ON THE THEORY OF PARAMAGNETIC SPIN-SPIN RELAXATION

W. J. CASPERS

ON THE THEORY OF
PARAMAGNETIC SPIN-SPIN RELAXATION

ON THE THEORY OF PARAMAGNETIC SPIN-SPIN RELAXATION

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WIS-
EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE LEIDEN,
OP GEZAG VAN DE RECTOR MAGNIFICUS MR J. V. RIJPPERDA
WIERDSMA, HOOGLERAAR IN DE FACULTEIT DER RECHTSGE-
LEERDHEID, PUBLIEK TE VERDEDIGEN OP WOENSDAG
23 NOVEMBER 1960 TE 14 UUR

DOOR

WILLEM JAN CASPERS

GEBOREN TE LEEUWARDEN IN 1929

Promotor: PROF. DR C. J. GORTER

Aan mijn ouders
Aan Elly

The author is a member of the scientific staff of the „Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)", which is financially supported by the Netherlands Organization for pure scientific Research (Z.W.O.).

Op verzoek van de Faculteit der Wis- en Natuurkunde volgen hier enkele gegevens over mijn studie.

In 1947 legde ik het eindexamen h.b.s.-b af aan de rijks-h.b.s. te Zwolle. In hetzelfde jaar begon ik mijn studie aan de universiteit te Groningen; ik legde in april 1951 het candidaatsexamen natuur- en wiskunde (d) af. In januari 1955 volgde het doctoraalexamen met hoofdvak theoretische natuurkunde en het bijvak wiskunde. In de periode tussen deze beide examens ontving ik een studietoelage van de „Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)" en verrichtte ik onderzoek omtrent neutronenverstrooiing en over georienteerde atoomkernen in kristallen; dit onderzoek geschiedde onder leiding van Prof. Dr H. J. Groenewold en stond in verband met experimenten van O. J. Poppema, die in zijn proefschrift beschreven zijn.

Na het vervullen van mijn militaire dienstplicht trad ik in januari 1957 in dienst van de Stichting F.O.M. en werd ik in Leiden te werk gesteld, waar ik theoretisch onderzoek verrichtte op het gebied van de spin-spinrelaxatie. Dit onderzoek vond plaats op voorstel van Prof. Dr C. J. Gorter en de resultaten ervan zijn voor het grootste gedeelte vermeld in dit proefschrift.

De discussies die ik heb gevoerd met Prof. Dr S. R. de Groot, Prof. Dr N. G. van Kampen en Prof. Dr J. H. Van Vleck zijn van grote betekenis geweest bij het tot stand komen ervan.

Momenteel ben ik medewerker van de werkgroep VS V van genoemde Stichting F.O.M.

Op verzoek van de Faculteit der Wis- en Natuurkunde volgen hier enkele gegevens over mijn studie.

In 1947 legde ik het eindexamen h.b.s.-b af aan de rijks-h.b.s. te Zwolle. In hetzelfde jaar begon ik mijn studie aan de universiteit te Groningen; ik legde in april 1951 het candidaatsexamen natuur- en wiskunde, (d) af. In januari 1955 volgde het doctoraalexamen met hoofdvak theoretische natuurkunde en het bijvak wiskunde. In de periode tussen deze beide examens ontving ik een studietoelage van de „Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)" en verrichtte ik onderzoek omtrent neutronenverstrooiing en over georiënteerde atoomkernen in kristallen; dit onderzoek geschiedde onder leiding van Prof. Dr H. J. Groenewold en stond in verband met experimenten van O. J. Poppema, die in zijn proefschrift beschreven zijn.

Na het vervullen van mijn militaire dienstplicht trad ik in januari 1957 in dienst van de Stichting F.O.M. en werd ik in Leiden te werk gesteld, waar ik theoretisch onderzoek verrichtte op het gebied van de spin-spinrelaxatie. Dit onderzoek vond plaats op voorstel van Prof. Dr C. J. Gorter en de resultaten ervan zijn voor het grootste gedeelte vermeld in dit proefschrift.

De discussies die ik heb gevoerd met Prof. Dr S. R. de Groot, Prof. Dr N. G. van Kampen en Prof. Dr J. H. Van Vleck zijn van grote betekenis geweest bij het tot stand komen ervan.

Momenteel ben ik medewerker van de werkgroep VS V van genoemde Stichting F.O.M.

---

*) The author is a member of the scientific staff of the „Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)", which is financially supported by the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.).

INTRODUCTION

In this thesis part of the magnetic properties of isolated paramagnetic spin systems will be analysed from a theoretical point of view. Isolated spin systems are systems of paramagnetic spins, arranged in a rigid lattice. In the general theory of paramagnetism the interaction between the spin systems and the lattice vibrations is also taken into account and this gives rise to the so-called spin-lattice relaxation. In the present investigation we concentrate our attention on the internal properties of the spin systems and of these properties specifically the first-orderresponse to a change in the external magnetic field. This response is given by the relaxation function (chapter III). Equivalent information is given by the high-frequency susceptibilities $\chi'(\omega)$ and $\chi''(\omega)$, which are related to the relaxation function by a Fourier transformation (ch. III).

Special attention is paid to χ' for frequency zero (ch. I, II) and the discrepancy between the value of this quantity computed in a thermodynamical way (χ_{S}) and that found with the aid of the theory of the adiabatic approximation (χ_{is}), in the case of a large constant external field, if use is made of standard perturbation methods. For large macroscopic systems in which there is a dipole-dipole interaction between the spins, one should expect these two susceptibilities to be equal and we are of the opinion that the discrepancy for these systems is determined by the misuse of perturbation calculus. If one makes certain hypotheses, of a very general character, about the nature of the energy spectrum of such large systems, it is possible to prove that $\chi_{\mathrm{S}} = \chi_{\mathrm{is}}$, for all values of the constant external field (ch. II). We have the opinion that we can give these hypotheses plausibility by relating them to well-known properties of the energy spectrum of small systems. One of the hypotheses is equivalent to the second law of thermodynamics.

For small systems and large constant external fields a general relation between χ_{S} and χ_{is}, in the case of powdered crystals, is derived on the basis of a perturbation calculation (ch. I). For a large class of systems without exchange interaction between the spins, we found $\chi_{\mathrm{is}}/\chi_{\mathrm{S}} = 4/5$; this ratio is determined by the tensorial character of the different terms in the spin hamiltonian.

If there is an exchange interaction this value obeys the inequality:

$$0 \leqslant \chi_{\mathrm{is}}/\chi_{\mathrm{S}} \leqslant 4/5, \text{ if } S \leqslant 3/2.$$

The value of χ_{is} computed in this way with the aid of perturbation methods, also has a physical meaning for large systems (ch. II) and is denoted by $\chi_{\text{is}}^{\text{sm}}$ for these systems, to distinguish between this quantity and the correct value of the isolated susceptibility: $\chi_{\text{is}}(=\chi_{\text{S}})$, determined in chapter II. $\chi_{\text{is}}^{\text{sm}}$ does not correspond to the susceptibility for frequency zero for these large systems, but gives the value of χ' in a certain frequency interval, the lower boundary of which is of the order of the so-called spin-spin relaxation time. The upper limit of this interval is of the order of the Larmor frequency ω_H (ch. II).

For simple systems, containing only one kind of magnetic spins, the change from χ_{S} to $\chi_{\text{is}}^{\text{sm}}$ is marked by the spin-spin relaxation time τ, *i.e.* in the neighbourhood of the frequency $1/\tau$, χ' drops from χ_{S} to $\chi_{\text{is}}^{\text{sm}}$, when the frequency increases. A more precise definition of τ may be given by means of the asymptotic behaviour of the relaxation function, showing an exponential form:

$$A \exp\,(-t/\tau) + B.$$

For the computation of τ a detailed analysis of this relaxation function is necessary.

In the chapters III, IV and V a general method is developed for computing spin-spin relaxation times for two different cases. In the first one the constant external magnetic field is large as compared to the total internal field H_i; a general definition of this quantity is given in chapter III.

$(H_i^2 = H_{i_{dd}}^2 + H_{i_{ex}}^2 + H_{i_{st}}^2$; $H_{i_{dd}}$, $H_{i_{ex}}$ and $H_{i_{st}}$ correspond respectively to the contributions of the dipole-dipole interaction, the exchange interaction and the electric splitting to this internal field).

The relaxation is effected by the non-secular part of the interaction, *i.e.* that part that does not commute with the component of the total magnetic moment in the direction of the constant external field. It is shown that τ is, in first order, given by the zero-value of the frequency distribution of the matrix elements of this non-secular part in a representation diagonalizing the secular part and the magnetic moment simultaneously. This result was already known, but a detailed derivation has never been given, since standard perturbation methods cannot be used for this problem. Also, higher order corrections to the value of τ are given for the general case of simple systems containing only one group of spins (all spins are of the same kind). A generalization for the systems containing more groups is indicated. For these systems the number of relaxation times equals the number of such groups (ch. III).

In chapter IV a numerical illustration of the theory developed in chapter III is given. A comparison with the experiments is made for the ammonium cupric Tutton salt. Another part of this chapter is devoted to discussion and criticism of previous theories on the subject.

The final chapter of this thesis is devoted to the second case of spin-spin relaxation; a special mechanism is observed in salts in which there is a large electric splitting due to the crystalline field (ch. V).

When the Zeeman splitting and the electric splitting are of the same order of magnitude we may expect the possibility of two-spin processes for which the sum of Zeeman and electric energy is approximately conserved, giving, nevertheless, a net change of the total magnetic moment of the system. The corresponding relaxation time(s) is (are) computed with a method quite similar to that developed in chapter III. For this relaxation mechanism we restrict ourselves to the case that:

$$H, H_{i_{st}} \gg \sqrt{H_{i_{dd}}{}^2 + H_{i_{ex}}{}^2},$$

i.e. the splittings in the one-ion spectra are large as compared to the shifts caused by the interactions. Only part of the operator of the total spin moment contributes to the relaxation, *i.e.* the part that commutes with the zero order hamiltonian containing the Zeeman and the electric terms. Also, in this case the relaxation is effected by the non-secular part of the interaction and, for the simple systems, the corresponding relaxation time is given, in first order, by the zero-value of the frequency distribution of this non-secular part in a representation diagonalizing the secular part and the zero-order hamiltonian simultaneously. In a way quite similar to that indicated in chapter III, a generalization for more complicated systems, containing different groups, is given.

We think that in this thesis we have given a general theory of paramagnetic spin-spin relaxation phenomena, in the case of relatively large splittings in the one spin energy spectra. For the case that neither H nor $H_{i_{st}}$ is large as compared to $H_{i_{dd}}$ and $H_{i_{ex}}$, we do not believe that there will be relaxation phenomena in the sense of the chapters III, IV, and V, *i.e.* in general, the relaxation function will not have an asymptotic exponential form.

CHAPTER I

THE RATIO OF THE ISOLATED AND THE ADIABATIC SUSCEPTIBILITY OF PARAMAGNETIC CRYSTALS

Synopsis

For certain powdered crystals the value 4/5 is derived for the ratio of the isolated susceptibility (χ_{is}) and the adiabatic susceptibility (χ_{S}) in the case of a high-frequency field parallel to a strong constant field $\boldsymbol{H}$. The derivation is given by means of geometrical arguments which give an insight into the remarkable fact that for so many crystals one finds the same value for the ratio of the two susceptibilities.

1. *Introduction.* The purpose of this chapter is to compute the ratio of the isolated magnetic susceptibility χ_{is} and the adiabatic magnetic susceptibility χ_{S} for certain powdered crystals, in the case of large values of H (the constant external field).

In section 2 the spin hamiltonian is given in its most general form in the case that we restrict ourselves to ions with a nondegenerate lowest orbital level and $S \leqslant 3/2$ for the lowest multiplet. Exchange interactions are not considered.

Section 3 gives explicit expressions for the two susceptibilities in terms of the energy eigenvalues of the spin system and a simple expression for $(\chi_{\mathrm{S}} - \chi_{\mathrm{is}})/\chi_{\mathrm{S}}$ in the case of large values of H. In section 4 we find the simple result $\chi_{\mathrm{is}}/\chi_{\mathrm{S}} = 4/5$ for those cases mentioned in section 2, making use of general geometrical arguments.

2. *The spin hamiltonian.* Let us consider magnetic ions with a nondegenerate lowest orbital level. The spin-degeneracy of this level is removed by an external magnetic field $\boldsymbol{H}$, an electrostatic interaction of the ions with their surroundings and a dipole-dipole interaction between the different magnetic ions.

The magnetic and electric splittings are supposed to be small compared to the distance to the next orbital level.

We confine ourselves to the case of an isotropic g-tensor for the lowest multiplet with $g = 2$ for all the ions (no orbital contribution to the magnetic splitting in the lowest multiplet). The susceptibilities are calculated for those temperatures for which kT is small compared to the excitation energy of the next orbital level, but large compared to the splittings in the lowest multiplet.

If we neglect exchange interactions and restrict ourselves to the case $S \leqslant 3/2$ for all the magnetic ions, the so-called spin hamiltonian has the form [1]) [2]):

$$\mathscr{H} = - g\beta_0 H \sum_i S_{iz} + \sum_h [D_h\{S_{h\bar{z}}^2 - \tfrac{1}{3}S_h(S_h + 1)\} + E_h(S_{h\bar{x}}^2 - S_{h\bar{y}}^2)] + \\ + g^2\beta_0^2 \sum_{j<k} r_{jk}^{-3} [\boldsymbol{S}_j \cdot \boldsymbol{S}_k - 3(\boldsymbol{S}_j \cdot \boldsymbol{r}_{jk})(\boldsymbol{S}_k \cdot \boldsymbol{r}_{jk})/r_{jk}^2]. \qquad (1)$$

In formula (1) the indices i, h, j and k number the different magnetic ions. $S_{h\bar{x}}$, $S_{h\bar{y}}$ and $S_{h\bar{z}}$ are the components of the spinvector $\boldsymbol{S}_h$ of the h-th ion in the directions of the magnetic anisotropy axes $(\bar{x}_h, \bar{y}_h, \bar{z}_h)$ of this ion. S_{iz} is the component of the spinvector $\boldsymbol{S}_i$ in the direction of the external magnetic field, β_0 is the Bohr magneton and $\boldsymbol{r}_{jk}$ the radius vector of the distance between the ions j and k.

The magnetic anisotropy is induced by the anisotropic electric interaction of the ions with their surroundings. The electric interaction gives rise only to quadratic terms in the spin operators in the case $S \leqslant 3/2$; a transformation to principal axes for every ion separately gives the most general form: $\sum_h [D_h\{S_{h\bar{z}}^2 - \frac{1}{3}S_h(S_h + 1)\} + E_h(S_{h\bar{x}}^2 - S_{h\bar{y}}^2)]$, in which a constant is added to make the trace zero; D_h and E_h are constants, depending on the asymmetry of the electric interaction. For $S > 3/2$ we have in the most general case a more complicated form; higher order terms in the spin operators will appear in the hamiltonian of the electric interaction.

Besides the individual systems $(\bar{x}_h, \bar{y}_h, \bar{z}_h)$ we consider one general system (x, y, z) whose z-axis is directed along the external magnetic field.

Now we take such large values of H that we can consider the second and third terms in (1) as small perturbations and we write formula (1) in the following form:

$$\mathscr{H} = - g\beta_0 H S_z + \mathscr{H}' = \mathscr{H}_0 + \mathscr{H}', \; (S_z = \textstyle\sum_i S_{iz}). \qquad (2)$$

An elementary perturbation calculation gives a convergent series for the eigenvalues of (2) only if we restrict ourselves to the case of a small number of ions (see e.g. Bloembergen [3])). In the following we restrict ourselves to small numbers of ions though in all practical cases this number is so large that our series diverges. In the case that there is no dipole-dipole interaction the given result still holds for larger numbers. (See also the remark at the end of this chapter).

3. *The susceptibilities* χ_{is} and χ_{S}. For the definition of the isolated and adiabatic susceptibility (χ_{is} and χ_{S}) we refer to Broer [4]), who gives general formulae for these quantities. We consider only the case of high-frequency

fields parallel to the constant field $\boldsymbol{H}$ and in that case from Broer's results we can, making use of the fact that Tr $\mathscr{H} = 0$, in a simple manner derive:

$$\chi_{\mathrm{is}} = \frac{1}{p}\,\frac{1}{kT}\,\Sigma_\alpha\, \mathscr{E}_\alpha \frac{\partial^2 \mathscr{E}_\alpha}{\partial H^2}\,, \tag{3}$$

$$\chi_{\mathrm{S}} - \chi_{\mathrm{is}} = \frac{1}{p}\,\frac{1}{kT}\left[\Sigma_\alpha \left(\frac{\partial \mathscr{E}_\alpha}{\partial H}\right)^2 - (\Sigma_\gamma \mathscr{E}_\gamma{}^2)^{-1} \left(\Sigma_\alpha \mathscr{E}_\alpha \frac{\partial \mathscr{E}_\alpha}{\partial H}\right)^2\right]. \tag{4}$$

$\mathscr{E}_\alpha(\alpha = 1, \ldots, p)$ are the eigenvalues of (1) and (2), p is their total number. For large isolated systems of ions these two quantities χ_{S} and χ_{is}, and their difference, have a simple interpretation in certain cases. If an interaction between the ions is not included in our hamiltonian $\mathscr{H}_0 + \mathscr{H}'$, the χ_{S} can be interpreted as the susceptibility to be found when, during the whole period of the high-frequency field, an equilibrium distribution over the discrete one-ion levels is conserved by means of the interaction, the χ_{is} being the susceptibility in the case that no transitions, that would maintain an equilibrium distribution, take place. χ_{is} is only different from zero when the expectation value of the magnetic moment for one or more of the one-ion states depends on the value of H, the non-diagonal elements of μ, the magnetic moment in the direction of the external field, not all being zero ($\mu_\alpha = -\,\partial\mathscr{E}_\alpha/\partial H$; $\partial\mu_\alpha/\partial H = -\,\partial^2\mathscr{E}_\alpha/\partial H^2 \neq 0$ for one or more α's). Perturbation calculation gives in the lowest order of $1/H$:

$$(\chi_{\mathrm{S}} - \chi_{\mathrm{is}})/\chi_{\mathrm{S}} = \mathrm{Tr}\,\mathscr{H}'_{sec}{}^2/\mathrm{Tr}\,\mathscr{H}'^2. \tag{5}$$

$\mathscr{H}'_{sec}$ is that part of $\mathscr{H}'$ that commutes with $\mathscr{H}_0$. Calculating the quantity (5) for a crystal powder, we must average the right member over all directions of the external field $\boldsymbol{H}$ with respect to the crystal axes.

There is some discussion as to which of the two quantities χ_{S} and χ_{is} is to be identified with an experimental high-frequency susceptibility, measured in the frequency interval $(1/\tau_r \leqslant \omega \leqslant 1/\tau_s)$ (τ_r = spin-lattice relaxation time and τ_s = spin-spin relaxation time). In the remark at the end of this chapter we shall pay some attention to the value of (4) for large systems. In connection with this problem, the computation of $\chi_{\mathrm{S}} - \chi_{\mathrm{is}}$ for large systems, we also refer to Klein [5]).

4. *The ratio of* χ_{is} *and* χ_{S} *for powdered crystals.* Before starting the computation of (5) we introduce the Eulerian angles $(\alpha_{jk}, \beta_{jk})$ and $(\alpha_h, \beta_h, \gamma_h)$ which respectively define the position of the vectors $\boldsymbol{r}_{jk}$ and the systems $(\bar{x}_h, \bar{y}_h, \bar{z}_h)$ with respect to the axes (x, y, z).

The last step in our computation of (5) for a powder will be the averaging over these Eulerian angles.

These angles are defined in the following way: β_{jk} is the angle between the z-axis and the vector $\boldsymbol{r}_{jk}$, α_{jk} indicates the angle between the projection of the vector $\boldsymbol{r}_{jk}$ on the xy-plane and the x-axis; β_h is the angle between the z-axis and the $\bar{z}_h$-axis, α_h that between the projection of the $\bar{z}_h$-axis on the xy-plane and the x-axis and γ_h measures the angle between the $\bar{x}_h$-axis and the $z\bar{z}_h$-plane.

We now can write $\mathcal{H}$ in the form:

$$\begin{aligned}\mathcal{H} = {} & -g\beta_0 H S_z + \Sigma_h \Sigma_{M=-2}^{+2} (-)^M\, U^r{}_{2M}(\alpha_h, \beta_h, \gamma_h)\, U^s{}_{2-M}(\boldsymbol{S}_h) + \\ & + \Sigma_{j<k} \Sigma_{M=-2}^{+2} (-)^M\, T^r{}_{2M}(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk}))\, T^s{}_{2-M}(\boldsymbol{S}_j, \boldsymbol{S}_k). \qquad (6)\end{aligned}$$

In this formula $U^{r(s)}{}_{2M}$ and $T^{r(s)}{}_{2M}$ are components of irreducible tensors of rank 2. If we have exchange terms in (1), we should also have terms of the form const. $\times\, T^s{}_{00}(\boldsymbol{S}_j, \boldsymbol{S}_k)$ in (6), whereas S values larger than 3/2 lead to the appearance of tensor components $U^{r(s)}{}_{LM}$ with $L > 2$, in the spin hamiltonian. For the definition of irreducible tensor operators, the components of which we have characterized by the symbols T_{LM} and U_{LM} (in our case $L = 0,2$), we refer to Edmonds [6]).

In (6) the tensor operators $U^s{}_{2M}$ and $T^s{}_{2M}$ have the following form:

$$\begin{aligned} U^s{}_{2\pm2}(\boldsymbol{S}_h) &= S_{h\pm}{}^2, \\ U^s{}_{2\pm1}(\boldsymbol{S}_h) &= \mp (S_{h\pm} S_{hz} + S_{hz} S_{h\pm}), \\ U^s{}_{20}(\boldsymbol{S}_h) &= \tfrac{2}{3}\sqrt{6}\,[S_{hz}{}^2 - \tfrac{1}{4}(S_{h+} S_{h-} + S_{h-} S_{h+})], \\ T^s{}_{2\pm2}(\boldsymbol{S}_j, \boldsymbol{S}_k) &= S_{j\pm} S_{k\pm}, \\ T^s{}_{2\pm1}(\boldsymbol{S}_j, \boldsymbol{S}_k) &= \mp (S_{j\pm} S_{kz} + S_{jz} S_{k\pm}), \\ T^s{}_{20}(\boldsymbol{S}_j, \boldsymbol{S}_k) &= \tfrac{2}{3}\sqrt{6}\,[S_{jz} S_{kz} - \tfrac{1}{4}(S_{j+} S_{k-} + S_{j-} S_{k+})]. \end{aligned} \qquad (7)$$

The $S_\pm$ are step operators: $S_\pm = S_x \pm iS_y$.

In the appendix we have given explicit expressions for $U^r{}_{2M}(\alpha_h, \beta_h, \gamma_h)$ and $T^r{}_{2M}(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk}))$. In our calculations we only need their transformation properties:

$$\begin{aligned} T^r{}_{2M}(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk})) &= \Sigma_{M'}\, \mathcal{D}^2{}_{M'M}(\alpha_{jk}, \beta_{jk}, 0)\, T^r{}_{2M'}(0, 0)_{jk} = \\ &= \mathcal{D}^2{}_{0M}(\alpha_{jk}, \beta_{jk}, 0)\, T^r{}_{20}(0, 0)_{jk}, \\ U^r{}_{2M}(\alpha_h, \beta_h, \gamma_h) &= \Sigma_{M'}\, \mathcal{D}^2{}_{M'M}(\alpha_h, \beta_h, \gamma_h)\, U^r{}_{2M'}(0, 0)_h. \end{aligned} \qquad (8)$$

The $\mathcal{D}^2{}_{M'M}$ are the matrix elements of the irreducible representation of the rotation group for $L = 2$.

We shall also need the following properties of the $T^s{}_{2M}$ and $U^s{}_{2M}$:

$$\mathrm{Tr}\, T^{s\dagger}{}_{2M}(\boldsymbol{S}_j, \boldsymbol{S}_k)\, T^s{}_{2M'}(\boldsymbol{S}_j, \boldsymbol{S}_k) \begin{cases} = 100\ \delta_{M,M'}\ (S_j = S_k = 3/2), \\ = \ \ 16\ \delta_{M,M'}\ (S_j = S_k = 1), \\ = \ \ \ \ 1\ \delta_{M,M'}\ (S_j = S_k = 1/2), \end{cases} \qquad (9)$$

$\mathrm{Tr}\, T^{s\dagger}{}_{2M}(\boldsymbol{S}_j, \boldsymbol{S}_k)\, T^s{}_{2M'}(\boldsymbol{S}_{j'}, \boldsymbol{S}_{k'}) = 0$ for $j \neq j'$ and/or $k \neq k'$

$(j < k$ and $j' < k')$,

$$\operatorname{Tr} U^{s\dagger}{}_{2M}(\boldsymbol{S}_h)\, U^{s}{}_{2M'}(\boldsymbol{S}_h) \begin{cases} = 24\ \delta_{M,M'} & (S_h = 3/2), \\ = \ \ 4\ \delta_{M,M'} & (S_h = 1), \\ = \ \ 0 & (S_h = \tfrac{1}{2})\ ^{*)}, \end{cases} \tag{10}$$

$$\operatorname{Tr} U^{s\dagger}{}_{2M}(\boldsymbol{S}_h) U^{s}{}_{2M'}(\boldsymbol{S}_{h'}) = \ 0 \text{ for } h \neq h'.$$

The calculation of $\operatorname{Tr} T^{s\dagger}{}_{2M}(\boldsymbol{S}_j, \boldsymbol{S}_k)\, T^{s}{}_{2M'}(\boldsymbol{S}_j, \boldsymbol{S}_k)$ with $S_j \neq S_k$ is omitted. In the general case we find:

$$\begin{aligned} &\operatorname{Tr} T^{s\dagger}{}_{2M}(\boldsymbol{S}_j, \boldsymbol{S}_k)\, T^{s}{}_{2M'}(\boldsymbol{S}_j, \boldsymbol{S}_k) = A(S_j, S_k)\, \delta_{M,\,M'}, \\ &\operatorname{Tr} U^{s\dagger}{}_{2M}(\boldsymbol{S}_h)\, U^{s}{}_{2M'}(\boldsymbol{S}_h) \qquad\quad\ = B(S_h)\, \delta_{M,\,M'}. \end{aligned} \tag{11}$$

The $\mathscr{D}^2{}_{M'M}$ obey the following orthogonality relations:

$$\begin{aligned} &\overline{\mathscr{D}^{2*}{}_{MM'}(\alpha_h, \beta_h, \gamma_h)\, \mathscr{D}^2{}_{M''M'''}(\alpha_h, \beta_h, \gamma_h)}^{\alpha_h\beta_h\gamma_h} = \tfrac{1}{5}\delta_{MM''}\, \delta_{M'M'''}, \\ &\overline{\mathscr{D}^{2*}{}_{0M}(\alpha_{jk}, \beta_{jk}, 0)\, \mathscr{D}^2{}_{0M'}(\alpha_{jk}, \beta_{jk}, 0)}^{\alpha_{jk}\beta_{jk}} \qquad = \tfrac{1}{5}\delta_{MM'}. \end{aligned} \tag{12}$$

The bar indicates averaging over the variables indicated at the right end. From (6) we have:

$$\begin{aligned} \mathscr{H}' &= \textstyle\sum_h \sum_M (-)^M U^r{}_{2M}(\alpha_h, \beta_h, \gamma_h)\, U^s{}_{2-M}(\boldsymbol{S}_h) + \\ &\quad + \textstyle\sum_{j<k} \sum_M (-)^M T^r{}_{2M}(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk}))T^s{}_{2-M}(\boldsymbol{S}_j, \boldsymbol{S}_k), \\ \mathscr{H}'_{sec} &= \textstyle\sum_h U^r{}_{20}(\alpha_h, \beta_h, \gamma_h)\, U^s{}_{20}(\boldsymbol{S}_h) + \\ &\quad + \textstyle\sum_{j<k} T^r{}_{20}(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk}))T^s{}_{20}(\boldsymbol{S}_j, \boldsymbol{S}_k). \end{aligned} \tag{13}$$

$\operatorname{Tr} \mathscr{H}'^2$ is independent of the angles $\alpha_{jk}, \beta_{jk}, \alpha_h, \beta_h, \gamma_h$; this is to be expected on geometrical grounds because of the non-existence of interference terms between the electric and the dipole-dipole part of the perturbation. From (13) we find, with the help of (8), (11) and (12):

$$\begin{aligned} &\overline{\operatorname{Tr} \mathscr{H}'^2}^{\alpha,\beta,\gamma} = \overline{\operatorname{Tr} \mathscr{H}'^{\dagger}\, \mathscr{H}'}^{\alpha,\beta,\gamma} = \\ &\qquad = \textstyle\sum_h \sum_{M_1M_2} \sum_{M'_1M'_2} (-)^{M_1+M_2} \operatorname{Tr} U^{s\dagger}{}_{2-M_1}(\boldsymbol{S}_h) U^s{}_{2-M_2}(\boldsymbol{S}_h) \cdot \\ &\cdot \overline{\mathscr{D}^{2*}{}_{M'_1M_1}(\alpha_h, \beta_h, \gamma_h)\, \mathscr{D}^2{}_{M'_2M_2}(\alpha_h, \beta_h, \gamma_h)}^{\alpha_h,\beta_h,\gamma_h}\, U^{r*}{}_{2M'_1}(0,0)_h U^r{}_{2M'_2}(0,0)_h + \\ &+ \textstyle\sum_{j<k} \sum_{M_1M_2} (-)^{M_1+M_2} \operatorname{Tr} T^{s\dagger}{}_{2-M_1}(\boldsymbol{S}_j, \boldsymbol{S}_k)\, T^s{}_{2-M_2}(\boldsymbol{S}_j, \boldsymbol{S}_k) \cdot \\ &\cdot \overline{\mathscr{D}^{2*}{}_{0M_1}(\alpha_{jk}, \beta_{jk}, 0)\, \mathscr{D}^2{}_{0M_2}(\alpha_{jk}, \beta_{jk}, 0)}^{\alpha_{jk},\beta_{jk}}\, T^r{}_{20}(0,0)_{jk}\, T^r{}_{20}(0,0)_{jk} = \\ &= \textstyle\sum_h \sum_{M_1M_2} \sum_{M'_1M'_2} (-)^{M_1+M_2} \delta_{M_1M_2} \tfrac{1}{5} \delta_{M'_1M'_2} U^{r*}{}_{2M'_1}(0,0)_h U^r{}_{2M_2'}(0,0)_h B(S_h) + \\ &+ \textstyle\sum_{j<k} \sum_{M_1M_2} (-)^{M_1+M_2} \delta_{M_1M_2} \tfrac{1}{5} T^r{}_{20}(0,0)_{jk}\, T^r{}_{20}(0,0)_{jk} A(S_j, S_k) = \\ &\qquad = \textstyle\sum_h B(S_h) \sum_M U^{r*}{}_{2M}(0,0)_h\, U^r{}_{2M}(0,0)_h + \\ &\qquad\quad + \textstyle\sum_{j<k} A(S_j, S_k)\, T^r{}_{20}(0,0)_{jk}\, T^r{}_{20}(0,0)_{jk}. \end{aligned}$$

Thus we have:

$$\begin{aligned} \operatorname{Tr} \mathscr{H}'^2 = \overline{\operatorname{Tr} \mathscr{H}'^2}^{\alpha,\beta,\gamma} &= \textstyle\sum_h B(S_h) \sum_M U^{r*}{}_{2M}(0,0)_h\, U^r{}_{2M}(0,0)_h + \\ &\quad + \textstyle\sum_{j<k} A(S_j, S_k)\, T^r{}_{20}(0,0)_{jk}\, T^r{}_{20}(0,0)_{jk}. \end{aligned} \tag{14}$$

---

*) In the case of $S = \frac{1}{2}$ there is no "crystal splitting".

