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INVESTIGATIONS ON PARAMAGNETIC SPIN-SPIN RELAXATION

P. R. LOCHER

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJKSUNIVERSITEIT TE LEIDEN,
OP GEZAG VAN DE RECTOR MAGNIFICUS
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GEBOREN TE 'S-GRAVENHAGE IN 1930

KONINKLIJKE DRUKKERIJ VAN DE GARDE N.V. - ZALTBOMMEL

Promotor: PROF. DR. C. J. GORTER

Aan mijn ouders
Aan mijn vrouw

Promotor: PROF. DR. C. J. GORTER

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

In 1949 legde ik het eindexamen β af aan het Stedelijk Gymnasium te Leiden. In hetzelfde jaar begon ik mijn studie aan de Rijksuniversiteit te Leiden. Het candidaatsexamen wis- en natuurkunde, letter A, legde ik af in 1954. Hierna vervulde ik mijn militaire dienstplicht en in 1956 hervatte ik mijn studie te Leiden. Aanvankelijk werkte ik mee met Dr. J. C. Verstelle en Drs. G. W. J. Drewes bij het onderzoek van paramagnetische relaxatie bij frequenties tussen 1 en 100 MHz, onder leiding van Prof. Dr. C. J. Gorter. Een uitbreiding naar hogere frequenties bij dit onderzoek was reeds opgezet door Drs. H. Hadders en werd, na zijn vertrek, in 1957 door mij voortgezet. In 1959 legde ik het doctoraalexamen experimentele natuurkunde met bijvak mechanica af, waarna ik de onderzoekingen in het frequentiegebied tussen 200 en 3000 MHz uitbreidde. De resultaten hiervan zijn in dit proefschrift verwerkt.

Van 1959 tot 1961 ontving ik van de N.V. Philips' Gloeilampenfabrieken een studietoelage, die het mij financieel mogelijk maakte het onderzoek voort te zetten. In juli 1961 werd ik benoemd tot wetenschappelijk ambtenaar.

Bij de voorbereiding en uitvoering van de experimenten en bij de uitwerking van de resultaten verleenden voornamelijk Drs. E. R. Reddingius en Drs. D. A. Smink hun medewerking. In de laatste stadia werkten de heren R. G. van Welzenis en P. W. Verbeek mee aan het onderzoek. Technische hulp werd verleend door verscheidene leden van de staf van het Kamerlingh Onnes Laboratorium, in het bijzonder door de heren A. R. B. Gerritse, J. W. Groenewold, J. Hoogwerf, D. de Jong en H. R. Nater. Dr. W. Duffy corrigeerde het Engels in een gedeelte van het proefschrift.

De discussies die ik heb gevoerd met mijn promotor Prof. Dr. C. J. Gorter, met Dr. J. C. Verstelle en met Dr. W. J. Caspers waren van groot belang voor het onderzoek.

CONTENTS

Chapter I has also been published as: Locher, P. R. and Gorter, C. J., Commun. Kamerlingh Onnes Lab., Leiden No. 329*a*; Physica **27** (1961) 997, and chapter II as: Locher, P. R. and Gorter, C. J., Commun. Leiden No. 334*c*; Physica **28** (1962) 797.

INTRODUCTORY REMARKS

In this thesis certain aspects of paramagnetic spin-spin relaxation have been studied experimentally. A somewhat detailed introduction to these investigations will be given in section 1 of chapter I. In addition, some introductory remarks of a more general character will be given here, especially for readers who are not so familiar with the topic.

Paramagnetic relaxation refers to the processes whereby the magnetization of a paramagnetic crystal tends to an equilibrium value when it has initially a different value. The non-equilibrium state may arise as a consequence of a change of the external magnetic field applied to the crystal. The relaxation processes can be divided into two groups: spin-spin relaxation and spin-lattice relaxation. Spin-spin relaxation is connected with the interactions (dipole-dipole and exchange) among the magnetic moments (spins) of the ions, whereas spin-lattice relaxation is due to the interactions between the spins and the lattice vibrations. Phenomenologically, these two processes can well be distinguished in a number of paramagnetic crystals at low temperatures, the respective relaxation times being widely separated. Spin-spin relaxation occurs in times of 10^{-7} to 10^{-10} seconds, which are in general independent of the temperature. Spin-lattice relaxation requires much longer times, at least at low temperatures. This makes it possible to study pure spin-spin relaxation.

The spin-spin relaxation times are too short and the effects would often be too small for a direct observation of the variation of magnetization with time after a change of the external field. Instead, the samples are placed in a weak high frequency (h.f.) harmonically alternating magnetic field, superimposed on a static magnetic field. Confining ourselves to isotropic materials, the varying part of the resulting magnetization is in the same direction as the h.f. field and varies also harmonically with the same frequency, but it may have a different phase. The in-phase component of the magnetization is given by the susceptibility component χ' and is called the high-frequency susceptibility, whereas the 90^0-out-of-phase component is described by χ'', which is also called the absorption coefficient since it gives rise to absorption of energy by the crystal from the h.f. field. The h.f. magnetic field may be oriented parallel or perpendicular to the static field, which distinction is not relevant if the static field is zero.

In the past, mainly two regions of frequencies have been investigated. Several measurements of χ' and χ'' have been carried out below 100 MHz, under a variety of conditions regarding the applied static fields. Above 3000 MHz, a great deal of information has been obtained for the situation involving static fields perpendicular to the alternating fields (paramagnetic resonance studies). However, the intermediate region (100 to 3000 MHz) has so far hardly been explored and it is the purpose of our present research to obtain additional information on spin-spin relaxation from measurements in this region.

CHAPTER I

SPIN-SPIN RELAXATION AND MAGNETIC RESONANCES IN TWO COPPER TUTTON SALTS

Synopsis

The real and imaginary components χ' and χ'' of the paramagnetic susceptibilities of $CuCs_2(SO_4)_2.6H_2O$ and $Cu(NH_4)_2(SO_4)_2.6H_2O$ have been studied at frequencies of 0.41, 1.21, 1.76 and 3.2 GHz. The powdered samples were placed in transmission cavities (cf. Fig. 1 and 2) and nearly all measurements have been carried out at 20°K. The accuracy of the absolute values is of the order of 5%.

The exchange interaction in the Cs Tutton salt is small while in the NH_4 Tutton salt (Table IV) it is of the same order as the dipole-dipole interaction. This leads to a very different magnetic behaviour as may be seen from the figures 4–9, where χ'' is given in perpendicular magnetic fields, and χ'' as well as χ' in parallel fields. In the figures 10–13 the data obtained in some of the fields have been plotted as a function of the frequency.

In zero field (Fig. 10 and 11) reasonably good agreement with Gauss curves is found for the Cs Tutton salt. The high top value of χ'' and the negative values of χ' at high frequencies are striking. A line shape function (Form. 6) for intermediate cases having the Gauss and Lorentz shapes as the two limits is proposed. The results for the NH_4 Tutton salt fit well with the shape function which is expected to apply in view of the ratio of exchange to dipole-dipole interaction derived from the specific heat of the spin system.

The decrease of width of the χ'' curve in a perpendicular field due to truncation of the Hamiltonian of dipole-dipole interaction is observed for the Cs Tutton salt as well as a weak absorption band at half the field H_L of the Larmor resonance (Fig. 4). The exchange narrowing of the Larmor resonance in the NH_4 Tutton salt is observed and, in accordance with the 10/3 factor, the width is found to decrease with increasing field (Fig. 7).

In large parallel fields marked resonances at the Larmor frequency and the double Larmor frequency (at constant frequency occurring at the Larmor field and half the Larmor field) are observed in the Cs Tutton salt (Fig. 5, 6 and 13). The absolute values, as well as the ratio of the intensities agree satisfactorily with the formulae taking the hyperfine interaction of the copper nuclei into account, which have been developed by Caspers.

On the whole good agreement is found with the theoretical expectations.

1. *Introduction.* In the first successful investigation [1]) on paramagnetic relaxation, carried out on salts obeying Curie's law in the absence of a

constant magnetic field at liquid hydrogen temperatures, the imaginary part χ'' of the magnetic susceptibility was found to be proportional to the frequency ν and, just as the static susceptibility χ_0, inversely proportional to the temperature T. In the expression

$$\chi'' = \chi_0 \nu \rho' \tag{1}$$

$\rho'/2\pi$ was of the order of 10^{-9} seconds. Previously Waller [2]) had already predicted the occurrence of a relaxation time of this order of magnitude due to the dipole-dipole magnetic interaction between the different magnetic moments (spins) in the substance.

Later experiments [3]), carried out in a constant magnetic field oriented parallel to the high frequency magnetic field, revealed the existence of a second phenomenon that could very well be described by a temperature dependent relaxation time $\rho/2\pi$ which, at low temperatures, was often several orders of magnitude longer than $\rho'/2\pi$. This relaxation time was identified with that describing, according to Waller, the transfer of energy between the spins and the heat waves in the substance [3]) and is called the spin-lattice relaxation time [4]). At frequencies large compared with ρ^{-1} a constant so-called adiabatic susceptibility χ_{ad} is found which is identical with the static susceptibility in small parallel fields but which is considerably lower in fields of the order of the field $H_i \approx h/g\beta\rho'$ characterizing the dipole-dipole interaction between the spins, h being Planck's constant, β the Bohr magneton and g the Landé *) factor [5])[4]). In very strong parallel fields χ_{ad} disappears. Exchange interaction leads to higher values of χ_{ad}, which are sometimes formally described by an increase of H_i above its dipole-dipole value and, somewhat unexpectedly, leads also to an increase of ρ' connected with the well known exchange narrowing of paramagnetic resonance in a perpendicular field [6])[7]).

According to Casimir and Du Pré's phenomenological description [8]) the system of magnetic spins is, at every moment, in internal equilibrium at the frequencies concerned and so χ_{ad} is a property of that spin system.

In the present paper we do not investigate the spin-lattice relaxation, but are concerned with the variations of the real part χ' of the susceptibility at higher frequencies from the value of χ_{ad} and with the corresponding absorption coefficient χ''.

At relatively low frequencies where χ' differs little from χ_{ad}, only χ'' can be measured accurately but the fact that generally (1) is obeyed is no indication that at higher frequencies χ' and χ'' behave according to a relaxation mechanism connected with the loss of internal equilibrium of the spin system. They might just as well have a resonance character. The final result must be anyhow that both χ' and χ'' disappear at extremely high

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*) For non-free ions, Landé's g is replaced by the spectroscopic splitting factor g (cf. for instance reference [11]) in chapter II).

frequencies. Generally we may expect χ'/χ_0 and χ''/χ_0 to be independent of the temperature both for resonances and relaxations.

Broer[9]) and Miss Wright[10]) have made theoretical suggestions and some computations about the behaviour of χ' and χ'' in the absence of an external field and of electrical splittings, considering the influence of exchange interaction. One may expect that χ''/ν behaves approximately in accordance with a Gauss function in the absence of exchange interaction between the spins and with a Debije (relaxation) function in case of very strong exchange interaction.

The paramagnetic resonance in perpendicular fields is adequately described by the present theories as a broadened resonance [7]).

A number of conflicting views [9])[11]) have been presented on the behaviour in parallel external fields $H_{//}$. Recently Caspers has arrived at a series of satisfactory conclusions concerning the susceptibility of isolated spin systems for zero frequency [12])[13]) and has given a theory for the relaxation with a Debije character to be expected for the case that the external field is large compared with the internal fields [14]). This so-called Kronig-Bouwkamp relaxation shifts rapidly to low frequencies with increasing $H_{//}$. In the absence of exchange interaction and for $S \leq 3/2$, χ' should decrease in this region to $\frac{4}{5}\chi_{\mathrm{ad}}$; in case of strong exchange the decrease should be larger. At higher frequencies two resonance bands of equal intensity should occur for the case of $S = \frac{1}{2}$: at the Larmor frequency $g\beta H_{//}/h$ and at twice that frequency.

At most a few incidental theoretical remarks have been made about the influence of electrical splittings and on hyperfine interaction between spins and nuclear moments. It is clear that electrical splittings will lead to resonance phenomena in zero field and to related complications in parallel as well as in perpendicular fields. Caspers [31]) has made some theoretical remarks and computations, in connection with our investigations, on the influence of hyperfine interaction.

Experimental observations should be made in the region between the radiowaves and the microwaves – roughly between 10 and 10000 MHz. In order to avoid complications with spin-lattice relaxation phenomena the measurements should be done at sufficiently low temperatures preferably liquid hydrogen temperatures, where no complications yet occur because of paramagnetic saturation in high fields or of nearby antiferromagnetic or ferromagnetic transitions and where there is no danger to heat up the spin system. A number of incidental observations have been made in Russia and in the Netherlands [15])[16]). Recently a few preliminary results have been published on data obtained at 1325 MHz [17]).

In this chapter, results obtained on powdered $Cu(NH_4)_2(SO_4)_2 . 6H_2O$ and $CuCs_2(SO_4)_2 . 6H_2O$ at frequencies from 400 to 3000 MHz are given. Many investigations on other magnetic properties of these well known

Tutton salts have been carried out. It is a simplifying circumstance that $S = \frac{1}{2}$ and that there are thus no electric splittings. It is known that there is a relatively weak exchange interaction in the Cs salt while that is much stronger in the NH_4 salt [18][19]. Complicating factors are, however, the magnetic anisotropy, the occurrence of two non-identical copper ions in the unit cell and the considerable hyperfine interaction.

In section 2 the experimental set-up is described and discussed as well as the method used to derive χ'/χ_0 and χ''/χ_0 from the observations.

In section 3 the results are presented with a short discussion.

In the sections 4 and 5 the cases of zero field and large fields are discussed also from a theoretical view point.

In the second chapter, somewhat less complete results will be presented on a series of other paramagnetic salts.

2. *Experimental method.* The sample is placed in the magnetic h.f. (high frequency) field of a resonant cavity of the rectangular type, the inner conductor being a strip, which is about $\lambda/4$ long. We use three cavities, each of them having a fixed strip-length. Two of these cavities are used at only one frequency, respectively 0.41 and 3.2 GHz ($\lambda = 73$ and 9.4 cm); the third one is used at two frequencies (1.21 and 1.76 GHz), the lower frequency being obtained by filling the cavity – besides the sample – with polystyrene. Fig. 1 shows how the two 50 Ω silvered coaxial lines are coupled to the 3.2 GHz cavity at two places of its electrical h.f. field and also where the sample is placed.

The magnetic absorption and dispersion coefficients χ'' and χ' are measured by usual microwave techniques using a cavity in transmission. The measurements of χ' enable us to express χ' and χ'' in units χ_0, the static susceptibility, with a reasonable accuracy (about 5%). We shall now give some more details about the experimental method.

Fig. 2 gives a block diagram of the experimental set-up. We use the Rohde and Schwarz generators type SDR (0.30 up to 1.00 GHz) and type SCR (1.00 up to 1.90 GHz). For our highest frequency (3.2 GHz) we used a dump generator "AM type 41" with a klystron. The detector is a General Radio type 874 VQ with a silicon crystal nr. 1N21B. Both the generator and the detector are matched to the characteristic impedance of the coaxial lines (50 Ω). A possible mismatch is corrected with adjustable lines and adjustable stubs (General Radio type 874). We have used unmodulated signals and the resulting D.C. voltage V from the detector has been measured by means of a Philips electronic D.C. microvoltmeter (type GM 6020). The detector has been used in its square-law region ($V \lesssim 10$ mV).

We recall the following formulae, which describe how V depends on the frequency ν and via $\chi'(H)$ and $\chi''(H)$ on the external static field H. If we denote the frequency at which V reaches its maximum by ν_r – the cavity-resonance frequency – we have for V at a field H and a frequency ν

$$V_H(\nu) = V_H(\nu_r)/\{1 + 4(\nu - \nu_r)^2 Q_H{}^2/\nu_r{}^2\} \tag{2}$$

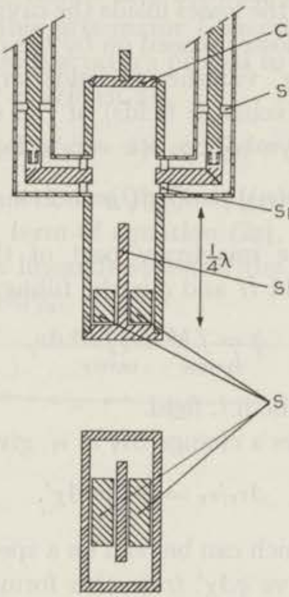

Fig. 1. Vertical and horizontal cross sections of the 3.2 GHz cavity. St = strip. S = sample, contained in a small polystyrene box, which is not indicated in the figure. Sp = polystyrene spacer. C = the cover of the cavity, soldered with Woods metal. The indicated distance $\frac{1}{4}\lambda = \frac{1}{4}\, c/\nu = 2.36$ cm.

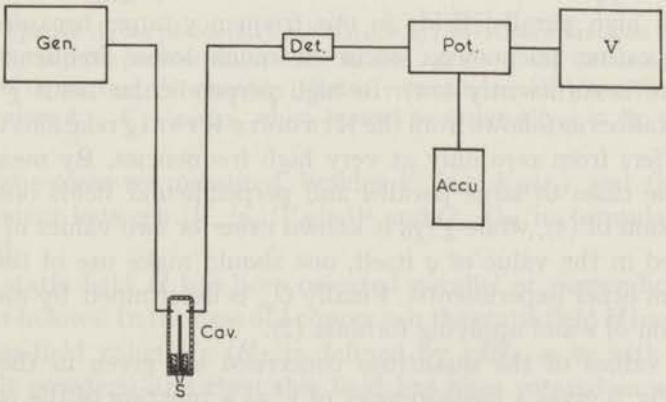

Fig. 2. Block diagram of the experimental set-up. *Gen.* = generator. *Cav.* = cavity. S = sample. *Det.* = crystal detector. V = electronic D.C. microvoltmeter. *Pot.* = = potentiometer. *Accu* = 2 Volt accu. The greater part of the detector D.C. voltage V can be compensated with the aid of the accu and the potentiometer in order to measure small changes of V.

if Q_H is sufficiently large ($Q_H \gtrsim 100$) and if only a small frequency region near ν_r is considered ($|\nu - \nu_r| \lesssim \nu_r/Q_H$). The quality factor Q_H is defined by

$$Q_H = 2\pi \frac{\text{energy stored in the cavity}}{\text{energy loss per cycle in the whole system}}.$$

The denominator contains the losses inside the cavity, including the magnetic losses, as well as external losses passed on by the couplings.

It is well known that χ'' vanishes in fields large compared to the total internal field (including exchange fields) of the substance. If one denotes these large fields by the symbol ∞, one can write

$$\{V_\infty(\nu_{\mathrm{r}})/V_H(\nu_{\mathrm{r}})\}^{\frac{1}{2}} = Q_\infty/Q_H = 1 + 4\pi q Q_\infty \chi'' \tag{3}$$

in which χ'' is minus the imaginary part of the dimensionless volume susceptibility *) at the field H and q is the filling factor defined by

$$q = \int_{\text{sample}} h^2 \,\mathrm{d}v \Big/ \int_{\text{cavity}} h^2 \,\mathrm{d}v,$$

h being the amplitude of the h.f. field.

A change $\Delta\chi'$ in χ' causes a change $\Delta\nu_{\mathrm{r}}$ in ν_{r}, given by

$$\Delta\nu_{\mathrm{r}}/\nu_{\mathrm{r}} = -2\pi q \Delta\chi'. \tag{4}$$

After measuring $\Delta\nu_{\mathrm{r}}$, which can be read on a specially mounted microscale on the generator, we derive $q\Delta\chi'$ from this formula (4). We obtain $qQ_\infty\chi''$ by measuring $V_\infty(\nu_{\mathrm{r}})$ and $V_H(\nu_{\mathrm{r}})$, using formula (3). In order to obtain then the absolute values of χ'/χ_0 and χ''/χ_0 we still have to determine $q\chi_0$, χ'/χ_0 at one value of H and finally Q_∞. This is done as follows. It is well known that in the copper Tutton salts – and also in many other substances – χ' vanishes in high parallel fields in our frequency-range because the spin-lattice relaxation phenomena occur at much lower frequencies (if the temperature is sufficiently low). In high perpendicular fields χ' equals χ_0 in our substances as follows from the Kramers-Kronig relations for the case that χ'' differs from zero only at very high frequencies. By measuring $\Delta\nu_{\mathrm{r}}$ between the cases of large parallel and perpendicular fields one finds $q\chi_0$ by application of (4), while χ'/χ_0 is known even for two values of H. (If one is interested in the value of q itself, one should make use of the χ_0-value, known from other experiments). Finally Q_∞ is determined by measuring V as a function of ν and applying formula (2).

