic interaction is respondible for the shift of the line remains true even near the '*Curie* point'.

Summarising we can say that from an experimental point of view it is certain that the resonance shifts markedly as a function of temperature in the region of the '*Curie* point'. The suggested description however is rather speculative and a definite conclusion only can be drawn if more detailed information about the susceptibility at different fieldstrengths will be known. Moreover resonance experiments at other wavelengths and in the whole temperature region between 4 and 90 °K are desirable, possibly including measurement of the line width.

About the line width one remark may be added. The preliminary experiments of *Bagguley* et al. (B7) indicate that in the liquid hydrogen region the line width increases strongly with decreasing temperatures. At room temperature the line width was found to be about 50 Oersted. The line width to be expected from the magnetic interaction would be about 1500 Oersted, so that probably the line is narrowed considerably by the exchange interaction. At 14 °K however the line width found by these authors was of the order 2000 Oersted. Our own experiments indicate as well an increase of line width at lower temperatures, but certainly not as much as indicated by *Bagguley* at al. As the determination of line widths are rather uncertain more reliable measurements of the line widths are desirable.

* * * *

SAMENVATTING

In dit proefschrift worden enige eigenschappen van paramagnetische stoffen beschouwd, welke onderzocht kunnen worden door een paramagnetische stof te onderwerpen aan de invloed van een constant magneetveld waarop een wisselend magneetveld is gesuperponeerd. De meeste proeven zijn uitgevoerd bij lage temperatuur en hadden ten doel

a) het bestuderen van de wijze waarop zich thermodynamisch evenwicht instelt tussen het systeem van de elementaire magnetische momenten in de stof en de roostertrillingen (proeven over paramagnetische relaxatie),

b) het bestuderen van de laagste energieniveaux van de paramagnetische ionen in een kristal (proeven over paramagnetische resonantie absorptie).

In Deel I wordt een overzicht gegeven van enkele aspecten van de theorie van de eigenschappen van paramagnetische stoffen welke van belang zijn voor het te bespreken onderzoek. Hierbij is in het bijzonder aandacht besteed aan de theorie van de energieniveaux van paramagnetische ionen in een kristal.

In Deel II wordt een overzicht gegeven van de proeven over paramagnetische relaxatie. Het blijkt dat - in tegenstelling tot de resultaten bij hogere temperatuur - de paramagnetische relaxatie in het temperatuurgebied van vloeibaar helium (1-4 °K) in het algemeen niet beschreven kan worden met een enkele relaxatie constante. Verschillende mogelijke verklaringen worden besproken, maar het blijkt niet mogelijk te zijn op grond van de huidige kennis van zaken een eenvoudige verklaring te geven. Verder onderzoek is hiertoe nodig en een aantal voorstellen in deze richting wordt gedaan.

Een analyse van de afhankelijkheid van de gemiddelde relaxatie constante van de temperatuur en de waarde van het constante magneetveld levert het resultaat dat waarschijnlijk in verschillende stoffen tussen 1 en 4 °K de energie overdracht tussen de elementaire magnetische momenten en de roostertrillingen tot stand komt door z.g. quasi-*Raman* processen, hetgeen in tegenstelling is tot de theoretische verwachtingen van *Van Vleck*, Indien deze conclusie juist is - hetgeen als waarschijnlijk wordt beschouwd - is de theorie van *Van Vleck* niet in staat de invloed van verdere magnetische verdunning op de relaxatie constante te verklaren, Ook hier zijn verder gaande proeven ten zeerste gewenst.

In Deel III worden enkele proeven over paramagnetische resonantie absorptie besproken. Allereerst wordt een kort overzicht gegeven van de gebruikte techniek voor het werken met radiogolven met een golflengte van enkele centimeters, waarbij enkele onderdelen, welke van bijzonder belang zijn voor het te bespreken onderzoek, uitvoeriger worden beschouwd. Tenslotte werd de besproken techniek gebruikt voor het bestuderen van een drietal stoffen, welke om verschillende redenen met voordeel bij lage temperatuur kunnen worden onderzocht.

* * * *

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STELLINGEN

1

Waarschijnlijk leveren quasi-*Raman* processen ook in het temperatuurgebied van vloeibaar helium een belangrijke bijdrage tot de paramagnetische relaxatie.

(Hoofdstuk II,3 van dit proefschrift)

2

Het resonantie-absorptiespectrum van ijzerammoniumaluin kan niet verklaard worden op grond van de onderstelling, dat het electrische veld, waarin de ijzerionen zich bevinden, een kubische symmetrie heeft.

(Hoofdstuk III,2 van dit proefschrift)

3

In sommige gevallen verdient het gebruik van magnetische thermometers bij metingen van de warmtegeleiding bij lage temperaturen de voorkeur boven het gebruik van weerstands- of gasthermometers.

(D.Bijl, Physica, 14 (1949) 684)

4

Het is niet mogelijk de ligging van de energieniveaus van de configuratie $3d^9 4s5s$ van het koperatoom te verklaren op grond van de vereenvoudigende onderstellingen, dat de invloed van andere configuraties verwaarloosbaar is en het probleem behandeld kan worden als een drie-electronenprobleem.

(D.Bijl, Physica, 11 (1944-1946) 287)

5

Men moet verwachten, dat trillingskringen met een zeer hoge kwaliteitsfactor vervaardigd kunnen worden van metalen, welke supergeleidend kunnen worden gemaakt. Een zodanige trillingskring zou het meten van uitzettingscoëfficienten bij lage temperaturen op eenvoudige en nauwkeurige wijze mogelijk maken.

6

Het is van belang de *Raman*- en infraroodspectra van vloeibaar en vast methaan en ammoniak te onderzoeken.

7

De keuze van de stoffen welke men tot dusverre bij voorkeur heeft gebruikt voor proeven over adiabatische demagnetisatie is op grond van recente experimentele resultaten voor bedenkingen vatbaar.

8

Met behulp van de ‘molecular-orbital’methode kan op eenvoudige wijze verklaard worden, dat het MnO_4^--ion licht van betrekkelijk lange golflengte absorbeert.

9

‘Hyperconjugation’ moet worden beschouwd als het gevolg van een verdere benadering van de gebruikelijke theorieen van de chemische binding. Het is nog niet proefondervindelijk bewezen dat ‘hyperconjugation’ merkbaar kan bijdragen tot de chemische binding.

(R.S.Mulliken, C.A.Rieke, W.G.Brown, J.Am.Chem.Soc.,63 (1941) p.41; M.Szwarc, J.Chem.Phys., 16 (1948) 128)

10

Voor het uitvoeren van oude muziek op toetsinstrumenten verdient de middentoonstemming de voorkeur boven de normale halftoonstemming.

11

Het is zeer wel denkbaar dat het gebruik van metaal in de constructie van het mechanisme van de piano een goedkopere vervaardiging van dit instrument mogelijk maakt.

12

Een betere kennis van c_p/c_v van waterstof, bij temperaturen tussen 100 en 1000 °K en onder drukken tot enige duizenden atmosferen, is gewenst voor een nauwkeuriger berekening van de dikte van de dampkring van verschillende planeten.

13

Een studie van de absorptie- en emissiespectra van vastgemaakte gassen kan van groot belang zijn voor de identificatie van, tot dusverre niet geïdentificeerde, lijnen en banden van het absorptiespectrum van de interstellaire ruimte.