The computation of $\overline{\mathrm{Tr}\ \mathscr{H}'^2_{sec}}^{\alpha,\beta,\gamma}$ is now easily performed. In the derivation of (14) we met a summation over M_1 and M_2; for $\overline{\mathrm{Tr}\ \mathscr{H}'^2_{sec}}^{\alpha,\beta,\gamma}$ we have to leave out this summation and to take only the term which corresponds to $M_1 = M_2 = 0$. Thus we find:

$$\overline{\mathrm{Tr}\ \mathscr{H}'^2_{sec}}^{\alpha,\beta,\gamma} = \tfrac{1}{5}\,\overline{\mathrm{Tr}\ \mathscr{H}'^2}^{\alpha,\beta,\gamma} = \tfrac{1}{5}\,\mathrm{Tr}\ \mathscr{H}'^2, \tag{15}$$

and for a crystal powder we have:

$$(\chi_\mathrm{S} - \chi_\mathrm{is})/\chi_\mathrm{S} = \overline{\mathrm{Tr}\ \mathscr{H}'^2_{sec}}^{\alpha,\beta,\gamma}/\mathrm{Tr}\mathscr{H}'^2 = \tfrac{1}{5},$$

or

$$\chi_\mathrm{is}/\chi_\mathrm{S} = 4/5.$$

This result has a very simple qualitative explanation: in χ_S we have an equal contribution from all the tensor components ($M = -2, \ldots, +2$) and in χ_is contributions only from the non-secular ones ($M \neq 0$), all of them having the same value. In all the cases that there are only tensors with $L \geqslant 2$ (no exchange) the fraction $\chi_\mathrm{is}/\chi_\mathrm{S}$ will obey the inequality $4/5 \leqslant \chi_\mathrm{is}/\chi_\mathrm{S} \leqslant 1$. If there are only tensors with $L = 0$ (exchange, no crystal splitting and no dipole-dipole interaction) $\chi_\mathrm{is}/\chi_\mathrm{S} = 0$ and in the most general case ($L = 0,2,\ldots$) this fraction can have all possible values between 0 and 1.

Remark: The given result holds only for a small number of ions, if there is a dipole-dipole interaction. In all practical cases measurements are done on large (macroscopic) systems for which the perturbation calculation we have used does not converge, since a dipole-dipole interaction is present.

In the case of large systems with a dipole-dipole interaction present and all the dimensions of the system becoming infinitely large for $N \to \infty$ (N = the total number of ions), we hope to be able to prove the following relation between χ_S and χ_is:

$$\lim_{N\to\infty} (\chi_\mathrm{S} - \chi_\mathrm{is})/\chi_\mathrm{S} = 0.$$

Appendix: Explicit expressions for the tensor components $U^{r(s)}{}_{LM}$

$$U^r{}_{2\pm2}(\alpha,\beta,\gamma) = \tfrac{1}{4}\mathrm{e}^{\pm 2i\alpha}[D\sin^2\beta + \tfrac{1}{2}E\,\{(1-\cos\beta)^2\,\mathrm{e}^{\mp 2i\gamma} + (1+\cos\beta)^2\,\mathrm{e}^{\pm 2i\gamma}\}],$$

$$U^r{}_{2\pm1}(\alpha,\beta,\gamma) = \mp\tfrac{1}{2}\mathrm{e}^{\pm i\alpha}\,[D\sin\beta\cos\beta + \tfrac{1}{2}E\,\{\sin\beta\,(1-\cos\beta)\,\mathrm{e}^{\mp 2i\gamma} - \sin\beta\,(1+\cos\beta)\mathrm{e}^{\pm 2i\gamma}\}],$$

$$U^r{}_{20}(\alpha,\beta,\gamma) = \tfrac{1}{12}\sqrt{6}\,[D(3\cos^2\beta - 1) + 3E\sin^2\beta\cos 2\gamma],$$

$$T^r{}_{2\pm2}(\boldsymbol{r}_{jk}) = -\tfrac{3}{4}\,(g\beta_0)^2\,\frac{1}{r_{jk}{}^5}\,(x_{jk} \pm iy_{jk})^2,$$

$$T^r{}_{2\pm1}(\boldsymbol{r}_{jk}) = \pm\tfrac{3}{2}\,(g\beta_0)^2\,\frac{1}{r_{jk}{}^5}\,(x_{jk} \pm iy_{jk})\,z_{jk},$$

$$T^{r}{}_{20}(\boldsymbol{r}_{jk}) = -\tfrac{1}{4}\sqrt{6}(g\beta_0)^2 \frac{1}{r_{jk}{}^5}(3z_{jk}{}^2 - r_{jk}{}^2).$$

x_{jk}, y_{jk} and z_{jk} are the components of $\boldsymbol{r}_{jk}$ in the system (x, y, z). They are well known functions of α_{jk}, β_{jk}.

REFERENCES

1) Bowers, K. D. and Owen, J., Rep. Progr. Phys. **18** (1955) 304.
2) Abragam, A. and Pryce, M. H. L., Proc. roy. Soc. A **205** (1951) 135.
3) Bloembergen, N., thesis Leiden (1948), p. 30.
4) Broer, L. J. F., Physica **17** (1951) 531.
5) Klein, M. J., Phys. Rev. **86** (1952) 807.
6) Edmonds, A. R., Angular momentum in quantum mechanics (Princeton University Press, 1957).

CHAPTER II

THE ISOLATED AND ADIABATIC SUSCEPTIBILITIES OF LARGE SYSTEMS

Synopsis

It can be shown that for large systems of magnetic ions with dipole-dipole interaction the isolated susceptibility χ_{is} and the adiabatic susceptibility χ_{S} are identical, if two hypotheses are made about the nature of the energy spectrum of such systems. These hypotheses say that the density of energy levels of such systems and the derivative of every energy eigenvalue with respect to H, the constant external field, can be approximated by continuous functions of the energy, for a fixed value of H. The derivation of the equivalence of χ_{is} and χ_{S} is given for single crystals for all directions of the external field with respect to the crystal axes and for all values of H, whereas the ratio $\chi_{\mathrm{is}} : \chi_{\mathrm{S}} = 4 : 5$, derived in the previous chapter [1]) for a certain class of small systems, refers to powders only and to large values of H.

Finally it is shown that in the case of large H there is always a frequency interval in which the high-frequency susceptibility of a powder has the value of χ_{is}, computed in the previous chapter, though the single crystals in a powder are expected to be much larger than those systems for which the computation given in that chapter is correct.

1. *Introduction*. In the previous chapter [1]), to be referred to hereafter as I, the value 4/5 was found for the ratio of the isolated and the adiabatic susceptibility of certain powdered crystals. In the case of systems with dipole-dipole interaction a restriction was made as to the number of magnetic ions (the number of ions in one single crystal in the powder has to be very small; the heat contact between the single crystals was supposed to be negligible). In a concluding remark the result, to be expected for large systems, was given. By large systems were meant such systems for which elementary perturbation calculation does not give a convergent series for the energy eigenvalues.

The purpose of this chapter is to show the identity of χ_{is} and χ_{S} for large systems of magnetic ions with dipole-dipole interaction. One only considers ions with a zero orbital momentum. The result $\chi_{\mathrm{is}} = \chi_{\mathrm{S}}$ refers to single crystals as well as to powders, χ_{is} being independent of the direction of the external field $\boldsymbol{H}$ with respect to the crystal axes. The restriction $S \leqslant 3/2$, made in I, can be abandoned too and the equivalence of the two susceptibilities holds for all values of H.

Only those lattices are considered which contain one sort of magnetic ions and for which $\sum_{k(k\neq j)} (r_{jk})^{-6}$ is independent of j (r_{jk} is the distance between the j–th ion and the k-th ion).

In section 2 the hamiltonian of our system is given. Section 3 contains formulae for the quantities χ_{S} and χ_{is}, valid for arbitrary systems. It is shown that the main point of our derivation will be the computation of $\sum_\alpha(\partial\mathscr{E}_\alpha/\partial H)^2$, where $\mathscr{E}_\alpha(\alpha = 1, 2, \ldots)$ are the energy eigenvalues of the system. The quantity $\sum_\alpha(\partial\mathscr{E}_\alpha/\partial H)^2$ is a rather complicated symmetric function of the eigenvalues $\mathscr{E}_\alpha$; an explicit expression of this function is given in section 4. In principle this symmetric function can be expressed in terms of the trace of powers of $\mathscr{H}$, the hamiltonian; one has thus a straightforward method to compute the value of $\sum_\alpha(\partial\mathscr{E}_\alpha/\partial H)^2$ as a function of H. But this method leads to insurmountable difficulties in the case of large N, the total number of ions. Therefore in section 5 asymptotic values of $\mathrm{Tr}\,\mathscr{H}^{2n} = \sum_\alpha\mathscr{E}_\alpha{}^{2n}$ for large N are given, which enable us to compute the value of the quantity $\sum_\alpha(\partial\mathscr{E}_\alpha/\partial H)^2$ for systems, all dimensions of which are of the order $N^{\frac{1}{3}}$. Use is made of two hypotheses concerning the properties of the energy spectrum of our systems. These hypotheses can be given well defined physical contents. The first one says that the level density can be approximated by a continuous function of the energy, for a fixed value of H. In the second one the same is postulated for the derivative with respect to H of every energy eigenvalue.

In both hypotheses our magnetic system has an arbitrary but fixed position with respect to the direction of $\boldsymbol{H}$.

In section 6 it is shown that for large values of H there is always a frequency interval in which the high-frequency susceptibility of a powder has the value of χ_{is} derived in I. One can thus distinguish between two extensive quantities: the value of χ_{is} computed in a way which is correct for small systems only, if one defines χ_{is} by means of formula (3) of I, and the value of χ_{is}, defined in the same way, computed with the aid of the method given in this chapter, a method which is only correct for large systems. For the first quantity we introduce the new symbol $\chi_{\mathrm{is}}{}^{\mathrm{sm}}$, whereas we reserve the symbol χ_{is} for the last one.

One expects that the greater part of the single crystals in a powder are much larger than the so-called small systems, for every practical value of H. The powdering has only the effect that the measured value of χ_{is} takes the value of χ_{is} for a single crystal averaged over all directions of the field $\boldsymbol{H}$.

2. *The hamiltonian*. The hamiltonian of our system only contains a Zeeman term and an interaction term, since only the case of zero orbital momentum is considered. If the ions have higher orbital levels with $L \neq 0$, our hamiltonian is, as a matter of fact, a spin hamiltonian. In all cases kT

is supposed to be small compared to the orbital excitation energy, but large compared to the splittings in the lowest orbital level.

Consequently the hamiltonian has the form:

$$\mathscr{H} = - g\beta_0 H \textstyle\sum_i S_{iz} + \\ + (g\beta_0)^2 \textstyle\sum_{j<k} \dfrac{1}{r_{jk}^3} \left[(\boldsymbol{S}_j \cdot \boldsymbol{S}_k) - 3\, \dfrac{(\boldsymbol{S}_j \cdot \boldsymbol{r}_{jk})(\boldsymbol{S}_k \cdot \boldsymbol{r}_{jk})}{r_{jk}^2} \right]. \quad (1)$$

In formula (1) the indices i, j and k number the magnetic ions. S_{iz} is the component of the spinvector $\boldsymbol{S}_i$ of the i-th ion in the direction of the magnetic field $\boldsymbol{H}$, β_0 is the Bohr magneton and $\boldsymbol{r}_{jk}$ the radius vector of the distance between the ions j and k, r_{jk} being its length. The Landé g-factor will have the value 2 in all cases. Only those lattices are considered which contain one sort of magnetic ions and for which $\sum_{k(k \neq j)} r_{jk}^{-6}$ is independent of j.

3. *The susceptibilities* χ_{is} *and* χ_{S}. In I formulae for χ_{is} and $\chi_{\mathrm{S}} - \chi_{\mathrm{is}}$ were given, both in the high temperature approximation:

$$\chi_{\mathrm{is}} = \frac{1}{p}\,\frac{1}{kT}\, \textstyle\sum_\alpha \mathscr{E}_\alpha \dfrac{\partial^2 \mathscr{E}_\alpha}{\partial H^2}, \quad (2)$$

$$\chi_{\mathrm{S}} - \chi_{\mathrm{is}} = \frac{1}{p}\,\frac{1}{kT} \left[\textstyle\sum_\alpha \left(\dfrac{\partial \mathscr{E}_\alpha}{\partial H} \right)^2 - (\textstyle\sum_\gamma \mathscr{E}_\gamma^{\,2})^{-1} \left(\textstyle\sum_\alpha \mathscr{E}_\alpha \dfrac{\partial \mathscr{E}_\alpha}{\partial H} \right)^2 \right]. \quad (3)$$

For a discussion of the physical meaning of these quantities one is referred to the chapter mentioned. In (2) and (3) $\mathscr{E}_\alpha$ ($\alpha = 1,2, \ldots, p$) are the eigenvalues of (1) (p being their total number).

For the computation of χ_{S} and χ_{is} in the present case no use will be made of perturbation calculation and the result $\chi_{\mathrm{S}} = \chi_{\mathrm{is}}$ is valid for all values of H.

One can write (2) and (3) in terms of $\sum_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2$, $T_2 = \sum_\alpha \mathscr{E}_\alpha^{\,2} = \mathrm{Tr}\, \mathscr{H}^2$ and the derivatives of the latter with respect to H; so one has:

$$\chi_{\mathrm{is}} = \frac{1}{p}\,\frac{1}{kT} \left[- \textstyle\sum_\alpha \left(\dfrac{\partial \mathscr{E}_\alpha}{\partial H} \right)^2 + \tfrac{1}{2}\, \dfrac{\partial^2}{\partial H^2}\, T_2 \right], \quad (4)$$

$$\chi_{\mathrm{S}} - \chi_{\mathrm{is}} = \frac{1}{p}\,\frac{1}{kT} \left[\textstyle\sum_\alpha \left(\dfrac{\partial \mathscr{E}_\alpha}{\partial H} \right)^2 - \tfrac{1}{4}\, \dfrac{((\partial/\partial H) T_2)^2}{T_2} \right]. \quad (5)$$

The most important part of the sections 4 and 5 will be formed by the computation of $\sum_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2$.

4. *Explicit expression for* $\sum_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2$ *in terms of the energy eigenvalues.* In this section a system of linear equations is given for the quantities $(\partial \mathscr{E}_\alpha / \partial H)^2$ in terms of the energy eigenvalues $\mathscr{E}_\beta$.

First definitions of the quantities T_n and A_n, which play an important role in the following derivation, are given:

$$T_n = \Sigma_\alpha \mathscr{E}_\alpha{}^n = \operatorname{Tr} \mathscr{H}^n, \tag{6}$$

$$A_n = \frac{1}{(n+1)(n+2)} \frac{\partial^2}{\partial H^2} T_{n+2}. \tag{7}$$

The unknown quantities $(\partial \mathscr{E}_\alpha / \partial H)^2$ and $\partial^2 \mathscr{E}_\alpha / \partial H^2$ $(\alpha = 1, \ldots, p)$ obey the linear equations:

$$\Sigma_\alpha \mathscr{E}_\alpha{}^l \left(\frac{\partial \mathscr{E}_\alpha}{\partial H} \right)^2 + \frac{1}{l+1} \Sigma_\alpha \mathscr{E}_\alpha{}^{l+1} \frac{\partial^2 \mathscr{E}_\alpha}{\partial H^2} = A_l \; (l = 1, 2, \ldots, 2p). \tag{8}$$

If all energy levels are non-degenerate, Cramer's rule leads to the following expressions for $(\partial \mathscr{E}_\alpha / \partial H)^2$ $(\alpha = 1, \ldots, p)$:

$$(\partial \mathscr{E}_\alpha / \partial H)^2 = D_\alpha / D,$$

$$D = \textstyle\int_0^{\varepsilon_1} \mathrm{d}x_1 \ldots \int_0^{\varepsilon_p} \mathrm{d}x_p \, \Pi_{\gamma=1}^p \, \mathscr{E}_\gamma \, \Pi_{\delta=1}^p \, x_\delta \, D_{2p}(\mathscr{E}_1 \ldots \mathscr{E}_p, x_1 \ldots x_p), \tag{9}$$

$$D_\alpha = \Sigma_{k=1}^{2p} \frac{A_k}{k!} \int_0^{\varepsilon_1} \mathrm{d}x_1 \ldots \int_0^{\varepsilon_p} \mathrm{d}x_p \left[\left(\frac{\partial}{\partial \mathscr{E}_\alpha} \right)^k \cdot \right.$$
$$\left. \cdot \, \Pi_{\gamma=1}^p \, \mathscr{E}_\gamma \, \Pi_{\delta=1}^p \, x_\delta D_{2p}(\mathscr{E}_1 \ldots \mathscr{E}_p, x_1 \ldots x_p) \right]_{\mathscr{E}_\alpha = 0}.$$

In this formula D_{2p} is a Vandermonde determinant of degree $2p$, also called an alternant, see e.g. Aitken 2). In his notation our determinant $D_{2p}(\mathscr{E}_1 \ldots \mathscr{E}_p, x_1 \ldots x_p)$ takes the form:

$$|\mathscr{E}_1{}^0 \, \mathscr{E}_2{}^1 \, \mathscr{E}_3{}^2 \ldots \mathscr{E}_p{}^{p-1} \, x_1{}^p \ldots x_p{}^{2p-1}|.$$

One can prove now, in an easy way, that:

$$\Sigma_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2 = \Sigma_\alpha D_\alpha / D, \tag{10}$$

is a symmetric expression in the eigenvalues $\mathscr{E}_\alpha$; this form can be reduced to an expression in terms of the T_n's and these quantities T_n can be found by a straightforward calculation. For a system with a discrete non-degenerate energy spectrum (9) and (10) give a general way for computing χ_{ls}. In the present case, however, (N very large) this method has no practical usefulness, the computations being too complicated, and in section 5 another method for the determination of the value of $\Sigma_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2$ is given.

5. *Explicit expressions for $\Sigma_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2$ and $\Sigma_\alpha \mathscr{E}_\alpha{}^{2n}$ for large N. Proof of the equality of χ_{ls} and χ_{s}.* In this section only large systems are considered, the dimensions of these systems all being of the order $N^{1/3}$ (e.g. a cube with an edge of length $aN^{1/3}$, a being the interionic distance).

In section 1 we gave a definition of large systems in general. Two hypotheses are made about the nature of the energy spectrum of such systems:

Hypothesis I: The level density can be approximated by a continuous function of the energy, with an arbitrary accuracy, taking N sufficiently large.

Hypothesis II: The derivative with respect to H of every energy eigenvalue can be approximated by one continuous function of the energy, also with an arbitrary accuracy, N being sufficiently large.

Both hypotheses are supposed to be valid for arbitrary direction and length of the vector $\boldsymbol{H}$.

In 5.1 it is explained why one is induced to expect such properties of the energy spectrum as formulated in a qualitative way in the hypotheses I and II. This part of the section has a pure heuristic character.

In 5.2 the hypotheses are given in a pure mathematical form (hypotheses I^{a} and II^{a}) and it is shown that, making use of these hypotheses, the equality of χ_{is} and χ_{S} can be derived.

5.1 The hypotheses I and II are based on the special character of the hamiltonian which gives a mutual coupling of all the ions. This hamiltonian cannot be separated in parts which contain different groups of degrees of freedom which do not interfere. If one has a small number of ions it is a well known fact that the total number of crossings of energy levels is very small for such values of H for which we can look at the dipole-dipole interaction as a perturbation. In this case one can divide the perturbation into two parts: a secular one and a non-secular one. The zero order hamiltonian (Zeeman energy) and the secular part can be diagonalized simultaneously and the corresponding eigenvalues are all linear functions of H, for all directions of $\boldsymbol{H}$. There are many points of intersection and in the neighbourhood of such a point the non-secular part of the perturbation gives a modification of the two corresponding levels, which can be described to a good approximation in terms of the matrix element of the interaction between those two states only. In the case that this matrix element is zero the point of intersection is not taken away, in all other cases the levels "repel" each other. We suppose that this repulsion also works in the case of small H and large N and that this is the cause of the particular properties of the energy spectrum formulated in the hypotheses (for large N the number of pairs of neighbouring levels for certain value of H is very large; these pairs, being made up of levels with much differing slope in many cases, would lead to a great number of intersection points. In the case that the slopes of the two levels in one pair are approximately equal, the number of intersection points is small).

The two hypotheses are given quantitative contents in 5.2.

For systems of ions without interaction the given argument does not hold. All energy eigenvalues of the system are the result of an addition of the eigenvalues of the individual ions. There is in general no relation between the value of the derivative of such an energy eigenvalue, being a composition of innumerable parts, and the eigenvalue itself and one expects that one cannot approximate this derivative by a continuous function of the energy. In this connection we refer to I, in which we derived $\chi_{\mathrm{is}} = 4/5\chi_{\mathrm{s}}$ and where we excluded an interaction in the case of large N.

The first step in the proof of the equality of χ_{is} and χ_{s} will be the computation of asymptotic values of T_{2n} ($n = 1, 2, \ldots$) and of the level density as a function of the energy.

From (6) it follows that:

$$\frac{1}{(2S+1)^N}\frac{1}{N}T_2 = \frac{1}{(2S+1)^N}\frac{1}{N}\,\mathrm{Tr}\,\mathscr{H}^2 = \overline{\epsilon^2}, \tag{11}$$

$$\overline{\epsilon^2} = \tfrac{1}{3}S(S+1)(g\beta_0)^2\,[H^2 + \tfrac{1}{2}H_i^2].$$

In section 2 we have restricted ourselves to systems which contain only one sort of ion, the spin of all the ions thus being the same; the corresponding eigenvalue is denoted by the letter S. $\overline{\epsilon^2}$ is the mean square of the energy per ion, which is a simple function of H and the internal field H_i, defined in the following way:

$$H_i^2 = 2S(S+1)(g\beta_0)^2 \sum_{\substack{j \\ (j\neq k)}} r_{jk}^{-6}. \tag{12}$$

The sum $\sum_{j(j\neq k)} r_{jk}^{-6}$ is independent of the index k, as assumed in section 2.

We now define $(2S+1)^{-N}N^{-\frac{1}{2}n}\,T_n$ as the moments of the energy distribution function.

For large N the higher moments can all be expressed in terms of $\overline{\epsilon^2}$, apart from terms of the order $1/N$:

$$\frac{1}{(2S+1)^N}\frac{1}{N^m}T_{2m} = \frac{1}{(2S+1)^N}\frac{1}{N^m}\,\mathrm{Tr}\,\mathscr{H}^{2m} = \frac{1}{2^m}\frac{(2m)!}{m!}(\overline{\epsilon^2})^m + 0\left(\frac{1}{N}\right). \tag{13}$$

Only the even moments are of interest, the odd being of vanishing order for large N.

From (13) it follows that for $N \to \infty$ the moments are those of a Gaussian distribution function and the continuous density function (hypothesis I) will have the following form:

$$\rho(E/N^{\frac{1}{2}}) = \frac{1}{\sqrt{2\pi}}\frac{1}{(\overline{\epsilon^2})^{\frac{1}{2}}}\,e^{-\frac{1}{2}E^2/N\overline{\epsilon^2}}. \tag{14}$$

5.2 Restricting oneself to one special kind of systems as defined in the first lines of this section (e.g.: in the case of a lattice structure which is simple cubic one only considers cubes or only rectangular parallelepipeds with a fixed ratio of the lengths of the edges), it is supposed that one can give an exact mathematical formulation of hypothesis I:

Hypothesis I$^{\mathrm{a}}$: For an arbitrary energy ε and an arbitrary positive energy $\Delta\varepsilon$, one can find a natural number N_0, so that for every number of ions N, with $N > N_0$, one can find an energy ε', in the interval $|\varepsilon' - \varepsilon| < \frac{1}{2}\Delta\varepsilon$, giving the total number of energy levels in the interval $|\mathscr{E}_\alpha - N^{\frac{1}{2}}\varepsilon| < \frac{1}{2}N^{\frac{1}{2}}\Delta\varepsilon$ by the formula: $(2S+1)^N \Delta\varepsilon\, \rho(\varepsilon')$. $\rho(\varepsilon)$ is defined by:

$$\rho(\varepsilon) = \frac{1}{\sqrt{2\pi}} \frac{1}{(\overline{\epsilon^2})^{\frac{1}{2}}} \mathrm{e}^{-\frac{1}{2}\varepsilon^2/\overline{\epsilon^2}}. \tag{14a}$$

Similar limiting procedures can be given for one- or two-dimensional lattices. Also in those cases we expect that an asymptotic expression (14*a*) for the level density can be given; the parameter H_i figuring in (14*a*) has different values for the different cases.

Differentiating both members of (13) with respect to H, one sees that the derivatives $\partial\mathscr{E}_\alpha/\partial H$ obey the equations:

$$\frac{1}{(2S+1)^N}\frac{1}{N^m}\Sigma_\alpha \mathscr{E}_\alpha{}^{2m-1}\frac{\partial\mathscr{E}_\alpha}{\partial H} = \frac{1}{2^m}\frac{(2m)!}{m!}(\overline{\epsilon^2})^{m-1}\,\tfrac{1}{2}\,\frac{\partial\overline{\epsilon^2}}{\partial H} + 0\left(\frac{1}{N}\right) =$$

$$= \frac{1}{2^m}\frac{(2m)!}{m!}(\overline{\epsilon^2})^m \frac{H}{H^2+\frac{1}{2}H_i{}^2} + 0\left(\frac{1}{N}\right). \tag{15}$$

In hypothesis II it was supposed that for large N $\partial\mathscr{E}_\alpha/\partial H$ as a function of $\mathscr{E}_\alpha$ can be well approximated by a continuous function. Formula (15) gives the values of the odd moments of the product of this function and ρ, the even ones all being zero.

Hypothesis II can now be given in an exact formulation too:

Hypothesis II^{a}: A continuous function $\partial E/\partial H(\varepsilon)$ can be defined with the following properties: For an arbitrary ε and $\delta > 0$ one can find a $\Delta\varepsilon > 0$ and a natural number M_0 so that for every $\mathscr{E}_\alpha$ in an interval $|N^{\frac{1}{2}}\varepsilon - \mathscr{E}_\alpha| < \frac{1}{2}\Delta\varepsilon N^{\frac{1}{2}}$ with $N > M_0$ (N is the number of ions) the following inequality is obeyed:

$$\left|\frac{1}{N^{\frac{1}{2}}}\frac{\partial\mathscr{E}_\alpha}{\partial H} - \frac{\partial E}{\partial H}(\varepsilon)\right| < \delta.$$

Making use of the two hypotheses I^{a} and II^{a} one can derive:

$$\lim_{N\to\infty}\frac{1}{(2S+1)^N}\frac{1}{N^m}\Sigma_\alpha\, \mathscr{E}_\alpha{}^{2m-1}\frac{\partial\mathscr{E}_\alpha}{\partial H} = \frac{1}{2^m}\frac{(2m)!}{m!}(\overline{\epsilon^2})^m\frac{H}{H^2+\frac{1}{2}H_i{}^2} =$$

$$= \int_{-\infty}^{+\infty} \mathrm{d}\varepsilon\, \frac{\partial E}{\partial H}(\varepsilon)\, \varepsilon^{2m-1}\rho(\varepsilon). \tag{16}$$

For $m = 1, 2, \ldots$ (16) gives the values of the odd moments of the function $\partial E/\partial H\,(\varepsilon)\,\rho(\varepsilon)$. If we want to find the form of the function $\partial E/\partial H\,(\varepsilon)$ we have to solve the moment problem given by (16). One sees immediately that our problem has the simple solution:

$$\partial E/\partial H\,(\varepsilon) = \varepsilon(H/(H^2+\tfrac{1}{2}H_i{}^2)). \tag{17}$$

It follows from (17) and hypothesis II^{a} that the energy eigenvalues obey the following asymptotic differential equation:

$$\partial \mathscr{E}_\alpha / \partial H \sim \mathscr{E}_\alpha (H / (H^2 + \tfrac{1}{2} H_i^2)). \tag{18}$$

The equation $\partial \mathscr{E}_\alpha / \partial H = \mathscr{E}_\alpha (H / (H^2 + \tfrac{1}{2} H_i^2))$ has the general solution:

$$\mathscr{E}_\alpha = c_\alpha \sqrt{H^2 + \tfrac{1}{2} H_i^2}. \tag{19}$$

Our hypothesis II^{a} has now the following meaning: for large N all the energy eigenvalues as a function of H can be written in the form (19) apart from a difference which is negligibly small.

For the whole energy spectrum the numbers c_α are distributed in a Gaussian way; this follows from the Gaussian distribution of the energy eigenvalues.

One now has an energy spectrum for which the condition, formulated by Klein 3), for the equivalence of χ_{is} and χ_{S}, is fulfilled. This condition l.c. formula (13), has the form:

$$\overline{(\partial E / \partial H - \partial E / \partial H) / (\bar{E} - E)} = \gamma, \tag{20}$$

γ being independent of E. One sees that in our case $\overline{\partial E / \partial H}$ and $\bar{E}$, denoting mean values for the whole spectrum, are zero and that γ has the value $H / (H^2 + \tfrac{1}{2} H_i^2)$.