Typical values of the quantities concerned are given in the following example. Fig. 3 gives a measurement of χ' as a function of the parallel and perpendicular fields. In this case our experiments yield $2\pi q\chi_0 = 1.15 \times 10^{-4}$ (thus $q = 0.17$ since $\chi_0 = 1.0_5 \times 10^{-4}$ at 20.4°K) and for the absorption in zero field we measure $V_\infty/V_{H=0} = 1.30_0$ which gives $4\pi q Q_\infty \chi''_{H=0} = 0.14_0$. The value of Q_∞ is measured to be $Q_\infty = 1.07 \times 10^3$ and from these data we calculate $\chi''_{H=0}/\chi_0 = 0.57$.

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*) If rationalized quantities χ'' are used, the factor 4π must be omitted.

Checks and some more details of the experimental method.

a) The square-law of the crystals has been checked by means of the calibrated attenuators of the Rohde and Schwarz generators and at 3.2 GHz by means of the adjustable attenuator General Radio type 874-GA. The deviations from the square-law ratio's proved to be $\lesssim 3\%$.

b) Formula (2) can be rewritten as

$$\{V_H(\nu_r)/V_H(\nu) - 1\}^{\frac{1}{2}} = 2Q_H\,|\nu - \nu_r|/\nu_r. \tag{2a}$$

Measuring $V_H(\nu)$ as a function of the frequency-microscale positions and calculating the left hand term of equation (2*a*), we can check whether the microscale readings are a linear function of the frequency. This proved to be the case within about 5%.

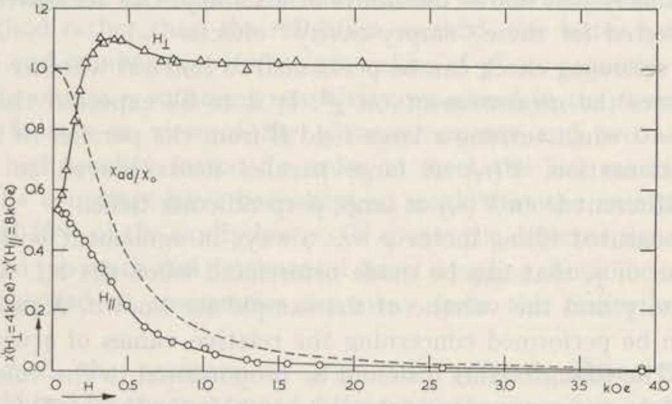

Fig. 3. The change $\Delta\chi'$ in powdered $Cu(NH_4)_2(SO_4)_2 . 6H_2O$ as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$ at $\nu = 0.409$ GHz and $T = 20.4$°K. As indicated in the text the quantity plotted vertically equals χ'/χ_0. The dashed line gives $1 - F = \chi_{ad}/\chi_0$, which is used to derive χ'/χ_{ad} in fig. 9.

c) In some cases we measured, besides $V_\infty(\nu_r)$, $V_H(\nu_r)$ and Q_∞, also Q_H. The agreement between $\{V_\infty(\nu_r)/V_H(\nu_r)\}^{\frac{1}{2}}$ and Q_∞/Q_H in formula (3) proved to be good.

d) The static field $\boldsymbol{H}$ has been oriented parallel or perpendicular to the h.f. field as follows. In the case of a copper salt the static field $\boldsymbol{H}$ has been given the Larmor-field value H_L (H_L is defined by $g\beta H_L = h\nu$ with $g = 2.2$ in copper salt powders) and then this field has been rotated in a horizontal plane. The direction of $\boldsymbol{H}$ at which the absorption reaches its minimum value is assumed to be the direction in which $\boldsymbol{H}$ is as nearly as possible parallel to the h.f. field. We used a $CuCl_2 . 2H_2O$ sample (powder) in order to check the deviations from the parallelism, which might be due to a curvature of the h.f. field lines. It is known that the large exchange field in copper chloride causes a narrowing of the perpendicular-field Larmor line, but broadens the parallel-field Larmor lines. Thus the remaining weak, narrowed, absorption line, which we measured in the case of the best parallel orientation, must be due to deviations from the parallelism. This remaining absorption amounted to only 0.1% of the perpendicular-field absorption at 1.76 GHz and 0.05% at 3.2 GHz. It is necessary that these deviations are so small in order to obtain reliable measurements of the parallel-field Larmor lines. These lines will be discussed in the sections 3 and 5.

e) With the same copper chloride sample we measured how χ'' at the Larmor-field depends on the angle φ between the static field and the h.f. field. $\chi''(\varphi)$ proved to be proportional to $\sin^2\varphi$ with an accuracy of about 3% of the χ''-values. This confirms that it is correct to use formula (3) for calculating χ'' from the measured V-values.

f) When measuring with an empty cavity we still found small changes of $V(\nu_r)$ and ν_r just above the limits of accuracy. Our measurements have been corrected for these "empty-cavity" effects.

g) The following check can be performed to find out whether a change of χ' influences the measurements of χ''. It is to be expected that $\Delta\chi' = \chi_0$ and $\Delta\chi'' = 0$ when turning a large field $\boldsymbol{H}$ from the parallel to the perpendicular orientation. $V(\nu_r)$ at large parallel fields proved to be slightly (or not) different from $V(\nu_r)$ at large perpendicular fields.

h) A measured filling factor q was always in agreement with the rough calculation of q, that can be made beforehand when the h.f. field pattern of the cavity and the volume of the sample are known. A more accurate check can be performed concerning the relative values of q with different samples. The filling factors q should be proportional to the volumes of the samples if they are put at about the same place in the cavity. This proportionality proved to be realised within the 5% accuracy, mentioned under *b*).

i) A direct check of the χ''/χ_0-values can be obtained in cases of a narrow perpendicular-field paramagnetic resonance line at the Larmor field H_L. In this case it will make little difference if we replace $\int_0^\infty(\chi''/\chi_0\nu)\,\mathrm{d}\nu$ – which has the theoretical value $\pi/2$ – by $(1/H_L)\int_{H_L\text{-line}}(\chi''/\chi_0)\,\mathrm{d}H$ (see also formula (16) in section 5). In several cases we calculated this latter integral from our measurements by simply determining the area below the χ''/χ_0 *versus* H graph. We did not find deviations from the theoretical value within the limits of accuracy (5%).

j) Usually χ''/χ_0 and χ'/χ_0 have been measured at 20.4°K only. In several cases we also performed measurements at 77.3°K. In the copper Tutton salts χ' is too small for a measurement with reasonable accuracy at that temperature but χ'' could be measured quite well and, using the filling factor of the 20.4°K-measurement, χ''/χ_0-values could be calculated. They proved not to differ from those at 20.4°K.

k) The high frequency power used is so low that the spin system is not heated up. To check this we sometimes varied the h.f. power and did not find any change of χ''.

l) The relative values of the static magnetic field have been calibrated by the ballistic galvanometer method, while the absolute values have been determined with the DPPH resonance absorption line at different frequencies ranging from 0.1 to 9 GHz. The inhomogeneity of the field amounts to about 1% in our samples which is of no importance.

m) Finally we give some general remarks about our experimental arrangements. Realizing that measurements of χ'' and χ' as a function of the frequency give more insight in the relaxation phenomena than those as a function of the static field, we concentrated our attention, when setting up our arrangements, rather on obtaining absolute values than on high sensitivity. We intend to increase the number of frequencies in future. Working with a number of circuits at different frequencies, it is efficient to keep the single set-up simple. For this reason we have chosen the transmission method rather than the reflection method, the latter being more complicated and cumbersome if absolute values of χ'' are required.

In order to obtain a sufficient sensitivity we aimed in the first place at high filling factors in view of the χ'-measurements and secondly at a sufficiently high quality factor. In order to meet the last mentioned requirement the couplings have been kept so weak that the external losses do not exceed 10% of the cavity losses. Of course the detector signal should not be reduced too much and detrimental direct coupling should be negligible as can be checked at frequencies far away from the cavity resonance frequency.

As mentioned, the accuracy of χ'/χ_0 and χ''/χ_0 is about 5%. The accuracy is limited by the mentioned different kinds of random and systematic errors, but at small susceptibilities certain absolute limits of the accuracy are dominating. These absolute limits correspond to a lowest detectable change of the quality factor of 0.1% and a lowest observable relative frequency change of 1×10^{-6}. With $q = 0.16$ and $Q_\infty = 2.5 \times 10^3$ (typical values) this corresponds to the volume susceptibilities $\chi'' = 2 \times 10^{-7}$ and $\chi' = 1 \times 10^{-6}$.

3. *Results.* The results on χ'' and χ' in powdered $CuCs_2(SO_4)_2.6H_2O$ and powdered $Cu(NH_4)_2(SO_4)_2 . 6H_2O$ are given in the figures 4, 5, 6, 7, 8 and 9. In order to avoid confusion it may be stressed that other figures in this chapter only give the same experimental data, plotted in another way.

Describing the results, we start remarking that in zero field $\chi''/\chi_0\nu(=$ $=(\pi/2kT\chi_0)\,f(\nu)$; see section 4) decreases monotonically with increasing frequency.

In perpendicular fields (fig. 4 and 7) one finds at the higher frequencies the well known paramagnetic resonance absorption line at the Larmor field $H_L = h\nu/g\beta$ with $g \approx 2.2$ while in the case of $CuCs_2(SO_4)_2.6H_2O$ (fig. 4) at $\nu = 3.178$ GHz the weak second line at $\frac{1}{2}H_L$ is partly resolved.

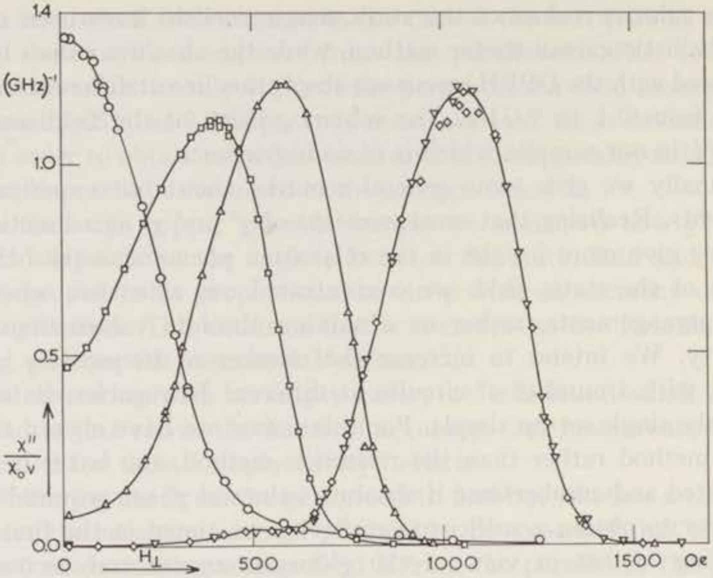

Fig. 4. $\chi''/\chi_0\nu$ in powdered $CuCs_2(SO_4)_2.6H_2O$ as a function of the perpendicular static field $H_\perp$ at different frequencies.

○ ≙ 0.407 GHz, 20.4°K
□ ≙ 1.213 GHz, 20.4°K
△ ≙ 1.761 GHz, 20.4°K
◇ ≙ 3.178 GHz, 20.4°K
▽ ≙ 3.178 GHz, 77.3°K

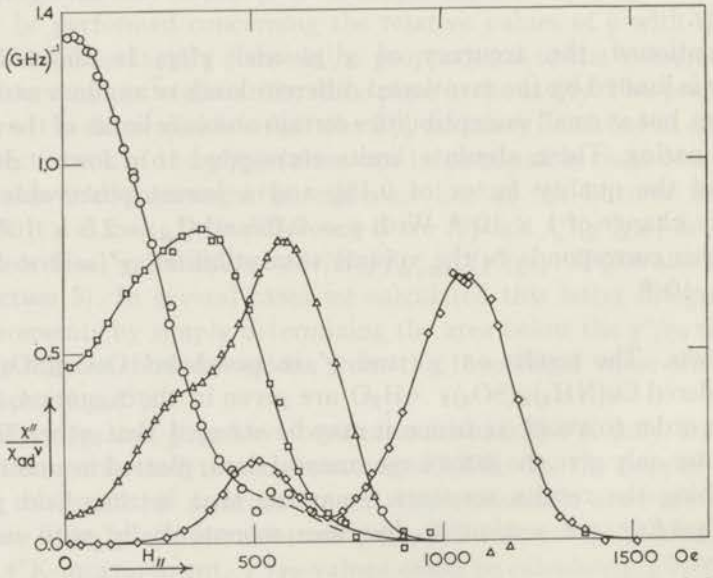

Fig. 5. $\chi''/\chi_{ad}\nu$ at 20.4°K in powdered $CuCs_2(SO_4)_2.6H_2O$ as a function of the parallel static field $H_{//}$ at different frequencies.

○ ≙ 0.407 GHz
□ ≙ 1.213 GHz
△ ≙ 1.761 GHz
◇ ≙ 3.178 GHz

$\chi_{ad} = \chi_0/\{1 + H^2_{//}/(b/C)\}$ with $(b/C)^{\frac{1}{2}} = 215$ Oe.

In the case of the CuCs Tutton salt the line shapes have a more Gaussian character compared with the lines of the $CuNH_4$ Tutton salt which have a more Lorentzian shape. In both salts the line width expressed in oersteds decreases with increasing frequency which effect could only be more pronounced in the hypothetical case of no anisotropy of *g*.

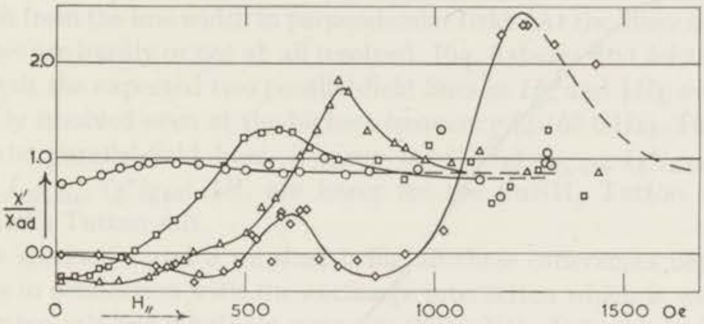

Fig. 6. χ'/χ_{ad} at 20.4°K in powdered $CuCs_2(SO_4)_2.6H_2O$ as a function of the parallel static field $H_{//}$ at different frequencies.

○ ≙ 0.407 GHz
△ ≙ 1.761 GHz
□ ≙ 1.213 GHz
◇ ≙ 3.178 GHz

For χ_{ad} see fig. 5.

Fig. 7. $\chi''/\chi_0\nu$ in powdered $Cu(NH_4)_2(SO_4)_2.6H_2O$ as a function of the perpendicular static field $H_\perp$ at different frequencies.

○ ≙ 0.409 GHz, 20.4°K
△ ≙ 1.760 GHz, 20.4°K
◇ ≙ 3.167 GHz, 77.3°K

In the case of parallel fields the total intensity $\int_{ss}(\chi''/\chi_0\nu)\,d\nu$ of the spin-spin absorption – ss denotes the total spin-spin absorption frequency range – is equal to $(\pi/2)\,\chi_{ad}/\chi_0$. Therefore it is useful to plot $\chi''/\chi_{ad}\nu$ instead of $\chi''/\chi_0\nu$ when discussing the field-dependence of χ''. We also plot χ'/χ_{ad}. But

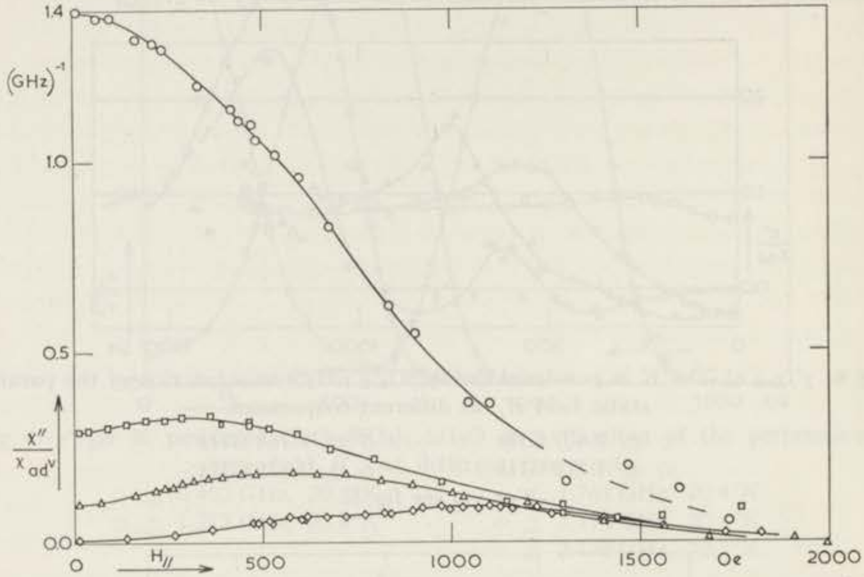

Fig. 8. $\chi''/\chi_{ad}\nu$ at 20.4°K in powdered $Cu(NH_4)_2(SO_4)_2.6H_2O$ as a function of the parallel static field $H_{//}$ at different frequencies.

○ ≙ 0.409 GHz   △ ≙ 1.760 GHz

□ ≙ 1.203 GHz   ◇ ≙ 3.167 GHz

$\chi_{ad} = \chi_0/\{1 + H^2_{//}/(b/C)\}$ with $(b/C)^{\frac{1}{2}} = 390$ Oe.

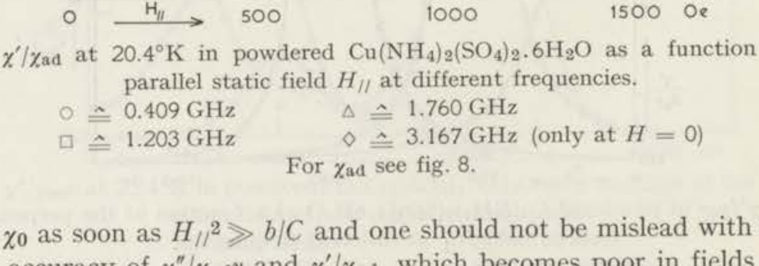

Fig. 9. χ'/χ_{ad} at 20.4°K in powdered $Cu(NH_4)_2(SO_4)_2.6H_2O$ as a function of the parallel static field $H_{//}$ at different frequencies.

○ ≙ 0.409 GHz   △ ≙ 1.760 GHz

□ ≙ 1.203 GHz   ◇ ≙ 3.167 GHz (only at $H = 0$)

For χ_{ad} see fig. 8.