One now can evaluate the value of $\sum_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2$ for large N making use of hypotheses I^{a} and II^{a} and formula (17):

$$\lim_{N \to \infty} \frac{1}{p} \frac{1}{N} \sum_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2 = \int_{-\infty}^{+\infty} \mathrm{d}\varepsilon \, \rho(\varepsilon) \left[\frac{\partial E}{\partial H} (\varepsilon) \right]^2 = \frac{\overline{\epsilon^2}}{(H^2 + \tfrac{1}{2} H_i^2)^2} H^2. \tag{21}$$

So one can derive from (4), (11) and (21):

$$\lim_{N \to \infty} \frac{\chi_{\mathrm{is}}}{N} = \lim_{N \to \infty} \frac{1}{kT} \left[- \frac{1}{p} \frac{1}{N} \sum_\alpha (\partial \mathscr{E}_\alpha / \partial H)^2 + \tfrac{1}{2} \frac{1}{pN} \partial^2 / \partial H^2 \, T_2 \right] =$$

$$= \frac{1}{kT} \frac{\overline{\epsilon^2}}{H^2 + \tfrac{1}{2} H_i^2} \left[1 - \frac{H^2}{H^2 + \tfrac{1}{2} H_i^2} \right] = \frac{1}{kT} \frac{1}{3} S(S+1)(g\,\beta_0)^2 \frac{\tfrac{1}{2} H_i^2}{H^2 + \tfrac{1}{2} H_i^2} =$$

$$= \frac{\tfrac{1}{2} H_i^2}{H^2 + \tfrac{1}{2} H_i^2} \lim_{N \to \infty} \frac{\chi_0}{N} = \lim_{N \to \infty} \frac{\chi_{\mathrm{S}}}{N},$$

and

$$\lim_{N \to \infty} (\chi_{\mathrm{S}} - \chi_{\mathrm{is}}) / N = 0. \tag{22}$$

This is in contradiction with the result given by Broer 5). One can say that the difference of χ_{is} and χ_{S} is zero for infinitely large systems.

The derivation of the equivalence of χ_{is} and χ_{S} for large systems can readily be generalized to more complicated cases in which the ions have a Stark splitting and when there is an exchange interaction. In all cases we take it for granted that there is a dipole-dipole interaction.

6. *The susceptibility for large values of H, as a function of the frequency.* In I we called special attention to the fact that there is some discussion as to which of the two quantities χ_S and $\chi_{\mathrm{is}}{}^{\mathrm{sm}}$ is to be identified with an experimental high-frequency susceptibility $\chi'(\omega)$ measured in the frequency interval $(1/\tau_r < \omega \leqslant 1/\tau_s)$; in this expression τ_r is the spin-lattice relaxation time and τ_s the so-called spin-spin relaxation time. There are many definitions of the quantity τ_s. We introduce a more suitable parameter ω_0, being the lower boundary of the frequency region in which there is a measurable spin absorption. In the following lines it is made plausible that for the frequencies in the region $(1/\tau_r < \omega \leqslant \omega_0)$, in the case that $1/\tau_r < \omega_0$, the high-frequency susceptibility $\chi'(\omega)$ has the value $\chi_S = \chi_{\mathrm{is}}$ and that there will be an interval $(\omega_1 \leqslant \omega \leqslant \omega_2)$ in which $\chi'(\omega)$ for a powder has the value $\chi_{\mathrm{is}}{}^{\mathrm{sm}}$. ω_0, ω_1 and ω_2 obey the inequality $\omega_0 < \omega_1 < \omega_2 < \omega_H$, ω_H being the Larmor frequency $g\beta_0 H/\hbar$.

In the argument use will be made of the two quantities $f(\omega)$, the shape function, and $\chi''(\omega)$, the imaginary part of the complex susceptibility. In our definition $f(\omega)$ will be normalized in such a way that:

$$\int_0^\infty f(\omega)\,\mathrm{d}\omega = \lim\nolimits_{N\to\infty} \frac{1}{N} \frac{(g\,\beta_0)^2}{(2S+1)^N} \, \Sigma_{\alpha\neq\beta}\, |S_{z\alpha\beta}|^2. \qquad (23)$$

We suppose that this limit exists if we restrict ourselves to those systems as defined in the first lines of section 5. The moments of the function $f(\omega)$ are given by the formulae:

$$\int_0^\infty f(\omega)\,\omega^{2n}\,\mathrm{d}\omega = \lim\nolimits_{N\to\infty} \frac{1}{N} \frac{(g\,\beta_0)^2}{(2S+1)^N} \, \Sigma_{\alpha\neq\beta}\, |S_{z\alpha\beta}|^2\, \omega_{\alpha\beta}{}^{2n}. \qquad (24)$$

In (23) and (24) α and β label the different energy eigenstates of the spin system, S_z is the operator of the z-component of the total spin moment, i.e. the component in the direction of $\boldsymbol{H}$. $S_{z\alpha\beta}$ is the matrix element of this operator corresponding to the eigenstates α and β; $\omega_{\alpha\beta} = (\mathscr{E}_\alpha - \mathscr{E}_\beta)/\hbar$, $\mathscr{E}_\alpha$ and $\mathscr{E}_\beta$ being respectively the energy eigenvalues for the eigenstates α and β.

One can write $\chi''(\omega)$ in terms of $f(\omega)$ by means of the asymptotic expression:

$$\chi''(\omega)/N \sim (\pi\omega/2kT)\, f(\omega). \qquad (25)$$

In the following lines our system has to be considered as an essentially isolated system so that for all finite values of N $\chi'(\omega)$ and $\chi''(\omega)$ are continuous functions of ω *). We take N so large that the asymptotic equality of (25) can be replaced by the formula:

$$\chi''(\omega)/N = (\pi\omega/2kT)\, f(\omega), \qquad (26)$$

---

*) The surroundings of our system proper consist of the lattice, the bath in which the crystal or crystal powder is placed, etc. The energy spectrum of these surroundings is supposed to be continuous (see e.g. Tolman [4])).

the difference between the two members of (25) being negligibly small. $\chi'(\omega)$ and $\chi''(\omega)$ obey the well-known Kramers-Kronig relations:

$$\begin{aligned} \chi'(\omega) &= \frac{2}{\pi}\int_0^\infty \frac{\omega'\,\chi''(\omega')}{\omega'^2-\omega^2}\,\mathrm{d}\omega', \\ \chi''(\omega) &= -\frac{2}{\pi}\int_0^\infty \frac{\omega\,\chi'(\omega')}{\omega'^2-\omega^2}\,\mathrm{d}\omega'. \end{aligned} \tag{27}$$

From (26) and (27) it follows that:

$$\frac{1}{N}\,\chi'(\omega) = \frac{1}{kT}\int_0^\infty \frac{\omega'^2}{\omega'^2-\omega^2}\,f(\omega')\,\mathrm{d}\omega'. \tag{28}$$

For the integrals in (27) and (28) one should take the principal value. In the following lines an analysis of the form of the function $f(\omega)$ is given. It was not possible to give this analysis with a great mathematical rigour.

In the most general case our spin hamiltonian has the form:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}'_{dd} + \mathscr{H}'_{ex} + \mathscr{H}'_{st} = \mathscr{H}_0 + \mathscr{H}'. \tag{29}$$

In (29) $\mathscr{H}'_{dd}$ contains the dipole-dipole interaction, $\mathscr{H}'_{ex}$ the exchange terms and $\mathscr{H}'_{st}$ the Stark splitting terms. $\mathscr{H}_0$ represents the Zeeman energy: $-g\,\beta_0 H S_z$. $\mathscr{H}'_{dd}$, $\mathscr{H}'_{ex}$ and $\mathscr{H}'_{st}$ can be expressed in terms of tensor operators:

$$\begin{aligned} \mathscr{H}'_{st} &= \textstyle\sum_h \sum_{L=2,4,6\ldots} \sum_{M=-L}^{+L} (-)^M\, U^r{}_{LM}\,(\alpha_h, \beta_h, \gamma_h)\, U^s{}_{L-M}\,(\boldsymbol{S}_h) = \\ &= \textstyle\sum_h \mathscr{H}'_{st}(h), \\ \mathscr{H}'_{dd} &= \tfrac{1}{2}\textstyle\sum_{j\neq k} \sum_{M=-2}^{+2} (-)^M\, T^r{}_{2M}(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk}))\,T^s{}_{2-M}\,(\boldsymbol{S}_j, \boldsymbol{S}_k) = \\ &= \tfrac{1}{2}\textstyle\sum_{j\neq k} \mathscr{H}'_{dd}(j,k), \\ \mathscr{H}'_{ex} &= \tfrac{1}{2}\textstyle\sum_{j\neq k} A_{jk}\, T^s{}_{00}(\boldsymbol{S}_j, \boldsymbol{S}_k) = \tfrac{1}{2}\textstyle\sum_{j\neq k} \mathscr{H}'_{ex}(j,k). \end{aligned} \tag{30}$$

For the definitions of the tensor operators $U^r{}_{LM}$, $U^s{}_{L-M}$, $T^r{}_{2M}$, $T^s{}_{2-M}$ and $T^s{}_{00}$ we refer to I. These operators are defined to within an arbitrary constant which is taken the same for all the components of one tensor. It is needless to say that in the inner products of two tensors $U^r{}_L$ and $U^s{}_L$, respectively $T^r{}_2$ and $T^s{}_2$, figuring in (30) the two corresponding constants are not independent.

As already presumed in (23) and (24) all ions have the same S and g-value. In fact we make the same restrictions as given in section 2: only those lattices are considered which contain one sort of magnetic ions and for which $\sum_{k(k\neq j)} r_{jk}^{-6}$ is independent of j.

Further restrictions are made regarding the quantities $\overline{\epsilon^2}(j)$, $\overline{\epsilon^2}_z(j)$, $\overline{\epsilon^2}_{st}(j)$, $\overline{\epsilon^2}_{dd}(j)$ and $\overline{\epsilon^2}_{ex}(j)$ defined in the following way:

$$\overline{\epsilon^2(j)} = \overline{\epsilon^2}_z(j) + \overline{\epsilon^2}_{st}(j) + \overline{\epsilon^2}_{dd}(j) + \overline{\epsilon^2}_{ex}(j), \tag{31}$$

$$\begin{aligned}
\overline{\epsilon^2}_z(j) &= (g\beta_0)^2\, H^2 \,\mathrm{Tr}\, S_z{}^2/(2S+1) = \tfrac{1}{3}S(S+1)(g\,\beta_0)^2\, H^2,\\
\overline{\epsilon^2}_{st}(j) &= \mathrm{Tr}\{\mathscr{H}'_{st}(j)\}^2/(2S+1),\\
\overline{\epsilon^2}_{dd}(j) &= \tfrac{1}{2}\sum_{\substack{k\\(k\neq j)}} \mathrm{Tr}\,\{\mathscr{H}'_{dd}(j,k)\}^2/(2S+1)^2,\\
\overline{\epsilon^2}_{ex}(j) &= \tfrac{1}{2}\sum_{\substack{k\\(k\neq j)}} \mathrm{Tr}\,\{\mathscr{H}'_{ex}(j,k)\}^2/(2S+1)^2.
\end{aligned} \tag{32}$$

We restrict ourselves to lattices for which the quantities $\overline{\epsilon^2}_{st}(j)$, $\overline{\epsilon^2}_{dd}(j)$ and $\overline{\epsilon^2}_{ex}(j)$ are independent of j.

Finally we introduce the operators $\mathscr{H}'_M$ and the quantities $\overline{\epsilon^2}_M$, b_M and b:

$$\begin{aligned}
\mathscr{H}'_M = \textstyle\sum_h \sum_{L=2,4,6\ldots} (-)^M\, U^r{}_{L-M}(\alpha_h, \beta_h, \gamma_h)\, U^s{}_{LM}(\boldsymbol{S}_h) &+\\
+ \tfrac{1}{2} \textstyle\sum_{j\neq k} (-)^M\, T^r{}_{2-M}(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk}))\,T^s{}_{2M}(\boldsymbol{S}_j, \boldsymbol{S}_k) &+\\
+ \delta_{0M}\, \tfrac{1}{2} \textstyle\sum_{j\neq k} A_{jk}\, T^s{}_{00}(\boldsymbol{S}_j, \boldsymbol{S}_k)&,
\end{aligned} \tag{33}$$

$$\overline{\epsilon^2}_M = \frac{1}{N}\,\frac{1}{(2S+1)^N}\,\mathrm{Tr}\,\mathscr{H}'_{-M}\,\mathscr{H}'_M = \frac{1}{N}\,\frac{1}{(2S+1)^N}\,\mathrm{Tr}\,\mathscr{H}'^{\dagger}_M\,\mathscr{H}'_M, \tag{34}$$

$$b_M = (\overline{\epsilon^2}_M/\overline{\epsilon^2}_z)\; CH^2, \qquad b = \textstyle\sum_M b_M. \tag{35}$$

C is the Curie constant which is equal to $\frac{1}{3}S(S+1)(g\,\beta_0)^2/k$, k being the Boltzmann constant.

The mean square energy per ion can be expressed in terms of H, b and C:

$$\overline{\epsilon^2} = \tfrac{1}{3}S(S+1)(g\,\beta_0)^2\,(H^2 + b/C). \tag{36}$$

Following the same lines of argument as given in section 5 the level density can be approximated by a continuous function of the energy of the form:

$$\rho(E/N^{\frac{1}{2}}) = \frac{1}{\sqrt{2\pi}}\,\frac{1}{(\overline{\epsilon^2})^{\frac{1}{2}}}\,\mathrm{e}^{-\frac{1}{2}E^2/N\overline{\epsilon^2}}. \tag{37}$$

It is possible now to evaluate the right member of equation (23):

$$\begin{aligned}
\int_0^\infty f(\omega)\mathrm{d}\omega &= \lim_{N\to\infty}\frac{1}{N}\,\frac{(g\,\beta_0)^2}{(2S+1)^N}\,\textstyle\sum_{\alpha\neq\beta}|S_{z\alpha\beta}|^2 =\\
&= \lim_{N\to\infty}\frac{1}{N}\,\frac{(g\,\beta_0)^2}{(2S+1)^N}\,[\textstyle\sum_{\alpha,\beta}|S_{z\alpha\beta}|^2 - \sum_\alpha S_{z\alpha\alpha}{}^2] =\\
&= \lim_{N\to\infty}\frac{1}{N}\,\frac{1}{(2S+1)^N}\left[-\textstyle\sum_\alpha\left(\dfrac{\partial\mathscr{E}_\alpha}{\partial H}\right)^2 + \tfrac{1}{2}\,\dfrac{\partial^2}{\partial H^2}\sum_\alpha \mathscr{E}_\alpha{}^2\right] =\\
&= \lim_{N\to\infty}\frac{kT\,\chi_{\mathrm{is}}}{N} = \lim_{N\to\infty}\frac{kT\,\chi_{\mathrm{S}}}{N} = \lim_{N\to\infty}\frac{kT\,\chi_0}{N}\,\frac{b}{b+CH^2}.
\end{aligned} \tag{38}$$

For the details of the derivation we refer to sections 3 and 5 in which an entirely similar computation was carried out.

The moments of the function $f(\omega)$ can be expressed in terms of the commutators $\underbrace{[\mathscr{H}, [\mathscr{H}, [\mathscr{H}, \ldots [\mathscr{H}}_{n}, S_z] \ldots]$, $n = 1, 2, \ldots$.

In these expressions n indicates the total number of operators $\mathscr{H}$.

From (24) it follows:

$$\int_0^\infty f(\omega)\, \omega^{2n}\, \mathrm{d}\omega = \lim_{N\to\infty} \frac{1}{N} \frac{(g\,\beta_0)^2}{(2S+1)^N} \frac{1}{\hbar^{2n}} \Sigma_{\alpha\neq\beta}\, |S_{z\alpha\beta}|^2\, (\mathscr{E}_\alpha - \mathscr{E}_\beta)^{2n} =$$

$$= \lim_{N\to\infty} \frac{1}{N} \frac{(g\,\beta_0)^2}{(2S+1)^N} \frac{(-)^n}{\hbar^{2n}}\, \mathrm{Tr}\, \underbrace{[\mathscr{H}, [\mathscr{H}, [\mathscr{H}, \ldots [\mathscr{H}}_{n}, S_z] \ldots]^2. \tag{39}$$

For large values of H the moments corresponding to small values of n can be approximated in the following way, if one restricts oneself to such large values of N that terms of the order $1/N$ can be neglected:

$$\int_0^\infty f(\omega)\omega^{2n}\, \mathrm{d}\omega = \frac{1}{N} \frac{(g\,\beta_0)^2}{(2S+1)^N} \frac{(g\,\beta_0 H)^{2(n-1)}}{\hbar^{2n}}\, \Sigma_M\, M^{2n}\, \mathrm{Tr}\, \mathscr{H}'_M{}^{\dagger} \mathscr{H}'_M. \tag{40}$$

Use was made of the commutator rules $[S_z, \mathscr{H}'_M] = M\,\mathscr{H}'_M$ and of the fact that $\mathrm{Tr}\, \mathscr{H}'_M{}^{\dagger}\, \mathscr{H}'_{M'} = 0$ for $M' \neq M$.

From (40), (34) and (35) it follows:

$$\textstyle\int_0^\infty f(\omega)\, \omega^{2n}\, \mathrm{d}\omega = (g\,\beta_0 H/\hbar)^{2n}\, \Sigma_M\, M^{2n}\, (b_M/CH^2)\, kT\, (\chi_0/N). \tag{41}$$

It is easy to verify that for large H the function $f(\omega)$ can be approximated in a fairly good way by a function of the form:

$$f_1(\omega) + 2kT\, (\chi_0/N)\, \Sigma_{M>0}\, (b_M/CH^2)\, \delta(\omega - \omega_H M), \tag{42}$$

in which $\delta(\omega - \omega_H M)$ is the well known Dirac delta function and $\omega_H = g\,\beta_0 H/\hbar$. $f_1(\omega)$ obeys the normalization condition:

$$\textstyle\int_0^\infty f_1(\omega)\, \mathrm{d}\omega = kT\, (\chi_0/N)(b_0/CH^2). \tag{43}$$

In (42) we made use of the symmetry relation $b_M = b_{-M}$, whereas (43) was found by means of the normalization condition for $f(\omega)$ given in (38). We suppose that the function $f_1(\omega)$ is only appreciably different from zero in a bounded region of the ω-axis. Or, formulating the properties of $f(\omega)$ in a more quantitative manner, we make the following hypothesis:

For every α with $0 < \alpha < 1$ and an arbitrary small positive ε we can always find a field H and two frequencies ω_1 and ω_2, obeying the inequalities $0 < \omega_1 < \frac{1}{2}\alpha\omega_H$ and $0 < \omega_H - \omega_2 < \frac{1}{2}\alpha\omega_H$ in such a way that:

$$\textstyle\int_{\omega_1}^{\omega_2} f(\omega)\, \mathrm{d}\omega < kT\, (\chi_S\, \varepsilon/N). \tag{44}$$

Thus in a good approximation one has $f(\omega) = 0$ in an interval $(\omega_1 \leqslant \omega \leqslant \omega_2)$ of finite length, taking H sufficiently large. One has, in the same approximation $f_1(\omega) = 0$ for $\omega > \omega_1$.

It is possible now to evaluate $\chi'(\omega)$ for frequencies ω in the interval $(\omega_1 \leqslant \omega \leqslant \omega_2)$, making use of (28):

$$\chi'(\omega') = 2\chi_0 \textstyle\sum_{M>0} b_M / CH^2 \quad (\omega_1 \leqslant \omega' \leqslant \omega_2). \tag{45}$$

This quantity is equal to $\chi_{\mathrm{is}}{}^{\mathrm{sm}}$, which follows from formula (5) of I.

We already introduced the frequency ω_0, being the lower boundary of the frequency region, in which there is a measurable spin absorption. The frequency region in which $\omega f_1(\omega)$ is appreciably different from zero is thus the interval $\omega_0 \leqslant \omega \leqslant \omega_1$ and, in accordance with the experiment, our theory gives:

$$\chi'(\omega'') = \chi_0\, b/CH^2 = \chi_{\mathrm{S}} \quad (1/\tau_r + \delta \leqslant \omega'' \leqslant \omega_0). \tag{46}$$

In (46) δ is a small frequency.

In general one has, in the case of a powder:

$$\frac{\overline{\chi'(\omega')}}{\overline{\chi'(\omega'')}} = \frac{2\sum_{M>0} b_M}{\sum_M b_M} = \frac{\overline{\mathrm{Tr}\,\mathscr{H}'^2} - \overline{\mathrm{Tr}\,\mathscr{H}'^2}_{sec}}{\overline{\mathrm{Tr}\,\mathscr{H}'^2}} = \frac{\chi_{\mathrm{is}}{}^{\mathrm{sm}}}{\chi_{\mathrm{S}}}. \tag{47}$$

ω' and ω'' denote frequencies in the intervals $(\omega_1 \leqslant \omega' \leqslant \omega_2)$ and $(1/\tau_r + \delta \leqslant \omega'' \leqslant \omega_0)$ respectively.

In (47) the bar denotes averaging over all directions of $\boldsymbol{H}$ (see, for the details of the computation, chapter I). We cannot make any theoretical predictions about the form of $f_1(\omega)$ in the framework of this chapter.

If we restrict ourselves to the case that $S \leqslant 3/2$ and to systems in which there is no exchange interaction, $\mathscr{H}'$ has the form:

$$\begin{aligned}\mathscr{H}' = \textstyle\sum_M \mathscr{H}'_M = \sum_{h,M} (-)^M\, U^r{}_{2-M}(\alpha_h, \beta_h, \gamma_h)\, U^s{}_{2M}(\boldsymbol{S}_h) + \\ + \tfrac{1}{2} \textstyle\sum_{j \neq k, M} (-)^M\, T^r{}_{2-M}\,(\boldsymbol{r}_{jk}(\alpha_{jk}, \beta_{jk}))\, T^s{}_{2M}(\boldsymbol{S}_j, \boldsymbol{S}_k).\end{aligned} \tag{48}$$

In that case it can be proven that the average value of b_M for all directions of the external field $\boldsymbol{H}$ is independent of M. For the details of the necessary computations we refer to I.

Thus for a powder one has:

$$\chi'(\omega) = \tfrac{4}{5}\chi_0\, b/CH^2 = \chi_{\mathrm{is}}{}^{\mathrm{sm}} \qquad (\omega_1 \leqslant \omega \leqslant \omega_2), \tag{49}$$

$$\chi'(\omega) = \chi_0\, b/CH^2 = \chi_{\mathrm{is}} = \chi_{\mathrm{S}} \quad (1/\tau_r + \delta \leqslant \omega \leqslant \omega_0). \tag{50}$$

For frequencies in the interval $(\omega_H < \omega < 2\omega_H)$ one has:

$$\chi'(\omega) = \tfrac{2}{5}\,\chi_0\, b/CH^2 = \tfrac{1}{2}\chi_{\mathrm{is}}{}^{\mathrm{sm}},$$

whereas:

$$\chi'(\omega) = 0,$$

for $\omega > 2\omega_H$ in this approximation.

Broer ⁵) starts with the definitions of χ_{is} and χ_{S} as given in formulae (2) and (3) of this chapter. He computes the values of these quantities in the case of large H by means of a perturbation calculation which does not converge in any practical case. His result $\chi_{\text{is}} = \frac{4}{5}\chi_{\text{s}}$ is in contradiction with our result given in (50), but a quantity $\chi_{\text{is}}^{\text{sm}}$ can be defined for which Broer's relation holds. However, Broer does not give any specification as to the frequency of the high frequency field, whereas our result (49) is only given in a specified interval. One can say that in the interval $\omega_1 \leqslant \omega \leqslant \omega_2$ only the interaction of an ion with its nearby surroundings has practical importance. One is allowed to divide all single crystals in the powder in a large number of submicroscopic parts containing only a very small number of ions. In the region $\omega_1 \leqslant \omega \leqslant \omega_2$ the interaction between these submicroscopic parts can be neglected for the computation of $\chi'(\omega)$ and for these parts Broer's computations and ours given in I are correct.

REFERENCES

1) Caspers, W. J., Commun. Kamerlingh Onnes Lab., Leiden, Suppl. No. 115*b*; Physica **25** (1959) 43.
2) Aitken, A. C., Determinants and matrices (Interscience Publishers, Inc., New York 1956).
3) Klein, M. J., Phys. Rev. **86** (1952) 807.
4) Tolman, R. C., The principles of statistical mechanics (Oxford University Press, 1938).
5) Broer, L. J. F., Physica **17** (1951) 531.

CHAPTER III

ON THE THEORY OF SPIN-SPIN RELAXATION I

Synopsis

A method is developed that enables us to determine the asymptotic form for large times of the so-called relaxation function of spin systems, in the case of a large external magnetic field $\boldsymbol{H}$. The spin-spin relaxation phenomena are described within the framework of the spin hamiltonian; we restrict ourselves to those systems for which all g-tensors appearing in the spin hamiltonian are isotropic.

Most attention will be paid to those systems in which all ions are identical and occupy equivalent lattice sites. For these systems the asymptotic form of the relaxation function is given by a function of the type:

$$A \exp(-t/\tau) + B,$$

in which expression τ is the spin-spin relaxation time. For the quantity $1/\tau$ we find a series expansion:

$$1/\tau = \Sigma_{n=1}^{\infty} 1/\tau_n,$$

in which the different terms $1/\tau_n$ correspond to different relaxation processes.

For more complicated systems the ions are divided into groups, according to the kind of ion and the occupied lattice site. When all ions have the same g-value and the interaction between the different groups is strong enough, the asymptotic form of the relaxation function will be, in a good approximation, of the type indicated above, that means that there is only one relaxation time. If this coupling is small there will be in general a number of different relaxation times, this number being equal to the number of groups. The same will be true for systems, containing different groups, corresponding with different g-values.

1. *Introduction.* The purpose of this chapter is to compute spin-spin relaxation times of idealized paramagnetic crystals, the magnetic properties of which can be described partly in terms of a spin hamiltonian 1)2), in a certain temperature range. The dynamical system corresponding with the spin hamiltonian is called the spin system.

In the sections 2–6 our method for computing spin-spin relaxation times is developed for systems in which all magnetic ions are identical and occupy equivalent lattice sites. In section 7 a generalization of this method is indicated for more complicated systems, containing different groups of ions. Groups of ions are composed in such a way that the translation that carries one ion of a certain group into an arbitrary one of the same group, is a symmetry operation of the lattice as a whole.

For the simple systems with only one group of ions, the asymptotic form of the relaxation function, that will be defined in this introduction, is given by a function of the type:

$$A \exp(-t/\tau) + B,$$

that contains only one relaxation time τ.

More complicated systems, containing different groups, corresponding with different g-values, or being very weakly coupled, have a relaxation function that is asymptotically given by:

$$\Sigma_{\bar{v}} A_{\bar{v}} \exp(-t/\tau^{(\bar{v})}) + B,$$

in which the number of relaxation times is equal to the number of groups.

In all cases we restrict ourselves to systems of which all ions have isotropic g-tensors.

In section 2 the spin hamiltonian for the simple systems is given in a general form. It can be divided into two parts: $\mathscr{H}_{\mathrm{I}}$, containing the Zeeman energy and all terms commuting with this Zeeman term, the so-called secular terms, and a part $\mathscr{H}_{\mathrm{II}}$, containing the non-commuting or non-secular terms.

The determination of the relaxation time τ for these systems results in the determination of the asymptotic form of the diagonal term $\varphi_{zz}(t)$ of the relaxation tensor $\varphi(t)$, following the method as given in the sections 2–6. The tensor $\varphi(t)$ describes the magnetic response of a system, after an external field $\boldsymbol{h}$, of vanishing modulus h, being cut down to zero at $t = 0$. We shall call $\varphi_{zz}(t)$ the relaxation function, the z-axis corresponding to the direction of $\boldsymbol{h}$. Besides the field $\boldsymbol{h}$ there will be a constant field $\boldsymbol{H}$, parallel to $\boldsymbol{h}$. We restrict ourselves to the case $H \gg H_i$; H_i is the so-called internal field, defined by $H_i = \sqrt{2b/C}$. In this formula C is Curie's constant: $C = \frac{1}{3}S(S+1)(g\beta_0)^2/k$; for the definition of the quantity b we refer to chapter II 3) (see e.g. formula (36) l.c.). For the case for which H and H_i are of the same order of magnitude our method will not be correct in general, as indicated in section 6. The same applies for the more complicated systems.

From $t = -\infty$ to $t = 0$ the total external field is equal to $\boldsymbol{H} + \boldsymbol{h}$; and for $t > 0$ it is equal to $\boldsymbol{H}$. The field $\boldsymbol{h}$ gives an extra contribution to the magnetic moment, which is given by:

$$\begin{gathered} \overline{\boldsymbol{M}}(t) - \overline{\boldsymbol{M}}_0 = \varphi(t)\, \boldsymbol{h}, \\ \overline{\boldsymbol{M}}_0 = \chi_0 \boldsymbol{H}, \qquad (1) \\ \varphi(t) = \chi_0, \text{ for } t \leqslant 0. \end{gathered}$$

χ_0 is the static susceptibility and $\overline{\boldsymbol{M}}(t)$ the total magnetic moment, being a function of the time. $\overline{\boldsymbol{M}}_0$ were the value of the moment if the field $\boldsymbol{h}$ would not have been applied. Kubo and Tomita [4]) have given a general expression for the relaxation tensor $\varphi(t)$. In their formalism $\overline{\boldsymbol{M}}(t)$ and $\overline{\boldsymbol{M}}_0$ are ensemble averages, corresponding to a canonical distribution:

$$\rho_0 = \exp(-\beta\mathscr{H})/\mathrm{Tr}\exp(-\beta\mathscr{H}).$$

$\mathscr{H}$ describes the unperturbed motion of the system, *i.e.* the motion in the absence of the disturbing field $\boldsymbol{h}$. $\beta = 1/kT$, T being the absolute temperature and k Boltzmann's constant.

The asymptotic form of $\varphi_{zz}(t)$ will be discussed in the case of large T and N, the latter being the total number of spins. In section 3 general expressions for $\varphi_{zz}(t)$ and:

$$\Gamma(t) = \lim_{\substack{\beta\to 0\\ N\to\infty}} \frac{\varphi_{zz}(t)}{\beta N},$$

are given for simple spin systems, these expressions being the starting point of the determination of the asymptotic form of $\varphi_{zz}(t)$.

Section 4 gives developments of $\Gamma(t)$ and the related function $\Omega(t)$ in a series of powers of $\mathscr{H}_{\mathrm{II}}$. A systematic reduction of the terms of the series for $\Omega(t)$ is given in section 5. The section 6 will be devoted to the asymptotic form of $\Gamma(t)$ and $\varphi_{zz}(t)$, derived on the base of this reduction. So we find $\varphi_{zz}(t) \sim A\exp(-t/\tau) + B$; the value of $1/\tau$, being the sum of an infinite number of terms: $1/\tau = \sum_{n=1}^{\infty} 1/\tau_n$, is also given in section 6.

A generalization for the systems containing different groups of ions is outlined in section 7. In this case the relaxation function will have the asymptotic form:

$$\varphi_{zz}(t) \sim \sum_{\bar{v}} A_{\bar{v}} \exp(-t/\tau^{(\bar{v})}) + B,\ 1/\tau^{(\bar{v})} = \sum_{n=1}^{\infty} 1/\tau_n{}^{(\bar{v})}.$$

In chapter IV the results of our theory will be worked out in detail for the ammonium cupric Tutton salt and compared with the experimental data. Besides a comparison with other theories on spin-spin relaxation will be given.