$\chi_{ad} \ll \chi_0$ as soon as $H_{//}^2 \gg b/C$ and one should not be mislead with regard to the accuracy of $\chi''/\chi_{ad}\nu$ and χ'/χ_{ad}, which becomes poor in fields $H_{//} \gg (b/C)^{\frac{1}{2}}$, as can be seen from the spread of the measuring points. Similarly the spread in $\chi''/\chi_{\mathrm{ad}}\nu$ increases with decreasing frequency. In χ_{ad} we have used the b/C-values derived from unpublished χ'-measurements by Verstelle which agree very well (to 1% in $(b/C)^{\frac{1}{2}}$) with the data given by Benzie, Cooke and Whitley (1955) [19]. Fig. 5 shows that for the CuCs Tutton salt at the highest frequency (3.178 GHz) two lines at H_{L} and $\frac{1}{2}H_{\mathrm{L}}$ of the same order of intensity are detected, both having a line width, which differs not much from the line width in perpendicular fields. At the lower frequencies these lines are hardly or not at all resolved. Fig. 8 shows that for the CuNH$_4$ Tutton salt the expected two parallel-field lines at H_{L} and $\frac{1}{2}H_{\mathrm{L}}$ overlap and are hardly resolved even at the highest frequency (3.167 GHz). The intensities of the parallel-field lines, if given by $(1/H_{\mathrm{L}}) \int_{H_{\mathrm{L}}\text{-line}} (\chi''/\chi_{\mathrm{ad}})\, \mathrm{d}H$ and $(1/\frac{1}{2}H_{\mathrm{L}}) \int_{\frac{1}{2}H_{\mathrm{L}}\text{-line}} (\chi''/\chi_{\mathrm{ad}})\, \mathrm{d}H$, are lower for the CuNH$_4$ Tutton salt than for the CuCs Tutton salt.

In the sections 4 and 5 we shall bring all these differences between the two salts in connection with the exchange interaction which is weak in the CuCs Tutton salt but relatively strong in the CuNH$_4$ Tutton salt.

The measurements of χ' in parallel fields are given in the figures 6 and 9. The remarkable negative values of $\chi'(H = 0)$ at the higher frequencies will be discussed in section 4. In view of the absorption lines observed at H_{L} and $\frac{1}{2}H_{\mathrm{L}}$ (fig. 5) the usual anomalous behaviour of χ', consisting in a rapid rise between two regions of descent, should be expected. These anomalies can indeed be seen in fig. 6 at the higher frequencies although they are only partly resolved. In the limit of high fields it is expected theoretically [13]) that χ'/χ_{ad} approaches the value $\chi'_{\mathrm{between}}/\chi_{\mathrm{ad}}$ (χ'_{between} has been denoted by $\chi_{\mathrm{is}}^{\mathrm{sm}}$ in reference [13])). Our measurements (fig. 6 and 9) yield for this limit the values

$$\chi'_{\mathrm{bet}}/\chi_{\mathrm{ad}} = 0.8_5 \pm 0.1_5 \text{ for the CuCs Tutton salt} \quad \text{and}$$
$$\chi'_{\mathrm{bet}}/\chi_{\mathrm{ad}} = 0.3 \pm 0.1 \text{ for the CuNH}_4 \text{ Tutton salt.}$$

4. *Discussion. Analysis of the line shape at $H = 0$.* For the discussion of our results we shall refer mainly to theoretical papers of Broer [9]), Van Vleck [7]), Miss Wright [10]) and Caspers [12])[13])[14]). Moreover we shall make use of theoretical results computed by Dr. Caspers [31]) for our investigations. We would like to acknowledge his valuable co-operation in our discussions.

The discussions are divided into two parts, this section 4 dealing with the case of zero field ($H = 0$) and section 5 with the cases of large parallel and perpendicular fields ($H \gg H_{\mathrm{i}}$). Thus far no satisfactory theory has been given for the case of external fields of the order of H_{i}.

The only general method for analysing the line shape in the case of $H = 0$ is the method of moments introduced by Van Vleck [7]), these moments being defined by

$$\langle\nu^{2n}\rangle = \int_0^\infty (\chi''/\chi_0\nu)\, \nu^{2n}\, \mathrm{d}\nu \Big/ \int_0^\infty (\chi''/\chi_0\nu)\, \mathrm{d}\nu = \int_0^\infty f(\nu)\, \nu^{2n}\, \mathrm{d}\nu \Big/ \int_0^\infty f(\nu)\, \mathrm{d}\nu,\ n = 1, 2, 3, \ldots$$

where $f(\nu) = 2kT\chi''/\pi\nu$. Only for the lower order moments ($2n = 2,4$ and 6) expressions have been given in terms of the constants of the spin-hamiltonian, the calculation of higher order moments requiring very much time. Thus some assumptions must be made concerning the shape-function $f(\nu)$. Provisionally we only consider the case in which there are no zero-field splittings. In the Cu^{++} salts ($S = \frac{1}{2}$) such splittings are absent if the nuclear hyperfine structure is neglected. For example Broer[9]) considers a Gauss-function:

$$f_G(\nu) = (2/\pi)^{\frac{1}{2}}\,(kT\chi_0/\langle\nu^2\rangle^{\frac{1}{2}})\,\exp(-\nu^2/2\langle\nu^2\rangle)$$

and later on Miss Wright[10]) computes the fourth moment for a simple cubic lattice, arriving at the conclusion that for pure dipole-dipole interactions a reasonable agreement is found with the value $\langle\nu^4\rangle/\langle\nu^2\rangle^2 = 3$ which results from $f_G(\nu)$. But no such agreement is found in the presence of strong exchange interactions. Therefore Miss Wright[10]) proposes a set of functions $f_{2n}(\nu)$ ($n = 1, 2, \ldots$) which give the correct values for the first n moments. In particular she considers the following expression:

$$f_4(\nu) = (2/\pi)^{\frac{1}{2}}(kT\chi_0/\langle\nu^2\rangle^{\frac{1}{2}})\{1 + (1/4!)(\langle\nu^4\rangle - 3\langle\nu^2\rangle^2)(\mathrm{d}/\mathrm{d}\nu)^4\}\exp(-\nu^2/2\langle\nu^2\rangle),$$

which can be worked out, giving:

$$f_4(\nu) = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{kT\chi_0}{\langle\nu^2\rangle^{\frac{1}{2}}} \left\{1 + \frac{1}{4!}\left(\frac{\langle\nu^4\rangle}{\langle\nu^2\rangle^2} - 3\right)\left(3 - \frac{6\nu^2}{\langle\nu^2\rangle} + \frac{\nu^4}{\langle\nu^2\rangle^2}\right)\right\} . \exp\left(-\frac{\nu^2}{2\langle\nu^2\rangle}\right). \qquad (5)$$

Miss Wright remarks that this gives only a reasonable approximation if the exchange interaction, for which $\langle\nu^4\rangle/\langle\nu^2\rangle^2$ is a measure, is not too strong. From an estimate of the sixth moment she calculates that her parameter A which characterizes the relative magnitude of the exchange interaction should be small compared with 7. In terms of the fourth moment this means that $\langle\nu^4\rangle/\langle\nu^2\rangle^2$ should be small compared with 24. In addition to this we remark that already at $(\langle\nu^4\rangle/\langle\nu^2\rangle^2) > 7$ the expression (5) is quite unsatisfactory since it is negative at the moderate frequency given by $\nu^2 = 3\langle\nu^2\rangle$.

We would rather construct a function $f(\nu)$ which also holds in the case of strong exchange interaction. In that case a Lorentzian line shape is observed in experiments on paramagnetic resonance and accordingly a Debije-function for the zero-field absorption [20])[21]), though far away from the centre of the line still an exponential decay should be expected to occur in view of the convergence of all the moments. Accordingly a product of a Lorentzian and a Gaussian shape function has already been used for an exchange-narrowed resonance absorption line by Lacroix[22]), this product being

$$\chi''/\chi_0\nu \propto [\rho/\{1 + \rho^2(\nu - \nu_L)^2\}]\,\exp\{-\alpha^2\rho^2(\nu - \nu_L)^2\}$$

in which ν_L is the Larmor frequency, $\nu_L = g\beta H/h$. For application of this formula at low fields and low frequencies a term should be added *) which accounts for the line at $\nu = -\nu_L$ for the case of a linearly polarized h.f. field – just as is done in the usual expression of Kronig, Van Vleck, Weisskopf and Fröhlich for the Lorentzian line shape function –, thus giving

$$\frac{\chi''}{\chi_0\nu} = \frac{\rho}{2(\exp\alpha^2)\,\mathrm{Erfc}\,\alpha}\left[\frac{\exp\{-\alpha^2\rho^2(\nu-\nu_L)^2\}}{1+\rho^2(\nu-\nu_L)^2} + \frac{\exp\{-\alpha^2\rho^2(\nu+\nu_L)^2\}}{1+\rho^2(\nu+\nu_L)^2}\right] \tag{6}$$

in which Erfc α is the complementary error function defined by Erfc $\alpha =$ $= (2/\pi^{\frac{1}{2}})\int_\alpha^\infty(\exp - \xi^2)\,\mathrm{d}\xi$. The coefficient in (6) has been chosen so as to comply with the normalization condition $\int_0^\infty(\chi''/\chi_0\nu)\,\mathrm{d}\nu = \pi/2$.

The introduction of the second term in (6) made it possible to derive a corresponding expression for χ' with the aid of the Kramers-Kronig relations, this expression being

$$\begin{aligned}\frac{\chi'}{\chi_0} = 1 - \frac{\rho\nu}{2}\left\{\frac{\rho(\nu-\nu_L)}{1+\rho^2(\nu-\nu_L)^2} + \frac{\rho(\nu+\nu_L)}{1+\rho^2(\nu+\nu_L)^2}\right\} - \\ - \frac{\rho\nu(\exp-\alpha^2)}{\pi^{\frac{1}{2}}\,\mathrm{Erfc}\,\alpha}\left[\frac{F\{\alpha\rho(\nu-\nu_L)\}}{1+\rho^2(\nu-\nu_L)^2} + \frac{F\{\alpha\rho(\nu+\nu_L)\}}{1+\rho^2(\nu+\nu_L)^2}\right]\end{aligned} \tag{7}$$

in which $F(x) = (\exp -x^2)\int_0^x(\exp t^2)\,\mathrm{d}t$. Tables of the function $F(x)$ have been given by Miller and Gordon [23]). In our case of $H = 0$ we shall make use of these formulae which then have the more simple form ($\nu_L = 0$):

$$\chi''/\chi_0\nu = \{\rho'/(1+\rho^2\nu^2)\}\exp(-\alpha^2\rho^2\nu^2) \tag{8}$$

in which

$$\rho' = \rho/(\exp\alpha^2)\,\mathrm{Erfc}\,\alpha$$

and

$$\chi'/\chi_0 = \{1 - 2\rho\nu F(\alpha\rho\nu)/\pi^{\frac{1}{2}}(\exp\alpha^2)\,\mathrm{Erfc}\,\alpha\}/(1+\rho^2\nu^2) \tag{9}$$

in accordance with the formulae given by Lacroix *l.c.* for this case. Thus we shall confront our measurements with these formulae (8) and (9) rather than with $f_4(\nu)$ of Miss Wright.

Before doing so we would like to make the following remarks about (8). The parameter α can be given all values between 0 and ∞. In the case of $\alpha = 0$ (8) is a simple Debije-function and in the limit of $\alpha \to \infty$ (with a fixed value of $\alpha\rho$, being equal to $(2\langle\nu^2\rangle)^{-\frac{1}{2}}$) (8) is the simple Gauss-function of Broer: $\chi''/\chi_0\nu = (\pi/2)^{\frac{1}{2}}\langle\nu^2\rangle^{-\frac{1}{2}}\exp(-\nu^2/2\langle\nu^2\rangle)$. The relaxation function $\Phi(t)$, which describes the response of the total magnetic moment after a small field $\boldsymbol{h}$ is suddenly switched out at $t = 0$, is generally given by $\Phi(t) = \chi_0$ for $t = 0$ and by $\mathrm{d}\Phi/\mathrm{d}t = -(2/\pi)\int_0^\infty\chi''(\omega)\sin\omega t\,\mathrm{d}\omega$ for $t > 0$; ($\omega = 2\pi\nu$);

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*) We are indebted to Dr. J. C. Verstelle who suggested the resulting line shape function and who performed calculations concerning it, especially on χ'.

($\Phi(\infty) = 0$). Cf. [24]) and $\varphi_{zz}(t)$ in [14]). For the $\chi''(\nu)$-function (8) this yields:

$$\frac{1}{\chi_0}\frac{\mathrm{d}\Phi(t)}{\mathrm{d}t} = -\frac{\exp(-t/\tau)}{2\tau\,\mathrm{Erfc}\,\alpha}\left[\mathrm{Erfc}\left(\alpha-\frac{t}{2\alpha\tau}\right)-\mathrm{e}^{2t/\tau}\,\mathrm{Erfc}\left(\alpha+\frac{t}{2\alpha\tau}\right)\right] \quad (10)$$

with $\tau = \rho/2\pi$. In the limit of $t \to \infty$ $\Phi(t)$ approaches the simple form $\Phi(t) = \chi_0 \exp(-t/\tau)$, whereas in the special case of $\alpha = 0$ (Debije-function) this simple form holds for all values of t. The asymptotic form, however, is not valid in the case of $\alpha = \infty$, the relaxation function corresponding to the Gauss-function being $\Phi_G(t) = \chi_0 \exp(-\langle\omega^2\rangle\, t^2/2)$ for all values of t.

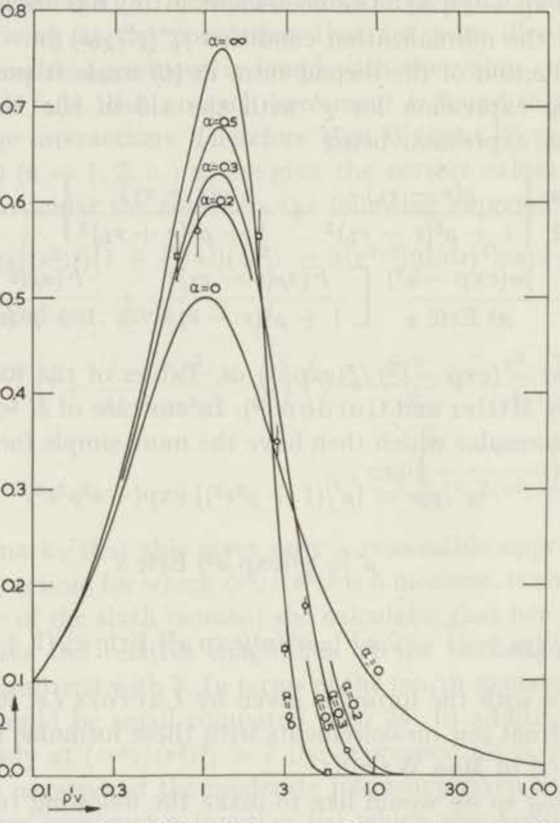

Fig. 10. Theoretical curves for $\chi''(H = 0)/\chi_0$ according to formula (8) as a function of log $\rho'\nu$ for different values of α.

□ ≙ $CuCs_2(SO_4)_2 \cdot 6H_2O$, $\rho' = 1.7\ (\mathrm{GHz})^{-1}$

○ ≙ $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $\rho' = 2.2\ (\mathrm{GHz})^{-1}$

The vertical lines through the measured points indicate the experimental error.

In the derivation of the asymptotic behaviour of (10) use has been made of the relation $\lim_{\alpha\to\infty} B = 1$ in which $B = \{\alpha\pi^{\frac{1}{2}}(\exp\alpha^2)\,\mathrm{Erfc}\,\alpha\}^{-1}$. The 2nd and 4th moment of (8) are given by

$$\langle\nu^2\rangle = (B-1)/\rho^2 \quad (11)$$

and

$$\langle\nu^4\rangle/\langle\nu^2\rangle^2 = \{1 + B(\tfrac{1}{2}\alpha^{-2} - 1)\}/(B-1)^2 \tag{12}$$

the latter expression being a function of α only. Apparently α can also be considered as a parameter characterizing the relative magnitude of the exchange.

Now our procedure will be to choose such values of the parameters ρ' and α in (8) and (9) so as to obtain the best fit to the experimental data. Then the resulting moments $\langle\nu^2\rangle$ and $\langle\nu^4\rangle$ will be compared with theory.

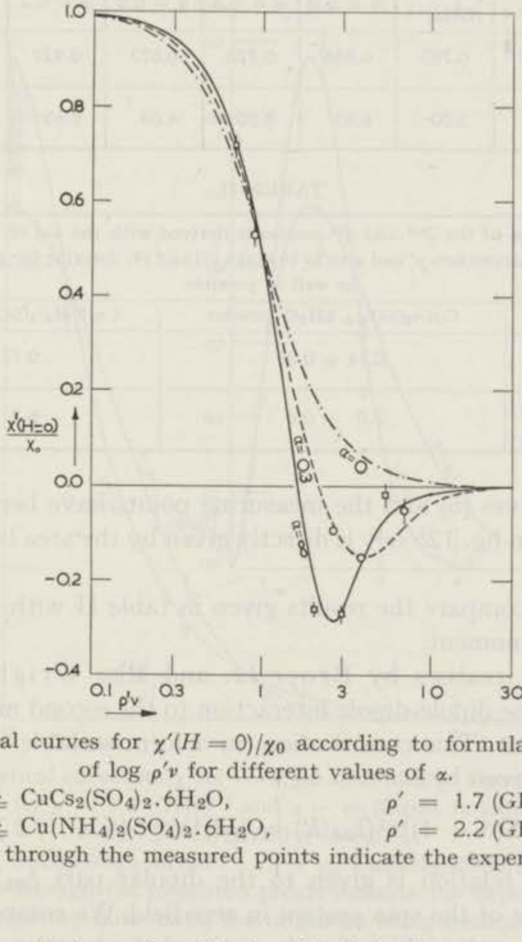

Fig. 11. Theoretical curves for $\chi'(H=0)/\chi_0$ according to formula (9) as a function of log $\rho'\nu$ for different values of α.

□ ≙ $CuCs_2(SO_4)_2.6H_2O$, $\rho' = 1.7\ (GHz)^{-1}$
○ ≙ $Cu(NH_4)_2(SO_4)_2.6H_2O$, $\rho' = 2.2\ (GHz)^{-1}$

The vertical lines through the measured points indicate the experimental error.

The choice of ρ' and α is made with the aid of the figures 10 and 11. In these figures a change of ρ' merely results in an equal horizontal shift of all the measuring points. In the case of $CuCs_2(SO_4)_2.6H_2O$ we find $\alpha \approx \infty$ and $\rho' = 1.7$ (GHz)$^{-1}$ while for $Cu(NH_4)_2(SO_4)_2.6H_2O$ we find $\alpha = 0.3$ and $\rho' = 2.2$ (GHz)$^{-1}$. In choosing this latter value $\rho' = 2.2$ (GHz)$^{-1}$, the measurements of Verstelle[21]) at low frequencies ($\rho'\nu \ll 1$) and at 20°K, giving $\rho' = 1.9 \pm 0.1$ (GHz)$^{-1}$, have been taken into account **). Some values of the moments at different values of ρ' and α are given in table I, from which we derive the experimental values of the moments and their accuracy, given in table II.

TABLE I

The 2nd and 4th moments of the curve given by formula (8) at some values of the parameters ρ' and α

	$\alpha = \infty$		$\rho' = 2.2$ (GHz)$^{-1}$			$\rho' = 2.1$ (GHz)$^{-1}$		
	$\rho' = 1.7$ (GHz)$^{-1}$	$\rho' = 1.6$ (GHz)$^{-1}$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.5$	$\alpha = 0.2$	$\alpha = 0.3$	$\alpha = 0.5$
$\langle\nu^2\rangle^{\frac{1}{2}}$ in units GHz	0.737	0.783	0.886	0.773	0.673	0.929	0.818	0.705
$\dfrac{\langle\nu^4\rangle}{\langle\nu^2\rangle^2}$	3.00	3.00	6.63	5.20	4.09	6.63	5.20	4.09

TABLE II

Experimental values of the 2nd and 4th moments derived with the aid of formula (8) using such values of the parameters ρ' and α so as to make (8) and (9) describe the experimental data as well as possible

	$CuCs_2(SO_4)_2.6H_2O$ powder	$Cu(NH_4)_2(SO_4)_2.6H_2O$ powder
$\langle\nu^2\rangle^{\frac{1}{2}}$ in units GHz	0.74 ± 0.05	0.77 ± 0.05
$\dfrac{\langle\nu^4\rangle}{\langle\nu^2\rangle^2}$	3.0 ± 0.4	5.2 ± 0.6

In fig. 12 the curves (8) and the measuring points have been plotted again in another way. In fig. 12*b* $\langle\nu^2\rangle$ is directly given by the area below the curves.