2. *The spin hamiltonian.* The spin hamiltonian contains different terms, corresponding to the Zeeman energy, the Stark splitting and the two spin interactions (dipole-dipole interaction and exchange; more complicated forms of interaction are neglected). The Stark splitting terms and the interaction terms together are denoted by $\mathscr{H}'$, whereas the Zeeman energy is represented by $\mathscr{H}_0$.

For the simple systems we have:

$$\mathscr{H}_0 = -g\beta_0 H \sum_j S_{jz} = -H\sum_j M_{jz} = -HM_z. \tag{2}$$

In (2) the index j numbers the magnetic ions; β_0 is the Bohr magneton.

$\mathscr{H}'$ can be split up into different terms:

$$\mathscr{H}' = \Sigma_M\,(M),$$

corresponding to the commutation rules:

$$[S_z, (M)] = M(M), \quad M = 0, \pm 1, \pm 2, \dots \tag{3}$$

The total spin hamiltonian can be written now in the form:

$$\begin{gathered} \mathscr{H} = \mathscr{H}_0 + \mathscr{H}' = \mathscr{H}_{\mathrm{I}} + \mathscr{H}_{\mathrm{II}}, \\ \mathscr{H}_{\mathrm{I}} = \mathscr{H}_0 + (0), \\ \mathscr{H}_{\mathrm{II}} = \Sigma_{M\neq 0}(M). \end{gathered} \tag{4}$$

In formulae (4) $\mathscr{H}_{\mathrm{I}}$ contains the secular terms and $\mathscr{H}_{\mathrm{II}}$ the non-secular terms of the hamiltonian. (M) corresponds to the operator $\mathscr{H}'_M$, defined in the previous chapter [3]).

In general the spin hamiltonian gives a good description of a part of the magnetic properties of a group of paramagnetic crystals in a certain temperature range (cf. our references [1])[2])). It is supposed that in this range a series expansion, in terms of powers of $1/T$, of the measurable quantities, pertaining to the spin system, is possible and that the first term gives a good approximation. Our calculations correspond with the experimental situation in which the spin-lattice and spin-spin relaxation (or absorption) can be observed seperately.

From an experimental point of view, the best way to study spin-spin relaxation phenomena is by investigating the low frequency absorption. In general this low frequency absorption has not a pure relaxation character, part of it being resonance absorption. By means of perturbation calculation it can be derived that the total contribution of the low frequency resonance absorption to the integral: $\int_0^\infty f_1(\omega)\, \mathrm{d}\omega$ is of the order of $kT(\chi_0/N)(H_i/H)^4$ in the case of $H \gg H_i$, (see for the definition of the function $f_1(\omega)$ chapter II [3])), whereas the contribution of the relaxation absorption is equal to $kT(\chi_0/N)\,(b_0/CH^2)$, in which form b_0 is a quantity of the order of CH_i^2.

Therefore in the case of $H \gg H_i$ the low frequency resonance absorption may be neglected in the region where the relaxation absorption is appreciably different from zero, so a detailed study of relaxation phenomena is possible. This agrees with the theoretical situation: As indicated in section 6, our formalism can only be applied in the case of $H \gg H_i$.

In all cases one may expect that spin-spin relaxation phenomena cannot be described well within the framework of standard perturbation methods. Our method, developed in the subsequent sections shows considerable differences with the standard perturbation methods, especially on the point of the long-time behaviour of the systems.

3. *The relaxation function.* In the linear theory, developed by Kubo and Tomita [4]), the relaxation function $\varphi_{zz}(t)$ is given by the formula:

$$\varphi_{zz}(t) = \int_0^\beta \mathrm{d}\lambda \, \langle M_z M_z(t + i\hbar\lambda)\rangle - \beta(\bar{M}_{0z})^2, \tag{5}$$

in which formula $\beta = 1/kT$. $M_z(t + i\hbar\lambda)$ is the Heisenberg representation of the magnetic moment operator, for the complex time $t + i\hbar\lambda$:

$$M_z(t + i\hbar\lambda) = \exp(-\lambda\mathscr{H}) \exp(it\mathscr{H}/\hbar) \, M_z \exp(-it\mathscr{H}/\hbar) \exp(\lambda\mathscr{H}).$$

The brackets $\langle , \rangle$ denote the average value for the canonical distribution: $\rho_0 = \exp(-\beta\mathscr{H})/\mathrm{Tr}\exp(-\beta\mathscr{H})$. For an arbitrary operator A we have:

$$\langle A\rangle = \mathrm{Tr}\,\rho_0 A.$$

For simple spin systems, we have in the high temperature limit:

$$\bar{\boldsymbol{M}}_0 = \langle \boldsymbol{M}\rangle = \mathrm{Tr}\,\rho_0 \boldsymbol{M} = \chi_0 \boldsymbol{H},$$

$$\chi_0 = \frac{C}{T} N, \tag{6}$$

$$C = \tfrac{1}{3} S(S+1)(g\beta_0)^2/k.$$

In (6) C is Curie's constant and N the number of spins.

The function $\varphi_{zz}(t)/\beta N$ will be studied in the limit of $\beta \to 0$ and $N \to \infty$. From (5) and (6) it follows that:

$$\lim_{\beta \to 0} \varphi_{zz}(t)/\beta N = \langle\langle M_z M_z(t)\rangle\rangle/N,$$

for all finite values of N. $\langle\langle A\rangle\rangle$ denotes the normalized trace of an operator:

$$\langle\langle A\rangle\rangle = \mathrm{Tr}\,A/\mathrm{Tr}\,1.$$

For a definite limiting procedure (cf. ch. II), we suppose that the following limit exists:

$$\lim_{N\to\infty} \varphi_{zz}(t)/N = \Phi(t, \beta),$$

for all values of β in an interval, containing the point $\beta = 0$. Finally it is supposed that the repeated and the double limit exist; so we can write:

$$\begin{gathered} \lim_{\substack{\beta\to 0\\ N\to\infty}} \frac{\varphi_{zz}(t)}{\beta N} = \lim_{\beta\to 0}\lim_{N\to\infty} \frac{\varphi_{zz}(t)}{\beta N} = \lim_{N\to\infty}\lim_{\beta\to 0} \frac{\varphi_{zz}(t)}{\beta N}, \\ \lim_{\beta\to 0} \frac{\Phi(t,\beta)}{\beta} = \lim_{N\to\infty} \frac{\langle\langle M_z M_z(t)\rangle\rangle}{N} = \Gamma(t). \end{gathered} \tag{7}$$

For a large essentially isolated spin system one has:

$$\frac{\varphi_{zz}(t)}{\beta N} \sim \Gamma(t),$$

in the high temperature limit *).

---

*) See the footnote on page 27 of chapter II [3]).

There exist simple relations between the function $\Gamma(t)$ and the susceptibilities χ_0 and $\chi^*(\omega)$, χ_0 being the static susceptibility and $\chi^*(\omega)$ the complex high-frequency susceptibility:

$$-\int_0^\infty \mathrm{d}\Gamma/\mathrm{d}t\,(t)\exp(-\,i\omega t)\,\mathrm{d}t = \lim_{\substack{\beta\to 0\\ N\to\infty}} \frac{\chi^*(\omega)}{\beta N} = \lim_{\substack{\beta\to 0\\ N\to\infty}} \frac{\chi'(\omega) - i\chi''(\omega)}{\beta N},$$

$$\Gamma(0) = \lim_{N\to\infty} \frac{\langle\langle M_z{}^2\rangle\rangle}{N} = \lim_{\substack{\beta\to 0\\ N\to\infty}} \frac{\chi_0}{\beta N}. \tag{8}$$

From (8) it can be seen that in the limit of $\beta \to 0$ and $N \to \infty$, all magnetic properties in the linear region, are given by the function $\Gamma(t)$.

For a finite spin system, containing only one magnetic specimen, the correlation function: $\langle\langle M_z M_z(t)\rangle\rangle$ can be written in the form:

$$\langle\langle M_z M_z(t)\rangle\rangle = \frac{(g\beta_0)^2}{p}\,[\Sigma_\alpha\,(S_{z\alpha\alpha})^2 + \Sigma_{\alpha\neq\gamma}\,S_{z\alpha\gamma}\{S_z(t)\}_{\gamma\alpha}]. \tag{9}$$

In (9) α, γ denote the different energy eigenstates of the system, $S_{z\alpha\alpha}$, $S_{z\alpha\gamma}$ and $\{S_z(t)\}_{\gamma\alpha}$ the corresponding matrix elements and p the total number of states.

For a simple (infinite) spin system it follows from ch. II [3]), formula (21):

$$\lim_{N\to\infty} \frac{(g\beta_0)^2}{p}\,\frac{\Sigma_\alpha\,(S_{z\alpha\alpha})^2}{N} = \tfrac{1}{3}S(S+1)(g\beta_0)^2\,\frac{CH^2}{b + CH^2}. \tag{10}$$

In this formula, the quantity b is given by:

$$b = \frac{1}{k}\,[\overline{\epsilon^2}_{st} + \overline{\epsilon^2}_{dd} + \overline{\epsilon^2}_{ex}].$$

For the definition of the mean square energy values $\overline{\epsilon^2}_{st}$ etc. we refer to formula (32) l.c.

Combining (7), (9) and (10) we find the following expression for $\Gamma(t)$:

$$\Gamma(t) = \tfrac{1}{3}S(S+1)(g\beta_0)^2\,\frac{CH^2}{b + CH^2} + \Omega(t), \tag{11}$$

in which expression:

$$\Omega(t) = \lim_{N\to\infty} \frac{(g\beta_0)^2}{p}\,\frac{1}{N}\,\Sigma_{\alpha\neq\gamma}\,S_{z\alpha\gamma}\,\{S_z(t)\}_{\gamma\alpha}. \tag{12}$$

The following section will be devoted to the evaluation of an expansion of $\Gamma(t)$ and $\Omega(t)$ in a series of powers of $\mathscr{H}_{\mathrm{II}}$.

The concluding part of this section will be devoted to the discussion of one aspect of formula (11), well in accordance with thermodynamical considerations concerning isolated spin systems ($\tau_r = \infty$, τ_r is the spin-lattice relaxation time), for which we refer to Casimir and Du Pré [5]).

In section 5 it will be shown that $\lim_{t\to\infty} \Omega(t) = 0$, so that:

$$\lim_{t\to\infty} \Gamma(t) = \tfrac{1}{3}S(S+1)(g\beta_0)^2 \frac{CH^2}{b+CH^2} = \lim_{\substack{\beta\to 0\\ N\to\infty}} \frac{\chi_0 - \chi_S}{\beta N}.$$

χ_S is the adiabatic susceptibility.

For a large essentially isolated spin system one has in the high temperature approximation:

$$\lim_{t\to\infty} \varphi_{zz}(t) \sim \chi_0 - \chi_S.$$

This result has a simple thermodynamical meaning:

At the time $t = 0$ the ensemble average for the magnetic moment has the value:

$$\overline{M}_z(0) = \overline{M}_{0z} + \varphi_{zz}(0)\, h = (H+h)\,\chi_0 = \frac{C(H+h)}{T} N,$$

and the average value of the energy, before demagnetizing, is given by:

$$\overline{E}(0) = -\frac{C(H+h)^2 + b}{T} N \approx -\frac{CH(H+2h)+b}{T} N\ ^{*)}.$$

After demagnetizing this average value is equal to:

$$\overline{E}'(0) = \overline{E}(0) + h\overline{M}_z(0) \approx -\frac{CH(H+h)+b}{T} N.$$

For $t = \infty$ there is again an equilibrium distribution; the corresponding temperature is given by:

$$\overline{E}\,(\infty) = \overline{E}'(0) = -\frac{CH^2+b}{T'} N \approx -\frac{CH(H+h)+b}{T} N,$$

from which formula it follows that:

$$\frac{1}{T'} \approx \frac{CH(H+h)+b}{CH^2+b} \frac{1}{T},$$

so that:

$$\overline{M}_z(\infty) \approx \frac{CH}{T} \frac{CH(H+h)+b}{CH^2+b} N.$$

We find in this way:

$$\lim_{\to\infty} \varphi_{zz}(t) = \frac{\overline{M}_z(\infty) - \overline{M}_{0z}}{h} \approx \frac{CH}{T} N \left[\frac{CH(H+h)+b}{CH^2+b} - 1 \right] \frac{1}{h} =$$

$$= \frac{C}{T} N \frac{CH^2}{CH^2+b} = \chi_0 - \chi_S.$$

So one may say that the well-known thermodynamical properties of spin systems follow from our formalism in a simple way.

---

*) In all formulae of this section the sign $\approx$ denotes equality in the lowest order of h.

A detailed comparison between our hypotheses, made in this chapter anp in ch. II [3]), and those of statistical thermodynamics has not yet been worked out, but it is clear that there exists an intimate relation between hypothesis II of ch. II [3]) and the second law.

4. *Expansion of $\Gamma(t)$ and $\Omega(t)$ in series of powers of $\mathscr{H}_{\mathrm{II}}$.* Using the methods of Kubo and Tomita l.c., the correlation function $\langle\langle M_z M_z(t)\rangle\rangle$ of a finite system can be expanded in the following way:

$$\langle\langle M_z M_z(t)\rangle\rangle = \Sigma_{n=0}^{\infty} \frac{1}{(i\hbar)^n} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \dots \int_0^{t_{n-2}} \mathrm{d}t_{n-1} \int_0^{t_{n-1}} \mathrm{d}t_n \,. \langle\langle [M_z; \mathscr{H}_{\mathrm{II}}(t_1), \mathscr{H}_{\mathrm{II}}(t_2), \dots, \mathscr{H}_{\mathrm{II}}(t_n)]\, M_z \rangle\rangle, \tag{13}$$

$$\mathscr{H}_{\mathrm{II}}(t) = \exp(it\mathscr{H}_{\mathrm{I}}/\hbar)\mathscr{H}_{\mathrm{II}} \exp(-it\mathscr{H}_{\mathrm{I}}/\hbar).$$

In the n-th order term of the series in (13) we have used the abbreviated notation:

$$[M_z; \mathscr{H}_{\mathrm{II}}(t_1), \mathscr{H}_{\mathrm{II}}(t_2), \dots, \mathscr{H}_{\mathrm{II}}(t_n)] = = [\dots[[M_z, \mathscr{H}_{\mathrm{II}}(t_1)], \mathscr{H}_{\mathrm{II}}(t_2)], \dots], \mathscr{H}_{\mathrm{II}}(t_n)].$$

For the proof of (13) use is made of a series expansion of the operator $M_z(t)$ in terms of $\mathscr{H}_{\mathrm{II}}$, which is found by solving the equation of motion, obeyed by $M_z(t)$, by means of an iteration method.

The equation of motion has the form:

$$i\hbar \dot{M}_z(t) = [M_z(t), \mathscr{H}] = [M_z(t), \mathscr{H}_{\mathrm{I}} + \mathscr{H}_{\mathrm{II}}], \tag{14}$$

and the iterated solution is given by:

$$\begin{aligned} &M_z(t) = M_z^{(0)}(t) + M_z^{(1)}(t) + M_z^{(2)}(t) + \dots, \\ &M_z^{(0)}(t) = M_z, \\ &M_z^{(n)}(t) = \frac{1}{(i\hbar)^n} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \dots \int_0^{t_{n-2}} \mathrm{d}t_{n-1} \int_0^{t_{n-1}} \mathrm{d}t_n \,. \\ &\qquad .[M_z; \mathscr{H}_{\mathrm{II}}(t_1), \mathscr{H}_{\mathrm{II}}(t_2), \dots, \mathscr{H}_{\mathrm{II}}(t_n)]. \end{aligned} \tag{15}$$

For the derivation of (15) use is made of the interaction representation:

$$M_z(t) = \exp(it\mathscr{H}_{\mathrm{I}}/\hbar)\, M_z^*(t) \exp(-it\mathscr{H}_{\mathrm{I}}/\hbar). \tag{16}$$

Differentiating (16) with respect to t gives:

$$\begin{aligned} i\hbar\dot{M}_z(t) &= \exp(it\mathscr{H}_{\mathrm{I}}/\hbar)\, \{[M_z^*(t), \mathscr{H}_{\mathrm{I}}] + i\hbar\dot{M}_z^*(t)\} \exp(-\,it\mathscr{H}_{\mathrm{I}}/\hbar) = \\ &= [M_z(t), \mathscr{H}_{\mathrm{I}}] + \exp(it\mathscr{H}_{\mathrm{I}}/\hbar) i\hbar\dot{M}_z^*(t) \exp(-it\mathscr{H}_{\mathrm{I}}/\hbar). \end{aligned} \tag{17}$$

From (14) and (17) it follows that:

$$[M_z(t), \mathscr{H}_{\mathrm{II}}] = \exp(it\,\mathscr{H}_{I}/\hbar)\; i\hbar\dot{M}_z^*(t) \exp(-it\,\mathscr{H}_{\mathrm{I}}/\hbar),$$

or:

$$[M_z^*(t), \mathscr{H}_{\mathrm{II}}(-\,t)] = i\hbar\dot{M}_z^*(t). \tag{18}$$

Integrating (18) with the initial condition: $M_z^*(0) = M_z$, one finds:

$$M_z^*(t) = M_z + \frac{1}{i\hbar}\int_0^t [M_z^*(t'), \mathscr{H}_{\mathrm{II}}(-t')]\,\mathrm{d}t'. \tag{19}$$

The integral equation (19) is solved by means of iteration, giving:

$$M_z^*(t) = M_z + \Sigma_{n=1}^{\infty} \frac{1}{(i\hbar)^n}\int_0^t \mathrm{d}t_n \int_0^{t_n} \mathrm{d}t_{n-1} \ldots \int_0^{t_2} \mathrm{d}t_1 .$$

$$.[M_z; \mathscr{H}_{\mathrm{II}}(-t_1), \mathscr{H}_{\mathrm{II}}(-t_2), \ldots, \mathscr{H}_{\mathrm{II}}(-t_n)]. \tag{20}$$

Inserting (20) into (16) one arrives at:

$$M_z(t) = M_z + \Sigma_{n=1}^{\infty} \frac{1}{(i\hbar)^n}\int_0^t \mathrm{d}t_n \int_0^{t_n} \mathrm{d}t_{n-1} \ldots \int_0^{t_2} \mathrm{d}t_1 .$$

$$.[M_z; \mathscr{H}_{\mathrm{II}}(t-t_1), \mathscr{H}_{\mathrm{II}}(t-t_2), \ldots, \mathscr{H}_{\mathrm{II}}(t-t_n)],$$

which solution can be readily transformed into the series given by (15). Inserting the series expansion (15) into the correlation function $\langle\langle M_z M_z(t)\rangle\rangle$ immediately gives the formula (13).

On certain general conditions, that will be supposed to be fulfilled, $\Gamma(t)$ can now be expanded in the following way:

$$\Gamma(t) = \Sigma_{n=0}^{\infty} \Gamma_n(t),$$

$$\Gamma_n(t) = \lim_{N\to\infty} \frac{1}{(i\hbar)^n}\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n . \tag{21}$$

$$\cdot\Sigma_{M_1, M_2, \ldots, M_n \neq 0} \frac{\langle\langle [M_z; (M_1, t_1), (M_2, t_2), \ldots, (M_n, t_n)] M_z \rangle\rangle}{N},$$

in which expressions the time-dependent operators (M, t) are defined by:

$$(M, t) = \exp(it\mathscr{H}_{\mathrm{I}}/\hbar)\,(M)\,\exp(-it\mathscr{H}_{\mathrm{I}}/\hbar).$$

The said conditions being fulfilled (21) immediately follows from (4), (7) and (13). Making use of the identity:

$$\langle\langle \exp(\alpha\mathscr{H}_0)\, A \exp(-\alpha\mathscr{H}_0)\rangle\rangle = \langle\langle A \rangle\rangle,$$

in which A is an arbitrary operator and α an arbitrary complex number, and of the identity:

$$\exp(\alpha\mathscr{H}_0)\,(M, t)\,\exp(-\alpha\mathscr{H}_0) = \exp(-\alpha M\Delta)\,(M, t),\ \Delta = g\beta_0 H,$$

it can be proved that only terms with $\Sigma M_k = 0$ contribute to (21), so that $\Gamma_n(t)$ can also be written in the form:

$$\Gamma_n(t) = \lim_{N\to\infty} \frac{1}{(i\hbar)^n}\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n .$$

$$\cdot\Sigma' \frac{\langle\langle [M_z; (M_1, t_1), (M_2, t_2), \ldots, (M_n, t_n)]\, M_z \rangle\rangle}{N}, \tag{22}$$

in which formula $\sum'$ stands for the summation $\sum_{\sum^{n}_{k=1} M_k = 0,\, M_k \neq 0}$. In the same way a similar expansion for the function $\Omega(t)$ can be found. This expansion has the form:

$$\Omega(t) = \textstyle\sum_{n=0}^{\infty} \Omega_n(t),$$

$$\Omega_n(t) = \lim_{N\to\infty} \frac{1}{(i\hbar)^n} \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n \cdot \tag{23}$$

$$\cdot \textstyle\sum_{\alpha\neq\gamma} \dfrac{\sum'[M_z; (M_1, t_1), (M_2, t_2), \ldots, (M_n, t_n)]_{\alpha\gamma}\, M_{z\gamma\alpha}}{pN}.$$

Now it is supposed that the second line of (23) can be replaced by:

$$\Omega_n(t) = \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n \cdot$$

$$\cdot \lim_{N\to\infty} \textstyle\sum_{\alpha\neq\gamma} \dfrac{(i\hbar)^{-n} \sum'[M_z; (M_1, t_1), (M_2, t_2), \ldots, (M_n, t_n)]_{\alpha\gamma} M_{z\gamma\alpha}}{pN}. \tag{24}$$

The next section will be devoted to a reduction of every term $\Omega_n(t)$ to a sum of terms of rather simple form.

5. *Reduction of the $\Omega_n(t)$*. The reduction of the $\Omega_n(t)$ consists in writing the commutators: $(i\hbar)^{-n} \sum'[M_z; (M_1, t_1), (M_2, t_2), \ldots, (M_n, t_n)]$ in terms of components of irreducible tensors, and we are particularly interested in the part of each commutator that is of the form: $-g_n M_z$, g_n being a *c*-number. This part will be called the principal diagonal part. For the definition and the general mathematical properties of tensor operators, we refer to Edmonds[6]).

For simple spin systems, in the limit of $N \to \infty$, the coefficient $-g_n$ is uniquely defined, being a function of the form: $-g_n(t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n)$, depending only on the differences: $t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n$. This follows from the symmetry of the commutators, being invariant for translations carrying one ion into other ones, and from the orthogonality of the different irreducible, symmetric tensor components that appear in the commutators. For the n-th commutator the coefficient of M_z, in the limit of $N \to \infty$ is given by:

$$-g_n(t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n) =$$

$$= \lim_{N\to\infty} \frac{\mathrm{Tr} \sum' [M_z; (M_1, t_1), (M_2, t_2), \ldots, (M_n, t_n)]\, M_z}{(i\hbar)^n\, \mathrm{Tr}\, M_z^2} =$$

$$= \lim_{N\to\infty} \mathrm{Tr} \textstyle\sum' [M_z; (M_1, t_1 - t_2 + t_2 - t_3 + \ldots + t_{n-1} - t_n),$$

$$(M_2, t_2 - t_3 + \ldots + t_{n-1} - t_n), \ldots, (M_{n-1}, t_{n-1} - t_n), (M_n)] M_z / (i\hbar)^n\, \mathrm{Tr}\, M_z^2. \tag{25}$$

The operator:

$$-g_n(t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n)\, M_z, \tag{26}$$

is called the principal diagonal part of the commutator: $(i\hbar)^{-n} \sum'[M_z; (M_1, t_1), \ldots, (M_n, t_n)]$. In general the g_n contain a sum of products of g_k with $k < n$, which can be found by means of repeated reductions of lower order. That part of (26), that cannot be reduced to products of g_k of lower index, is called the irreducible principal diagonal part of the n-th commutator and is written as:

$$- h_n(t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n)\, M_z.$$

So the functions g_n can be brought into the form:

$$\begin{aligned} g_n(t_1 - t_2, \ldots, t_{n-1} - t_n) &= h_n(t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n) - \\ - \textstyle\sum_{p=2}^{n-2} h_p(t_1 - t_2, \ldots, t_{p-1} - t_p)\, &h_{n-p}\,(t_{p+1} - t_{p+2}, \ldots, t_{n-1} - t_n) + \\ + \textstyle\sum_{q=2}^{n-4} \sum_{r=2}^{n-q-2} h_q(t_1 - t_2, \ldots, t_{q-1} - t_q)\, &h_r(t_{q+1} - t_{q+2}, \ldots, t_{q+r-1} - t_{q+r}) \,. \\ &. h_{n-q-r}(t_{q+r+1} - t_{q+r+2}, \ldots, t_{n-1} - t_n) - \ldots, \end{aligned} \tag{27}$$

and the reduced form of the n-th commutator is given by:

$$\begin{aligned} (i\hbar)^{-n} \textstyle\sum' [M_z; (M_1, t_1), \ldots, (M_n, t_n)] &= \\ = - M_z[h_n(t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n) &- \\ - \textstyle\sum_{p=2}^{n-2} h_p(t_1 - t_2, \ldots, t_{p-1} - t_p)\, h_{n-p}\,(t_{p+1} - t_{p+2}, \ldots, t_{n-1} - t_n) &+ \\ + \textstyle\sum_{q=2}^{n-4} \sum_{r=2}^{n-q-2} h_q(\,..)h_r(\ldots)\, h_{n-q-r}(\,..) - \ldots] + T_n(t_1, t_2, \ldots, t_n)&. \end{aligned} \tag{28}$$

In (28) $T_n(t_1, t_2, \ldots, t_n)$ stands for the sum of all parts of the commutator that are not principal diagonal. Now it is supposed that the contribution of the tensors T_n to the relaxation part of $\Omega(t)$ can be neglected in the case of large external fields ($H \gg H_i$). This statement can be formulated in a more accurate way in terms of the function $f(\omega)$, defined in section 6 of ch. II [3]). This function is given by the formula:

$$f(\omega) = \frac{2}{\pi\beta\omega} \frac{\chi''(\omega)}{N},$$

for a large essentially isolated spin system. From (23) and (24) l.c. and formula (12) of this chapter it follows that:

$$\Omega(t) = \int_0^\infty f(\omega) \cos(\omega t)\, \mathrm{d}\omega. \tag{29}$$

On general physical grounds we suppose that $f(\omega)$ is a continuous function of ω. So we have:

$$\lim_{t \to \infty} \Omega(t) = 0.$$

In the case of a large external field ($H \gg H_i$) $f(\omega)$ is composed of three parts, as shown in ch. II [3]), except for very special cases ($S > 3/2$; Stark splitting terms (M) with $M > 2$). The first part $f_1(\omega)$ is only different from zero in the neighbourhood of the point $\omega = 0$; the two other ones correspond with the Larmor peaks, situated at the points $\omega = \omega_H$ and $\omega = 2\omega_H$ respectively,

ω_H being the Larmor frequency: $g\beta_0 H/\hbar$. The breadth of the two peaks, being of the order of $g\beta_0 H_i/\hbar$, will be independent of the value of H, for $H \gg H_i$.

From (29) it follows that also the function $\Omega(t)$ is composed of three parts, two of them corresponding with damped oscillations, with a characteristic time of the order of $\hbar/g\beta_0 H_i$, independent of the value of H in our case. We now suppose that the T_n only contribute to the oscillating parts, so the function $f_1(\omega)$ is only determined by the principal diagonal parts of the commutators. In section 6 it will be proved that the characteristic time of the part of $\Omega(t)$ corresponding with $f_1(\omega)$, the spin-spin relaxation time, is a rapidly increasing function of H, so that for asymptotic values of H and t the contribution of T_n to $\Omega_n(t)$ can be neglected.

So the functions $\Omega_n(t)$ are asymptotically given by:

$$\Omega_n(t) = -\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n \,.$$

$$.[h_n(t_1 - t_2, \ldots, t_{n-1} - t_n) - \textstyle\sum_{p=2}^{n-2} h_p(\ldots)\, h_{n-p}(\ldots) + \ldots].$$

$$.\lim_{N\to\infty} \textstyle\sum_{\alpha \neq \gamma} \dfrac{M_{z\alpha\gamma} M_{z\gamma\alpha}}{pN} =$$

$$= -\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n \,.$$

$$.[h_n(t_1 - t_2, \ldots, t_{n-1} - t_n) - \textstyle\sum_{p=2}^{n-2} h_p(\ldots)\, h_{n-p}(\ldots) + \ldots].$$

$$.\tfrac{1}{3} S(S+1)(g\beta_0)^2 \frac{b}{b + CH^2},\ n = 2,3,\ldots, \tag{30}$$

which follows from the argument given above and from (24). Also use is made of formula (38) of ch. II [3]).

For the computation of the spin-spin relaxation time it will be convenient to write the functions h_p in the form of a complex Fourier integral:

$$h_p(t_1, t_2, \ldots, t_{p-1}) = \int \mathrm{d}\omega_1\, \mathrm{d}\omega_2 \ldots \mathrm{d}\omega_{p-1} \exp i(\omega_1 t_1 + \omega_2 t_2 + \ldots + \omega_{p-1} t_{p-1})\,.$$

$$.F^{(p-1)}(\omega_1, \ldots, \omega_{p-1}), \tag{31}$$

$$F^{(p-1)}(\omega_1, \omega_2, \ldots, \omega_{p-1}) = \textstyle\sum' f^{(p-1)}_{M_1 M_2 \ldots M_p}(\omega_1, \omega_2, \ldots, \omega_{p-1}).$$

In (31) the function $f^{(p-1)}_{M_1 M_2 \ldots M_p}$ corresponds with the commutator:

$$(i\hbar)^{-p}[M_z; (-M_1, t_1), (-M_2, t_2), \ldots, (-M_p, t_p)].$$

For all functions $f^{(p-1)}_{M_1 M_2 \ldots M_p}$ there is a straightforward method for computing the moments:

$$\int \mathrm{d}\omega_1\, \mathrm{d}\omega_2 \ldots \mathrm{d}\omega_{p-1} (\omega_1)^{n_1} (\omega_2)^{n_2} \ldots (\omega_{p-1})^{n_{p-1}} f^{(p-1)}_{M_1 M_2 \ldots M_p}(\omega_1, \omega_2, \ldots, \omega_{p-1}).$$

All these moments can be expressed in terms of traces of commutators of the operators (M) and $\mathscr{H}_{\mathrm{I}}$. For instance the function $f^{(1)}_{-M,M}(\omega)$ is given by:

$$\lim_{N\to\infty} \frac{(i\hbar)^{-2}\,\mathrm{Tr}\,[M_z;\,(M,t_1),\,(-M,t_2)]\,M_z}{\mathrm{Tr}\,M_z{}^2} =$$

$$= -\int \mathrm{d}\omega \exp\{i\omega(t_1-t_2)\}\, f^{(1)}_{-M,M}(\omega),$$

which formula can be transformed into:

$$\lim_{N\to\infty} \frac{M^2\,\mathrm{Tr}\,(M,t)(-M)}{\hbar^2\,\mathrm{Tr}\,S_z{}^2} = \int \mathrm{d}\omega \exp(i\omega t)\, f^{(1)}_{-M,M}(\omega). \tag{32}$$

From (32) it follows that the k-th moment of $f^{(1)}_{-M,M}(\omega)$ is given by:

$$\int \mathrm{d}\omega\, \omega^k f^{(1)}_{-M,M}(\omega) = \lim_{N\to\infty} \frac{M^2\,\mathrm{Tr}\underset{k}{[}\mathscr{H}_{\mathrm{I}},[\mathscr{H}_{\mathrm{I}},[\ldots[\mathscr{H}_{\mathrm{I}},(M)]\ldots](-M)}{\hbar^{2+k}\,\mathrm{Tr}\,S_z{}^2},$$

in which expression $\underset{k}{[}\mathscr{H}_{\mathrm{I}},[\mathscr{H}_{\mathrm{I}},[\ldots[\mathscr{H}_{\mathrm{I}},(M)]\ldots]$ denotes the k-th commutator of $\mathscr{H}_{\mathrm{I}}$ and (M). For the determination of the moments of the functions $f^{(3)}_{M_1M_2M_3M_4}$, $f^{(4)}_{M_1M_2M_3M_4M_5}$, ... we have first to substract the reducible parts of the corresponding commutators:

$$[M_z;\,(-M_1,t_1),\,(-M_2,t_2),\,(-M_3,t_3),\,(-M_4,t_4)]\ \ldots\ etc.$$

It should be noted that the second and third order commutators do not contain reducible parts, whereas there are no first order ones ($\Omega_1(t) = = \Gamma_1(t) \equiv 0$).

The definition of the functions $f^{(p)}_{M_1M_2\ldots M_{p+1}}$ is given in such a way that the absolute values of these functions show maxima in the neighbourhood of the points:

$$\{\omega_1 = M_1\omega_H,\ \omega_2 = (M_1+M_2)\,\omega_H,\ \ldots,\ \omega_p = (M_1+M_2+\ldots+M_p)\omega_H\},$$

respectively, which follows from the commutation rules (3). The functions:

$$g^{(p)}_{M_1M_2\ldots M_{p+1}}(\omega_1,\omega_2,\ldots,\omega_p) = f^{(p)}_{M_1\ldots M_{p+1}}(\omega_1+M_1\omega_H,\ \omega_2+(M_1+M_2)\,\omega_H,\ldots),$$

are independent of the value of H, so the shape of the functions: $f^{(p)}_{M_1\ldots M_{p+1}}(\omega_1,\omega_2,\ldots,\omega_p)$, for all values of H, is entirely determined by the values of the moments for $H = 0$. This enables us to give an estimate of the field dependence of τ, assuming a reasonable form for the functions $f^{(1)}{}_{-1,1}$ and $f^{(1)}{}_{1,-1}$, giving the main contribution to $1/\tau$, as shown in the next section. In that section it will be shown that in general the asymptotic form of $\Omega(t)$ is given by a function of the type:

$$\Omega(t) = \bar{A} \exp -t/\tau,$$

in which expression τ, the spin-spin relaxation time, can be expressed in terms of the functions $f^{(p-1)}_{M_1\ldots M_p}$.

6. *Determination of the relaxation time* τ. From formula (30) it follows that the functions $\Omega_n(t)$ obey the asymptotic integral equations:

$$\begin{aligned}\Omega_n(t) = -\,[\textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 h_2(t_1 - t_2)\, \Omega_{n-2}\,(t_2) + \\ + \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 h_3(t_1 - t_2, t_2 - t_3)\, \Omega_{n-3}(t_3) + \ldots],\ n \geqslant 2. \qquad (33)\end{aligned}$$

Adding up all equations (33) we arrive at the equation:

$$\begin{aligned}\Omega(t) - \Omega(0) = -\,[\textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 h_2(t_1 - t_2)\, \Omega(t_2) + \\ + \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 h_3(t_1 - t_2, t_2 - t_3)\, \Omega(t_3) + \ldots], \qquad (34)\end{aligned}$$

that can be transformed, after differentiating with respect to t, into the equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\Omega(t) + \textstyle\int_0^t \mathrm{d}t_1 h_2(t_1)\, \Omega(t-t_1) + \int_0^t \mathrm{d}t_1 \int_0^{t-t_1} \mathrm{d}t_2 h_3(t_1, t_2)\, \Omega(t-t_1-t_2) + \ldots = 0. \qquad (35)$$

Now we shall show, without going into all mathematical detail, that (35) is asymptotically obeyed by:

$$\Omega(t) = \bar{A} \exp -t/\tau, \quad H \gg H_i, \quad t \gg \hbar/g\beta_0 H_i, \qquad (36)$$

in which expression the relaxation time τ is given by:

$$1/\tau = \textstyle\sum_{n=1}^{\infty} 1/\tau_n,\ 1/\tau_1 = \int_0^\infty \mathrm{d}t_1 h_2(t_1),\ 1/\tau_2 = \int_0^\infty \mathrm{d}t_1 \int_0^\infty \mathrm{d}t_2 h_3(t_1, t_2), \ldots. \qquad (37)$$

From the properties of the functions $F^{(p)}$ it follows that $1/\tau_1$, $|1/\tau_2|$, $|1/\tau_3|$, ... are rapidly decreasing functions of H and that they obey the inequality:

$$\ldots\ |1/\tau_3| \ll |1/\tau_2| \ll 1/\tau_1,\ H \gg H_i. \qquad (38)$$

For the proof of (36) we shall study in some detail the properties of the functions $h_2(t_1)$, $h_3(t_1, t_2)$, ... These functions have an oscillating character and from section 5 it follows that their characteristic frequencies, determined by the moments of their Fourier transforms $F^{(1)}$, $F^{(2)}$, ... are multiples of the Larmor frequency ω_H. To give a prediction of the long time behaviour of the functions h_p, we have to look at the different components of the Fourier transforms: $f^{(p-1)}_{M_1 M_2 \ldots M_p}$. The function $f^{(p-1)}_{M_1 M_2 \ldots M_p}$ has an extremum in the neighbourhood of the point:

$$\{\omega_1 = M_1\omega_H,\ \omega_2 = (M_1 + M_2)\,\omega_H,\ \ldots,\ \omega_{p-1} = (M_1 + M_2 + \ldots + M_{p-1})\omega_H\},$$

and the root mean square deviation of all variables ω_1, ω_2, ... will be of the order of $g\beta_0 H_i/\hbar$, independent of H, which follows from the computation of the moments, as indicated in the preceding section. So the regions in which the functions $h_2(t_1)$, $h_3(t_1, t_2)$, ... are considerably different from zero, are in general given by:

$\{|t_1| \leqslant \delta_1\}$, $\{|t_1| \leqslant \delta_2,\ |t_2| \leqslant \delta_2\}$, ... in which δ_1, δ_2, ... are times of the order of $\hbar/g\beta_0 H_i$ (independent of H).

Now the validity of the solution (36) can be demonstrated by direct inserting in equation (35). For $t \gg \hbar/g\beta_0 H_i$ and $H \gg H_i$, the main contribution to the integrals in (35) comes from the regions:

$$\{|t_1| \leqslant \delta_1\}, \{|t_1| \leqslant \delta_2, |t_2| \leqslant \delta_2\}, \ldots$$

which follows from the fact that the rate of decay of $\Omega : 1/\tau$ is a rapidly decreasing function of H, whereas those of $h_2, h_3, \ldots$ as functions of t_1, t_1 and $t_2, \ldots$ are not. $1/\tau$ being very small (35) can be replaced by:

$$\frac{\mathrm{d}}{\mathrm{d}t}\Omega(t) + [\textstyle\int_0^t \mathrm{d}t_1 h_2(t_1) + \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 h_3(t_1, t_2) + \ldots]\, \Omega(t) = 0,$$

which is in accordance with (36) and (37) for $t \gg \hbar/g\beta_0 H_i$.

To compute the different terms $1/\tau_n$ in the series for $1/\tau$ we make use of the formula:

$$\int_0^\infty \mathrm{d}t_1 \int \mathrm{d}\omega \exp(i\omega t_1)\, F(\omega) = \pi F(0) + i \int \mathrm{d}\omega\, F(\omega) \left(\frac{1}{\omega}\right)_P, \tag{39}$$

and of certain symmetry properties of the functions $F^{(p)}$. From formula (25) it follows that the functions $g_n(t_1, t_2, \ldots, t_{n-1})$ show the symmetry:

$$g_n(t_1, t_2, \ldots, t_{n-1}) = (-)^n\, g_n(-t_{n-1}, -t_{n-2}, \ldots, -t_1).$$

From (27) it can be proved that the functions h_n obey the same equality, that immediately gives the following symmetry property of the functions $F^{(p)}$:

$$F^{(p)}(\omega_1, \omega_2, \ldots, \omega_p) = (-)^{p+1}\, F^{(p)}(-\omega_p, -\omega_{p-1}, \ldots, -\omega_1). \tag{40}$$

So one finally arrives at the following expressions for the lowest order terms in the series for $1/\tau$:

$$\begin{aligned} 1/\tau_1 &= \pi F^{(1)}(0), \\ 1/\tau_2 &= 2i\pi \int \mathrm{d}\omega\, F^{(2)}(\omega, 0) \left(\frac{1}{\omega}\right)_P, \ldots \end{aligned} \tag{41}$$

Assuming a Gaussian shape for the functions $f^{(1)}{}_{1,-1}$ and $f^{(1)}{}_{-1,1}$ (these functions obey the relation $f^{(1)}{}_{1,-1}(\omega) = f^{(1)}{}_{-1,1}(-\omega)$, that follows from (32)), and neglecting the contributions of the functions $f^{(1)}{}_{M,-M}$ ($|M| > 1$) to $1/\tau_1$, and all $1/\tau_n$ ($n \geqslant 2$) in the series expansion for $1/\tau$, we find that asymptotically τ shows a field dependence of the form:

$$\tau = \tau_0 \exp(cH^2),$$

in which expression c is a quantity of the order of $1/H_i^2$. This field dependence shows great analogy with that, predicted by Kronig and Bouwkamp 7)). A detailed comparison of our theory with those of other authors will be given in the following chapter.

The contributions of $\pi f^{(1)}{}_{M,-M}(0)$ to the reciprocal relaxation time $1/\tau$

can be related with "single flips" ($M = \pm 1$, $\Delta S_z = 1$) and "double flips" ($M = \pm 2$, $\Delta S_z = 2$) etc. These "single" and "double flips" (of which the second ones are highly forbidden as compared to the single flips) have an essentially collective character, this unlike the single spin reversals, in terms of which the relaxation mechanism is interpreted in the theory of Kronig and Bouwkamp.

"Triple flips" ($|M| > 2$) do not occur in first order except for very special cases (see the remark after (29)).

The higher order terms in the series for $1/\tau$, given in (37), correspond with contributions of more complicated character, that are highly forbidden if $H \gg H_i$. In general they are related with multiple spin flips and small corrections to the single and double flips included in $1/\tau_1$.

For practical computations we always restrict ourselves to the contributions to the first order term, corresponding with $M = \pm 1$. In that case the relaxation time τ is given by the formula:

$$\tau = [2\pi f^{(1)}{}_{1,-1}(0)]^{-1}. \tag{42}$$

From (11) and (36) it follows that $\Gamma(t)$ has the asymptotic form:

$$\Gamma(t) = \tfrac{1}{3}S(S+1)(g\beta_0)^2 \frac{CH^2}{b + CH^2} + \\ + \bar{A} \exp -t/\tau,\ t \gg \hbar/g\beta_0 H_i,\ H \gg H_i. \tag{43}$$

Now the quantity $\bar{A}$ is determined by formula (43) of ch. II [3]), if one allows for the fact that the contribution of the low frequency resonance absorption to the integral: $\int_0^\infty f_1(\omega)\,\mathrm{d}\omega$, being of the order of $kT(\chi_0/N)(H_i/H)^4$ can be neglected if $H \gg H_i$(cf. section 2 of this chapter).

So one finds:

$$\bar{A} = \tfrac{1}{3}S(S+1)(g\beta_0)^2 b_0/CH^2,$$

$$b_0 = \lim_{N\to\infty} \frac{1}{k}\,\frac{\mathrm{Tr}\,(0)(0)}{N\,\mathrm{Tr}\,1},$$

and the asymptotic form of the relaxation function $\varphi_{zz}(t)$ is given by:

$$\varphi_{zz}(t) = A \exp(-t/\tau) + B,$$

$$A = \chi_0 b_0/CH^2, \quad B = \chi_0\, CH^2/(b + CH^2).$$

As indicated in section 2, the best way to measure spin-spin relaxation times, will be by investigating the low frequency part of $\chi''(\omega)$ (one may also investigate the corresponding part of $\chi'(\omega)$, giving essentially the same information). This part of $\chi''(\omega)$ corresponds with the relaxation part of $f_1(\omega)$, having the form:

$$f_1(\omega) = f_1(0)\frac{1}{1 + \omega^2\tau^2}, \tag{44}$$

in which formula τ is given, in our approximation by formula (42). In the following chapter the experimental value of τ, measured in a way as indicated above, will be compared with our theoretical value, given by (42), in the case of the ammonium cupric Tutton salt.

7. *Systems containing different groups of ions.* For systems containing different groups of ions, a generalization of the formalism, developed in the preceding sections can be given; in the following lines a brief outline of this generalization will be given.

A group consists of ions that are identical and occupy equivalent lattice sites, so that the translation that carries one ion into any other one of the same group is a symmetry operation for the lattice as a whole.

The zero-order hamiltonian $\mathscr{H}_0$, is now given by:

$$\mathscr{H}_0 = - H \textstyle\sum_v M_z{}^v = - \beta_0 H \sum_v g^{(v)} S_z{}^v, \quad v = 1,2, \ldots, P. \tag{45}$$

The index v in formula (45) numbers the different groups, P being the total number of them. $M_z{}^v$ is the z-component of the total magnetic moment of the group v and $S_z{}^v$ that of the corresponding total spin moment, while $g^{(v)}$ stands for the g-value of the same group.

The perturbation hamiltonian $\mathscr{H}'$ can be split up as indicated in section 2. Now a further differentiation of the terms, contributing to (0) will be made. We do not take into account Stark splitting terms in this section, so all terms of (0) have a two spin character. Consequently (0) can be divided into the parts: $(0)^{(v,v')}$, the indices v and v' indicating that in each term of $(0)^{(v,v')}$ one of the spins belongs to the group v and the other one to group v'. It will be clear that $(0)^{(v,v')}$ commutes with S_z and $S_z{}^v + S_z{}^{v'}$. That part of $(0)^{(v,v')}$ that commutes with $S_z{}^v$ and $S_z{}^{v'}$ separately will be denoted by $(0)_{zz}{}^{(v,v')}$; the other part will be indicated by: $(0)_{\pm}{}^{(v,v')}$. So we have:

$$(0)^{(v,v')} = (0)_{zz}{}^{(v,v')} + (0)_{\pm}{}^{(v,v')}.$$

If the g-values of all groups are different the secular and non secular parts of the total spin-hamiltonian will be given by:

$$\begin{aligned} \mathscr{H}_{\mathrm{I}} &= \mathscr{H}_0 + \textstyle\sum_v (0)^{(v,v)} + \sum_{v<v'} (0)_{zz}{}^{(v,v')}, \\ \mathscr{H}_{\mathrm{II}} &= \textstyle\sum_{v<v'} (0)_{\pm}{}^{(v,v')} + \sum_{M\neq 0} (M). \end{aligned} \tag{46}$$

$\mathscr{H}_{\mathrm{I}}$ obeys the commutation rules:

$$[\mathscr{H}_{\mathrm{I}}, S_z{}^v] = 0, \quad v = 1,2, \ldots, P,$$

thus commuting with the z-component of the spin and magnetic moment operator of the individual groups.

The functions Γ and Ω can be defined in an analogous way as for the simple spin systems, and also a series expansion for these functions can be given in terms of $\mathscr{H}_{\mathrm{II}}$. So we have:

$$\Omega_n(t) = \textstyle\sum_v \Omega_n{}^{(v)}(t),$$

$$\Omega(t) = \textstyle\sum_v \Omega^{(v)}(t),\ \Omega^{(v)}(t) = \sum_{n=0}^{\infty} \Omega_n{}^{(v)}(t), \tag{47}$$

$$\Omega_n{}^{(v)}(t) = \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \dots \int_0^{t_{n-1}} \mathrm{d}t_n \,.$$

$$.\lim_{N\to\infty} \frac{\sum_{\alpha\neq\gamma} (i\hbar)^{-n} \sum{}' [M_z{}^v;\ (M_1,t_1), (M_2,t_2) \dots (M_n, t_n)]_{\alpha\gamma} M_{z\gamma\alpha}}{pN}.$$

In (47) N is the total number of ions and in the summation $\sum{}'$ the terms $(0)_{\pm}{}^{(v,v')}$ should be included. Now we have to find the different principal diagonal parts of the commutators:

$(i\hbar)^{-n} \sum{}'[M_z{}^v; (M_1, t_1) \dots (M_n, t_n)]$, that will have the form:

$$- M_z{}^{v'} . g_n{}^{(v,v')}(t_1 - t_2, t_2 - t_3, \dots, t_{n-1} - t_n).$$

The functions $g_n{}^{(v,v')}$ are given by the formulae:

$$- g_n{}^{(v,v')}(t_1 - t_2, t_2 - t_3, \dots, t_{n-1} - t_n) =$$

$$= \lim_{N\to\infty} \frac{\operatorname{Tr} \sum{}' [M_z{}^v; (M_1, t_1), (M_2, t_2), \dots, (M_n, t_n)]\, M_z{}^{v'}}{(i\hbar)^n \operatorname{Tr} \{M_z{}^{v'}\}^2}, \tag{48}$$

and may contain products of $g_k{}^{(v_1,v_2)}$ of lower index, in the same way as in the case of simple spin systems.

So the reduced form of the different parts of the total n-th commutator is given by:

$$\begin{aligned} &(i\hbar)^{-n} \textstyle\sum{}' [M_z{}^v; (M_1, t_1), (M_2, t_2), \dots, (M_n, t_n)] = \\ &\qquad = - \textstyle\sum_{v'} M_z{}^{v'} [h_n{}^{(v,v')}(t_1 - t_2, t_2 - t_3, \dots, t_{n-1} - t_n) - \\ &\qquad - \textstyle\sum_{v_1} \sum_{p=2}^{n-2} h_p{}^{(v,v_1)}(t_1 - t_2, t_2 - t_3, \dots, t_{p-1} - t_p) . \\ &. h_{n-p}{}^{(v_1,v')}(t_{p+1} - t_{p+2}, \dots, t_{n-1} - t_n) + \dots] + T_n{}^{(v)}(t_1, t_2, \dots, t_n). \end{aligned} \tag{49}$$

In formula (49) the functions $h_n{}^{(v,v')}$ correspond with the irreducible principle diagonal parts of the n-th commutator:

$$(i\hbar)^{-n} \textstyle\sum{}'[M_z{}^v; (M_1, t_1), \dots, (M_n, t_n)].$$

Inserting (49) into (47) we arrive at the following asymptotic formula for $\Omega_n{}^{(v)}(t)$ (cf. formula (30)):

$$\begin{aligned} \Omega_n{}^{(v)}(t) = &- \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \dots \int_0^{t_{n-1}} \mathrm{d}t_n \,. \\ &. \textstyle\sum_{v'} [h_n{}^{(v,v')}(t_1 - t_2, t_2 - t_3, \dots, t_{n-1} - t_n) - \\ &- \textstyle\sum_{v_1} \sum_{p=2}^{n-2} h_{n-p}{}^{(v,v_1)}(\dots)\, h_p{}^{(v_1,v')}(\dots) + \dots] . \\ &. \lim_{N\to\infty} \textstyle\sum_{\alpha\neq\gamma} \frac{\{M_z{}^{v'}\}_{\alpha\gamma} M_{z\gamma\alpha}}{pN}, \end{aligned} \tag{50}$$

from which the integral equations:

$$\Omega^{(v)}(t) - \Omega^{(v)}(0) = - \Sigma_{v'} \left[\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 h_2^{(v,v')}(t_1 - t_2)\, \Omega^{(v')}(t_2) + \right.$$
$$\left. + \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 h_3^{(v,v')}(t_1 - t_2, t_2 - t_3)\, \Omega^{(v')}(t_3) + \ldots \right], \tag{51}$$

follow in a straight forward way.

After differentiating with respect to t the equations (51) go over into:

$$\frac{\mathrm{d}}{\mathrm{d}t} \Omega^{(v)}(t) + \Sigma_{v'} \left[\int_0^t \mathrm{d}t_1 h_2^{(v,v')}(t_1)\, \Omega^{(v')}(t - t_1) + \right.$$
$$\left. + \int^t \mathrm{d}t_1 \int_0^{t-t_1} \mathrm{d}t_2\, h_3^{(v,v')}(t_1, t_2)\, \Omega^{(v')}(t - t_1 - t_2) + \ldots \right] = 0. \tag{52}$$

Following an analogous reasoning as given in section 6, we can find the asymptotic form of (52), given by:

$$\frac{\mathrm{d}}{\mathrm{d}t} \Omega^{(v)}(t) + \Sigma_{v',n} \frac{1}{\tau_n^{(v,v')}} \Omega^{(v')}(t) = 0, \tag{53}$$

in which the quantities $1/\tau_n^{(v,v')}$ are given by:

$$\frac{1}{\tau_n^{(v,v')}} = \int_0^\infty \mathrm{d}t_1 \int_0^\infty \mathrm{d}t_2 \ldots \int_0^\infty \mathrm{d}t_n\, h_{n+1}^{(v,v')}(t_1, t_2, \ldots, t_n). \tag{54}$$

By choosing the right linear combinations of the functions $\Omega^{(v)}(t)$ the matrix $\Sigma_n\, 1/\tau_n^{(v,v')}$ can be diagonalized and we have:

$$\frac{\mathrm{d}}{\mathrm{d}t} \Lambda^{(\bar{v})}(t) + \frac{1}{\tau^{(\bar{v})}} \Lambda^{(\bar{v})}(t) = 0,\ \bar{v} = 1, 2, \ldots, P, \tag{55}$$

from which it follows that the asymptotic forms of $\Omega(t)$ and $\varphi_{zz}(t)$ are respectively given by:

$$\begin{aligned} \Omega(t) &= \Sigma_{\bar{v}} \bar{A}_{\bar{v}} \exp -t/\tau^{(\bar{v})}, \\ \varphi_{zz}(t) &= \Sigma_{\bar{v}} A_{\bar{v}} \exp -t/\tau^{(\bar{v})} + B. \end{aligned} \tag{56}$$

The reciprocal relaxation times $1/\tau^{(\bar{v})}$, found by diagonalizing the matrix $\Sigma_n\, 1/\tau_n^{(v,v')}$, will be given by a series expansion in terms of $\mathscr{H}_{\mathrm{II}}$:

$$1/\tau^{(\bar{v})} = \Sigma_{n=1}^{\infty}\, 1/\tau_n^{(\bar{v})},\ \bar{v} = 1, 2, \ldots, P,$$

the number of relaxation times thus being equal to the number of groups in the general case. Some of the $1/\tau^{(\bar{v})}$ may be complex, this follows from the fact that the matrix: $\Sigma_n\, 1/\tau_n^{(v,v')}$ need not be symmetric; so part of the relaxation may have an oscillatory character.

For the case that two or more g-values, corresponding with different groups are equal and the coupling terms for these groups: $(0)_\pm^{(v,v')}$ are large enough we expect that the exchange of magnetization between these groups is so rapid that they can be treated as one and the same group, so the number of relaxation times will be reduced, being equal to the total number of different g-values. For computations of relaxation times in this case the terms $(0)_{\pm}^{(v,v')}$ $(g_v = g_{v'})$ should be included in $\mathscr{H}_{\mathrm{I}}$.

For two different groups having the same or nearly the same g-value, but being very weakly coupled (the matrix elements of $(0)_{\pm}^{(v,v')}$ being very small, which may be the case for special crystal structures) there is no reduction of the number of relaxation times in general and $(0)_{\pm}^{(v,v')}$ should be included in $\mathscr{H}_{\mathrm{II}}$.

It need not be said that in the general case, one or more of the $\tau^{(\bar{v})}$ may be equal, but this degeneracy seems to be very exceptional.

Our method for determining relaxation times for simple spin systems, as developed in the sections 2–6, has a great analogy with the method of Van Hove[8]) for computing the relaxation time for more general phenomena, in the case of systems with a continuous energy spectrum.

REFERENCES

1) Bowers, K. D. and Owen, J., Rep. Progr. Phys. **18** (1955) 304.

2) Abragam, A. and Pryce, M. H. L., Proc. roy. Soc. A **205** (1951) 135.

3) Caspers, W. J., Commun. Kamerlingh Onnes Lab., Leiden, Suppl. No. 116*a*; Physica **25** (1959) 645.

4) Kubo, R. and Tomita, K., J. phys. Soc. Japan **9** (1954) 888.

5) Casimir, H. B. G. and Du Pré, F. K., Physica **5** (1938) 507.

6) Edmonds, A. R., Angular momentum in quantum mechanics (Princeton University Press, 1957).

7) Kronig, R. de L. and Bouwkamp, C. J., Physica **5** (1938) 521.

8) Van Hove, L., Physica **21** (1955) 517.

CHAPTER IV

ON THE THEORY OF SPIN-SPIN RELAXATION II

Synopsis

The method for computing spin-spin relaxation times, developed in chapter III *) will be worked out in more detail for systems containing only one magnetic specimen. Numerical calculations are performed for two types of lattices, and the results are compared with the experimental value of τ for the ammonium cupric Tutton salt. Besides a discussion of older theories on spin-spin relaxation is given and a comparison of these theories with our one is made, regarding the theoretical foundation as well as the numerical results.

1. *Introduction.* In chapter III 1) we derived an asymptotic expression for the spin-spin relaxation time τ, in the case of large external fields, for magnetic crystals, containing only one magnetic specimen. This expression was given by formula (42) l.c. In section 2 the function $f^{(1)}{}_{1,-1}(\omega)$, given by formula (32) of ch. III 1), will be determined with the aid of its moments of zero and second order, assuming a Gaussian shape.

So we arrive at a field dependence of τ that is of the form:

$$\tau = \tau_0 \exp\,(cH^2).$$

Numerical calculations are given for two types of lattices *i.e.*: those in which the magnetic ions are arranged in a simple cubic lattice and in a face centered cubic lattice.

In the final results, expressed in terms of the internal fields, the values of $H_{i_{dd}}$ and $H_{i_{ex}}$, corresponding with the contributions of the dipolar interaction and the exchange interaction to the specific heat, are inserted for the ammonium cupric Tutton salt, and a comparison with the experimental value of τ, as a function of the external field H, is made. Only for this salt detailed experimental data were available in the region where a comparison with our results is possible ($H \gg H_i$). The actual structure of this Tutton salt is more complicated than that of the two types of lattices, for which our computations are given, but more realistic calculations corresponding with this actual structure seem to be very time-devouring, whereas those for the more simple lattices may give a good approximation, if one uses the

---

*) Reference 1.

actual values of $H_{i_{dd}}$ and $H_{i_{ex}}$. Besides the experiments are performed with powders, whereas our calculations refer to single crystals and special directions of the external field $\boldsymbol{H}$, with respect to the crystal axes. Section 3 is devoted to a discussion of older theories on spin-spin relaxation. The numerical results of the theory of Kronig and Bouwkamp [3]) are also compared with the experimental ones for the ammonium cupric Tutton salt. So one sees that our theory, leading to a field dependence of τ that is quite similar to that of these authors, but giving another value for certain constants, gives a better agreement with the experiments. Besides we may remark that the underlying ideas of their theory, describing the relaxation mechanism in terms of reversals of individual spins, are quite different from the fundamentals of our formalism.

In the first theory of spin-spin relaxation, given by Waller [2]), only the case $H = 0$ is treated. Broer [4])[5]) gave an extension of this theory for the case $H \neq 0$ and his results are quite different from those of Kronig and Bouwkamp and of this chapter. However his results do not refer to the "relaxation" part of the low frequency absorption, as is suggested, but to the "resonance" part. The distinction between these two parts can be made in a theoretical way and the two parts show a quite different dependence on H. In the previous chapter [1]) we showed that the "resonance" part can be neglected in the region where there is "relaxation" absorption. As to the computations of Wright [6]) of the field dependence of spin-spin relaxation times the same remarks can be made.

The results of Bloembergen [7]) and Pershan [8]) are quite similar to our ones for the first order contribution to $1/\tau$, but in their method a straightforward correspondence with thermodynamical considerations concerning spin systems cannot be shown in a simple way.

Finally attention is drawn to the similarity between the field dependence of $1/\tau$ in our case and that of the line breadth of resonance lines, as computed by Kubo and Tomita [9]).