We shall now compare the results given in table II with theory, starting with the second moment.

In the earlier treatises by Broer *l.c.* and Miss Wright *l.c.* only the contribution of the dipole-dipole interaction to the second moment has been taken into account. This contribution, in a form suitable for our analysis, is for a powder given by

$$\nu_{\mathrm{dd}}^2 = 6k^2h^{-2}\{S(S+1)\}^{-1}(b_{\mathrm{dd}}/R) = (g\beta)^4 h^{-2}\, S(S+1)\, 2\sum_{j(\neq i)} r_{ij}^{-6}. \quad (13)$$

In (13) also the relation is given to the dipolar part b_{dd}/T^2 of the heat capacity per mole of the spin system in zero field. We computed the lattice-sum for a Tutton salt, taking for the ratio of the lengths of the crystallografic axes $a : b : c = 3 : 4 : 2$ and a monoclinic angle of 105° between the a- and the c-axis and taking the neighbouring ions at the lattice positions $(0, 0, \pm 1)$, $(\pm\frac{1}{2}, \pm\frac{1}{2}, 0)$, $(\pm\frac{1}{2}, \pm\frac{1}{2}, \pm 1)$ *etc.*, these conditions all being

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**) Volger's [25]) [4]) value $\rho' = 5.7$ (GHz)$^{-1}$ obtained at 77°K has not been confirmed whereas Dijkstra's [26]) value $\rho' = 2.0$ (GHz)$^{-1}$ obtained at 77°K and 90°K is confirmed.

approximately fulfilled in Tutton salts. Our computation arrives at $\sum_j r_{ij}^{-6} = (9.0 \pm 0.1)\, n^2$, n being the number of ions per unit volume. This result is in accordance with the computation of Daniels [27]). (For comparison we mention that this lattice-sum has the values $8.4\, n^2$, $7.2\, n^2$ and $7.2_5\, n^2$ for respectively s.c., f.c.c. and b.c.c. lattices [5])). In $CuCs_2(SO_4)_2.6H_2O$ one has $g_{//} = 2.43$ and $g_\perp = 2.06$ [28]) and about the same values are found in $Cu(NH_4)_2(SO_4)_2.6H_2O$. This gives $g = 2.20$ for the g-value of the powders.

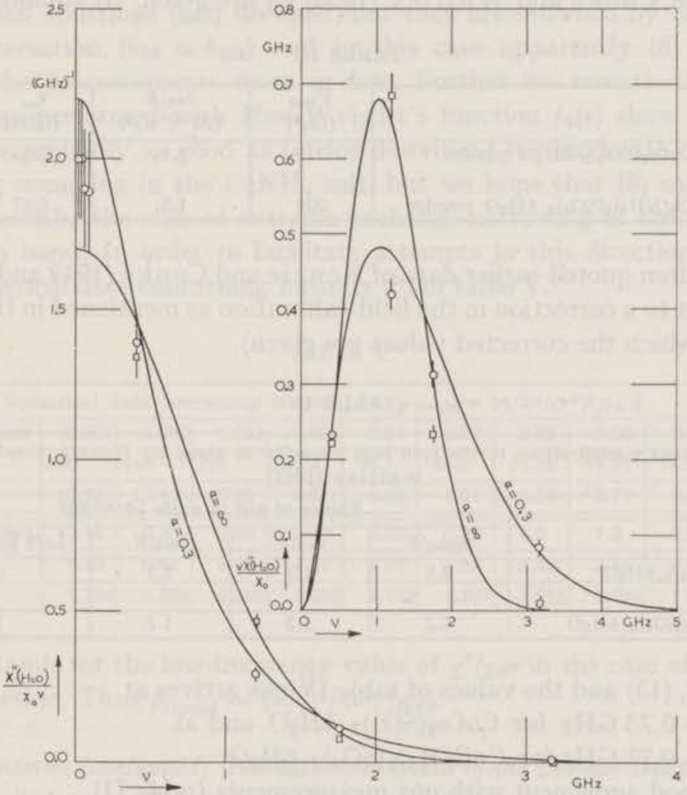

Fig. 12. *a*) Theoretical curves for $\chi''(H = 0)/\chi_0\nu$ according to formula (8) as a function of the frequency ν for $\rho' = 1.7$ (GHz)$^{-1}$ and $\alpha = \infty$ (Gauss function) and for $\rho' = 2.2$ (GHz)$^{-1}$ and $\alpha = 0.3$.

□ $\triangleq$ $CuCs_2(SO_4)_2.6H_2O$ ○ $\triangleq$ $Cu(NH_4)_2(SO_4)_2.6H_2O$

The vertical lines through the measured points indicate the experimental error.

b) The inlay gives the same data, the ordinates being multiplied by ν^2.

With this g-value and with the molar volumes 219 cm³ and 206 cm³ [28]) in the CuCs and the $CuNH_4$ salts respectively, one arrives at the values given in table III.

This is of course in agreement with the values of b_{dd}/R [19]) in table IV (see below).

In part *a*) of reference [31]) Caspers has calculated the contribution of the nuclear hyperfine structure (hfs) to the second moment. In the case of a bilinear form in the components of ***S*** and ***I*** for the hfs-term in the spin-hamiltonian of one single ion he arrives for the total second moment for a powder in zero field at

$$\langle\nu^2\rangle_{H=0} = \nu_{\mathrm{dd}}^2(b_{\mathrm{dd}} + \tfrac{1}{3}b_{\mathrm{hfs}})/b_{\mathrm{dd}}. \tag{14}$$

In table IV the different contributions to the spin heat capacity, as analysed by Benzie, Cooke and Whitley (1955) [19]) are given. (It should be noted that the often quoted earlier data of Benzie and Cooke (1949 and 1950) [18]) are subject to a correction in the field-calibration as mentioned in the (1955)-paper in which the corrected values are given).

TABLE III

	V_{mol} (cm^3)	b_{dd}/R (10^{-4}(°K)^2)	ν_{dd} (GHz)
$CuCs_2(SO_4)_2.6H_2O$ powder	219	1.1_6	0.63
$Cu(NH_4)_2(SO_4)_2.6H_2O$ powder	206	1.3_1	0.67

TABLE IV

The different contributions to the spin heat capacity as given by Benzie, Cooke and Whitley (1955)

	Values of b/R in units 10^{-4}(°K)^2			
	b_{total}/R	b_{dd}/R	b_{hfs}/R	Left for b_{ex}/R
$CuCs_2(SO_4)_2.6H_2O$	2.5	1.2	1.1	0.2
$Cu(NH_4)_2(SO_4)_2.6H_2O$	8.2	1.3	1.2	5.7

With (14), (13) and the values of table IV one arrives at

$\langle\nu^2\rangle^{\frac{1}{2}} = 0.73$ GHz for $CuCs_2(SO_4)_2.6H_2O$ and at

$\langle\nu^2\rangle^{\frac{1}{2}} = 0.77$ GHz for $Cu(NH_4)_2(SO_4)_2.6H_2O$,

in very good agreement with our measurements (table II).

As to $\langle\nu^4\rangle/\langle\nu^2\rangle^2$ we can compare our values in table II only with calculations for a simple cubic lattice and thus we may only expect a rough agreement. Caspers (see reference [31]) under *b*)) has extended Miss Wright's computation by taking the main corrections due to the hfs interaction into account for the case that $b_{\mathrm{ex}} \gg b_{\mathrm{hfs}}$, which corresponds to the $CuNH_4$ salt. He arrives for a powder at

$$\left(\frac{\langle\nu^4\rangle}{\langle\nu^2\rangle^2}\right)_{H=0} = \{0.43A^2 + (2.5 \pm 0.6)\}\left(\frac{b_{\mathrm{dd}}}{b_{\mathrm{dd}} + \frac{1}{3}b_{\mathrm{hfs}}}\right)^2 + \frac{2}{9}\,\frac{b_{\mathrm{hfs}}\,b_{\mathrm{ex}}}{(b_{\mathrm{dd}} + \frac{1}{3}b_{\mathrm{hfs}})^2}\,. \tag{15}$$

The exchange constant A is for a s.c. lattice related to the b's by $b_{\mathrm{ex}}/b_{\mathrm{dd}} = 0.36\,A^2$, so A^2 can be computed from the values of B.,C. and W. (table IV).

Then (15) can be applied, the result being $(\langle\nu^4\rangle/\langle\nu^2\rangle^2)_{H=0} = 5.0 \pm 0.4$ for the $CuNH_4$ salt. This is in excellent agreement with the experimental value $(\langle\nu^4\rangle/\langle\nu^2\rangle^2)_{H=0} = 5.2 \pm 0.6$ (see table II), although this could hardly be expected.

Formula (15) can not be expected to give a good result for the CuCs salt, terms of the order b_{hfs}^2 being neglected in the computed value of $\langle\nu^4\rangle$.

At the end of this discussion of the zero-field measurements we want to remark that (8) has been introduced for the case of no zero-field splittings. In fact such splittings (hfs) do exist, but they are drowned by the dipole-dipole interaction ($b_{\text{dd}} \approx b_{\text{hfs}}$) and in this case apparently (8) can still describe the measurements more or less. Further we remark that some calculations performed with Miss Wright's function $f_4(\nu)$ show that this function is probably as good as (8) for describing the moderate exchange-narrowing occurring in the $CuNH_4$ salt, but we hope that (8) can also be used to describe the case of extreme exchange-narrowing of the zero-field absorption band. In order to facilitate attempts in this direction we give some numerical data concerning formula (8) in table V.

TABLE V

Numerical data concerning formula (8). $\rho'_{\text{Gauss}} = (\pi/2)^{\frac{1}{2}}/\langle\nu^2\rangle^{\frac{1}{2}}{}_{H=0}$.

α (exact value)	0.001	0.002	0.003	0.005	0.01	0.02	0.03	0.05	0.07	0.10
$\langle\nu^4\rangle/\langle\nu^2\rangle^2$	888	445	297	179.4	90.7	46.6	31.75	19.91	14.83	11.03
$\rho'/\rho'_{\text{Gauss}}$	18.92	13.43	10.98	8.51	6.05	4.31	3.54	2.79	2.39	2.05
α (exact value)	0.15	0.20	0.30	0.40	0.50	0.70	1.0	1.5	2.0	∞
$\langle\nu^4\rangle/\langle\nu^2\rangle^2$	8.10	6.63	5.20	4.49	4.09	3.63	3.32	3.18	3.14	3.00
$\rho'/\rho'_{\text{Gauss}}$	1.734	1.556	1.357	1.250	1.182	1.107	1.055	1.022	1.007	1.000

ρ'_{Gauss} stands for the low-frequency value of $\chi''/\chi_0\nu$ in the case of Broer's Gauss-function. Thus $\rho'_{\text{Gauss}} = (\pi/2)^{\frac{1}{2}}/\langle\nu^2\rangle^{\frac{1}{2}}{}_{H=0}$.

5. *Discussion (continued). Intensity and width of the Larmor lines.* Already much detailed research has been done concerning the shape of the (first) Larmor line in perpendicular fields, for instance by Bleaney, Penrose and Plumpton (1949) [28]) who examined single crystals. Although our main research concerns the parallel and zero-field measurements we shall also discuss our data on the perpendicular field lines in powders in view of their relation to the absorption in zero and parallel fields.

Before considering the different cases separately we shall discuss how the intensity of an absorption line as a function of ν can be derived from the measurements as a function of H. Considering, to begin with, the first perpendicular-field line, cf. the curves for the two highest frequencies in the figures 4 and 7, we see that in the relatively small interval of H where the absorption is almost entirely due to this line, $\chi''/\chi_0\nu$ is (in a good approximation) a function of $\nu - \nu_L$ only. Under this condition it can readily be derived that we have for this intensity:

$$I_{1\perp} \equiv \int_{\nu_L\text{-line}} (\chi''/\chi_0\nu)\,\mathrm{d}\nu = (1/H_L)\int_{H_L\text{-line}} (\chi''/\chi_0)\,\mathrm{d}H. \qquad (16)$$

For the first parallel-field line the same holds (fig. 5) or can be expected to hold (fig. 8) if $\chi''/\chi_0\nu$ is replaced by $\chi''/\chi_{ad}\nu$ and thus

$$I_{1//} \equiv \int_{\nu_L\text{-line}} (\chi''/\chi_0\nu)\,\mathrm{d}\nu = (\chi_{ad}/\chi_0)(1/H_L)\int_{H_L\text{-line}} (\chi''/\chi_{ad})\,\mathrm{d}H. \qquad (17)$$

For the second parallel-field line (at $\nu = 2\nu_L$ or correspondingly at $H = \frac{1}{2}H_L$ in a fixed frequency plot) again the same is expected to be valid if $\nu - \nu_L$ is replaced by $\nu - 2\nu_L$, giving

$$I_{2//} \equiv \int_{2\nu_L\text{-line}} (\chi''/\chi_0\nu)\,\mathrm{d}\nu = (\chi_{ad}/\chi_0)(1/\tfrac{1}{2}H_L)\int_{\frac{1}{2}H_L\text{-line}} (\chi''/\chi_{ad})\,\mathrm{d}H. \qquad (18)$$

For the second perpendicular-field line it can not be said that in a certain region of H $\chi''/\chi_0\nu$ is a function of $\nu - 2\nu_L$ only, its intensity being expected to decrease rapidly with increasing H. The rate of the decrease not being precisely known we shall, at the present stage, merely use the approximate relation for a narrow-line:

$$I_{2\perp} \equiv \int_{2\nu_L\text{-line}} (\chi''/\chi_0\nu)\,\mathrm{d}\nu \approx (1/\tfrac{1}{2}H_L)\int_{\frac{1}{2}H_L\text{-line}} (\chi''/\chi_0)\,\mathrm{d}H. \qquad (19)$$

Of course (16), (17), (18) and (19) can only be applied if the lines are well separated. When this is not the case we shall extrapolate each line into the region of overlap and derive approximate values of the intensities from (16) ... (19).

a) $CuCs_2(SO_4)_2.6H_2O$ in perpendicular fields. At the highest frequency used (3.2 GHz) the intensity of the first line (at $H = H_L = 1032$ Oe, fig. 4) is measured to be $I_{1\perp} = 0.95\ (\pi/2)$. Because of the intensities of the satellite lines this value should be somewhat lower than 1.00 $(\pi/2)$ but in view of the inaccuracy of the measurements (cf. section 2*i*) the 5% deviation can not be identified as such. The intensity of the poorly resolved second line at $\frac{1}{2}H_L = 516$ Oe can only roughly be estimated, giving $I_{2\perp} \approx 0.04\ (\pi/2)$. We may remark, that this is roughly the same value as we shall find later for $I_{2//}$ at 516 Oe where $\chi_{ad}/\chi_0 = 0.15$ and $I_{2//} = 0.15 \times 0.21\ (\pi/2) = 0.031\ (\pi/2)$.

Van Vleck's theory 7) of the line width of the first line in perpendicular fields gives a mean square moment $\langle(\nu - \nu_L)^2\rangle = (3/10)\ \langle\nu^2\rangle_{H=0}$, the factor 3/10 being due to the so-called truncation for the case $H \gg H_i$. If one has Gaussian line shapes, the full width $\Delta\nu$ of the line at half height decreases from $(\Delta\nu)_{H=0} = 2\{(\ln 4)\ \langle\nu^2\rangle_{H=0}\}^{\frac{1}{2}}$ to $(\Delta\nu)_{H\gg H_i} = (3/10)^{\frac{1}{2}}(\Delta\nu)_{H=0}$. Using $\langle\nu^2\rangle^{\frac{1}{2}}_{H=0} = 0.74$ GHz (see section 4) one obtains $(\Delta\nu)_{H\gg H_i} = 0.95$ GHz corresponding to $\Delta H = 308$ Oe ($g = 2.20$). Our measurements (fig. 4) give $\Delta H = 410$ and 390 Oe at 1.76 and 3.18 GHz respectively. For the latter frequency we estimated the increase of ΔH due to the anisotropy of g for the hypothetical case of an isotropic line width, the result being an increase of only 3% of ΔH. We did not examine the field dependence of the contribution of the unresolved hyperfine structure to the line width. We may conclude, nevertheless, that the effect of truncation has qualitatively been confirmed by our measurements. There exists also a rough agreement with the measurements at 9 GHz (3 cm) of Bleaney *e.a.* 28) which give a rather strongly anisotropic line width in single crystals, varying from 260 to 630 Oe in the *ac*-plane.

b) $Cu(NH_4)_2(SO_4)_2.6H_2O$ in perpendicular fields. The zero-field line width obtained from fig. 12*a* is $(\Delta\nu)_{H=0} = 1.14$ GHz. Our measurements (fig. 7) give $\Delta H = 230$ and 185 Oe at 1.76 and 3.17 GHz respectively. This corresponds ($g = 2.20$) to $\Delta\nu = 0.71$ and 0.57 GHz respectively, the latter value being a factor 2 smaller than $(\Delta\nu)_{H=0}$. An estimation of the influence of the anisotropy of g gives that without this anisotropy the factor might have been about 2.6 instead of 2. It is plausible that the decrease of the width is due to the so-called 10/3 effect 29) in the line width when going from $H \ll H_{ex}$ up to $H \gg H_{ex}$ in cases of $H_{ex} \gg H_{dd}$. It should be noted that this effect is not quite the same as the effect mentioned under *a*) for the CuCs salt where $\Delta\nu$ should change by $(10/3)^{\frac{1}{2}}$, although both effects have the same origin (truncation). Again the measurements at 9 GHz 28) agree roughly with our results, the line width varying from 85 to 230 Oe in the *ac*-plane.

The intensity $I_{1\perp}$ is found to be 1.01 $(\pi/2)$ and 0.92 $(\pi/2)$ at 1.76 and 3.17 GHz respectively, the 8% deviation in the last result probably being due to the experimental inaccuracy, which may be somewhat increased above the 5% mentioned in section 2 by the indirect calibration of the 77°K measurement using the 20°K data for this case.

c) Intensities in parallel fields. As mentioned already in the introduction one has in the case of $S = \frac{1}{2}$ in large parallel fields three frequency regions of absorption (exclusively the spin-lattice absorption), namely the low frequency (l.f.) or Kronig-Bouwkamp relaxation band, (which has been studied experimentally by Verstelle 21) and theoretically by Caspers 14) and with which our present experiments are not directly concerned) and the first and the second Larmor line. We shall denote the intensity of the l.f. band by

$$I_{\text{l.f.}//} = \int_{\text{l.f. band}} (\chi''/\chi_0\nu)\, d\nu.$$

Caspers has derived in reference 31) that one should expect for a powder:

$$(\chi_0/\chi_{ad})(2/\pi)\, I_{\text{l.f.}//} = (\tfrac{1}{5}b_{dd} + \tfrac{1}{3}b_{hfs} + b_{ex})/b_{total},$$
$$(\chi_0/\chi_{ad})(2/\pi)\, I_{1//} = (\tfrac{2}{5}b_{dd} + \tfrac{2}{3}b_{hfs})/b_{total} \qquad \text{and}$$
$$(\chi_0/\chi_{ad})(2/\pi)\, I_{2//} = \tfrac{2}{5}b_{dd}/b_{total}.$$

TABLE VI

Theoretical and experimental values of the intensities of the three bands in large parallel fields and the related values of $\chi'_{\text{bet}}/\chi_{\text{ad}}$.