2. *Computation of τ for special cases.* The asymptotic formula for the spin-spin relaxation time given in ch. III [1]), formula (42), will be worked out for the case that the perturbation hamiltonian $\mathscr{H}'$ (see section 2 l.c.) does not contain Stark splitting terms. So the hamiltonian $\mathscr{H}'$ contains two parts, $\mathscr{H}'_{dd}$ and $\mathscr{H}'_{ex}$, corresponding respectively with the dipole-dipole and the exchange interaction. A partition, as given in formulae (3) and (4) l.c., will now be given for $\mathscr{H}'_{dd}$ and $\mathscr{H}'_{ex}$ separately. One has:

$$\mathscr{H}' = \mathscr{H}'_{dd} + \mathscr{H}'_{ex},$$

$$\mathscr{H}'_{dd} = \tfrac{1}{2}(g\beta_0)^2 \textstyle\sum_{j\neq k}(r_{jk})^{-3}\,[(\boldsymbol{S}_j\cdot\boldsymbol{S}_k) - 3\,(r_{jk})^{-2}\,(\boldsymbol{S}_j\cdot\boldsymbol{r}_{jk})(\boldsymbol{S}_k\cdot\boldsymbol{r}_{jk})] =$$

$$= \textstyle\sum^{2}_{M=-2}(M)_{dd}, \qquad (1)$$

$$\mathscr{H}'_{ex} = \tfrac{1}{2}\textstyle\sum_{j\neq k} A_{jk}(\boldsymbol{S}_j\cdot\boldsymbol{S}_k) = (0)_{ex}.$$

The operators $(M)_{dd}$ and $(0)_{ex}$ can be written as products of components of irreducible tensors, for the definition and properties of which we refer to Edmonds 10). Making use of the tensor notation we have for the dipole-dipole interaction:

$$\begin{aligned}
&(M)_{dd} = \tfrac{1}{2} \textstyle\sum_{j\neq k} T^{r}{}_{2M}{}^{\dagger}(\boldsymbol{r}_{jk})\, T^{s}{}_{2M}(\boldsymbol{S}_j, \boldsymbol{S}_k),\\
&T^{s}{}_{2\pm2}(\boldsymbol{S}_j,\boldsymbol{S}_k) = S_{j\pm}S_{k\pm},\\
&T^{s}{}_{2\pm1}(\boldsymbol{S}_j, \boldsymbol{S}_k) = \mp\,(S_{j\pm} S_{kz} + S_{jz}S_{k\pm}),\\
&T^{s}{}_{20}(\boldsymbol{S}_j, \boldsymbol{S}_k) = \tfrac{2}{3}\sqrt{6}\,[S_{jz}S_{kz} - \tfrac{1}{4}(S_{j+} S_{k-} + S_{j-}S_{k+})],\\
&T^{r}{}_{2\pm2}(\boldsymbol{r}_{jk}) = -\tfrac{3}{4}(g\beta_0)^2\,(r_{jk})^{-3}\,(\xi_{jk} \pm i\eta_{jk})^2,\\
&T^{r}{}_{2\pm1}(\boldsymbol{r}_{jk}) = \pm\,\tfrac{3}{2}(g\beta_0)^2\,(r_{jk})^{-3}\,(\xi_{jk} \pm i\eta_{jk})\,\zeta_{jk},\\
&T^{r}{}_{20}(\boldsymbol{r}_{jk}) = -\tfrac{1}{4}\sqrt{6}\,(g\beta_0)^2\,(r_{jk})^{-3}\,(3\zeta_{jk}{}^2 - 1),\\
&S_{\pm} = S_x \pm iS_y,\ (\xi_{jk}, \eta_{jk}, \zeta_{jk}) = \frac{1}{r_{jk}}(x_{jk}, y_{jk}, z_{jk}),
\end{aligned} \tag{2}$$

and for the exchange interaction:

$$\begin{aligned}
&(0)_{ex} = \tfrac{1}{2} \textstyle\sum_{j\neq k} A_{jk}T^{s}{}_{00}(\boldsymbol{S}_j, \boldsymbol{S}_k),\\
&T^{s}{}_{00}(\boldsymbol{S}_j, \boldsymbol{S}_k) = S_{jz}S_{kz} + \tfrac{1}{2}(S_{j+}S_{k-} + S_{j-}S_{k+}).
\end{aligned} \tag{3}$$

In the final expression for τ, use will be made of the quantities $H_{i_{dd}}$ and $H_{i_{ex}}$, defined in an analogous way as the total internal field H_i; for the definition of the latter quantity we refer to chapter III 1).

So we have:

$$\begin{aligned}
&\tfrac{1}{3}S(S+1)(g\beta_0)^2\,\tfrac{1}{2}H_{i_{dd}}{}^2 = \frac{1}{N}\frac{\mathrm{Tr}\,\mathscr{H}'_{dd}{}^2}{\mathrm{Tr}\,1}, \qquad (N\to\infty),\\
&\tfrac{1}{3}S(S+1)(g\beta_0)^2\,\tfrac{1}{2}H_{i_{ex}}{}^2 = \frac{1}{N}\frac{\mathrm{Tr}\,\mathscr{H}'_{ex}{}^2}{\mathrm{Tr}\,1}, \qquad (N\to\infty).
\end{aligned} \tag{4}$$

In (4) N is the total number of spins; these formulae are asymptotic expressions for large systems.

As was shown in ch. III 1), the determination of the relaxation time τ, in the case: $H \gg H_i$, comes down to the determination of the function $f^{(1)}{}_{1,-1}(\omega)$. This determination, in all details, from a straightforward computation of the moments, as indicated in section 5 of ch. III 1), is impossible in practice.

So we assume a Gaussian shape for this function and in this approximation the value of τ will be fully determined by the moments of zero and second order, and we have:

$$\begin{aligned}
&\frac{1}{\tau} = 2\pi\left[\int \mathrm{d}\omega\, f^{(1)}{}_{1,-1}(\omega)\right]\frac{1}{\{2\pi(\Delta\omega)^2\}^{\frac{1}{2}}}\exp -(g\beta_0H)^2/2\hbar^2(\Delta\omega)^2,\\
&(\Delta\omega)^2 = \frac{1}{\hbar^2}\,\frac{\mathrm{Tr}\,[(0),[(0),(-1)]](1)}{\mathrm{Tr}\,(-1)(1)} = \frac{1}{\hbar^2}\,\frac{\mathrm{Tr}\,[(0),(1)]^{\dagger}\,[(0),(1)]}{\mathrm{Tr}\,(1)^{\dagger}\,(1)},\\
&\int \mathrm{d}\omega\, f^{(1)}{}_{1,-1}(\omega) = \frac{1}{\hbar^2}\,\frac{\mathrm{Tr}(1)^{\dagger}\,(1)}{\mathrm{Tr}\,S_z{}^2}.
\end{aligned} \tag{5}$$

From (4) it follows that the internal fields $H_{i_{ad}}$ and $H_{i_{ex}}$ are given by:

$$\begin{aligned} H_{i_{ad}}^{\ 2} &= 2x(g\beta_0)^2\, a^{-6} \textstyle\sum_{k(\neq j)} \rho_{kj}^{-6}, \quad x = S(S+1), \\ H_{i_{ex}}^{\ 2} &= x(g\beta_0)^{-2} \textstyle\sum_{k(\neq j)} A_{jk}^2. \end{aligned} \tag{6}$$

In (6) a is the distance between nearest neighbours and $\rho_{jk} = r_{jk}/a$. The quantities $H_{i_{ad}}^{\ 2}$ and $H_{i_{ex}}^{\ 2}$ have, for the two types of lattices considered (simple cubic (s.c.) and face centered cubic (f.c.c.)) the values:

TABLE I

	s.c.	f.c.c.
$H_{i_{ad}}^{\ 2}$	$2x(g\beta_0)^2a^{-6}$ 8.36 (± 5‰)	$2x(g\beta_0)^2a^{-6}$ 14.39 (± 5‰)
$H_{i_{ex}}^{\ 2}$	$6x(g\beta_0)^{-2}\ A^2$	$12x(g\beta_0)^{-2}\ A^2$

For the computation of $H_{i_{ex}}^{\ 2}$ it was supposed that A_{jk} is only different from zero for nearest neighbours and has for all pairs of nearest neighbours the value A.

The quantities Tr $(1)^\dagger$ (1) and Tr $[(0), (1)]^\dagger$ $[(0), (1)]$ depend on the direction of the external field $\boldsymbol{H}$ with respect to the crystal axes. Three cases will be considered:

a. a simple cubic lattice, $\boldsymbol{H}$ parallel to the (100) direction: (s.c. (100)),

b. a face centered cubic lattice, $\boldsymbol{H}$ parallel to the (100) direction: (f.c.c. (100)),

c. a face centered cubic lattice, $\boldsymbol{H}$ parallel to the (111) direction: (f.c.c. (111)).

We shall first give explicit expressions for:

$$(N\,\mathrm{Tr}\,1)^{-1}\,\mathrm{Tr}\,\{(1)^\dagger\,(1)\} \text{ and } (N\,\mathrm{Tr}\,1)^{-1}\,\mathrm{Tr}\,\{[(0),(1)]^\dagger\,[(0),(1)]\},\ (N \to \infty),$$

in the general case and then give their values for the three cases a, b and c, in terms of the quantities a, A and x.

$$\frac{1}{N}\,\frac{\mathrm{Tr}\,(1)^\dagger\,(1)}{\mathrm{Tr}\,1} = \tfrac{1}{2}x^2(g\beta_0)^4\,a^{-6}\textstyle\sum_{k\neq j}(1-\zeta_{jk}^2)\,\zeta_{jk}^2\rho_{jk}^{-6},$$

$$\frac{1}{N}\,\frac{\mathrm{Tr}\,[(0),(1)]^\dagger\,[(0),(1)]}{\mathrm{Tr}\,1} = \frac{(g\beta_0)^8}{a^{12}}\left[\frac{7}{24}\,x^3\textstyle\sum_{k(\neq j)}\dfrac{(1-3\zeta_{jk}^2)^2}{\rho_{jk}^6}\,\cdot\right.$$

$$\cdot\textstyle\sum_{l(\neq j)}\dfrac{(1-\zeta_{jl}^2)\,\zeta_{jl}^2}{\rho_{jl}^6} - \dfrac{1}{80}\,(28x+9)\,x^2\textstyle\sum_{k(\neq j)}\dfrac{(1-3\zeta_{jk}^2)^2(1-\zeta_{jk}^2)\,\zeta_{jk}^2}{\rho_{jk}^{12}} +$$

$$+\frac{1}{12}\,x^3\left\{\textstyle\sum^*_{kl(j)\neq}\dfrac{(1-3\zeta_{jk}^2)^2\,(\xi_{kl}\xi_{jl}+\eta_{kl}\eta_{jl})\,\zeta_{kl}\zeta_{jl}}{\rho_{jk}^6\rho_{kl}^3\rho_{jl}^3}\right. +$$

$$+\textstyle\sum^*_{kl(j)\neq}\dfrac{(1-\zeta_{jk}^2)\,\zeta_{jk}^2(1-3\zeta_{kl}^2)(1-3\zeta_{jl}^2)}{\rho_{jk}^6\rho_{kl}^3\rho_{jl}^3} +$$

$$\left.\left.+\textstyle\sum^*_{kl(j)\neq}\dfrac{(1-3\zeta_{jk}^2)(1-3\zeta_{kl}^2)(\xi_{jk}\xi_{jl}+\eta_{jk}\eta_{jl})\zeta_{jk}\zeta_{jl}}{\rho_{jk}^6\rho_{kl}^3\rho_{jl}^3}\right\}\right] +$$

$$
\begin{aligned}
&+\frac{(g\beta_0)^4}{a^6}\left[\frac{1}{3}x^3\left\{2\,\Sigma_{k(\neq j)}\,A_{jk}^2\,\Sigma_{l(\neq j)}\,\frac{(1-\zeta_{jl}^2)\,\zeta_{jl}^2}{\rho_{jl}^6}-\right.\right.\\
&-2\Sigma_{kl(j)\neq}\frac{A_{jk}A_{jl}(\xi_{jl}\xi_{kl}+\eta_{jl}\eta_{kl})\,\zeta_{jl}\zeta_{kl}}{\rho_{jl}^3\rho_{kl}^3}-\\
&\left.-2\,\Sigma^*_{kl(j)\neq}\frac{A_{jk}^2(\xi_{jl}\xi_{kl}+\eta_{jl}\eta_{kl})\zeta_{jl}\zeta_{kl}}{\rho_{jl}^3\rho_{kl}^3}+\Sigma_{kl(j)\neq}\frac{A_{jk}A_{jl}(1-\zeta_{kl}^2)\,\zeta_{kl}^2}{\rho_{kl}^6}\right\}-\\
&\left.-\frac{1}{20}(8x+9)\,x^2\,\Sigma_{k(\neq j)}\frac{A_{jk}^2(1-\zeta_{jk}^2)\,\zeta_{jk}^2}{\rho_{jk}^6}\right]+\\
&+\frac{(g\beta_0)^6}{a^9}\tfrac{1}{6}x^3\left[\Sigma^*_{kl(j)\neq}\cdot\right.\\
&\cdot A_{jk}\left\{\frac{(1-3\zeta_{jk}^2)(\xi_{kl}\xi_{jl}+\eta_{kl}\eta_{jl})\zeta_{kl}\zeta_{jl}}{\rho_{jk}^3\rho_{kl}^3\rho_{jl}^3}-\frac{(1-3\zeta_{kl}^2)(\xi_{jk}\xi_{jl}+\eta_{jk}\eta_{jl})\,\zeta_{jk}\zeta_{jl}}{\rho_{jk}^3\rho_{kl}^3\rho_{jl}^3}\right\}+\\
&\left.+2\,\Sigma^*_{kl(j)\neq}\,A_{jk}\left\{\frac{(1-3\zeta_{jl}^2)(\xi_{jl}\xi_{kl}+\eta_{jl}\eta_{kl})\,\zeta_{jl}\zeta_{kl}}{\rho_{kl}^3\rho_{jl}^6}-\frac{(1-3\zeta_{kl}^2)(1-\zeta_{jl}^2)\,\zeta_{jl}^2}{\rho_{kl}^3\rho_{jl}^6}\right\}\right].
\end{aligned}
$$

In the numerical evaluation the sums marked with an asterisk, being small with respect to the sum of all other terms, will be neglected. The summation sign $\Sigma_{k(\neq j)}$ indicates a summation over all lattice sites k different from an arbitrary but fixed site j. In the summation $\Sigma_{kl(j)\neq}$ we sum over all sites $k \neq l$, both of them being different from an arbitrary but fixed j.

The values of the quantities $(N\,\mathrm{Tr}\,1)^{-1}\,\mathrm{Tr}\,\{(1)^\dagger\,(1)\}$ and $(N\,\mathrm{Tr}\,1)^{-1}\,\mathrm{Tr}\,\{[(0),(1)]^\dagger\,[(0),(1)]\}$, expressed in terms of x, a and A, for the three cases a, b and c, are given in Table II.

TABLE II

	s.c.(100)	f.c.c.(100)	f.c.c.(111)
$\dfrac{\mathrm{Tr}\,(1)^\dagger(1)}{N\,\mathrm{Tr}\,1}$	$x^2(g\beta_0)^4\,a^{-6}\,0.189$	$x^2(g\beta_0)^4\,a^{-6}\,1.123$	$x^2(g\beta_0)^4\,a^{-6}\,0.850$
$\dfrac{\mathrm{Tr}\,[(0),(1)]^\dagger[(0),(1)]}{N\,\mathrm{Tr}\,1}$	$x^3(g\beta_0)^8\,a^{-12}\cdot$ $\left[1.46-\dfrac{0.0009}{x}\right]+$ $+\,x^3(g\beta_0)^4\,a^{-6}\,A^2 1.51$	$x^3(g\beta_0)^8\,a^{-12}\cdot$ $\cdot\left[5.43-\dfrac{0.06}{x}\right]+$ $+\,x^3(g\beta_0)^4\,a^{-6}\,A^2\cdot$ $\cdot\left[16.71-\dfrac{0.9}{x}\right]$	$x^3(g\beta_0)^8\,a^{-12}\cdot$ $\cdot\left[6.21-\dfrac{0.15}{x}\right]+$ $+\,x^3(g\beta_0)^4\,a^{-6}\,A^2\cdot$ $\cdot\left[15.2-\dfrac{0.6}{x}\right]$

Now we are able to express the quantity $(\Delta\omega)^2$, that appears in (5), in terms of the internal fields $H_{i_{dd}}$ and $H_{i_{ex}}$, with the aid of the Tables I and II. The values of $\hbar^2(\Delta\omega)^2$ in the three cases are given in Table III.

TABLE III

	s.c.(100)	f.c.c.(100)	f.c.c.(111)
$\hbar^2(\Delta\omega)^2$	$(g\beta_0)^2[0.46H_{i_{dd}}^2+1.33\,H_{i_{ex}}^2]$	$(g\beta_0)^2\left[0.17H_{i_{dd}}^2+\right.$ $\left.+\left(1.24-\dfrac{0.07}{x}\right)H_{i_{ex}}^2\right]$	$(g\beta_0)^2\left[0.25H_{i_{dd}}^2+\right.$ $\left.+\left(1.49-\dfrac{0.06}{x}\right)H_{i_{ex}}^2\right]$

Now we shall first compare the theoretical and the experimental field dependence of τ for the ammonium cupric Tutton salt. In Table IV the results of measurements of Verstelle *) are given.

TABLE IV

H	τ
2000 Ø	$7.96 \cdot 10^{-8}$
1675	$1.28 \cdot 10^{-8}$
1550	$0.796 \cdot 10^{-8}$
1360	$0.404 \cdot 10^{-8}$
1250	$0.266 \cdot 10^{-8}$
1100	$0.175 \cdot 10^{-8}$

If one plots $\log \tau$ versus H^2, the corresponding points lay, within the experimental error, on a straight line and so all experimental results may be given by:

$$\tau = (0.35 \cdot 10^{-9}) \exp (H^2/0.78 \cdot 10^6) \text{ sec}, \quad (H \text{ in oersted}). \tag{7}$$

The experiments of Verstelle are done with powdered crystals.

For the theoretical value of τ we have to know the values of $H_{i_{dd}}{}^2$ and $H_{i_{ex}}{}^2$. These can be derived from the measurements of Benzie, Cooke and Whitley [11]). So we find:

$$H_i{}^2 = 311 \cdot 10^3 \text{ Ø}^2, \quad H_{i_{dd}}{}^2 = 58 \cdot 10^3 \text{ Ø}^2, \quad H_{i_{ex}}{}^2 = 253 \cdot 10^3 \text{ Ø}^2.$$

The quantity x for this salt has the value: $\frac{1}{2} \cdot \frac{3}{2} = \frac{3}{4}$, $(S = \frac{1}{2})$. Now the theoretical field dependence will be determined by the value of the quantity $2\hbar^2(\Delta\omega)^2/(g\beta_0)^2$, that is given, for the three cases considered in Table V.

TABLE V

	s.c.(100)	f.c.c.(100)	f.c.c.(111)
$2\hbar^2(\Delta\omega)^2/(g\beta_0)^2$	$73 \cdot 10^4$ Ø^2	$60 \cdot 10^4$ Ø^2	$74 \cdot 10^4$ Ø^2

If these values are inserted in formula (5) a reasonable agreement with the experimental field dependence, given by (7), is found. However it should be taken in mind that (7) refers to a powder, whereas in Table V, theoretical results are given for single crystals and special directions of the external field. We have omitted the rather complicated computations to determine $\hbar^2(\Delta\omega)^2$ for a powder, but our calculations are only performed to give an order of magnitude of the theoretical estimate.

If the extrapolated value of τ for $H = 0$ is denoted by τ_0 the theoretical formula for τ has the form:

$$\tau = \tau_0 \exp (cH^2), \tag{8}$$

---

*) Verstelle, J. C. to be published.

in which the quantity c is equal to: $(g\beta_0)^2/2\hbar^2(\Delta\omega)^2$. From (5) and (2) it follows that τ_0 is given by:

$$\tau_0 = \frac{\Delta\omega}{\sqrt{2\pi} \int \mathrm{d}\omega \, f^{(1)}{}_{1,-1}(\omega)}, \qquad (9)$$
$$\int \mathrm{d}\omega \, f^{(1)}{}_{1,-1}(\omega) = \tfrac{3}{2} x \frac{(g\beta_0)^4}{\hbar^2 a^6} \sum_{k(\neq j)} \frac{(1-\zeta_{jk}{}^2)\zeta_{jk}{}^2}{\rho_{jk}{}^6}.$$

The theoretical values of τ_0 for the three cases, derived from Table III and (9), are given in Table VI.

TABLE VI

	s.c.(100)	f.c.c.(100)	f.c.c.(111)
τ_0	$7.0 \cdot 10^{-9}$ sec	$1.8 \cdot 10^{-9}$ sec	$2.7 \cdot 10^{-9}$ sec

These results are in disagreement with the experimental value of τ_0, given by (7): $\tau_0 = 0.35 \cdot 10^{-9}$ sec. It has not been possible to give a satisfactory explanation of this discrepancy so far. We expect however that for this salt the contribution of the "double flips" to $1/\tau$ (see section 6 of ch. III [1])) is much more important than one should expect on the base of rough calculations as performed in this section. The field dependence of both contributions should be of the same form, roughly spoken, because of the simple quadratic dependence on H of the experimental value of $\log \tau$ and so the agreement as to this field dependence between theory and experiment as found in this section may have some significance. The coupling with the nuclear spins of the copper ions has not been taken into account: we expect that the corresponding contributions to the function $f^{(1)}{}_{1,-1}(\omega)$ have a breadth that is very small as compared to the total breadth of this function. Small deviations from the isotropy of the g-tensor ($g = 2$) are likewise neglected.

3. *Discussion of other theories on spin-spin relaxation.* The first theory of paramagnetic relaxation was given by Waller [2]). He confined himself to the case $H = 0$ and as for the amplitude of the variable field, he studied both cases $h \ll H_i$ and $h \gg H_i$ (in his notation H corresponds with our field h). The only interaction between the spins, being taken into account, is a dipole-dipole interaction. For the case $h \ll H_i$, he computed a characteristic frequency ν_0, $(\nu_0)^{-1}$ giving the order of magnitude of the time necessary for the spin system to reach internal equilibrium, after the field h being suddenly switched on at $t = 0$. The characteristic time $(\nu_0)^{-1}$ was found to be of the order of magnitude of $\hbar/g\beta_0 H_i$. Spin-lattice relaxation was not taken into account for this low field case.

As stressed by Broer [4])[5]), the frequency ν_0 corresponds to the breadth of the shape function $f(\omega)$, that can be computed in a simple way by the method of moments, developed by Van Vleck [12]). In general one cannot expect in this case that the relaxation function $\varphi_{zz}(t)$, related by $f(\omega)$ through the formulae (11) and (29) of ch. III [1]), has an asymptotic exponential form, and for the exceptional case that this will be true, the corresponding τ will not be related in a simple way with the quantity $(\nu_0)^{-1}$.

Kronig and Bouwkamp [3]) were the first to give an estimate of the field dependence of τ. In a rather simple model they computed the chance that the external field $\boldsymbol{H}$ is compensated by the local internal field, assuming a Gaussian distribution for the component of this internal field in the direction of $\boldsymbol{H}$. So they arrived at the formula: $\tau(H) = \tau(0) \exp H^2/H_0^2$. The quantity H_0 is of the order of $H_{i_{dd}}$, only the effect of the dipole-dipole interaction being taken into account. For a face centered cubic lattice they arrived at a value of H_0^2 that is given by:

$$H_0^2 = 19.2\frac{\mu^2}{a^6} = \frac{19.2x(g\beta_0)^2}{a^6} = \tfrac{2}{3}H_{i_{dd}}^2.$$

This value of H_0^2 refers to single crystals, for arbitrary directions of $\boldsymbol{H}$, and thus also to powders. For $\tau(0)$ they took the value of the relaxation time as computed by Waller.

As to the field dependence of τ for the ammonium cupric Tutton salt, discussed in section 2, this would lead in our language, in both cases b and c, to a value of $2(\hbar\Delta\omega)^2/(g\beta_0)^2$, that is equal to: $4 \cdot 10^4$ Ø^2, whereas the experimental value is: $78 \cdot 10^4$ Ø^2. So, in this form, the theory of Kronig and Bouwkamp shows a large discrepancy with the experimental results. When the formula of these authors is replaced by: $\tau(H) = \tau(0) \exp H^2/2H_i^2$, $H_i^2 = H_{i_{dd}}^2 + H_{i_{ex}}^2$, a rather good, but not very significant agreement with the experimental results is found. However Kronig and Bouwkamp, giving a primitive but clear description of a possible relaxation mechanism, succeeded in predicting the general character of the field dependence of τ, without computing the precise value of $2\hbar^2(\Delta\omega)^2/(g\beta_0)^2$. In our opinion this could only be done by means of a more detailed quantum mechanical treatment, as given in the foregoing section.

In general one cannot expect a simple connection between the relaxation time for large values of H and that of Waller, through a formula of the form: $\tau(H) = \tau(0) \exp H^2/H_0^2$, because of the entirely different nature of the two quantities $\tau(H)$ and $\tau(0) = (\nu_0)^{-1}$; the first one can be related with a relaxation mechanism, described in terms of individual spin flips, whereas such a relation does not exist for $\tau(0)$.

The similarity of the field dependence of the relaxation time computed with the method of this chapter and of that of the relaxation time of Kronig and Bouwkamp becomes clear if one considers that in both cases τ^{-1} gives the velocity of a rate process that becomes more and more forbidden as H grows larger. The difference between the two theories lays in the fact that in our case the elementary processes, giving rise to paramagnetic relaxation, are of a character, more complicated than that of the single spin flips of Kronig and Bouwkamp.

For the case $H = 0$, the asymptotic form of the equation (35) of ch. III 1), given in section 6 l.c., cannot be used, because of the fact that the contributions to the integrals originating from the neighbourhood of the point $(t_1, t_2, t_3, \ldots) = (0, 0, 0, \ldots)$ do not give a good approximation for the value of the total integrals, in this case, the characteristic times of the functions h_2, h_3, ... and of $\Omega(t)$ being of the same order of magnitude. We do not expect in general an asymptotic exponential decay in this case.

Broer 4)5) made use of standard perturbation methods to predict the field dependence of the low frequency part of $f(\omega)$ in the case: $H \gg H_i$ and doing so he arrived at a field dependence of τ that is of the form: $\tau = \text{const.} \times H_i^2/H^2$. This result is in contradiction with that of Kronig and Bouwkamp and that of our theory.

This discrepancy can be understood by means of the following argument: The absorption computed by Broer has not a relaxation character but it is resonance absorption, because it originates from small clusters of spins for which perturbation calculus does converge, whereas relaxation is a typical many spin phenomenon. Broer's absorption gives a contribution to the integral $\int f(\omega)\,d\omega$ that is of the order of $kT(\chi_0/N)(H_i/H)^4$ and we have neglected this contribution for the region in which there is relaxation absorption. (For large spin systems ($N \to \infty$) the perturbation calculus will diverge in the general case as can be seen from straightforward evaluation of the different terms in the series for the eigenfunctions).

Miss Wright 6) following the same line of thought as Broer, gave a more precise calculation of the field dependence of τ, arriving at a similar result.

An entirely different approach, more similar to that developed in ch. III 1), was given by Bloembergen *e.a.* 7). In a paper by Pershan 8) the method was worked out in detail for the cross relaxation in LiF, for which a comparison was made with the experimental results. The distinction between "cross relaxation" and the Kronig Bouwkamp relaxation does not become quite clear for simple spin systems in the paper 7). For these simple systems, containing only one magnetic specimen ($S = \frac{1}{2}$), their method leads to the following cross relaxation probability:

$$w = \frac{4\pi}{\hbar^2} \frac{\operatorname{Tr}(1)^\dagger (1)}{N \operatorname{Tr} 1} \frac{1}{\sqrt{\{2\pi(\Delta\omega)^2\}}} \exp - \frac{(g\beta_0 H)^2}{2\hbar^2(\Delta\omega)^2},$$

including only single jumps.

Introducing this transition probability into a rate equation for the magnetization, including the proper Boltzmann factors, we arrive at:

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{M}_z = N\frac{4\pi}{\hbar^2}g\beta_0\frac{\exp\dfrac{-g\beta_0 H}{2kT} - \exp\dfrac{g\beta_0 H}{2kT}}{2}\frac{\mathrm{Tr}\,(1)^\dagger\,(1)}{N\,\mathrm{Tr}\,1}\,\cdot$$

$$\cdot\,\frac{1}{\sqrt{\{2\pi(\varDelta\omega)^2\}}}\exp -\frac{(g\beta_0 H)^2}{2\hbar^2(\varDelta\omega)^2} = -\frac{1}{\tau}\overline{M}_z,$$

in which formula τ is the spin-spin relaxation time given in section 2 of this chapter. In this way the method of Bloembergen *e.a.* leads to the same value for τ if only spin reversals of first order are taken into account (cf. section 6 of ch. III 1)).

However the mechanism of the relaxation does not become quite clear in their hybrid method for computing relaxation times and the rate equation given above does not lead to the real asymptotic value of $\overline{M}_z$, prescribed by the rules of thermodynamics.

One cannot expect to find the good answer following their method because of the fact that typical collective properties of the relaxation mechanism were not taken into account in a proper way.

As to the computation of the cross relaxation time in the case of LiF (see Pershan l.c.) a method can be followed as indicated in section 7 of ch. III 1)).

The author also developed a method to compute the so called "cross relaxation" time in some paramagnetic alums 13)), for the case that the crystal splitting and the magnetic splitting are of the same order of magnitude. An outline of this method will be given in the next chapter.

Our formula for $1/\tau_1$, given in ch. III 1)) (41), shows a great analogy with the formula for the linebreadth $\varDelta\omega_{\frac{1}{2}}$ in the case of strong narrowing, given by Kubo and Tomita 9)), formula (8.14). Assuming that there are only contributions from $M = \pm 1, \pm 2$ and that the corresponding functions $f^{(1)}{}_{-M,M}(\omega)$ have a Gaussian shape, it follows from (32) and (41) of ch. III 1)) that the relaxation time τ_1, for the case: $H = 0$, is given by:

$$\frac{1}{\tau_1} = 2\pi\,\Sigma_{M=1,2}\frac{M^2\,\mathrm{Tr}\,(M)^\dagger\,(M)}{\hbar^2\,\mathrm{Tr}\,S_z{}^2}\frac{1}{\sqrt{2\pi}}\hbar\left[\frac{\mathrm{Tr}\,(M)^\dagger\,(M)}{\mathrm{Tr}\,[(0),(M)]^\dagger\,[(0),(\mathrm{M})]}\right]^{\frac{1}{2}}.\quad(10)$$

This formula is not simply identical with (8.14) of Kubo and Tomita l.c., but the latter can be transformed into (10) by replacing S_- and S_+ by S_z and writing $\omega_z = 0$ *). One should expect that the two quantities $\varDelta\omega_{\frac{1}{2}}$ and $1/\tau_1$ were equal for $H = 0$, because of the fact that for this case there is no longer a distinction between the parallel and the perpendicular components of S_z. However our formula (10) does not give a good approximation for $1/\tau$ in the case of $H = 0$, because of the higher order processes becoming very important for small values of H. So (10) only gives the

---

*) Strong narrowing implies that in our formula (10), (0) can be replaced by $\mathscr{H}'_{ex}$.

extrapolated value of the reciprocal relaxation time. Besides we do not expect a Debye form for the low frequency absorption curve in the case of small H and the asymptotic expression for $\Omega(t)$ given in ch. III $^{1})$ is not correct in this case. We can only state that for $H = 0 : 1/\tau_1$ and $\Delta\omega_{\frac{1}{2}}$ are of the same order of magnitude: $g\beta_0 {H_{i_{dd}}}^2/\hbar H_{i_{ex}}$. The difference between $\Delta\omega_{\frac{1}{2}}$ and $1/\tau_1$ can be further illustrated by evaluating their values in the limit of $H \rightarrow \infty$. In our case we have $1/\tau_1(H = \infty) = 0$, whereas:

$$\Delta\omega_{\frac{1}{2}}(H = \infty) = \sqrt{\frac{\pi}{2}} \cdot \frac{{\sigma_0}^2}{\omega_{e0}},$$

corresponding with the fact that for large values of H, only the secular part of the interaction contributes to the moments of the absorption line (truncation).