	$(\chi_0/\chi_{\text{ad}})(2/\pi)\ I_{\text{l.f.}//}$	$(\chi_0/\chi_{\text{ad}})(2/\pi)\ I_{1//}$	$(\chi_0/\chi_{\text{ad}})(2/\pi)\ I_{2//}$	$\chi'_{\text{bet}}/\chi_{\text{ad}}$
$CuCs_2(SO_4)_2.6H_2O$ powder	th: 0.32 exp: (0.2_5)	th: 0.49 exp: 0.46 (0.51 at 1.76 GHz)	th: 0.19 exp. 0.21	th: 0.68 exp: $0.8_5 \pm 0.1_5$
$Cu(NH_4)_2(SO_4)_2.6H_2O$ powder	th: 0.78 exp: 0.7_6	th: 0.16 exp: $\approx 0.1_7$	th: 0.06 exp:	th: 0.22 exp: 0.3 ± 0.1

Using the b-values from table IV one obtains the "theoretical" values of the intensities given in table VI, where also our experimental values, obtained from the 3.2 GHz measurements (fig. 5 and 8) are given. Moreover the values of χ'_{bet} (*i.e.*: χ' in the frequency region between the l.f. band and the Larmor lines) are given in this table. The theoretical value of χ'_{bet} is related to the intensities by the Kramers-Kronig relations and given by

$$\chi'_{\text{bet}}/\chi_{\text{ad}} = (\tfrac{4}{5}b_{\text{dd}} + \tfrac{2}{3}b_{\text{hfs}})/b_{\text{total}}.$$

The experimental values of $\chi'_{\text{bet}}/\chi_{\text{ad}}$ have already been mentioned in section 3. The experimental values of $I_{\text{l.f.}}$ have been obtained from the measurements of Verstelle [21]) for the $CuNH_4$ salt and from recent measurements of Ten Hove and Verstelle [30]) for the CuCs salt (provisional value). The agreement is satisfactory.

As to the line width of the parallel-field lines we prefer to give the detailed comparison with theory at a later stage (see also the remark at the end of this section). So we shall give the experimental values of the line widths without discussion. For the CuCs salt the 3.2 GHz measurement (fig. 5) gives for the first (H_{L}) line $\Delta H = 305$ Oe, corresponding to $\Delta\nu = 0.94$ GHz, while about the same value is determined from extrapolation of the partly resolved H_{L}-line at 1.76 GHz. The second ($\frac{1}{2}H_{\text{L}}$) line has a width of 225 Oe, corresponding to $\Delta\nu = 1.39$ GHz, at 3.2 GHz. (*N.B.*: $2\pi\Delta\nu = 2\gamma\Delta H$ for the second line whereas $2\pi\Delta\nu = \gamma\Delta H$ for the first line). The shape of the lines can be described reasonably well by Gauss functions. Taking the experimental values of the width and of the intensity, these functions have been plotted for $H = 600$ Oe as a function of the frequency in a log scale in fig. 13, in which the low frequency band has provisionally been indicated [30]). When the field is increased, the l.f. band (fig. 13) shifts rapidly to lower frequencies [30]) and the Larmor lines shift of course to higher frequencies, while these latter lines become higher and narrower in this graph, because of the method of plotting, if at least $\Delta\nu$ is constant under field variations. The area below each line in fig. 13 must remain constant because

$$\int_{\text{line}} (\chi''/\chi_{\text{ad}})\, \text{d}(\ln \nu) = \int_{\text{line}} (\chi''/\chi_{\text{ad}}\nu)\, \text{d}\nu.$$

In the same fig. 13 the bands of the $CuNH_4$ salt at $H = 1500$ Oe are given, the dotted Larmor lines being determined by extrapolation. The width of the first line (at H_L) in the $CuNH_4$ salt can roughly be determined from fig. 8, giving $\Delta H \approx 1.0$ kOe. We suppose that this line is broadened by the exchange. In the $CuNH_4$ salt the l.f. line shifts less rapidly than in the CuCs salt to lower frequencies upon increasing the field [21][30][14].

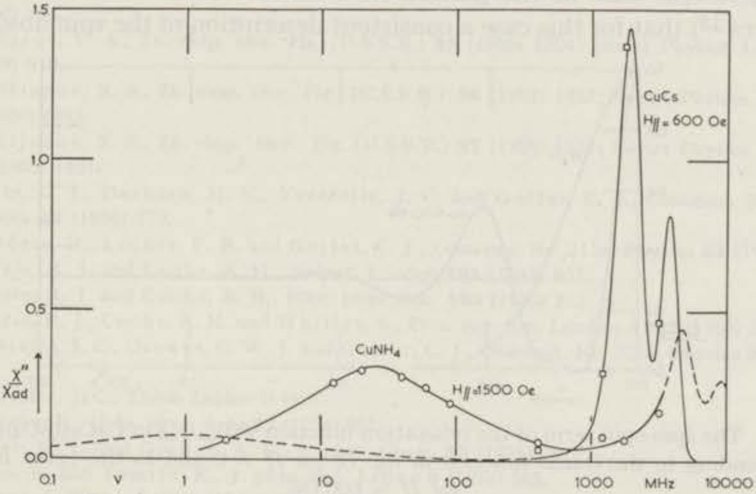

Fig. 13. χ''/χ_{ad} as a function of $\log \nu$. The line for the CuCs salt represents the sum of two Gauss curves fitted through the data (fig. 5). The line for the $CuNH_4$ salt is drawn through the data. The dotted lines give provisional or extrapolated values.

□ $\triangleq$ $CuCs_2(SO_4)_2 \cdot 6H_2O$, $H_{//} = 600$ Oe.
○ $\triangleq$ $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$, $H_{//} = 1500$ Oe.

The relaxation function $\Phi(t)$ (see section 4) generally consists (*e.g.* in our substances at low temperatures) of two separate terms $\Phi(t)_{ss}$ and $\Phi(t)_{sl}$, corresponding to the spin-spin absorption and to the spin-lattice absorption respectively. We have $\Phi(0)_{ss} = \chi_{ad}$ and $\Phi(0)_{sl} = \chi_0 - \chi_{ad}$. For $H = 0$: $\chi_{ad} = \chi_0$ and $\Phi(t)_{sl} = 0$. The spin-spin term $\Phi(t)_{ss}$, corresponding to the Larmor lines of the CuCs salt (fig. 13) has been computed from the data in fig. 13 and plotted in fig. 14. $\Phi(t)_{ss}$ is the sum of two damped cosine functions with respectively $\nu = \nu_L$ and $\nu = 2\nu_L$ and of a constant. The time in which these oscillations die out corresponds to the inverse line widths of the Larmor lines. The decrease from the value 0.3 to zero, corresponding to the Kronig-Bouwkamp (l.f.) band takes such a long time that it is not visible in the figure. For comparison the relaxation function for $H = 0$, computed from the Gauss function in fig. 12, has also been indicated in fig. 14.

Dr. A. G. Anderson kindly sent us a research memorandum, dated October 3, 1960, which gives a summary of theoretical work performed by

Hung Cheng on "Spin absorption of solids" at the I.B.M. Research Laboratory, San Jose, California, U.S.A. Hung Cheng's conclusions, given in that memorandum, about the intensity and the second moment of the first and second parallel-field line and of the second perpendicular-field line are in general agreement with our results as far as comparison is permitted. One might make some objections against the method of Hung Cheng for the case of the parallel-field Larmor lines. It is discussed by Caspers [13]) that for this case a consistent description of the spin absorption phenomena is not possible in the framework of standard perturbation methods, on which Hung Cheng's analysis is based. Publication of the theoretical work in a more detailed Research Report has been announced and a more precise confrontation with the experimental data is postponed.

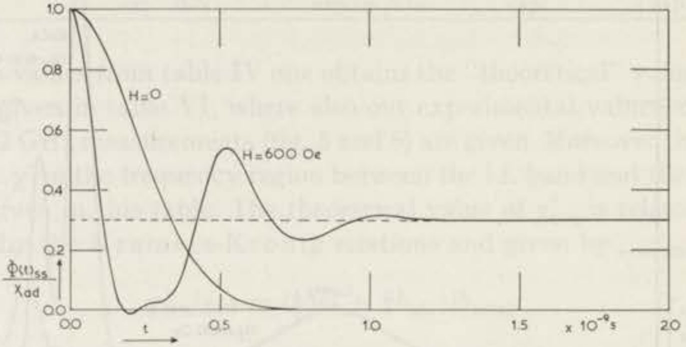

Fig. 14. The spin-spin term of the relaxation function $\Phi(t)_{ss}/\chi_{ad}$ in $CuCs_2(SO_4)_2.6H_2O$, corresponding to the Gauss function in fig. 12 for $H = 0$ and to the curve in fig. 13 for $H = 600$ Oe.

Note added in the proof. The theoretical work of Hung Cheng has recently been published in Phys. Rev. **124** (1961) 1359.

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CHAPTER II

SPIN-SPIN RELAXATIONS AND MAGNETIC RESONANCES IN A SERIES OF HYDRATED PARAMAGNETIC SALTS

Synopsis

The real and imaginary components χ' and χ'' of the paramagnetic susceptibilities of a series of powdered hydrated salts have been measured at frequencies between 0.18 and 3.2 GHz. Not all frequencies were applied to all substances. The measurements were carried out in perpendicular and parallel fields up to 8.2 or 9.5 kilooersted as well as in zero field. Nearly all measurements were performed at 20°K and no influence of spin-lattice relaxation was found.

In $Gd_2(SO_4)_3.8H_2O$, $CrK(SO_4)_2.12H_2O$, $Mn(NH_4)_2(SO_4)_2.6H_2O$ and $FeNH_4(SO_4)_2.12H_2O$ internal electric fields cause splittings which dominate over the dipole-dipole interaction or are at least of the same order of magnitude. Apart from a few indications in the chromic alum, the frequencies were not sufficiently high to resolve the structure of the energy levels. In perpendicular fields a clear satellite at zero frequency was found in some cases (fig. 3-5 and table III). In high parallel fields Kronig-Bouwkamp relaxations were found (figs. 3-2 and 5-2).

In $MnCl_2.4H_2O$, $CuSO_4.5H_2O$ and $CuCl_2.2H_2O$ exchange interaction is dominant. In perpendicular fields and in zero field Lorentz and Debije shapes (figs. 8-2 and 9-1) were found respectively. The available theoretical expressions for the exchange-narrowed line widths only permit a rough comparison with the observed widths. In the case of $CuSO_4.5H_2O$ there is a clear discrepancy, which may be due to the marked difference between the two copper sub-lattices, to which Miedema, Van Kempen, Haseda and Huiskamp attracted attention in connection with their observations below 1°K. The available parallel fields were not sufficiently high to permit observation of the Kronig-Bouwkamp relaxations. In agreement with the expectation, no parallel-field resonances were observed.

While Shaposhnikov's prediction for the dependence of χ'' at low frequencies on a parallel field gives in some cases satisfactory agreement with the data, this is not so in the presence of third relaxation, Kronig-Bouwkamp relaxation or when there is a strong exchange interaction.

1. *Introduction.* In addition to investigations (ch. I) on the high-frequency susceptibilities χ' and χ'' of $CuCs_2(SO_4)_2.6H_2O$ and $Cu(NH_4)_2(SO_4)_2.6H_2O$ and of the influence on them of perpendicular and parallel magnetic fields, similar measurements have been carried out on powders of a number of other hydrated paramagnetic salts.

The range of frequencies (0.41 to 3.2 GHz) has been extended at the low frequency side by 0.18 GHz and so the gap with the absorption measurements carried out by the calorimetric method, which go up to 0.09 GHz, has almost been closed. The choice of frequencies at which a substance has been investigated was, in a few cases, rather incidental and some of the earlier results, the accuracy of which was inferior to the data that were later obtained, have not been used or been used only qualitatively.

While in the copper Tutton salts there was no electric splitting ($S = \frac{1}{2}$), the electric splittings in $Gd_2(SO_4)_3.8H_2O$, $CrK(SO_4)_2.12H_2O$, $Mn(NH_4)_2(SO_4)_2.6H_2O$ and $FeNH_4(SO_4)_2.12H_2O$ are larger than the broadening due to dipole-dipole and exchange interaction between the magnetic ions or at least of the same order of magnitude. But only in the chromium potassium alum the electric splittings dominate to such an extent that irregularities due to a beginning resolution of the spectral lines are noticeable and that the so-called third relaxation phenomena are observed. A study of chromium alums in which the chromium has been diluted by non-magnetic ions would doubtlessly accentuate these two aspects. In the other three salts mentioned the so-called Kronig-Bouwkamp relaxation is observed in large parallel magnetic fields and above the frequencies of this relaxation the susceptibility χ'_{between}, also denoted by $\chi_{\text{is}}^{\text{sm}}$ 18), can be clearly detected. This susceptibility χ'_{bet} is approximately equal to the contribution of the non-diagonal elements of the magnetic moment of one single ion in the combined electric and external magnetic fields *), if the electric splittings dominate over the dipole-dipole interaction. In this case, χ'_{bet} has a simpler physical meaning than in cases of no electric splittings such as in the copper salts in which the dipole-dipole interaction is essential for χ'_{bet}. Hyperfine structure is only an important complicating factor in the manganese Tutton salt.

In the three other investigated salts, $MnCl_2.4H_2O$, $CuSO_4.5H_2O$ and $CuCl_2.2H_2O$ the exchange interaction is dominating in an even more pronounced way than this was the case in $Cu(NH_4)_2(SO_4)_2.6H_2O$. In zero field and in perpendicular fields Debije and Lorentz curves are found respectively. As to the widths of these curves it should be stressed that the available theoretical computations are not sufficient to permit an accurate comparison with the data obtained. Special attention to the theoretical computations is given in section 7. In parallel fields no resonance lines are found. This should be ascribed to the domination of exchange over dipole-dipole interaction. Study of the Kronig-Bouwkamp relaxation in these salts would require larger fields than the 9.5 kilooersted available to us.

Finally it may be mentioned that at the fields and temperatures used,

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*) The representation of the magnetic moment matrix is here the one that diagonalizes the energy of the ion in the electric and external magnetic fields.

paramagnetic saturation as well as deviations from Curie's law can be neglected apart from the latter effect for $MnCl_2.4H_2O$. This is a marked simplification in comparison with research on these phenomena at liquid helium temperatures.

2. *Experimental methods.* The greater part of the experimental results given in this chapter have been obtained by the method described in I. This concerns the measurements at the frequencies 0.41, 1.21, 1.76 and 3.2 GHz. The resonant cavities used for these frequencies consist of a rectangular outer conductor and of a strip inner-conductor, which is fixed to the bottom of the cavity and is unconnected at the upper side. These cavities are used in the lowest TEM-mode, the strip-length being approximately a quarter wavelength. We have used a transmission method for which the details have been given in I.

We have constructed a similar cavity for a frequency as low as 0.18 GHz ($\lambda = c/\nu = 167$ cm). The strip-length is 28 cm and the value of 0.18 GHz for the resonant frequency is obtained by filling the cavity with polystyrene. Using powdered samples a filling factor $q = 0.11$ could be obtained and at 20°K the loaded quality factor is $Q_\infty \approx 1400$. It will be clear that this is approximately the lowest frequency at which this type of cavity can be used in low temperature work. The nice fit in fig. 9-1 (section 9) of the points with the drawn lines (calculated from the Lorentz line-shape formulae (7.3) and (7.4)) gives a check on the experimental method used and on the way of deriving absolute values of χ'/χ_0 and χ''/χ_0 from the observations.

Some of the data are early results obtained at 1.33 GHz and a brief discussion of the set-up used will be given. The resonant cavity was cylindrically coaxial, one-half wavelength long. It was coupled magnetically to one silvered german silver coaxial transmission line and a reflection method was used. The coupling loop could be adjusted during the measurements from far undercoupled to slightly overcoupled. For separating the reflected wave from the incident wave we used a coaxial hybrid T. The reflected wave was detected with a silicon crystal detector (nr. 1N21B), used in its square law region, and thus the detected signal is proportional to Γ^2, Γ being the modulus of the complex voltage-reflection-coefficient. For the sake of brevity Γ will simply be called reflection coefficient in the following lines. At a frequency ν and an external static field H, this reflection coefficient will be denoted by $\Gamma_H(\nu)$. Near the cavity resonance frequency ν_r the function $\Gamma_H(\nu)$ is given by

$$1 - \Gamma_H^2(\nu) = \{1 - \Gamma_H^2(\nu_\mathrm{r})\}/\{1 + 4(\nu - \nu_\mathrm{r})^2\, Q_H^2/\nu_r^2\}, \qquad (2.1)$$

if Q_H, the loaded quality factor at the field H, is sufficiently large ($Q_H \gtrsim 100$). Formula (2.1) is analogous to formula (2) in I. In the undercoupled case, which we always used, $\Gamma_H(\nu_r)$ is related to χ'' by

$$\{1 - \Gamma_\infty(\nu_r)\}/\{1 - \Gamma_H(\nu_r)\} = Q_\infty/Q_H = 1 + 4\pi q Q_\infty \chi'', \qquad (2.2)$$

in which the symbol ∞ refers to very large fields H where χ'' is supposed to be zero, and in which q is the filling factor and χ'' is the negative of the imaginary part of the volume susceptibility. In the overcoupled case $\Gamma_\infty(\nu_r)$ and $\Gamma_H(\nu_r)$ change sign. Just as in I the real part χ' of the susceptibility is measured by observing the change of ν_r when varying the field H.

The method of deriving χ'/χ_0 and χ''/χ_0 from the observations is essentially the same as that given in I. Values χ'' in arbitrary units can be obtained (in a good approximation) from the ratios of the reflection coefficients, but for obtaining the values χ''/χ_0 one should measure the reflection coefficients themselves. This could not be done accurately as there were many frequency-sensitive components in the set-up. For instance, the level of total reflection far from cavity resonance could only be determined by extrapolation and then proved to be only 50 to 80% of the detector signal when introducing a total reflection directly on the hybrid T arm by a short-circuit element instead of the cavity. On the other hand, it can be shown that the accuracy of χ''/χ_0 is a few times better than that of the reflection coefficients, if these latter ones are of the order of 0.3 or less. The inaccuracy of the data obtained with the reflection set-up could be estimated by comparison with data of the transmission set-up at the nearby frequency of 1.21 GHz, the latter data having an accuracy of about 5%. In the case of the manganese ammonium Tutton salt and the gadolinium sulphate the older values of χ''/χ_0 were 20% and 25% smaller than would be expected from the newer data with the transmission set-up. In other cases there were no considerable differences. Only in those cases where we did not measure at 1.21 GHz, the older data will be presented and they are estimated to have an accuracy of 20% for the χ''/χ_0 values. The χ'/χ_0 data will have no other systematic errors than those mentioned in chapter I, but the random errors are much greater, due to the poor filling factor, which was another disadvantage of the older set-up. Besides, in large fields the small "empty cavity" effects (compare I section 2f) may have played a rôle in the older set-up. Some more details of this set-up can be found in reference[33]).

We shall now make some other remarks which apply to all our experimental set-ups. We can always measure only the change of χ' and χ'' when the external static field is varied. In I it was argued how χ'/χ_0 and χ''/χ_0 can be obtained from the observations in those cases where spin-lattice relaxation occurs at frequencies that are several orders of magnitude lower than the frequencies with which we are concerned. Futhermore the maximum external field should be of the order of ten times $(b/C)^{\frac{1}{2}}$ in order to be sure that χ' and χ'' disappear in the maximum external parallel field. This maximum field was usually 8.2 kOe, and 9.5 kOe if the measurement was done with the inner dewar vessel only. In the results on χ' and χ'' presented in the following sections, these conditions are not fulfilled for all substances. For instance in gadolinium sulphate and manganese chloride $(b/C)^{\frac{1}{2}}$ is 1.83 kOe and 4.24 kOe, respectively, so that extrapolations to $H_{//} = \infty$ should be made. These have been performed by making graphs of $\Delta\chi'$ and $\Delta\chi''$ as a function of H^{-2} and in the case of the parallel-field absorption also as a function of H^{-4}. For χ'' we can check in the salts of the sections 3, 4, 5 and 6 whether the extrapolations in $H_{//}$ and $H_{\perp}$ yield the same χ''-value (*i.e.*, both $\chi''(H_{//})$ and $\chi''(H_{\perp})$ are expected to disappear in strong fields), but very small differences may also be due to a slight influence of χ' on the χ'' data (compare I section 2g). In the salts of the sections 7, 8 and 9 the extrapolations of χ' and χ'' in parallel fields could not be carried out or are doubtful. In these cases $\chi''(H_{//})$ is obtained by comparison with $\chi''(H_{\perp})$, the latter quantity vanishing in large fields. For $\chi'(H_{//})$ special methods have been used which are described in the sections 7, 8 and 9.

3. $Gd_2(SO_4)_3.8H_2O$. *Results and discussion.* The results of our measurements have been given in the figures 3-1, 3-2 and 3-3. In section 2 we have described how the quantities plotted vertically have been derived from the observations. In addition, we mention that the measurement at 0.180 GHz has been performed with fields up to 9.5 kOe so that the extrapolation to high fields could be carried out adequately. For the case of parallel fields (fig. 3-2) this was done by linear extrapolation of a graph of $\Delta\chi''$ plotted against H^{-4}. After thus having determined the zero-level of χ'', the χ''-values were divided by χ_{ad}. The place and shape of the hump at 5.5 kOe will be modified somewhat if the mentioned extrapolation is made otherwise. The extrapolations in the figs. 3-1 and 3-3 were carried out linearly in a diagram *versus* H^{-2}. The data of fig. 3-2 have been plotted again in fig. 3-4 as a function of log ν.

Spin-lattice relaxation has been observed at several temperatures by De Vrijer 69) 67). His results indicate that at 20°K the absorptions measured by us cannot be due to spin-lattice relaxation within the experimental accuracy. For instance, the absorption measured at 0.180 GHz and $H_{//} = 3$ kOe is ten times as large as would be expected from spin-lattice absorption extrapolated with a Debije curve.

Our data for the zero-field absorption can be compared with the results of Volger 62) and De Vrijer 69) 67) at low frequencies. These are given together with our results in table I.

It would be expected that at low frequencies $(\chi''/\chi_0 < 0.1)$ $\chi''/\chi_0\nu$ is independent of the frequency. The accuracies are such that the results are not in contradiction with this expectation. At higher frequencies $\chi''/\chi_0\nu$ decreases notably and χ''/χ_0 will presumably pass a maximum at about 3

TABLE I

Zero-field absorption in $Gd_2(SO_4)_3.8H_2O$

Reference	Temperature in °K	Frequency in GHz	χ''/χ_0	$\chi''/\chi_0\nu$ in $(GHz)^{-1}$
De Vrijer 69)	77 and 90	0.01 and lower		0.3
67)	20			0.28
Volger 62)	77 and 90	0.078	0.028	0.36
Present results	20	0.180	0.062	0.34
	20 and 77	0.418	0.136	0.32_5
	20	1.214	0.28_5	0.23_5
	20	1.761	0.32	0.18_1

or 4 GHz. At still higher frequencies zero-field resonance lines will occur which are perhaps not all completely resolved from the low-frequency absorption band. In connection with this we shall sum up what is known about the zero-field energy levels. Assuming a cubic crystal field, there should be one 4-fold and two 2-fold degenerate levels ($J = S = \frac{7}{2}$), the distances between which could be derived from the value of b/C. About one quarter of the observed value of b/C should be due to dipole-dipole interaction and the remaining part to the zero-field splittings, if the reasonable supposition is made that contributions from exchange and hyperfine interaction can be neglected. Van Dijk and Auer 26) even derived from their results which level might be lowest, their values of the levels being $-\frac{7}{16}\delta$, $-\frac{1}{16}\delta$ and $\frac{9}{16}\delta$ with $\delta/hc = 0.94\,cm^{-1}$. The distances between the pairs of levels would then correspond to the frequencies $28._2$, $17._6$ and $10._6$ GHz. The value of the dipole-dipole field H_i is calculated to be about 1.4 kOe if an estimated value of $7.7\,n^2$ for $\sum_i r_{ij}^{-6}$ (compare I section 4) is assumed. This value of H_i corresponds to a splitting $\nu_{dd} = g\beta H_i/h = 3.9$ GHz for a splitting factor $g = 2$. This evaluation suggests that a certain separation exists between the resonance lines and the low frequency band. Bogle and Heine 10), however, carried out paramagnetic resonance experiments in the diluted salt $(Gd_{1/200}Sm_{199/200})_2(SO_4)_3.$ $.8H_2O$ (Sm^{3+} behaves like a diamagnetic ion, due to the extremely short spin-lattice relaxation time) and found that the crystal field is not purely cubic so that there are four twofold-degenerate levels in zero field. From the crystal field parameters $b_2^0 = (+)\ 0.0633\,cm^{-1}$, $b_2^2 = (+)\ 0.038\,cm^{-1}$ and $b_4^0 = (-)\ 0.0013\,cm^{-1}$ (the value of b_2^0 is the corrected value given by Bowers and Owen 11)) the zero-field levels can be calculated 11)), giving (+) 0.44, (+) 0.10, (−) 0.11 and (−) 0.42 cm^{-1}. These values are not very accurate since the condition $b_2^0 \gg b_2^2$ used is not well fulfilled. These data would indicate that some of the zero-field bands considerably overlap in the undiluted salt.

With reference to our measurements in perpendicular fields, it can be remarked that the curves in fig. 3-1 do not show maxima. This is in accord with the expectations, since ν_{dd} is considerably larger than our frequencies. At high fields (6 to 8 kOe) resolved lines must be expected to occur at high frequencies but the observed absorption can not merely be the tail of these lines, since $\chi''/\chi_0\nu$ decreases upon increasing frequency (fig. 3-5). This suggests that the observed absorption is mainly due to the zero-frequency satellite line[22]).

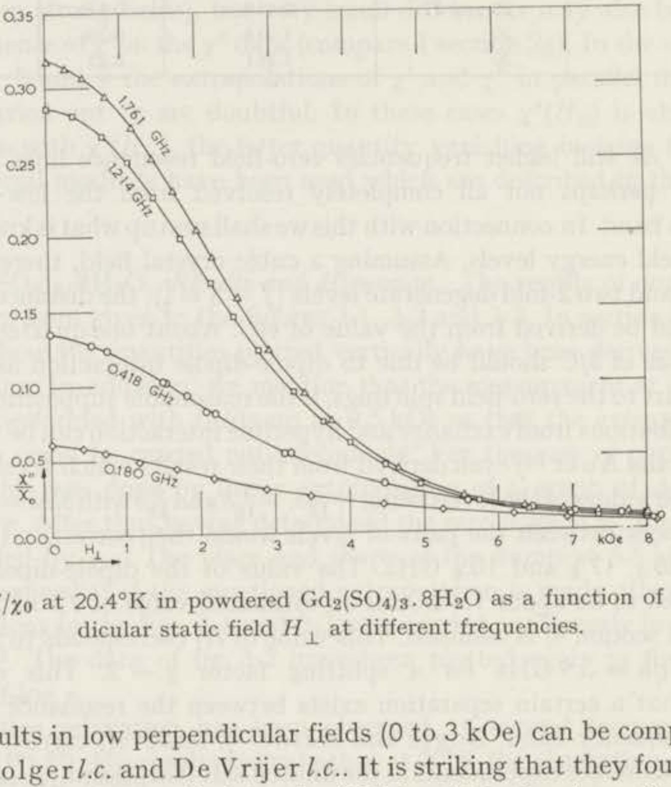

Fig. 3-1. χ''/χ_0 at 20.4°K in powdered $Gd_2(SO_4)_3 \cdot 8H_2O$ as a function of the perpendicular static field $H_\perp$ at different frequencies.

Our results in low perpendicular fields (0 to 3 kOe) can be compared with those of Volger *l.c.* and De Vrijer *l.c.*. It is striking that they found a lower value (1.6 kOe) than we find for the field in which the absorption has one-half the zero-field value (compare fig. 3-5), but this difference might be due to the uncertainty of the correction introduced for the non-magnetic absorption in the data of Volger and De Vrijer.

Finally, considering the results in parallel fields, we remark that their general structure indicates that at 0.180 GHz χ' equals χ_{ad} in low fields. Thus the value of b/C can be derived from our measurement (fig. 3-3), the result being $(b/C)^{\frac{1}{2}} = 1.83$ kOe or $b/C = 3.3_5$ $(\text{kOe})^2$. This value of b/C is somewhat lower than was found by Volger and De Vrijer at 20°K and higher temperatures (3.9 and 3.7 $(\text{kOe})^2$ respectively). We have used our value in calculating χ''/χ_{ad} in the figures 3-2 and 3-4.

In low parallel fields the absorption band shifts towards higher frequencies upon increasing the field as can be seen in fig. 3-4. In accordance with this picture it can be seen from Kurushin's[37]) result at 9.15 GHz and 290°K

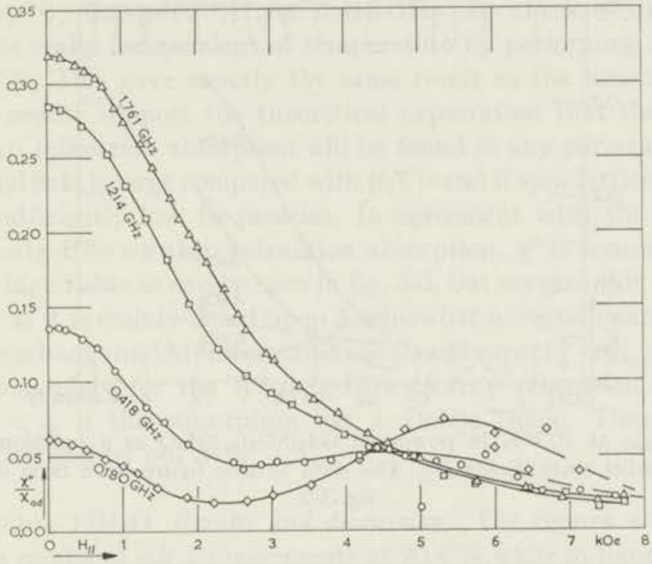

Fig. 3-2. χ''/χ_{ad} at 20.4°K in powdered $Gd_2(SO_4)_3 . 8H_2O$ as a function of the parallel static field $H_{//}$ at different frequencies.

$\chi_{ad} = \chi_0/\{1 + H^2_{//}/(b/C)\}$ with $(b/C)^{\frac{1}{2}} = 1.83$ kOe.

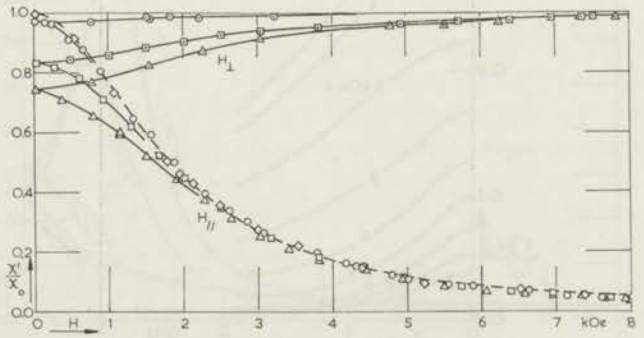

Fig. 3-3. χ'/χ_0 at 20.4°K in powdered $Gd_2(SO_4)_3 . 8H_2O$ as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$ at different frequencies.

◇ ≙ 0.180 GHz, $H_{//}$
○ ≙ 0.418 GHz, $H_{//}$ ⊙ ≙ 0.418 GHz, $H_\perp$
□ ≙ 1.214 GHz, $H_{//}$ ⊡ ≙ 1.214 GHz, $H_\perp$
△ ≙ 1.761 GHz, $H_{//}$ ◬ ≙ 1.761 GHz, $H_\perp$

The dashed line gives $1 - F = \chi_{ad}/\chi_0$; see the caption of fig. 3-2.

that $\chi''/\chi_{\mathrm{ad}}$ increases in low parallel fields and decreases again in fields above 2 kOe. In section 10 we shall consider Shaposhnikov's[50]) formula. The result of Garifianov[29]) at 0.546 GHz and 290°K agrees with our results.

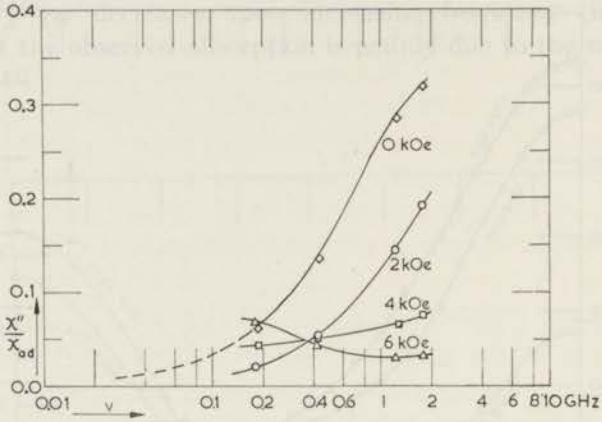

Fig. 3-4. $\chi''/\chi_{\mathrm{ad}}$ at 20.4°K in powdered $\mathrm{Gd_2(SO_4)_3.8H_2O}$ as a function of log ν at different parallel static fields $H_{//}$. The data in this figure have been derived from fig. 3-2.

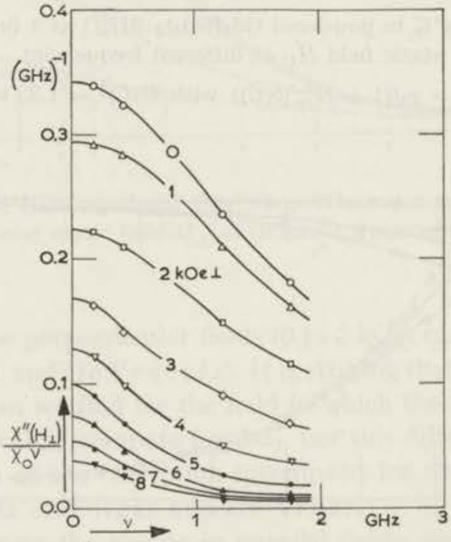

Fig. 3-5. $\chi''/\chi_0\nu$ at 20.4°K in powdered $\mathrm{Gd_2(SO_4)_3.8H_2O}$ as a function of the frequency ν at different perpendicular static fields $H_\perp$. The data in this figure have been derived from fig. 3-1.

In high parallel fields (4 to 8 kOe) a clear hump is observed at 0.180 GHz (mentioned already at the beginning of this section) and to a lesser degree in the 0.418 GHz measurement (fig. 3-2). In fig. 3-4 the same phenomenon is visible in the 6 kOe-line. It is evident that we are here concerned with the Kronig-Bouwkamp relaxation absorption in high parallel fields which shifts towards lower frequencies when the field is increased (Kronig and Bouwkamp[34]); Caspers[19])). At 0.418 GHz we checked whether the absorption is really independent of temperature by performing a measurement at 77°K. This gave exactly the same result as the measurement at 20°K. Our results support the theoretical expectation that the Kronig-Bouwkamp relaxation absorption will be found in any paramagnetic salt if the external field is large compared with $(b/C)^{\frac{1}{2}}$ and if spin-lattice relaxation occurs at sufficiently low frequencies. In agreement with the behaviour of the Kronig-Bouwkamp relaxation absorption, χ' is somewhat lower than χ_{ad} in high fields as can be seen in fig. 3-3, but we give this result with due reserve as it is mainly based upon a somewhat uncertain extrapolation. Neglecting exchange and hfs interaction one should expect $\frac{4}{5} < \chi'_{bet}/\chi_{ad} < 1$ [21]) and correspondingly for the Kronig-Bouwkamp relaxation absorption $(\chi''/\chi_{ad})_{max} < \frac{1}{10}$ if this absorption has a Debije shape. These relations seem to be fulfilled by our data.

4. $CrK(SO_4)_2 . 12H_2O$. *Results and discussion.* The figures 4-1, 4-2 and 4-3 give the results of our measurements at 20.4°K while in figure 4-4 some data obtained at 77.3°K are also given. The data in parallel and zero fields (figs. 4-2 and 4-3) have been plotted as a function of the frequency in the figures 4-5 and 4-6.

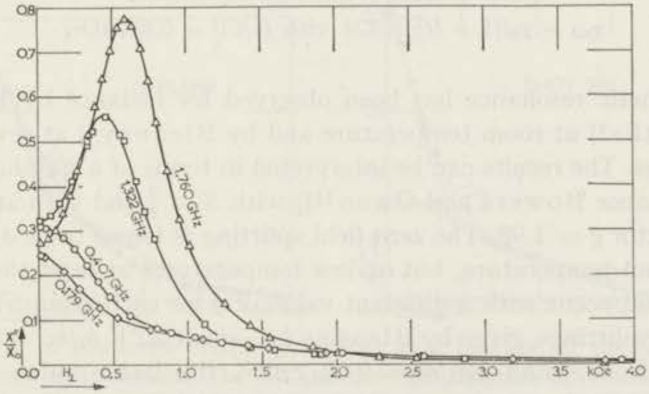

Fig. 4-1. χ''/χ_0 at 20.4°K in powdered $CrK(SO_4)_2 . 12H_2O$ as a function of the perpendicular static field $H_\perp$ at different frequencies.

Within the limits of accuracy, the absorption must be of the spin-spin type only, since spin-lattice absorption occurs at much lower frequencies: near 10^6 Hz at 77°K[27])[16]) and near 10^4 Hz at 20°K[68])[59]). This statement is perhaps not exactly true at 77°K since the spin-lattice relaxation time may be somewhat (by a factor 2 or so) different in different samples. It is, however, not likely that the heat contact between the spins and the lattice can explain the temperature dependence displayed in fig. 4-4. We shall return to this problem below.

A brief summary of previous experimental and theoretical results concerning the spin system in CrK alum will now be given.

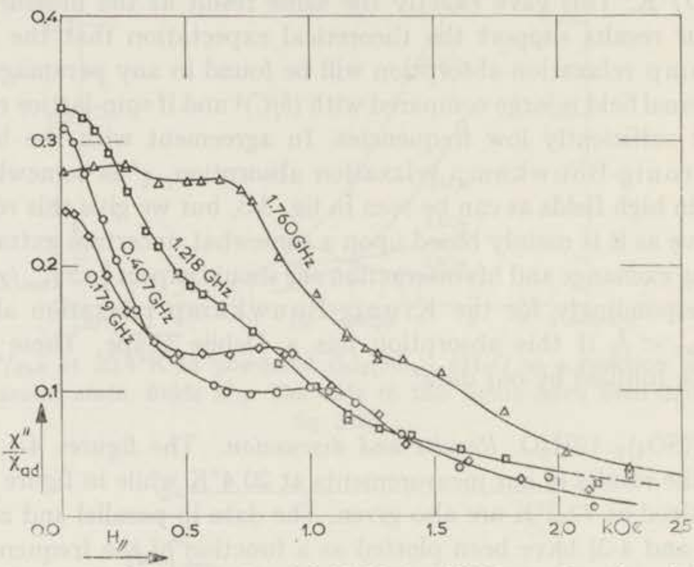

Fig. 4-2. χ''/χ_{ad} at 20.4°K in powdered $CrK(SO_4)_2 . 12H_2O$ as a function of the parallel static field $H_{//}$ at different frequencies.

$\chi_{ad} = \chi_0/\{1 + H_{//}^2/(b/C)\}$ with $(b/C)^{\frac{1}{2}} = 0.82_5$ kOe.

Paramagnetic resonance has been observed for instance by Bagguley and Griffiths[4]) at room temperature and by Bleaney[7]) at several lower temperatures. The results can be interpreted in terms of a spin hamiltonian (see for instance Bowers and Owen[11])) with $S = \frac{3}{2}$ and with an isotropic splitting factor $g = 1.98$. The zero-field splitting is found to be $\delta/hc = 0.12$ cm^{-1} at room temperature, but at low temperatures at least three groups of ions should occur with a different value of δ for each group. The values of the three splittings, given by Bleaney *l.c.*, are at 20°K $\delta_I/hc = 0.27$ cm^{-1}, $\delta_{II}/hc = 0.15$ cm^{-1} and $\delta_{III}/hc = 0.03_5$ cm^{-1}, the latter value being uncertain. At 90°K these values are approximately the same. The fractions of the ions with δ_I, δ_{II} or δ_{III} have been estimated by Beun, Miedema and Steenland[6]) from specific heat and entropy data at very low temperatures, the results being 32%, 42% and 26% respectively. The paramagnetic resonance data of Bleaney indicate that the abundance of the ions with δ_I and δ_{II} decreases with increasing temperature and as a result the percentages should be changed at 77°K. This might explain the temperature dependence in fig. 4-4. In connection with this, we should also mention the data on the optical spectrum by Ancenot and Mrs. Couture[23)] [1)], which indicate a phase transition at 60°K in CrK alum if the salt is cooled slowly. This transition does not occur if the cooling is performed rather rapidly. We do not know whether our salt has been cooled slowly or rapidly in this sense.