REFERENCES

1) Caspers, W. J., Commun. Kamerlingh Onnes Lab., Leiden, Suppl. No. 118*a*; Physica **26** (1960) 778.
2) Waller, I., Z. Phys. **79** (1932) 370.
3) Kronig, R. de L. and Bouwkamp, C. J., Physica **5** (1938) 521.
4) Broer, L. J. F., thesis Amsterdam (1945).
5) Broer, L. J. F., Physica **10** (1943) 801.
6) Wright, A., Phys. Rev. **76** (1949) 1826.
7) Bloembergen, N., Shapiro, S., Pershan, P. S. and Artman, J. O., Phys. Rev. **114** (1959) 445.
8) Pershan, P. S., Technical Report No. **308**, Cruft Laboratory, Harvard University, Cambridge, Massachusetts.
9) Kubo, R. and Tomita, K., J. phys. Soc. Japan **9** (1954) 888.
10) Edmonds, A. R., Angular momentum in quantum mechanics (Princeton University Press, 1957).
11) Benzie, R. J., Cooke, A. H. and Whitley, S., Proc. roy. Soc. A **232** (1955) 277.
12) Van Vleck, J. H., Phys. Rev. **74** (1948) 1168.
13) Verstelle, J. C., Drewes, G. W. J. and Gorter, C. J., Commun. No. 311*b*; Physica **24** (1958) 632.

CHAPTER V

ON THE THEORY OF SPIN-SPIN RELAXATION III

Synopsis

A typical relaxation mechanism is studied for which the change in magnetic energy, accompanying a spin flip, is compensated or partly compensated by the change in electric energy. The spin flips are all two or more spin processes for this mechanism. An essential part of the argument is the partition of the operators of the total magnetic moment and of the total spin moment in a diagonal and a non-diagonal part, in a representation diagonalizing the zero order hamiltonian, containing only the one spin parts of the total spin hamiltonian (Zeeman parts and electric parts). Only the diagonal part of the moments contribute to the spin-spin relaxation.

Just as for the more simple case, treated in previous chapters [1][2], the number of relaxation times equals the number of groups of ions. Most attention will be paid to simple systems, containing only one group.

1. *Introduction*. In this chapter a relaxation mechanism will be studied, first indicated in a paper by Verstelle, Drewes and Gorter [3]). A short discussion of this mechanism has already been given by Bloembergen *e.a.*[4]). It is expected to be very important if the Zeeman energy and the electric energy of the single spins are of the same order of magnitude. The characteristic processes are two spin flips for which the change in magnetic energy is compensated or partly compensated by the change in electric energy. Also more complicated processes of the same nature, in which three or more spins turn over simultaneously, are possible. (The electric energy arises from inhomogeneous electric fields acting on the paramagnetic ions; the corresponding contributions to the spin hamiltonian and general properties of this operator are discussed in the papers [5])[6])).

In section 2 the spin hamiltonian is given in its general form. The zero order part of this hamiltonian: $\mathscr{H}_0$, only contains the one spin parts: Zeeman energy and electric energy. Just as for the case treated in the chapters III and IV [1])[2]), the spins may be divided into different groups, according to the form of their contribution to $\mathscr{H}_0$ and the way they are surrounded by other spins. For simplicity we restrict ourselves to the case that all ions have an isotropic g-tensor, the g-values of all of them being the same. Throughout this chapter most attention will be paid to simple systems, containing only one group; the generalization for the more complicated systems will be shortly indicated.

The perturbation hamiltonian $\mathscr{H}'$, containing the two spin interaction terms, can be split up into different parts, that are characterized by their commutation relations with $\mathscr{H}_0$:

$$[\mathscr{H}_0, \mathscr{H}'(\Delta_n)] = \Delta_n \mathscr{H}'(\Delta_n), \qquad n = 1,2,3 \ldots,$$

in which the real quantities Δ_n are a number of differences of eigenvalues of $\mathscr{H}_0$.

All Δ_n are continuous functions of $\boldsymbol{H}$ and we choose them in such a way that they all have continuous derivatives with respect to the components of $\boldsymbol{H}$. For the secular part of $\mathscr{H}'$: $\mathscr{H}'(0)$, the quantity Δ_n obeys the equality: $\Delta_n(\boldsymbol{H}) \equiv 0$.

An analogue partition of the operators of the spin and of the magnetic moment may be given; doing so the z-components of these moments: S_z and M_z, corresponding with the direction of the field $\boldsymbol{H}$, have the secular parts $S_z(0)$ and $M_z(0)$ respectively, commuting with $\mathscr{H}'(0)$. The partition of the operators $\mathscr{H}'$, S_z and M_z, indicated above, is discussed in section 2.

The spin-spin relaxation time(s), given by the asymptotic form of the relaxation function $\varphi_{zz}(t)$[1]), will in this case be fully determined by the correlation function:
$\langle\langle M_z(0)\, M_z(0, t)\rangle\rangle = (g\beta_0)^2 \langle\langle S_z(0)\, S_z(0, t)\rangle\rangle$, in which formula $M_z(0, t)$ and $S_z(0, t)$ are the Heisenberg representation of the secular parts of the z-components of the magnetic moment and of the spin respectively; β_0 is the Bohr magneton. The operators $M_z(0, t)$ and $S_z(0, t)$ are given by:

$$M_z(0, t) = g\beta_0 S_z(0, t),$$

$$S_z(0, t) = \exp \frac{i}{\hbar}\, t\, (\mathscr{H}_0 + \mathscr{H}')\, S_z(0) \exp - \frac{i}{\hbar}\, t(\mathscr{H}_0 + \mathscr{H}').$$

In section 3 the asymptotic form of the relaxation function $\varphi_{zz}(t)$ and that of the related functions $\Gamma(t)$ and $\Omega(t)$ (ch. III [1])) are derived. In that section we made use of a method similar to that exposed in ch. III [1]); both methods are based on the formalism of Kubo and Tomita [7]). For the simple systems it will be shown that $\varphi_{zz}(t)$ has a simple asymptotic exponential form:

$$\varphi_{zz}(t) \sim A \exp - t/\tau + B,$$

in which formula τ is the single spin-spin relaxation time. It is shown briefly in the same section that in general, for the more complicated systems containing different groups, the number of relaxation times equals the number of groups.

2. *The spin hamiltonian. The operators* $S_z(0)$ *and* $M_z(0)$. The total spin

hamiltonian may be divided into two parts: the zero order hamiltonian $\mathscr{H}_0$ and the perturbation $\mathscr{H}'$. $\mathscr{H}_0$ only contains the one spin parts of the total hamiltonian, *i.e.*: the Zeeman energy and the electric or Stark energy, arising from asymmetric crystalline electric fields [5][6]. If the hamiltonian of the free i-th spin is denoted by $\mathscr{H}_0(i)$ we have:

$$\mathscr{H}_0 = \textstyle\sum_i \mathscr{H}_0(i).$$

All magnetic ions having the same spin S, the $\mathscr{H}_0(i)$ have in general $2S + 1$ non-degenerate eigenvalues ($H \neq 0$). There may be different groups of ions: for all ions of a certain group the contribution to $\mathscr{H}_0$ has the same form. Besides all ions of one group have the same surroundings of other magnetic ions, the translation that carries one ion of a certain group into another of the same group being a symmetry operation for the lattice as a whole. The zero order hamiltonian may thus be divided into the parts corresponding with the different groups:

$$\mathscr{H}_0 = \textstyle\sum_v \mathscr{H}_0^v, \qquad v = 1,2, \ldots, P.$$

In this formula v numbers the different groups, P being their total number. We shall mainly restrict ourselves to systems containing only one group ($P = 1$) and the generalization for more complicated systems will only be briefly indicated.

The perturbation hamiltonian $\mathscr{H}'$ may be written as a sum of two spin interaction terms, more complicated forms of interaction are negligible in general:

$$\mathscr{H}' = \textstyle\sum_{i<j} \mathscr{H}'(i,j), \qquad \mathscr{H}'(i,j) = \mathscr{H}'(j,i).$$

$\mathscr{H}'(i,j)$ is the operator of the interaction between the i-th and the j-th spin (dipole-dipole and exchange interaction).

Taking a representation for which $\mathscr{H}_0$ is diagonal it can be shown in a simple way that $\mathscr{H}'$ may be divided into different parts:

$$\mathscr{H}' = \textstyle\sum_n \mathscr{H}'(\Delta_n) + \mathscr{H}'(0), \tag{1}$$

that are characterized by the commutation rules:

$$[\mathscr{H}_0, \mathscr{H}'(\Delta_n)] = \Delta_n \mathscr{H}'(\Delta_n), \quad [\mathscr{H}_0, \mathscr{H}'(0)] = 0. \tag{2}$$

In formula (1) the real quantities Δ_n are equal to a finite number of differences of eigenvalues of $\mathscr{H}_0$, being functions of $\boldsymbol{H}$. These functions $\Delta_n(\boldsymbol{H})$ may be chosen in such a way that they have continuous derivatives with respect to the components of $\boldsymbol{H}$. $\mathscr{H}'(0)$ is called the secular part of $\mathscr{H}'$, corresponding with a difference Δ that obeys the equality: $\Delta(\boldsymbol{H}) \equiv 0$; it is supposed that none of the Δ_n figuring in the sum in (1) is identical to: 0. The Δ_n may be arranged in pairs of opposite values and from the hermiticity of the operator $\mathscr{H}'$ it follows:

$$\mathscr{H}'(\Delta_n)^\dagger = \mathscr{H}'(-\Delta_n), \qquad \mathscr{H}'(0)^\dagger = \mathscr{H}'(0). \tag{3}$$

Now we may write the total spin hamiltonian $\mathscr{H}$ in different ways:

$$\begin{aligned} \mathscr{H} &= \mathscr{H}_0 + \mathscr{H}' = \mathscr{H}_{\mathrm{I}} + \mathscr{H}_{\mathrm{II}}, \\ \mathscr{H}_{\mathrm{I}} &= \mathscr{H}_0 + \mathscr{H}'(0), \\ \mathscr{H}_{\mathrm{II}} &= \textstyle\sum_n \mathscr{H}'(\Delta_n). \end{aligned} \tag{4}$$

In formulae (4) $\mathscr{H}_{\mathrm{I}}$ contains all secular parts of $\mathscr{H}$ and $\mathscr{H}_{\mathrm{II}}$ all non-secular parts. An analogue division can be made for the operators for S_z and M_z. It is assumed that all ions have isotropic g-tensors with the same g-value for all of them. So we have $\boldsymbol{M} = g\beta_0\boldsymbol{S}$ and it suffices to give the said division for S_z only. (Just as in the chapters III and IV [1][2]) the z-axis corresponds with the direction of the constant external field $\boldsymbol{H}$ and that of the parallel high-frequency field).

The division of S_z takes the form:

$$\begin{gathered} S_z = \textstyle\sum_{\bar{n}} S_z(\Delta_{\bar{n}}) + S_z(0), \\ [\mathscr{H}_0, S_z(\Delta_{\bar{n}})] = \Delta_{\bar{n}} S_z(\Delta_{\bar{n}}), \qquad [\mathscr{H}_0, S_z(0)] = 0, \\ S_z(\Delta_{\bar{n}})^\dagger = S_z(-\Delta_{\bar{n}}), \qquad S_z(0)^\dagger = S_z(0). \end{gathered} \tag{5}$$

Every $\Delta_{\bar{n}}$ will be equal to one of the Δ_n; the Δ_n correspond with energy differences in the two spin spectra, whereas the $\Delta_{\bar{n}}$ give the energy differences in the one spin spectra. From the foregoing it is clear that none of the $\Delta_{\bar{n}}$ is identical to: 0.

The operators $\mathscr{H}'(0)$ and $S_z(0)$ may be determined without solving the secular problem for the unperturbed hamiltonian $\mathscr{H}_0$, as will be shown in the Appendix I.

To find the different non-secular parts $\mathscr{H}'(\Delta_n)$ and $S_z(\Delta_{\bar{n}})$ it is necessary to diagonalize $\mathscr{H}_0$, but for the determination of the spin-spin relaxation times it is not necessary in principle to have the explicit form of $\mathscr{H}'(\Delta_n)$ and $S_z(\Delta_{\bar{n}})$, neither the values of the Δ_n and $\Delta_{\bar{n}}$.

In the next section we shall analyse the asymptotic form of the relaxation function $\varphi_{zz}(t)$ and that of the related functions $\Gamma(t)$ and $\Omega(t)$. For the definition and the physical meaning of these quantities we refer to ch. III [1]). The asymptotic form for large times of these functions will be determined by the asymptotic behaviour of the correlation function $\langle\langle S_z(0)S_z(0, t)\rangle\rangle$, in the high temperature approximation. For the single spin systems $\varphi_{zz}(t)$ will have an asymptotic form as given in the introduction:

$$\varphi_{zz}(t) \sim A \exp - t/\tau + B,$$

in which formula τ is the spin-spin relaxation time. For more complicated systems the asymptotic form of $\varphi_{zz}(t)$ will be a sum of exponential functions, apart from a constant. These exponential functions correspond with the different relaxation times $\tau^{(\bar{\nu})}$. The total number of relaxation times will be in general equal to the number of groups of ions. As was done for the operator $\mathscr{H}_0$, the operator S_z may be divided into the parts corresponding with the different groups. So we have:

$$S_z = \sum_v S_z^v, \qquad v = 1,2, \ldots, P.$$

A division as made in (5) for the operator of the total spin moment can be made for the different groups individually:

$$S_z^v = \sum_{\bar{n}} S_z^v(\Delta_{\bar{n}}) + S_z^v(0), \tag{6}$$

and the determination of the relaxation times for the systems, containing different groups, consists in the analysis of the asymptotic form of the correlation functions:

$$\langle\langle S_z(0)\, S_z^v(0, t)\rangle\rangle.$$

If for reasons of symmetry or incidentally the one ion spectra of two different groups are identical and if the two spin interactions between these two groups are strong enough, there is a rapid exchange of magnetization between these two groups and it may be necessary, for an adequate description of the relaxation phenomena in this case, to treat them as one and the same group.

In the next section we mainly restrict ourselves to systems, containing only one group. The solution of the problem for the more complicated systems is only briefly indicated.

3. *Expansion of $S_z(t)$ and $\Omega(t)$. Determination of the relaxation time.* To determine the spin-spin relaxation time(s) of a spin system we have to analyse the asymptotic form of the relaxation function $\varphi_{zz}(t)$. The definition and the general properties of $\varphi_{zz}(t)$ and the related functions $\Gamma(t)$ and $\Omega(t)$ were discussed in some detail in ch. III [1]) section 3.

In the present case the functions $\varphi_{zz}(t)$, $\Gamma(t)$ and $\Omega(t)$ are composed of different parts corresponding with the different parts of S_z, given in (5). If one looks at the form of the shape function $f(\omega)$, being the Fourier cosine transform of $\Omega(t)$ (cf. ch. III [1]) section 5), it is easy to see that the operators $S_z(\Delta_{\bar{n}})$ give rise to resonance absorption lines at the frequencies $|\Delta_{\bar{n}}|/\hbar$, $\bar{n} = 1,2,\ldots$; the operator $S_z(0)$ is the origin of the low frequency relaxation absorption and gives relatively small corrections to the resonance absorption intensities (this may be seen from simple time-dependent perturbation methods).

We are only interested in the low frequency relaxation absorption, corresponding with that part of $\varphi_{zz}(t)$ that has, in general, the longest characteristic time(s), the spin-spin relaxation time(s). In most cases those parts of $\varphi_{zz}(t)$ that correspond with the resonance absorption have characteristic times of the order of $\hbar/g\beta_0 H_i$ ($H_i^2 = H_{i_{dd}}^2 + H_{i_{ez}}^2$, cf. ch. III [1])), whereas the relaxation time(s) is (are) expected to be much larger and showing a strong dependence on $\boldsymbol{H}$.

Our method for computing the relaxation time(s) only gives convergent results for the case that the distances between the two-spin levels Δ_n are large as compared to $g\beta_0 H_i$, for analogue reasons as those leading to the restriction: $H \gg H_i$ in ch. III [1]). Only the experimental results with diluted crystals are suited for an analysis following the lines of this chapter.

From the foregoing it will be clear that for asymptotic values of the time: $t \gg \hbar/g\beta_0 H_i$, the relaxation function $\varphi_{zz}(t)$ is given by (cf. ch. III[1])):

$$\varphi_{zz}(t) = \beta(g\beta_0)^2 \langle\langle S_z(0)\, S_z(0,t)\rangle\rangle, \qquad \beta = 1/kT, \tag{7}$$

if one uses the high temperature approximation (we are only interested in that temperature region for which higher powers of β may be neglected). In formula (7) $S_z(0,t)$ is the Heisenberg representation of the secular part of the operator of the z-component of the total spin moment. The z-axis corresponds with the direction of the external magnetic field $\boldsymbol{H}$. The operator $S_z(0,t)$ is given by:

$$S_z(0,t) = \exp(it\mathscr{H}/\hbar)\, S_z(0) \exp(-it\mathscr{H}/\hbar). \tag{8}$$

From (7) and the definitions of $\Gamma(t)$ and $\Omega(t)$ given in ch. III [1]) it follows that the asymptotic forms of these two functions are given by:

$$\left.\begin{aligned} \Gamma(t) &= \lim_{N\to\infty} (g\beta_0)^2 \frac{\langle\langle S_z(0)\, S_z(0,t)\rangle\rangle}{N}, \\ \Omega(t) &= \lim_{N\to\infty} \frac{(g\beta_0)^2}{pN} \textstyle\sum_{\alpha\neq\gamma} \{S_z(0)\}_{\alpha\gamma} \{S_z(0,t)\}_{\gamma\alpha}. \end{aligned}\right\} \quad t \gg \hbar/g\beta_0 H_i \tag{9}$$

In formulae (7) and (9) $\langle\langle A\rangle\rangle$ denotes the normalized trace of an operator A: Tr A/Tr 1. α, γ, ... indicate the eigenstates of $\mathscr{H}$, p being the total number of them. N is the total number of spins. As to the limit: $\lim_{N\to\infty}$ we refer to the corresponding remarks in section 3 of ch. III [1]).

To determine the asymptotic form of the functions $\varphi_{zz}(t)$, $\Gamma(t)$ and $\Omega(t)$ for times of the order of the relaxation time(s) we make use of a series expansion for the operator $S_z(0,t)$ in terms of $\mathscr{H}_{\mathrm{II}}$. Now we shall first give the analysis for the simple spin systems. At the end of this section the generalization for the more complicated systems will be briefly indicated.

The expansion for the operator $S_z(0,t)$ in terms of $\mathscr{H}_{\mathrm{II}}$ is the analogue of that given for $M_z(t)$ by Kubo and Tomita [7]), cited in ch. III [1]). From the definition of $S_z(0)$ it follows that the eigenvalues of this operator are single valued functions of the corresponding eigenvalues of $\mathscr{H}_0$, except for very special values of the components of $\boldsymbol{H}$ *i.e.*: those values for which multiple spin flips may occur, without changing the unperturbed energy. A representation, diagonalizing $\mathscr{H}_0$, may be chosen in such a way that $S_z(0)$ is diagonal and that its (diagonal) elements are all continuous functions of $\boldsymbol{H}$

for all values of the components of $\boldsymbol{H}$. The same is true for the operator $\mathscr{H}'(0)$ and it can be proved in an easy way that the commutator of $S_z(0)$ and $\mathscr{H}'(0)$ vanishes for all lengths and directions of $\boldsymbol{H}$:

$$[S_z(0), \mathscr{H}'(0)] = 0. \tag{10}$$

Following a derivation, analogue to that given by Kubo and Tomita, we find the following expansion for $S_z(0, t)$, starting from formulae (4) and (8):

$$\begin{gathered} S_z(0, t) = S_z{}^{(0)} + S_z{}^{(1)}(t) + S_z{}^{(2)}(t) + \ldots, \\ S_z{}^{(0)} = S_z(0), \\ S_z{}^{(n)}(t) = (i\hbar)^{-n} \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n [S_z{}^{(0)};\, \mathscr{H}_{\mathrm{II}}(t_1),\, \mathscr{H}_{\mathrm{II}}(t_2),\, \ldots,\, \mathscr{H}_{\mathrm{II}}(t_n)], \end{gathered} \tag{11}$$

in which formulae the time-dependent operators $\mathscr{H}_{\mathrm{II}}(t_1), \mathscr{H}_{\mathrm{II}}(t_2), \ldots$ are given by:

$$\mathscr{H}_{\mathrm{II}}(t) = \exp\left(\frac{i}{\hbar}\, t \mathscr{H}_{\mathrm{I}}\right) \mathscr{H}_{\mathrm{II}} \exp\left(-\frac{i}{\hbar}\, t\, \mathscr{H}_{\mathrm{I}}\right).$$

From (10) it follows that the first order term in the series in (11): $S_z{}^{(0)}$, is independent of t. Combining (9) and (11) we arrive at the following expansion of the function $\Gamma(t)$:

$$\begin{gathered} \Gamma(t) = \textstyle\sum_{n=0}^{\infty} \Gamma_n(t), \\ \Gamma_n(t) = \lim\limits_{N\to\infty} \dfrac{(g\beta_0)^2}{(i\hbar)^n} \displaystyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n. \\ \cdot \frac{\langle\langle [S_z{}^{(0)};\, \mathscr{H}_{\mathrm{II}}(t_1),\, \mathscr{H}_{\mathrm{II}}(t_2),\, \ldots,\, \mathscr{H}_{\mathrm{II}}(t_n)]\, S_z{}^{(0)} \rangle\rangle}{N}. \end{gathered} \tag{12}$$

The second line of (12) may be transformed into:

$$\begin{gathered} \Gamma_n(t) = \lim\limits_{N\to\infty} \dfrac{(g\beta_0)^2}{(i\hbar)^n} \displaystyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n. \\ \cdot \textstyle\sum'_{\Sigma_k \Delta_k = 0} \displaystyle\frac{\langle\langle [S_z{}^{(0)};\, \mathscr{H}'(\Delta_1, t_1),\, \mathscr{H}'(\Delta_2, t_2),\, \ldots,\, \mathscr{H}'(\Delta_n, t_n)]\, S_z{}^{(0)} \rangle\rangle}{N}, \end{gathered}$$

following the same lines of thought as those leading to formula (22) of ch. III 1).

As to the function $\Omega(t)$ we arrive at an analogue expansion (cf. formulae (23) and (24) l.c.):

$$\begin{gathered} \Omega(t) = \textstyle\sum_{n=0}^{\infty} \Omega_n(t), \\ \Omega_n(t) = \displaystyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n. \\ . \lim\limits_{N\to\infty} \textstyle\sum_{\alpha\neq\gamma} \displaystyle\frac{(g\beta_0)^2 \sum' [S_z{}^{(0)};\, \mathscr{H}'(\Delta_1, t_1), \mathscr{H}'(\Delta_2, t_2), \ldots, \mathscr{H}'(\Delta_n, t_n)]_{\alpha\gamma} \{S_z{}^{(0)}\}_{\gamma\alpha}}{(i\hbar)^n\, pN}, \end{gathered} \tag{13}$$

in which formula $\sum'$ stands for the summation $\sum'_{\Sigma_k \Delta_k = 0}$. Just as in formula (4) none of the Δ_k obeys the equality: $\Delta_k(\boldsymbol{H}) \equiv 0$. The time dependent operators $\mathscr{H}'(\Delta_k, t_k)$ are given by:

$$\mathscr{H}'(\Delta_k, t_k) = \exp\left(\frac{i}{\hbar} t_k \mathscr{H}_{\mathrm{I}}\right) \mathscr{H}'(\Delta_k) \exp\left(-\frac{i}{\hbar} t_k \mathscr{H}_{\mathrm{I}}\right).$$

To determine the asymptotic behaviour of the functions $\Omega_n(t)$ we have to look for the principal diagonal part of the commutators:

$$(i\hbar)^{-n} \textstyle\sum'[S_z{}^{(0)}; \mathscr{H}'(\Delta_1, t_1), \mathscr{H}'(\Delta_2, t_2), \ldots, \mathscr{H}'(\Delta_n, t_n)],$$

following the method developed in ch. III [1]). This principal diagonal part has the form:

$$- g_n(t_1 - t_2, t_2 - t_3, \ldots\ldots, t_{n-1} - t_n)\, S_z{}^{(0)}, \tag{14}$$

in which formula the c-number $g_n(t_1 - t_2, t_2 - t_3, \ldots, t_{n-1} - t_n)$ is given by:

$$- g_n(t_1 - t_2, \ldots, t_{n-1} - t_n) =$$

$$= \lim_{N\to\infty} \frac{\mathrm{Tr} \sum' [S_z{}^{(0)}; \mathscr{H}'(\Delta_1, t_1), \mathscr{H}'(\Delta_2, t_2), \ldots, \mathscr{H}'(\Delta_n, t_n)]\, S_z{}^{(0)}}{(i\hbar)^n\, \mathrm{Tr}\,\{S_z{}^{(0)}\}^2}. \tag{15}$$

If the irreducible part of (14) is denoted by:

$$- h_n(t_1 - t_2, t_2 - t_3, \ldots\ldots, t_{n-1} - t_n)\, S_z{}^{(0)},$$

$\Omega_n(t)$ may written in the form (t sufficiently large):

$$\Omega_n(t) = - \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n\, [h_n(t_1 - t_2, \ldots, t_{n-1} - t_n) -$$

$$- \textstyle\sum_{p=2}^{n-2} h_p(\ldots) h_{n-p}(\ldots) + \ldots]\, \displaystyle\lim_{N\to\infty} (g\beta_0)^2 \textstyle\sum_{\alpha\neq\gamma} \displaystyle\frac{\{S_z{}^{(0)}\}_{\alpha\gamma} \{S_z{}^{(0)}\}_{\gamma\alpha}}{pN}. \tag{16}$$

It is beyond the scope of this chapter to determine the quantity:

$$\lim_{N\to\infty} (g\beta_0)^2 \textstyle\sum_{\alpha\neq\gamma} \displaystyle\frac{\{S_z{}^{(0)}\}_{\alpha\gamma} \{S_z{}^{(0)}\}_{\gamma\alpha}}{pN},$$

but is not necessary to know its value for computing the relaxation time τ. Still following analogue lines of thought as those developed in ch. III[1]) we arrive at the following equation for the function $\Omega(t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t} \Omega(t) + \int_0^t \mathrm{d}t_1 h_2(t_1)\, \Omega(t - t_1) +$$

$$+ \int_0^t \mathrm{d}t_1 \int_0^{t-t_1} \mathrm{d}t_2 h_3(t_1, t_2)\, \Omega(t - t_1 - t_2) + \ldots = 0, \tag{17}$$

hat has the asymptotic solution:

$$\Omega(t) = \bar{A} \exp - t/\tau, \tag{18}$$

if certain general conditions are fulfilled. It was not possible to indicate in detail all the conditions, but we suppose that the following two are the most important of them:

a. the differences of the unperturbed energy eigenvalues of the system of two spins are large as compared to $g\beta_0 H_i : \Delta_n \gg g\beta_0 H_i$,

b. $t \gg \hbar / g\beta_0 H_i$.

In (18) τ is the spin-spin relaxation time, given by:

$$1/\tau = \textstyle\sum_{n=1}^{\infty} 1/\tau_n, \; 1/\tau_1 = \int_0^\infty \mathrm{d}t_1 h_2(t_1),$$
$$1/\tau_2 = \textstyle\int_0^\infty \mathrm{d}t_1 \int_0^\infty \mathrm{d}t_2 h_3(t_1, t_2), \ldots .$$

For the general case the quantities $1/\tau_1$, $1/\tau_2$, $1/\tau_3$, ... will obey the inequality:

$$\ldots \ll |1/\tau_3| \ll |1/\tau_2| \ll 1/\tau_1,$$

and may be expressed in terms of the complex Fourier transforms of the function h_n.

These Fourier transforms are given by:

$$\begin{aligned} h_n(t_1, t_2, \ldots, t_{n-1}) &= \\ &= \textstyle\int \mathrm{d}\omega_1\, \mathrm{d}\omega_2 \ldots\ldots \mathrm{d}\omega_{n-1} \exp i(\omega_1 t_1 + \omega_2 t_2 + \\ &\quad + \ldots \omega_{n-1} t_{n-1})\, F^{(n-1)}(\omega_1, \omega_2, \ldots, \omega_{n-1}), \end{aligned} \tag{19}$$

from which formula it follows that the quantities $1/\tau_1$, $1/\tau_2$, ... are given by (cf. ch. III [1])):

$$\begin{aligned} 1/\tau_1 &= \pi F^{(1)}(0), \\ 1/\tau_2 &= 2i\pi \int \mathrm{d}\omega F^{(2)}(\omega, 0) \left(\frac{1}{\omega}\right)_P, \; \ldots\ldots . \end{aligned} \tag{20}$$

For practical computations it will be sufficient to compute only the first order contribution to $1/\tau : 1/\tau_1$. The functions $F^{(n)}$ are in principle determined by their moments that can be computed in a straightforward way with the aid of formula (15) and (19). However, in a practical case it is more suitable to split up $F^{(n)}$ into different parts that correspond with the different commutators, figuring in (15). These different commutators correspond with different sets of values of the quantities Δ_1, Δ_2, ..., Δ_n.

So we have for instance:

$$\begin{aligned} F^{(1)}(\omega) &= \textstyle\sum_n f^{(1)}_{\Delta_n, -\Delta_n}(\omega), \\ \lim_{N\to\infty} \frac{\mathrm{Tr}\,[S_z{}^{(0)}; \mathscr{H}'(\Delta_n, t), \mathscr{H}'(-\Delta_n)]\, S_z{}^{(0)}}{\hbar^2\, \mathrm{Tr}\,\{S_z{}^{(0)}\}^2} &= \\ = \textstyle\int \mathrm{d}\omega \exp(i\omega t)\, f^{(1)}{}_{\Delta_n, -\Delta_n}(\omega). \end{aligned} \tag{21}$$

The definition of the functions $f^{(1)}{}_{\Delta_n, -\Delta_n}(\omega)$ is a straightforward generalization of that given for the functions $f^{(1)}{}_{-M,M}$ in ch. III [1]). In an analogue way the functions $f^{(2)}{}_{\Delta_1,\Delta_2,\Delta_3}$, $f^{(3)}{}_{\Delta_1,\Delta_2,\Delta_3,\Delta_4}$, ... may be defined. For the determination of the moments of the functions $f^{(3)}{}_{\Delta_1,\Delta_2,\Delta_3,\Delta_4}$, $f^{(4)}{}_{\Delta_1,\Delta_2,\Delta_3,\Delta_4,\Delta_5}$, ... we have first to substract the reducible parts of the corresponding commutators (cf. ch. III [1])).

The leading term in the series for $1/\tau : 1/\tau_1$ may be approximated in general by:

$$1/\tau_1 = 2\pi f^{(1)}{}_{\Delta_m,-\Delta_m}(0), \qquad \Delta_m = \text{Min.}(|\Delta_n|),$$

for analogue reasons as those leading to the approximated value of $1/\tau_1$, in ch. III [1]).

In this approximation the relaxation time τ will be given by:

$$\tau = [2\pi f^{(1)}{}_{\Delta_m,-\Delta_m}(0)]^{-1}. \tag{22}$$

For the computation of this approximated value of τ it will be necessary to solve the one spin eigenvalue problem, *i.e.* diagonalize the matrix of $\mathscr{H}_0(i)$ (cf. section 2).