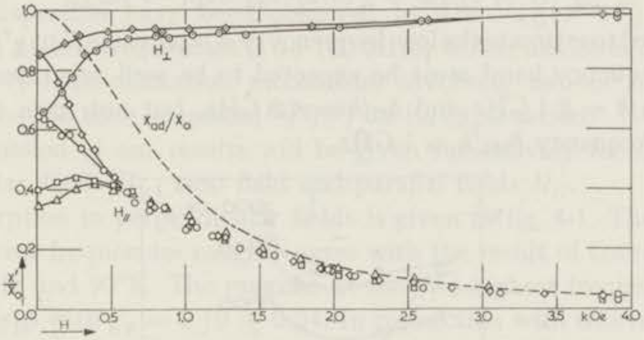

Fig. 4-3. χ'/χ_0 at 20.4°K in powdered $CrK(SO_4)_2 . 12H_2O$ as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$ at different frequencies.

◇ ≙ 0.179 GHz, $H_{//}$ ◇ ≙ 0.179 GHz, $H_\perp$
○ ≙ 0.407 GHz, $H_{//}$ ⊙ ≙ 0.407 GHz, $H_\perp$
□ ≙ 1.218 GHz, $H_{//}$
△ ≙ 1.760 GHz, $H_{//}$

The dashed line gives $1 - F = \chi_{ad}/\chi_0$; see the caption of fig. 4-2.

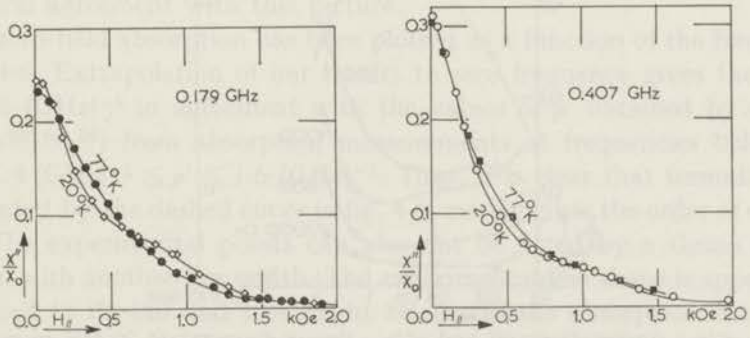

Fig. 4-4. χ''/χ_0 in powdered $CrK(SO_4)_2 . 12H_2O$ as a function of the parallel static field $H_{//}$ at two temperatures. The left and the right diagram have been obtained at 0.179 GHz and 0.407 GHz respectively.

The chromic ions form a face-centered cubic lattice and correspondingly the dipole-dipole field of CrK alum is calculated to be $H_i = 298$ Oe. This corresponds to a frequency $\nu_{dd} = g\beta H_i/h = 0.825$ GHz (if for g the value 1.98 is taken), giving the order of magnitude of the line widths.

In zero field one should expect[13)] [14)][15)] for $\chi''/\chi_0\nu$ a band near zero frequency with an intensity $\int_{0\text{-band}} (\chi''/\chi_0\nu)\, d\nu = \frac{3}{5}(\pi/2)$ and bands at the frequencies δ/h, having together the remaining intensity $\frac{2}{5}(\pi/2)$. In connection with our experimental results we are mainly interested in the low-frequency band but unfortunately no theoretical expectations have been given about the shape and width of this band, this problem being more difficult than ordinary line-width theory. Broer14)15) suggested that the expression

$$\chi''(H=0)/\chi_0\nu = \tfrac{3}{5}\,(\pi/2)^{\frac{1}{2}}\,\nu_{\mathrm{dd}}^{-1}\exp(-\nu^2/2\nu_{\mathrm{dd}}^2) \tag{4.1}$$

might be used to estimate the low-frequency ($\nu \ll \nu_{\mathrm{dd}}$) value ρ' of $\chi''(H=0)/\chi_0\nu$. The low-frequency band must be expected to be well separated from the bands at $\delta_{\mathrm{I}}/h = 8.1$ GHz and $\delta_{\mathrm{II}}/h = 4.5$ GHz, but not from that at the uncertain frequency $\delta_{\mathrm{III}}/h \approx 1$ GHz.

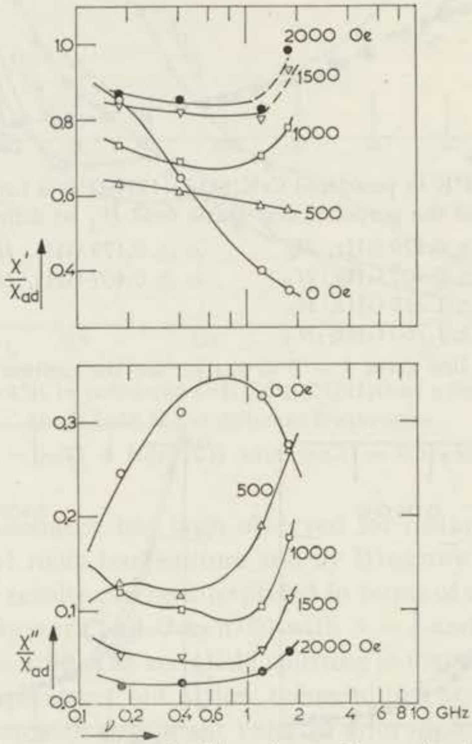

Fig. 4-5. χ'/χ_{ad} (upper diagram) and $\chi''/\chi_{\mathrm{ad}}$ (lower diagram) at 20.4°K in powdered $\mathrm{CrK(SO_4)_2 \cdot 12H_2O}$ as a function of log ν at different parallel static fields $H_{//}$. The data in this figure have been derived from the figures 4-2 and 4-3. The lines have been drawn through the points; in the lower diagram also the data of Verstelle below 0.1 GHz have been taken into account for drawing the lines.

In fields that are large compared with H_{i} and with $\delta/g\beta$ one should expect Kronig-Bouwkamp relaxation absorption at low frequencies34) 19) and parallel-field resonance lines at high frequencies. In the intermediate frequency-range, where we performed our measurements, χ' should equal

$\chi'_{\text{bet}} = \frac{4}{5}\,\chi_{\text{ad}}$ in a powder, if hyperfine and exchange interactions can be neglected. It is known[11]) that the hyperfine structure is small and is present only in ^{53}Cr which has a natural abundance of 9.5%. There are no indications for an appreciable exchange interaction. The Kronig-Bouwkamp relaxation absorption has not yet been found in CrK alum but in $CrNH_3CH_3$ alum there are experimental indications for it[52]) *).

At relatively low parallel fields (between H_i and $\delta/g\beta$) anomalous absorption and dispersion have been observed by De Vrijer[68]) [67]) and Verstelle[52]) [59]) at low frequencies (1 to 100 MHz) which has been called third relaxation. A cross-relaxation mechanism involving two or more neighbouring spins has been suggested[57]) [9]) [20]) for its explanation.

The discussion of our results will be given successively for the cases of perpendicular fields $H_\perp$, zero field and parallel fields $H_{//}$.

The absorption in perpendicular fields is given in fig. 4-1. The results at the two lowest frequencies roughly agree with the result of Garifianov[30]) at 0.545 GHz and 90°K. The maxima at the two highest frequencies occur at fields $h\nu/g_{\text{p}}\beta$ with $g_{\text{p}} = 2.10 \pm 0.04$. In connection with this result of our powder measurements, one should of course remember the considerable anisotropy of the resonance spectrum and the existence of several resolved resonance lines in single crystals. Thus, our results only give average data. In high fields (> 2 kOe) the accuracy is still sufficient for making the conclusion that $\chi''/\chi_0\nu$ at a fixed field $H_\perp$ decreases markedly with increasing frequency. Just as for $Gd_2(SO_4)_3.8H_2O$ this behaviour might be attributed to the zero-frequency satellite line. The early results of Volger[63]) [61]) at 0.078 GHz are in general agreement with this picture.

The zero-field absorption has been plotted as a function of the frequency in fig. 4-6. Extrapolation of our results to zero frequency gives the value $\rho' = 1.6$ (GHz)$^{-1}$ in agreement with the values of ρ' obtained by several authors[63]) [68]) [59]) from absorption measurements at frequencies below 0.1 GHz: 1.4 (GHz)$^{-1} \leqq \rho' \leqq 1.6$ (GHz)$^{-1}$. Thus, it is clear that formula (4.1), represented by the dashed curve in fig. 4-6, merely gives the order of magnitude. The experimental points can also not be fitted by a Gauss shape-function with another line width. The experimental line shape is apparently broadened in its tail and this might be due to the absorption line at the frequency $\delta_{\text{III}}/h \approx 1$ GHz, while the relatively steep fall at low frequencies is perhaps connected with the anisotropy of the splittings of the energy levels near zero field.

The behaviour in parallel fields (figs. 4-2, 4-3 and 4-5) is rather complicated. The hump near 1 kOe in the 0.179 and 0.407 GHz lines in fig. 4-2 is apparently related to the anomalies observed by De Vrijer and Verstelle at lower frequencies but the relation is not quite clear and will not be discussed here

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*) Dr. J. C. Verstelle has informed us that the figures 3 and 4 in reference [52]) have been interchanged.

in detail. At 77°K (fig. 4-4) the humps have disappeared and our results at this temperature agree with the result of Garifianov[30]) at 0.546 GHz and 90°K. The weak humps in the 1.760 GHz line (fig. 4-2) can be attributed to poorly resolved parallel-field resonance lines. In fig. 4-5 it can be seen that at $H_{//} = 2$ kOe the absorption is small in our frequency range. The χ'-data in the same figure indicate, in view of the Kramers-Kronig relations, that the greater part of the absorption at that field has shifted towards higher frequencies (resonance lines) and a small part must be expected to be present at lower frequencies (Kronig-Bouwkamp relaxation). As mentioned already, this Kronig-Bouwkamp absorption has not yet been found separately from the low-field absorptions and it might be that the effect has been overlooked in the early measurements[52]). In high parallel fields (2 to 3 kOe) our results on χ' give $\chi'_{\mathrm{bet}}/\chi_{\mathrm{ad}} = 0.8_5 \pm 0.1$ in accordance with the expected theoretical value $\frac{4}{5}$. In fields of 500 to 1000 Oe χ' is much lower, which must be connected with the mentioned anomalies observed by De Vrijer and Verstelle.

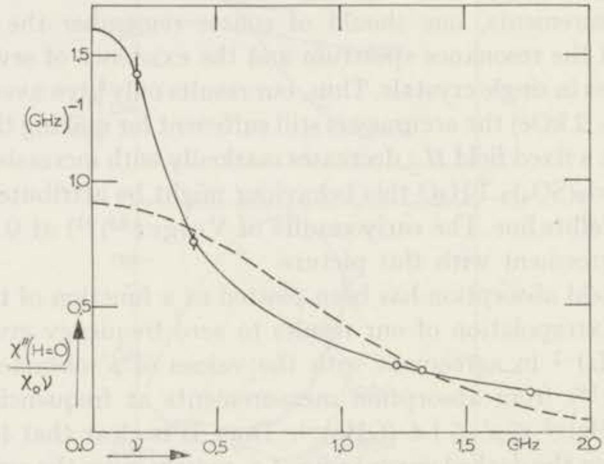

Fig. 4-6. $\chi''(H = 0)/\chi_0\nu$ at 20.4°K in powdered $CrK(SO_4)_2.12H_2O$ as a function of the frequency ν. The solid line is drawn through the points and the dashed line is according to formula (4.1).

Generally, our results should be considered as giving a first orientation and the qualitative behaviour of χ' and χ''. For obtaining more quantitative information, we suggest the examination of powders and single crystals of CrCs alum (or CrRb alum), in which so far only one zero-field splitting has been found in paramagnetic resonance experiments.

5. $Mn(NH_4)_2(SO_4)_2.6H_2O$. *Results and discussion.* The figures 5-1, 5-2 and 5-3 give our experimental results obtained at 20.4°K. The data in zero and parallel fields have been plotted again as a function of the frequency

(logarithmic scale) in fig. 5-4 together with results of Verstelle[43]) [59]) obtained at frequencies below 0.1 GHz.

Just as in Gd sulphate and CrK alum, the absorption must be of the spin-spin type only, since spin-lattice absorption in parallel fields occurs near 10^5 Hz at 77°K and 90°K [54]) [16]) [64]) and near 10^3 Hz at 20°K [17]) [46]).

In two cases, namely for the absorption χ''/χ_0 in parallel fields at 0.409 and 1.772 GHz, we also measured at 77°K; the results agreed with the corresponding data at 20°K.

Before discussing our data we sketch what would be expected from theoretical considerations in combination with previous experimental data concerning the $MnNH_4$ salt.

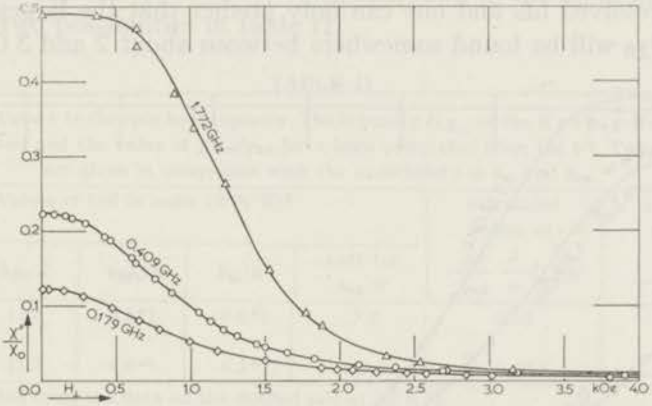

Fig. 5-1. χ''/χ_0 at 20.4°K in powdered $Mn(NH_4)_2(SO_4)_2.6H_2O$ as a function of the perpendicular static field $H_\perp$ at different frequencies.

The leading terms in the spin hamiltonian of one single ion ($S = \frac{5}{2}$) are the Zeeman energy term, the term for the axial crystal field (D-term) and the term for the nuclear ($I = \frac{5}{2}$) hyperfine structure (A-term). Further, there is a weak term for the deviations from axial symmetry (E-term) and a very small term for the cubical part of the crystal field (a-term) [11]). The paramagnetic resonance data in one $MnNH_4$ salt, highly diluted with Zn, could thus be explained satisfactorily by Bleaney and Ingram[8]) and the values of D, E, A and a have been given at 20°K and higher temperatures by these authors. The g-value is found to be 2.000, very near to the free spin value. From the data at 20°K Bleaney and Ingram have calculated the zero-field energy levels. Neglecting the hyperfine structure (hfs) there would be three twofold-degenerate levels at 0.093, −0.016 and −0.077 cm^{-1}. The D-term only ($D/hc = 0.0277\ \text{cm}^{-1}$ *)) would give $(10/3)\ D/hc = 0.092_3$ cm^{-1}, $-(2/3)\ D/hc = -0.018_5\ \text{cm}^{-1}$ and $-(8/3)\ D/hc = -0.073_9\ \text{cm}^{-1}$.

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*) In a discussion of the magnetic behaviour of the undiluted salt at very low temperatures Miedema[48]) arrives at $D/hc = -0.020\ \text{cm}^{-1}$, the main difference with Bleaney's result being the opposite sign of D.

The hfs gives a splitting in three groups of 12 levels each, which groups almost overlap each other as can be seen from fig. 8 in reference[8].

In the undiluted salt, taking the lattice-sum $\sum_j r_{ij}^{-6} = 9.0\, n^2$ for a Tutton salt (see I), the dipole-dipole field can be calculated giving $H_i = 0.65_6$ kOe which corresponds to a frequency $\nu_{dd} = 2\beta H_i/h = 1.84$ GHz and thus $\nu_{dd}/c = 0.061$ cm^{-1}. Taking the D-term only, one would expect zero-field absorption bands to lie near the frequencies 0, $2|D|/h$ and $4|D|/h$, having the intensities $(2/\pi) \int_{\text{band}} (\chi''/\chi_0\nu)\, d\nu = (53/105)$, $(32/105)$ and $(20/105)$ respectively in a powder, as can be calculated analogously to the case $S = \frac{3}{2}$[15]. These bands would overlap in the undiluted salt because of the dipole-dipole interaction. Moreover, the bands will actually be smeared out by the unresolved hfs and one can only predict that the largest values of $\chi''(H = 0)/\chi_0$ will be found somewhere between about 2 and 3 GHz.

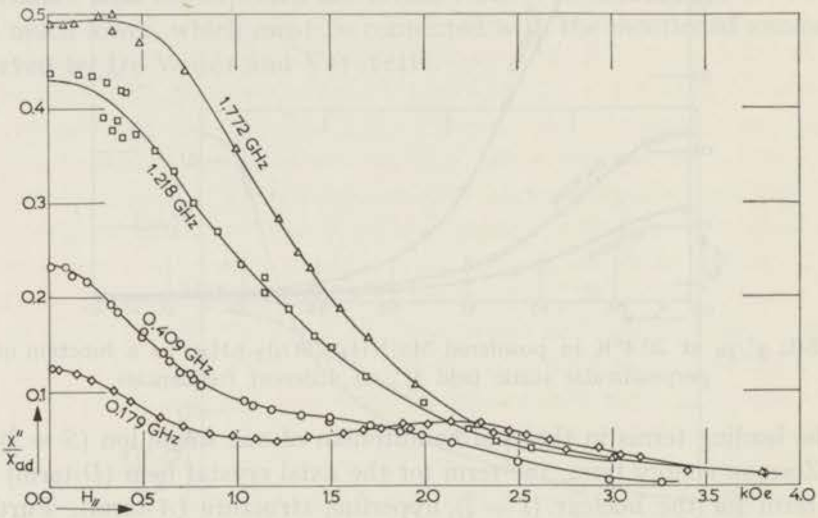

Fig. 5-2. χ''/χ_{ad} at 20.4°K in powdered $Mn(NH_4)_2(SO_4)_2 . 6H_2O$ as a function of the parallel static field $H_{//}$ at different frequencies.
$\chi_{ad} = \chi_0/\{1 + H_{//}^2/(b/C)\}$ with $(b/C)^{\frac{1}{2}} = 0.80$ kOe.

In parallel fields, that are large compared with H_i and with $|D|/g\beta$, the absorption spectrum should have the general character already described in section 4. The low frequency absorption (Kronig-Bouwkamp relaxation) has been found experimentally by Smits *e.a.*[52] [43] [59] and extrapolation of their results to higher frequencies indicates that this band should be observable, though only partly resolved, at our lowest frequency (0.18 GHz). Just as for the Cu Tutton salts (see I) the intensity of the Kronig-Bouwkamp relaxation band, $I_{\text{l.f.}//} \equiv \int_{\text{l.f.band}} (\chi''/\chi_0\nu)\, d\nu$, and the value of $\chi'_{\text{bet}}/\chi_{\text{ad}}$ can be predicted for a powder from the different contributions to the heat capacity per mole of the spin system in zero field. These contributions can be written b_{dd}/T^2, b_{ex}/T^2, b_{el}/T^2 (term due to the electrical crystal field splittings) and b_{hfs}/T^2 at our temperatures. The prediction of $I_{1.f.//}$ and χ'_{bet}/χ_{ad} can readily be made if the a-term (operator $S_x^4 + S_y^4 + S_z^4$) can be neglected. Actually the value of a is found to be only 3% of the value of D in the diluted salt at 20°K 8) and so we do not expect that neglecting the a-term will introduce an appreciable error either in the diluted or in the undiluted salt. One can then write for a powder (compare I):

$$(\chi_0/\chi_{ad})(2/\pi)\, I_{1.f.//} = (\tfrac{1}{5}\, b_{dd} + \tfrac{1}{5}\, b_{el} + \tfrac{1}{3}\, b_{hfs} + b_{ex})/b_{total} \qquad (5.1)$$

and

$$\chi'_{bet}/\chi_{ad} = (\tfrac{4}{5} b_{dd} + \tfrac{4}{5} b_{el} + \tfrac{2}{3} b_{hfs})/b_{total}. \qquad (5.2)$$

The values of b_{el} and b_{ex} are only roughly known in the undiluted salt and so we give two possibilities in table II.