In Appendix II some simple numerical illustrations of the theory, developed in this section, will be given.

For the more complicated systems, containing different groups of spins, there is a straightforward generalization of the method indicated above. The functions $\Omega_n(t)$ should be divided into different parts $\Omega_n{}^{(v)}(t)$, corresponding with the different groups. This division goes parallel with the partition of the operator $S_z : S_z = \sum_v S_z{}^v$, and a partition of the $S_z{}^v$ into a secular part and different non-secular parts, as indicated in formula (6). So we have:

$$\Omega(t) = \textstyle\sum_v \Omega^{(v)}(t),\ \Omega_n(t) = \sum_v \Omega_n{}^{(v)}(t), \quad \Omega^{(v)}(t) = \sum_{n=0}^{\infty} \Omega_n{}^{(v)}(t),$$

$$\Omega_n{}^{(v)}(t) = \textstyle\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \ldots \int_0^{t_{n-1}} \mathrm{d}t_n \, . \tag{23}$$

$$.\lim_{N\to\infty} \sum_{\alpha\neq\gamma} \frac{(g\beta_0)^2 \sum'[S_z{}^v(0)\,; \mathscr{H}'(\Delta_1, t_1), \ldots\ldots, \mathscr{H}'(\Delta_n, t_n)]_{\alpha\gamma}\{S_z{}^{(0)}\}_{\gamma\alpha}}{(i\hbar)^n pN}.$$

The second line of (23) leads to a system of linear integro-differential equations for the functions $\Omega^{(v)}(t)$, as indicated, for the analogue case, in section 7 of ch. III [1]).

The number of these equations, being given by the number of groups, is equal to the number of relaxation times, for the general case. For reasons of symmetry or accidentally two or more relaxation times, that may be computed from the asymptotic form of these equations, may be equal.

As to the field dependence of τ for the simple systems the following general remarks can be made. In first order the relaxation time is completely determined by the functions $f^{(1)}{}_{\Delta_n,-\Delta_n}(\omega)$, that have maxima for the frequencies: $\omega = \Delta_n/\hbar$ respectively.

The quantities Δ_n are functions of $\boldsymbol{H}$, but in general the dependence is not linear: That means that the shape of the functions $f^{(1)}{}_{\Delta_n,-\Delta_n}(\omega)$ depends on $\boldsymbol{H}$ in general, so that the field dependence of τ will be more complicated than that for the simple case treated in ch. III [1]). However, it may be possible that in the neighbourhood of a field $\boldsymbol{H}_0$, for which one of the Δ_n is equal to: 0, this Δ_n may be expanded into a series of the form:

$$\Delta_m(\boldsymbol{H}) = \boldsymbol{a}.(\boldsymbol{H} - \boldsymbol{H}_0) + \ldots, \tag{24}$$

and that for $|\boldsymbol{H} - \boldsymbol{H}_0|$ sufficiently small, the first term in this series gives a good approximation for the value of $\Delta_m(\boldsymbol{H})$. For H_i sufficiently small, that means for high magnetic dilution, there may be a range of values and directions of $\boldsymbol{H}$:

$$H_i \ll |\boldsymbol{H} - \boldsymbol{H}_0| < K, \qquad (K > 0),$$

for which (24) gives a good approximation of $\Delta_m(\boldsymbol{H})$, while in the same interval our method can be applied. In this region the relaxation time will be given by:

$$\tau = [2\pi f^{(1)}{}_{\Delta_m,-\Delta_m}(0)]^{-1},$$

and the function $f^{(1)}{}_{\Delta_m,-\Delta_m}(0)$ may be well approximated by an expression of the form: $C_0 \exp G(\boldsymbol{H} - \boldsymbol{H}_0)$. G is a quadratic expression (homogeneous) in the components of the vector $\boldsymbol{H} - \boldsymbol{H}_0$; the coefficients in this expression may be determined by computing the moments:

$$\int \mathrm{d}\omega f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) \text{ and } \int \mathrm{d}\omega(\omega - \Delta_m/\hbar)^2 f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega),$$

by means of formula (21). C_0 is a constant.

The relaxation mechanism exposed in this chapter is believed to be the origin of a typical phenomenon, indicated by Verstelle, Drewes and Gorter [3]). For certain paramagnetic alums, χ' and χ'', measured at a fixed frequency, show a sharp field dependence in a certain region of values H. A detailed comparison with the results of our theory is not possible because of the fact that the experiments are performed with powders, and the τ computed following the lines of this chapter shows a strong anisotropy. However, we have the impression that their results and the results of the theory given in this chapter are qualitatively in agreement with each other.

APPENDIX I

The determination of the operators $S_z(0)$ *and* $\mathscr{H}'(0)$. Formulating the problem in a general way we have to find that part of an operator B that commutes with a given operator A. As to the operator S_z the problem is reduced to the problem of finding that part of the operator S_{iz} that commutes with $\mathscr{H}_0(i)$, i denoting the i-th spin. The sum of all these secular parts is denoted by $S_z(0)$.

For the operator $\mathscr{H}'$ we have to find that part of the operator $\mathscr{H}'(i, j)$

that commutes with $\mathscr{H}_0(i) + \mathscr{H}_0(j)$; the sum of these parts is denoted by $\mathscr{H}'(0)$. For the solution of the general problem we suppose that all eigenvalues of A are different. For that case: $1, A, A^2, \ldots, A^{l-1}$ is a complete set of operators, commuting with A, if l is the total number of eigenvalues of this operator.

From this set an orthogonal set may be derived by means of Schmidt's orthogonalization method:

$$\begin{aligned}
C_0' &= 1, & C_0 &= 1/(\mathrm{Tr}\, 1)^{\frac{1}{2}},\\
C_1' &= A - (\mathrm{Tr}\, AC_0)\, C_0, & C_1 &= C_1'/(\mathrm{Tr}\, C_1'^2)^{\frac{1}{2}},\\
C_2' &= A^2 - (\mathrm{Tr}\, A^2C_1)\, C_1 - (\mathrm{Tr}\, A^2C_0)\, C_0, & C_2 &= C_2'/(\mathrm{Tr}\, C_2'^2)^{\frac{1}{2}},\\
C_3' &= A^3 - (\mathrm{Tr}\, A^3C_2)\, C_2 - (\mathrm{Tr}\, A^3C_1)\, C_1 - & C_3 &= C_3'/(\mathrm{Tr}\, C_3'^2)^{\frac{1}{2}},\\
&\quad - (\mathrm{Tr}\, A^3C_0)\, C_0, & &
\end{aligned}$$

……………………………

The diagonal part of the operator B is now given by:

$$\Sigma_{n=0}^{l-1}\, (\mathrm{Tr}\, BC_l)C_l.$$

For a practical case it may be more simple to diagonalize the operator A and to determine the diagonal elements of the operator B in the corresponding representation.

If two or more of the eigenvalues of $\mathscr{H}_0(i)$ or $\mathscr{H}_0(i) + \mathscr{H}_0(j)$ coincide for special directions and lengths of $\boldsymbol{H}$ the corresponding diagonal parts of S_{iz} and $\mathscr{H}'(i, j)$ can be determined from the diagonal parts for neighbouring values of the components of $\boldsymbol{H}$.

APPENDIX II

Numerical examples. To illustrate the results of this chapter we shall compute the relaxation time τ, for the case discussed in section 3, for some simple lattices. These lattices do not correspond with actual salts, but our calculations may give an insight in the qualitative behaviour of the spin-spin relaxation phenomena for the case that the Zeeman and the Stark splitting are of the same order of magnitude.

One of the most simple zero order hamiltonians, giving the typical relaxation phenomena, has the form:

$$\begin{aligned}
&\mathscr{H}_0 = \Sigma_i \mathscr{H}_0(i),\\
&\mathscr{H}_0(i) = -g\beta_0 HS_{iz} + D[S_{iz}{}^2 - \tfrac{5}{4}], \quad S_i = \tfrac{3}{2},\ g = 2.
\end{aligned} \tag{I}$$

$\mathscr{H}_0(i)$ commutes with S_{iz} and the energy eigenvalues for the free i-th spin may be characterized by the corresponding eigenvalue of S_{iz}: m.

So we have:

$$\begin{aligned} m &= \pm \tfrac{3}{2}\colon\ E_{\pm\frac{3}{2}} = D \mp \tfrac{3}{2} g\beta_0 H, \\ m &= \pm \tfrac{1}{2}\colon\ E_{\pm\frac{1}{2}} = -D \mp \tfrac{1}{2} g\beta_0 H. \end{aligned} \qquad \text{(II)}$$

The secular part of S_z: $S_z^{(0)}$ is simply given by: $S_z^{(0)} = S_z$. For all ions the crystalline field has axial symmetry and we study the case that the vector $\boldsymbol{H}$ is directed along the crystal axis, that is the same for all ions. For this case the one spin energy eigenvalues show a very simple dependence on D and H, whereas the corresponding eigenstates are fully characterized by the value of m, just like the energy eigenvalues.

There are real spin hamiltonians showing resemblance with (I), e.g. that of chromium potassium alum. This salt, however, contains four ions per unit cell, corresponding with four different magnetic axes. The perturbation hamiltonian $\mathscr{H}'$, giving rise to the two spin transitions we are interested in, contains two spin interaction terms. We only take into account the dipole-dipole interaction, and with this restriction $\mathscr{H}'$ is given by formula (1) of ch. IV[2]). The typical two spin transitions we are interested in, are the following ones: A couple of spins i and j, originally in the state ($m_i = -\frac{1}{2}$, $m_j = +\frac{1}{2}$), also indicated by $|-\frac{1}{2}, \frac{1}{2}\rangle$, makes a transition to the state $|\frac{1}{2}, \frac{3}{2}\rangle$. The difference between the energy of the initial and that of the final state is given by:

$$\Delta_m = 2(D - g\beta_0 H), \qquad \text{(III)}$$

and it follows from section 3 that this transition has a large probability for $\Delta_m \approx 0$ or $g\beta_0 H \approx D$. As already outlined in section 3 we restrict ourselves to the case that:

$$|\Delta_m| \gg g\beta_0 H_i,$$

for the computation of the relaxation time τ and suppose that all other differences $|\Delta_n|$ are large as compared to $|\Delta_m|$. The change of the z-component of the spin for the double jump, indicated above is: 2. (It is a whole number because of the fact that we study an exceptional case for which S_z commutes with $\mathscr{H}_0$).

Introducing the quantities $\bar{\omega}$ and $\bar{H}$ in the following way:

$$\bar{\omega} = 2(D - g\beta_0 H)/\hbar = -\,2g\beta_0 \bar{H}/\hbar, \quad \bar{H} = H - D/g\beta_0,$$

and assuming a Gaussian shape for the function $f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega)$ we have:

$$f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) = f^{(1)}{}_{\Delta_m,-\Delta_m}(\bar{\omega}) \exp -(\omega - \bar{\omega})^2/2(\Delta\omega)^2. \qquad \text{(IV)}$$

For the definition of the function $f^{(1)}{}_{\Delta_m,-\Delta_m}$ we refer to section 3. Now the relaxation time τ is given by:

$$\tau = [2\pi f^{(1)}{}_{\Delta_m,-\Delta_m}(0)]^{-1}, \qquad \text{(V)}$$

and its numerical value can be determined by computing the following moments, that are given by formula (21):

$$\int \mathrm{d}\omega f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) = \frac{4 \operatorname{Tr} \mathscr{H}'(\Delta_m)\{\mathscr{H}'(\Delta_m)\}^\dagger}{\hbar^2 \operatorname{Tr} S_z{}^2},$$

$$\int \mathrm{d}\omega(\omega - \bar{\omega})^2 f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) = \frac{4 \operatorname{Tr} [\mathscr{H}'(\Delta_m), \mathscr{H}'(0)][\mathscr{H}'(\Delta_m), \mathscr{H}'(0)]^\dagger}{\hbar^4 \operatorname{Tr} S_z{}^2}. \qquad \text{(VI)}$$

The different parts of $\mathscr{H}'$: $\mathscr{H}'(\Delta_n)$, $\mathscr{H}'(0)$, are defined in section 2. The operators $\mathscr{H}'(0)$ and $\mathscr{H}'(\Delta_m)$ are defined in the most simple way by giving the matrix elements in a representation, diagonalizing all S_{iz}. We have:

$$\mathscr{H}'(0) = \tfrac{1}{2} \frac{(g\beta_0)^2}{a^3} \Sigma'_{i \neq j} [S_{iz}S_{jz} - \tfrac{1}{4}\{(S_{i+}S_{j-}) + (S_{i-}S_{j+})\}] \cdot$$

$$\cdot (1 - 3\zeta_{ij}{}^2)\, \rho_{ij}{}^{-3}, \qquad \text{(VII)}$$

$$\mathscr{H}'(\Delta_m) = -\tfrac{3}{8} \frac{(g\beta_0)^2}{a^3} \Sigma'_{i \neq j} (S_{i+}S_{j+})(\xi_{ij} - i\eta_{ij})^2 \rho_{ij}{}^{-3}.$$

For the definition of the quantities: ξ_{ij}, η_{ij}, ζ_{ij}, ρ_{ij} and a we refer to ch. IV [2]). The same applies for S_{i+}, S_{j-}, etc.

$(S_{i+}S_{j-})$ and $(S_{i-}S_{j+})$ correspond with those parts of the operators $S_{i+}S_{j-}$ and $S_{i-}S_{j+}$ that obey the commutation relation:

$$[(S_{i\pm}S_{j\mp}), \mathscr{H}_0] = 0,$$

with the restrictions outlined in section 2 ($(S_{i\pm}S_{j\mp})$ should be continuous functions of H). In an analogous way $(S_{i+}S_{j+})$ is given by:

$$[\mathscr{H}_0, (S_{i+}\, S_{j+})] = \Delta_m.$$

The matrix elements are derived in an easy way and we have:

$$\begin{aligned} &\langle \tfrac{1}{2}, \tfrac{3}{2} |(S_{i+}S_{j+})| -\tfrac{1}{2}, \tfrac{1}{2}\rangle = 2\sqrt{3}, && \langle \tfrac{3}{2}, \tfrac{1}{2} |(S_{i+}S_{j-})| \tfrac{1}{2}, \tfrac{3}{2}\rangle = \\ & && \langle \tfrac{1}{2}, \tfrac{3}{2} |(S_{i-}S_{j+})| \tfrac{3}{2}, \tfrac{1}{2}\rangle = 3, \\ &\langle \tfrac{3}{2}, \tfrac{1}{2} |(S_{i+}S_{j+})| \tfrac{1}{2}, -\tfrac{1}{2}\rangle = 2\sqrt{3}, && \langle \tfrac{1}{2}, -\tfrac{1}{2} |(S_{i+}S_{j-})| -\tfrac{1}{2}, \tfrac{1}{2}\rangle = \\ & && \langle -\tfrac{1}{2}, \tfrac{1}{2} |(S_{i-}S_{j+})| \tfrac{1}{2}, -\tfrac{1}{2}\rangle = 4. \end{aligned} \qquad \text{(VIII)}$$

From (VI), (VII), (VIII) it follows that the moment of zero order is given by:

$$\int \mathrm{d}\omega f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) = \tfrac{27}{20} \frac{(g\beta_0)^4}{\hbar^2 a^6} \Sigma'_{j(\neq i)} \frac{(1 - \zeta_{ij}{}^2)^2}{\rho_{ij}{}^6}. \qquad \text{(IX)}$$

For the moment of second order we find a rather complicated expression. In the general case it is given by:

$$\int \mathrm{d}\omega(\omega - \bar{\omega})^2 f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) = \tfrac{9}{64} \frac{(g\beta_0)^8}{\hbar^4 a^{12}} \Sigma'_{i \neq j}\, \Sigma'_{h \neq k}\, \Sigma'_{\bar{i} \neq \bar{j}}\, \Sigma'_{\bar{h} \neq \bar{k}} \cdot$$

$$\cdot \operatorname{Tr} [(S_{i+}S_{j+}), S_{iz}S_{jz} - \tfrac{1}{4}\{(S_{\bar{i}+}S_{\bar{j}-}) + (S_{\bar{i}-}S_{\bar{j}+})\}] \cdot$$

$$\cdot [(S_{h+}S_{k+}), S_{\bar{h}z}S_{\bar{k}z} - \tfrac{1}{4}\{(S_{\bar{h}+}S_{\bar{k}-}) + (S_{\bar{h}-}S_{\bar{k}+})\}]^\dagger \cdot$$

$$\cdot (\xi_{ij} - i\eta_{ij})^2 (1 - 3\zeta_{\bar{i}\,\bar{j}}{}^2)(\xi_{hk} + i\eta_{hk})^2 (1 - 3\zeta_{\bar{h}\,\bar{k}}{}^2)(\rho_{ij}\, \rho_{\bar{i}\bar{j}}\, \rho_{hk}\, \rho_{\bar{h}\bar{k}})^{-3} / \hbar^4 \operatorname{Tr} S_z{}^2.$$

Now we suppose that the most important contribution to this second moment originates from the following combinations of indices:

$$(ij) = (hk) \quad \text{or} \quad (ij) = (kh),$$
$$(\bar{i}\bar{j}) = (\bar{h}\bar{k}) \quad \text{or} \quad (\bar{i}\bar{j}) = (\bar{k}\bar{h}).$$

So we find the following approximated value of the second moment:

$$\int \mathrm{d}\omega(\omega - \bar{\omega})^2 f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) =$$
$$= \tfrac{1}{320} \frac{(g\beta_0)^8}{\hbar^4 a^{12}} \left[1647 \, {\sum}'_{j,\bar{j}(\neq i)} \frac{(1-\zeta_{ij}{}^2)^2}{\rho_{ij}{}^6} \frac{(1-3\zeta_{i\bar{j}}{}^2)^2}{\rho_{i\bar{j}}{}^6} - \right. \qquad \text{(X)}$$
$$\left. - 729 \, {\sum}'_{j(\neq i)} \frac{(1-\zeta_{ij}{}^2)^2 (1-3\zeta_{ij}{}^2)^2}{\rho_{ij}{}^{12}} \right].$$

In formula (X) the summation ${\sum}'_{j,\bar{j}(\neq i)}$ indicates a summation over all indices j and $\bar{j}$ (that may be equal), different from a fixed index i. The summation ${\sum}'_{j(\neq i)}$, just as in formula (IX), indicates a summation over all indices j, different from a fixed index i. From (IV) it follows that the quantity $(\Delta\omega)^2$ is given by the quotient of (X) and (IX).

The relaxation time τ may be expressed in terms of $\Delta\omega$, $\bar{H}$ and $\int \mathrm{d}\omega f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega)$ and is then given by:

$$\tau = \Delta\omega \left\{ \sqrt{2\pi} \int \mathrm{d}\omega f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega) \right\}^{-1} \exp 2\bar{H}^2 \Big/ \left(\frac{\hbar\Delta\omega}{g\beta_0} \right)^2, \quad \bar{H} = H - D/g\beta_0. \qquad \text{(XI)}$$

It will be convenient to express the final results in terms of the internal field H_i, that is given by (cf. the chapters III and IV [1][2]):

$$H_i{}^2 = \tfrac{15}{2} \frac{(g\beta_0)^2}{a^6} {\sum}'_{j(\neq i)} \rho_{ij}{}^{-6}, \quad (S = \tfrac{3}{2}).$$

We made numerical calculations for two types of lattices: simple cubic and face centered cubic lattices, that are indicated by s.c. and f.c.c., respectively, in table VII. This table gives the values of the zero order moment and of $(\Delta\omega)^2$ for these two types of lattices. The combination of this table and formula (XI) immediately gives τ as a function of H in the range of values of H indicated in the beginning of this appendix.

TABLE VII

	$\int \mathrm{d}\omega f^{(1)}{}_{\Delta_m,-\Delta_m}(\omega)$	$(\Delta\omega)^2$	$\exp 2\bar{H}^2 \Big/ \left(\frac{\hbar\Delta\omega}{g\beta_0}\right)^2$
s.c.	$0.112(g\beta_0 H_i/\hbar)^2$	$0.79(g\beta_0 H_i/\hbar)^2$	$\exp \bar{H}^2/0.39 H_i{}^2$
f.c.c.	$0.109(g\beta_0 H_i/\hbar)^2$	$0.29(g\beta_0 H_i/\hbar)^2$	$\exp \bar{H}^2/0.15 H_i{}^2$

The results given above serve as an example for the application of our theory. For the greater part of the real cases the computations are far more complicated. In most salts there are more than one group of spins and there cannot be found directions of $\boldsymbol{H}$ for which the component of the spin of each group in the direction of $\boldsymbol{H}$ commutes with $\mathscr{H}_0$. For this reason the one spin eigenvalues and eigenstates depend in a complicated way on $\boldsymbol{H}$, and also the quantities Δ_n and $S_z^{(0)}$. However the general character of the field dependence of the relaxation time(s), in the neighbourhood of a value $\boldsymbol{H}_0$, for which one of the $\Delta_n = 0$, will be the same, having the form:

$$\tau = \tau(\boldsymbol{H} = \boldsymbol{H}_0) \exp \frac{|\boldsymbol{H} - \boldsymbol{H}_0|^2}{\alpha H_i^2},$$

in which formula α is a quantity of the order of 1, that depends in general on the direction of $\boldsymbol{H} - \boldsymbol{H}_0$. $\tau(\boldsymbol{H} = \boldsymbol{H}_0)$ is only a theoretical quantity, not corresponding with the actual value of τ for $\boldsymbol{H} = \boldsymbol{H}_0$.

REFERENCES

1) Caspers, W. J., Commun. Kamerlingh Onnes Lab., Leiden, Suppl. No.118*a*; Physica **26** (1960) 778.

2) Caspers, W. J., Commun. Suppl. No. 118*b*; Physica **26** (1960) 798.

3) Verstelle, J. C., Drewes, G. W. J. and Gorter, C. J., Commun. No. 311*b*; Physica **24** (1958) 632.

4) Bloembergen, N., Shapiro, S., Pershan, P. S. and Artman, J. O., Phys. Rev. **114** (1959) 445.

5) Bowers, K. D. and Owen, J., Rep. Progr. Phys. **18** (1955) 304.

6) Abragam, A. and Pryce, M. H. L., Proc. roy. Soc. A **205** (1951) 135.

7) Kubo, R. and Tomita, K., J. phys. Soc. Japan **9** (1954) 888.

SAMENVATTING

In dit proefschrift wordt een theoretische analyse van de paramagnetische spin-spinrelaxatieverschijnselen gegeven en een berekening van de verhouding van de geïsoleerde en de adiabatische susceptibiliteit van spinsystemen. De samenhang van deze onderwerpen wordt getoond in hoofdstuk II: de spin-spinrelaxatietijd markeert het frequentiegebied waarin $\chi'(\omega)$ daalt van de waarde van de adiabatische susceptibiliteit (χ_S) tot die van de geïsoleerde susceptibiliteit ($\chi_{is}{}^{sm}$). Er kunnen ook verschillende spin-spinrelaxatietijden zijn.

Van de geïsoleerde susceptibiliteit wordt een algemene definitie gegeven in hoofdstuk I. Onderscheid wordt gemaakt tussen de geïsoleerde susceptibiliteit, berekend op een wijze die alleen correct is voor kleine systemen en waarbij gebruik gemaakt wordt van elementaire storingsrekening ($\chi_{is}{}^{sm}$), en die welke gevonden wordt met methodes, die alleen van toepassing zijn voor grote systemen (χ_{is}).

Voor de laatste wordt bewezen dat deze gelijk is aan de adiabatische susceptibiliteit (hoofdstuk II). $\chi_{is}{}^{sm}$ correspondeert ook met een extensieve grootheid van grote systemen, maar komt voor deze systemen niet meer overeen met de susceptibiliteit voor de frequentie: $\omega = 0$. In hoofdstuk I wordt een eenvoudige relatie van $\chi_{is}{}^{sm}$ en χ_S afgeleid; we bewijzen: $\chi_{is}{}^{sm}/\chi_S = 4/5$ voor een grote klasse van poeders van magnetische zouten.

Spin-spinrelaxatietijden worden berekend in de hoofdstukken III, IV en V; in hoofdstuk III voor systemen in sterke uitwendige magneetvelden, met enkele numerieke resultaten in hoofdstuk IV (voor dit geval is de Zeemanterm in de spinhamiltoniaan zeer groot ten opzichte van alle andere termen. In hoofdstuk V wordt de invloed van relatief sterke kristalvelden op het relaxatiemechanisme onderzocht. Voor enkelvoudige spinsystemen, die slechts één type magnetische ionen bevatten, vinden we steeds één relaxatietijd, die wordt gegeven door de waarde voor frequentie nul van de frequentieverdelingsfunctie van de matrixelementen van het niet-seculaire deel van de wisselwerking, in een representatie waarin de nulde-orde-hamiltoniaan (Zeemanenergie en electrische energie) en het seculaire deel van de wisselwerking diagonaal zijn.

Een generalisatie voor meer gecompliceerde spinsystemen, die verscheidene groepen ionen bevatten, is aangegeven. De resultaten van de theorie worden in hoofdstuk IV vergeleken met die van andere auteurs, voor zover het de processen geanalyseerd in hoofdstuk III betreft.

STELLINGEN

I

Het is niet mogelijk een correcte beschrijving te geven van de paramagnetische spin-spinrelaxatieverschijnselen in termen van overgangen tussen de energie-eigentoestanden van de individuele spins.

N. Bloembergen, S. Shapiro, P. S. Pershan en J. O. Artman, Phys. Rev. **114** (1959) 445.
Hoofdstukken III, IV en V van dit proefschrift.

II

De controverse tussen de theoretische resultaten van Broer enerzijds en die van Kronig en Bouwkamp anderzijds, wat betreft de afhankelijkheid van de spin-spinrelaxatietijd van de grootte van het constante uitwendige magneetveld, vindt zijn oorzaak in het feit, dat uitgegaan wordt van verschillende definities van het begrip spin-spinrelaxatietijd.

R. Kronig en C. J. Bouwkamp, Physica **5** (1938) 521.
L. J. F. Broer, Physica **10** (1943) 801.
L. J. F. Broer, Proefschrift, Amsterdam (1945).
Hoofdstuk IV van dit proefschrift.

III

Ten onrechte maken Abragam en Proctor voor geïsoleerde spinsystemen in een quasistatisch veranderend magneetveld, onderscheid tussen adiabatisch in de zin van Ehrenfest en adiabatisch in thermodynamische zin.

A. Abragam en W. G. Proctor, Phys. Rev. **109** (1958) 1441.
H. A. Kramers, Quantum mechanics V, § 54, (North Holland Publishing Company, Amsterdam, 1957).
R. C. Tolman, The principles of statistical mechanics XIII, § 123, (Oxford University Press, 1938).
T. Yamamoto, Phys. Rev. **119** (1960) 701.
Hoofdstuk II van dit proefschrift.

IV

Zonder uitwendig magneetveld en bij een juiste keuze voor het coördinatenstelsel, wordt de spinhamiltoniaan van een paramagnetisch ion met spin S en kernspin 0, volledig bepaald door n constanten, waarbij n gegeven wordt door:

$$n = \sum_{k=1}^{[S]} (4k + 1) - 3 = [S]\,(3 + 2[S]) - 3, \quad S \geqslant 1,$$

($[S]$ is gelijk aan het grootste gehele getal x dat voldoet aan: $x \leqslant S$).

B. Bleaney en K. W. H. Stevens, Rep. Progr. Phys. **16** (1953) 108.
A. Abragam en M. H. L. Pryce, Proc. roy. Soc. A **205** (1951) 135.
Hoofdstuk I van dit proefschrift.

V

Een gedetailleerde theoretische discussie van de verschijnselen van de paramagnetische verzadiging en de z.g. „cross-saturation" is mogelijk op de basis van een uitbreiding van de theorie van Kubo en Tomita.

A. H. Eschenfelder en R. T. Weidner, Phys. Rev. **92** (1953) 869.
N. Bloembergen, S. Shapiro, P. S. Pershan en J. O. Artman, Phys. Rev. **114** (1959) 445.
B. Bölger, Proefschrift, Leiden (1959).
R. Kubo en K. Tomita, J. phys. Soc. Japan **9** (1954) 888.

VI

De magnetisatie van een spinsysteem, waarvan de toestand gekarakteriseerd kan worden door een Zeemantemperatuur en een temperatuur van de plaatsruilwisselwerking, op de door Van Vleck aangegeven wijze, hangt in het algemeen af van deze beide temperaturen.

J. H. Van Vleck, Suppl. Nuovo Cimento **6** (1957) 1081.
N. Bloembergen en S. Wang, Phys. Rev. **93** (1954) 72.

VII

De formule van Kubo voor de tensor van het „statisch geleidingsvermogen" van eindige systemen geeft de waarde: 0 voor alle componenten van deze tensor en heeft dus geen fysische zin.

R. Kubo, J. phys. Soc. Japan **12** (1957) 570.

VIII

De uitdrukking die Saitô geeft voor de entropieproductie in een systeem waarin een tijdafhankelijke veldsterkte heerst is niet in overeenstemming met de voorwaarde dat op ieder tijdstip deze entropieproductie positief moet zijn.

N. Saitô, Phys. Rev. **117** (1960) 1163.

IX

Bij de discussie van zijn metingen van de verzwakking van ultrageluid in aluminium besteedt Filson geen aandacht aan de door hem gevonden systematische verschillen tussen twee meetseries; het feit dat deze twee series zijn opgenomen met een tussentijd van verscheidene weken kan een verklaring bevatten van deze verschillen.

D. Filson, Phys. Rev. **115** (1959) 1516.

X

Het is gewenst dat bij de benaming van verschillende soorten vergroting in de optica een grotere eenheid wordt nagestreefd. Tussen deze benaming in verscheidene, veel gebruikte leerboeken voor het V.H.M.O. enerzijds en die in standaardleerboeken voor pre-candidaten anderzijds bestaan grote en deels systematische verschillen.

XI

Laat R_n de ring van de formele machtreeksen zijn in n variabelen met complexe coëfficienten; A_n de deelring bestaande uit de machtreeksen, convergent in een omgeving van de oorsprong.

In R_n en A_n geldt het Lemma van Euclides. Het bewijs, dat hiervan door Siegel is gegeven, kan worden vereenvoudigd.

C. L. Siegel, Analytic functions of several complex variables, (Lectures delivered at the Institute for Advanced Study, Princeton, 1948–1949).

XII

De veronderstelling van Sierksma van het bestaan van een hiaat tussen waarneming en reactie bij het dier, een hiaat waardoor het dier tot subject wordt, is een projectie in één van de door hemzelf geformuleerde betekenissen.

In eerste instantie is dit hiaat belevingsmoment en als zodanig niet op bevredigende wijze te analyseren; het aantreffen ervan ,,buiten'' zichzelf is dus noodzakelijkerwijs een projectie.

F. Sierksma, De religieuze projectie, 2e dr., p. 9, (W. Gaade N.V., Delft, 1957).