TABLE II

The contributions b to the spin heat capacity. The intensity $I_{1.f.//}$ of the Kronig-Bouwkamp relaxation band and the value of χ'_{bet}/χ_{ad} have been calculated from the b's. Two possibilities are given in connection with the uncertainty in b_{el} and b_{ex}.

Values of b/R in units $10^{-3}(°K)^2$					calculated value of	calculated value of
b_{total}/R	b_{dd}/R	b_{hfs}/R	b_{el}/R	Left for b_{ex}/R	$\frac{\chi_0}{\chi_{ad}} \frac{2}{\pi} I_{1.f.//}$	$\frac{\chi'_{bet}}{\chi_{ad}}$
$33._7$	11.3	4.6*)	10.8*)	7.0	0.38	0.62
$33._7$	11.3	4.6*)	6.2**)	$11._6$	0.49	0.51

*) Calculated from the data on the diluted salt at 20°K 8).

) Calculated from $D/hc = -0.020$ cm^{-1} 48) and from the E-value of the diluted salt at 20°K 8) *).

The values of $I_{1.f.//}$ and χ'_{bet}/χ_{ad} will respectively be somewhat decreased and increased 21) when taking an a-term into account.

Proceeding to the discussion of our data we first consider the absorption in perpendicular fields, given in fig. 5-1. The highest frequency used (1.772 GHz) is slightly lower than ν_{dd} (1.84 GHz) and therefore the qualitative behaviour is not surprising. At the relatively low frequencies 0.179 and 0.409 GHz the absorption coefficients $\chi''/\chi_0\nu$ do not differ very much from the early results of Volger 64) obtained at still lower frequencies as can be seen in table III. The data in large perpendicular fields (≥ 2.4 kOe) in this table give an indication for the existence of a low frequency satellite line, just as in the Gd and Cr salt.

The zero-field absorption data are in accordance with the rough expectation. The zero-field curve in fig. 5-4 will presumably pass a maximum at about 3 GHz and the following descent will be rather steep when plotted *versus* the logarithm of the frequency.

***) The value $b_{ex}/R = 9.1 \times 10^{-3}(°K)^2$ in reference 48) (pg. 67 in the thesis and pg. 257 in Proc. Kon. Acad.) is apparently in error.

TABLE III

Values of $\chi''/\chi_0\nu$ at several frequencies and perpendicular fields in powdered $Mn(NH_4)_2(SO_4)_2.6H_2O$, in units $(GHz)^{-1}$.

$H_\perp$ in kOe / ν in GHz	0.00	0.20	0.40	0.80	1.60	2.40	3.20	4.00
0.011 0.037 0.078 Volger [64])	0.79	0.77	0.58	0.40	0.12	0.05	0.02	
0.179	0.69	0.66	0.58	0.37	0.13	0.05_6	0.03_1	0.02
0.409	0.55	0.54	0.48	0.32	0.10	0.04_1	0.02_3	0.01_5
1.772	0.28	0.28	0.27_5	0.24	0.07_2	0.01_7	0.00_8	0.00_5

In parallel fields (fig. 5-2) the curve at 0.179 GHz has a broad hump, apparently due to the Kronig-Bouwkamp relaxation band, as can be seen from fig. 5-4 in which also the data of Verstelle[43]) [59]) (below 0.1 GHz) have been plotted. In this figure it can also be seen that the low-frequency tail of the parallel-field resonance bands decreases when these bands move towards higher frequencies in large fields. Kurushin[38]) has clearly detected these bands (at $\frac{1}{2}H_L$ and H_L, H_L being the Larmor field $h\nu/g\beta$) in his result at 9.377 GHz and 290°K. The result $\Delta H_{//} = 500$ Oe ($\Delta H_{//}$ is the field at which $\chi''(H_{//})/\chi_0$ has half its zero-field value) of Garifianov[31]) at 0.295 GHz and 90°K agrees with our results. The data on χ' in fig. 5-3 agree with the general picture. At parallel fields of about 3 kOe the value of χ'_{bet}/χ_{ad} can be estimated from fig. 5-3, giving $\chi'_{bet}/\chi_{ad} = 0.7 \pm 0.1$. This is in agreement

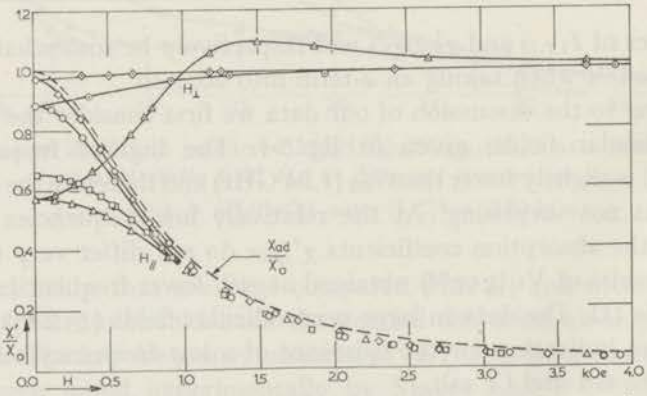

Fig. 5-3. χ'/χ_0 at 20.4°K in powdered $Mn(NH_4)_2(SO_4)_2.6H_2O$ as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$ at different frequencies.

◇ $\triangleq$ 0.179 GHz, $H_{//}$ ◈ $\triangleq$ 0.179 GHz, $H_\perp$
○ $\triangleq$ 0.409 GHz, $H_{//}$ ⊙ $\triangleq$ 0.409 GHz, $H_\perp$
□ $\triangleq$ 1.218 GHz, $H_{//}$
△ $\triangleq$ 1.772 GHz, $H_{//}$ ◬ $\triangleq$ 1.772 GHz, $H_\perp$

The dashed line gives $1 - F = \chi_{ad}/\chi_0$; see the caption of fig. 5-2.

with the value of $I_{l.f.//}$, derived from Verstelle's data: $(\chi_0/\chi_{ad})(2/\pi)\, I_{l.f.//} = 0.2_5$. Comparing this with the calculated values in table II one might conclude that the value $b_{ex}/R = 11._6 \times 10^{-3}(°K)^2$ is too high and that Verstelle's and our data indicate that $b_{ex}/R = 7 \times 10^{-3}(°K)^2$ or an even smaller value give a better agreement. Neglecting the a-term (cubical part of the crystal field) is, as mentioned, perhaps not allowed and therefore our conclusion on b_{ex} is not completely justified.

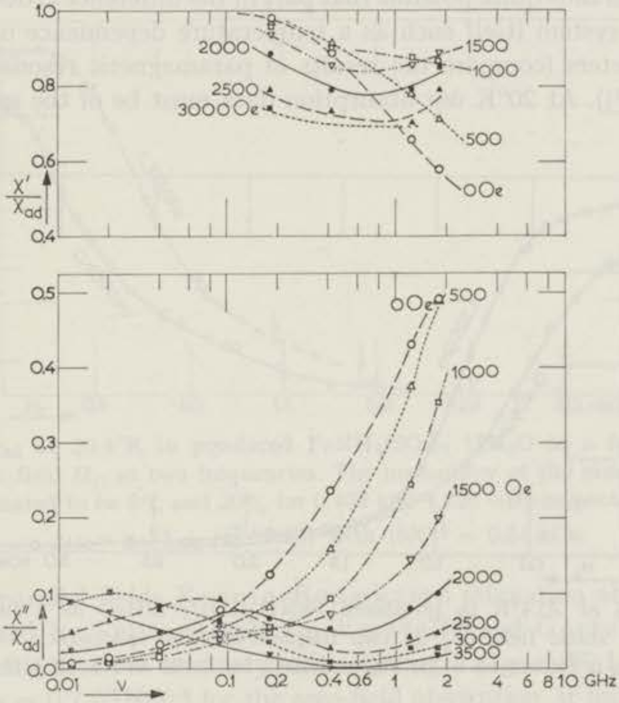

Fig. 5-4. χ'/χ_{ad} (upper diagram) and χ''/χ_{ad} (lower diagram) at 20.4°K in powdered $Mn(NH_4)_2(SO_4)_2.6H_2O$ as a function of log ν at different parallel static fields $H_{//}$. The data in this figure have been derived from the figures 5-2 and 5-3. The points in the lower diagram below 0.1 GHz have been obtained from measurements of Verstelle. The lines have been drawn through the points.

6. $FeNH_4(SO_4)_2.12H_2O$. *Results and discussion.* We have investigated $FeNH_4(SO_4)_2.12H_2O$ at 0.409 and 1.325 GHz only. The results obtained at 20.4°K have been presented in the figures 6-1, 6-2 and 6-3. As mentioned in section 2, the absolute values of χ''/χ_0 at 1.325 GHz might have a systematic error of plus or minus 20%. Also in some other respects the results at 1.325 GHz are less accurate then those at 0.409 GHz as can be seen from the spread of the points.

Spin-lattice relaxation occurs near 10^6 Hz at 77°K[54] and below 10^5 Hz at 20°K[60]. At 0.409 GHz we measured the absorption in parallel fields also at 77°K, which gave slightly larger values of χ''/χ_0 than at 20°K in fields above 500 Oe. The difference has a maximum value 0.01 near 800 Oe and has decreased to about 0.003 in fields of 1500 to 2000 Oe. At first sight one is inclined to attribute this difference to spin-lattice relaxation absorption at 77°K, but extrapolation with a Debije curve of the data of Teunissen and Gorter[54]) gives at 0.409 GHz a maximium spin-lattice absorption of only $\chi'' = 0.003\chi_0$ (roughly at 600 Oe) and an absorption $\chi'' = 0.002\chi_0$ at 1600 Oe. It is thus quite possible that part of the difference is due to a change in the spin system itself such as a temperature dependence of the crystal field parameters (compare the results of paramagnetic resonance in other iron alums[11])). At 20°K our absorption data must be of the spin-spin type only.

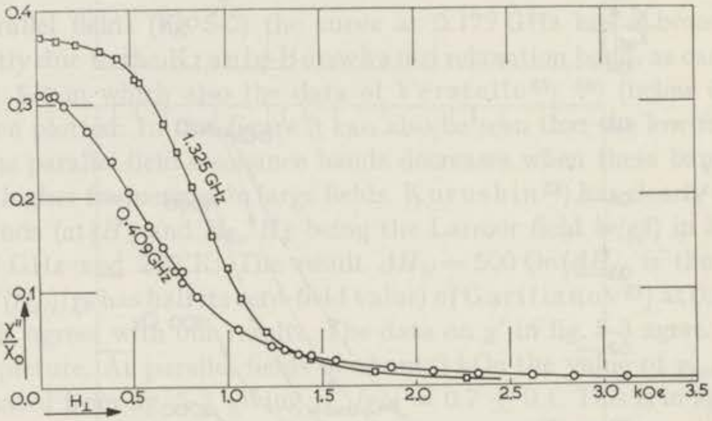

Fig. 6-1. χ''/χ_0 at 20.4°K in powdered $FeNH_4(SO_4)_2 . 12H_2O$ as a function of the perpendicular static field $H_\perp$ at two frequencies. The inaccuracy of the absolute values of χ''/χ_0 is estimated to be 5% and 20% for 0.409 and 1.325 GHz respectively.

$FeNH_4$ alum is in some respects similar to the $MnNH_4$ Tutton salt of the preceding section. In both salts $L = 0$, $S = \frac{5}{2}$ and $2\beta H_i$ is of the same order of magnitude as the zero-field splittings. Differences are, however, the crystal field symmetry, the absence in iron alum of an observable hyperfine interaction (only 2.17% of the iron ions have a nuclear spin $I \neq 0$) and likely also the absence of an appreciable exchange interaction.

The values of the dipole-dipole field H_i and of the corresponding frequency $\nu_{dd} = 2\beta H_i/h$ are calculated to be 445 Oe and 1.25 GHz.

Paramagnetic resonance has been observed by Ubbink, J. A. Poulis and Gorter[55]) in the diluted salt $Fe_{1/80}\,Al_{79/80}\,NH_4(SO_4)_2 . 12H_2O$ and P. H. E. Meijer[47]) could explain these data very well by assuming cubic and axial crystal fields of the same order of magnitude to be present *). As a

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*) It should be noted that Bowers and Owen[11]) have made a mistake when quoting Meijer's value $|c| = \frac{4}{3}\,|D| = 0.016 \pm 0.001\ \mathrm{cm}^{-1}$.

result of the unknown sign of the crystal field parameters, there are two possibilities for the three energy levels in zero field (see Meijer [47])). The first possibility would give zero-field absorption bands near the frequencies 0, 2.1, 2.4 and 4.5 GHz and the second possibility would give bands near 0, 0.9, 3.5 and 4.4 GHz. Some of the bands will of course overlap since $\nu_{dd} = 1.25$ GHz. The calculation of the intensities of the bands would be rather laborious and has been performed only for the simpler case of a pure cubic field [35]).

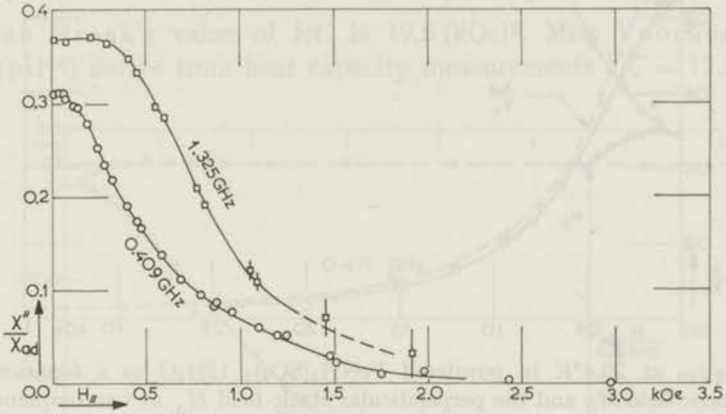

Fig. 6-2. χ''/χ_{ad} at 20.4°K in powdered $FeNH_4(SO_4)_2.12H_2O$ as a function of the parallel static field $H_{//}$ at two frequencies. The inaccuracy of the absolute values of χ''/χ_{ad} is estimated to be 5% and 20% for 0.409 and 1.325 GHz respectively.

$$\chi_{ad} = \chi_0/\{1 + H_{//}^2/(b/C)\} \text{ with } (b/C)^{\frac{1}{2}} = 0.51 \text{ kOe}.$$

In large parallel fields Kronig-Bouwkamp relaxation absorption has been observed by Smits, Derksen, Verstelle and Gorter [52]), the absorptions being given in arbitrary units. Taking Volger's [63]) low-frequency value $\chi''/\chi_0\nu = 0.7$ (GHz)$^{-1}$ for the zero-field absorption, it follows that the maxima of χ''/χ_{ad} have roughly the value 0.06. In case of a Debije curve for the Kronig-Bouwkamp absorption band, one would then expect $\chi'_{bet}/\chi_{ad} = 1 - 2 \times 0.06 = 0.88$, but it is quite possible that this band is somewhat broader than a Debije curve, just as in $Cu(NH_4)_2(SO_4)_2.6H_2O$ and $Mn(NH_4)_2(SO_4)_2.6H_2O$. In that case a lower value would be expected for χ'_{bet}/χ_{ad}. The theoretical value of χ'_{bet}/χ_{ad} in a powder should lie between $\frac{4}{5}$ and 1, if exchange and hfs interaction can be neglected [21]).

In view of the several uncertainties mentioned we shall restrict the discussion of our experimental results to the case of parallel fields. The qualitative behaviour of χ'' and χ' is similar to that of the three salts of the preceding sections, apart from the anomalies in CrK alum at low fields. Again, the main part of the absorption shifts towards higher frequencies upon increasing the field (fig. 6-2). Correspondingly, the data in fig. 6-3 yield $\chi'_{bet}/\chi_{ad} = 0.8 \pm 0.1$, which is in accordance with the rough expectation.

Just as in Kurushin's[38]) observation for $Mn(NH_4)_2(SO_4)_2.6H_2O$ the parallel-field resonance bands have been found qualitatively in $FeNH_4(SO_4)_2.12H_2O$ at 9.3 GHz and 295°K by Kutuzov[40]).

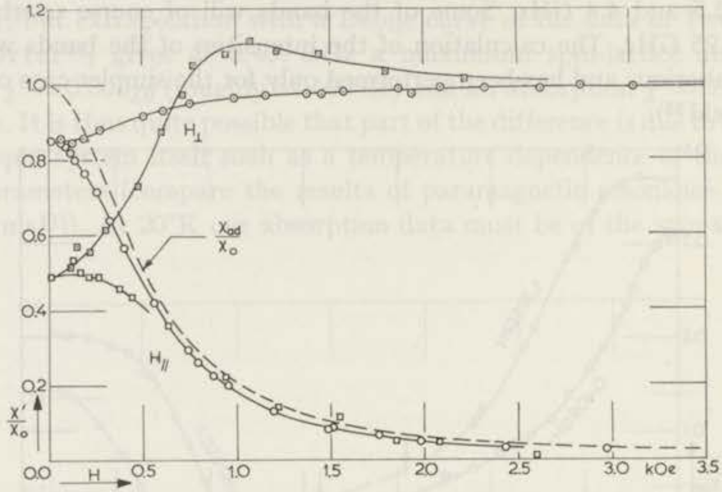

Fig. 6-3. χ'/χ_0 at 20.4°K in powdered $FeNH_4(SO_4)_2.12H_2O$ as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$ at two frequencies.

○ ≙ 0.409 GHz, $H_{//}$ ⊙ ≙ 0.409 GHz, $H_\perp$
□ ≙ 1.325 GHz, $H_{//}$ ⊡ ≙ 1.325 GHz, $H_\perp$

For the fields at which χ''/χ_0 has half its zero-field value Garifianov[30]) has observed $\Delta H_{//} = 480$ Oe and $\Delta H_\perp = 730$ Oe at 0.540 GHz and 90°K. These values are somewhat larger than our corresponding values at 0.409 GHz (20 and 77°K) : $\Delta H_{//} = 330$ Oe and $\Delta H_\perp = 630$ Oe. From interpolation between our different frequencies it follows that the rather serious discrepancy for $\Delta H_{//}$ cannot be attributed to a frequency difference.

7. $MnCl_2.4H_2O$. *Results and discussion. Remarks on exchange narrowing.* $MnCl_2.4H_2O$ has been investigated by us at the frequencies 0.411 GHz (figs. 7-1 and 7-2) and 1.327 GHz. The results of the early measurements at the latter frequency are rather inaccurate and we shall mention them without giving figures. Due to the large value of b/C (strong exchange interaction), we cannot derive the values χ'/χ_0 as easily from the observations as could be done in the salts of the preceding sections. It will be discussed how χ'/χ_0-values have nevertheless been derived from fig. 7-1.

Before doing so, we shall summarize the relevant data from other sources about $MnCl_2.4H_2O$. Below $T_N = 1.62$°K the salt is antiferromagnetic and above 3.5°K the static susceptibility follows the Curie-Weiss law $\chi_0 = C/(T - \Theta)$ with $\Theta = -2.0$°K for the powder[12]), $S = \frac{5}{2}$, $g = 2.0_0$

(isotropic) [32]). Van den Broek *e.a.* [12]) have examined spin-lattice relaxation at liquid helium temperatures and have discussed the relation between χ_{ad} and the heat capacity $C_{\mathrm{M}} = b/T^2$ of the spin system. At $T > 14°\mathrm{K}$ one has in a good approximation:

$$\chi_{\mathrm{ad}}/\chi_0 = (1 + H_{//}^2/H_{\mathrm{h}}^2)^{-1}, \tag{7.1}$$

in which

$$H_{\mathrm{h}}^2 = \{(T - \Theta)/T\}^3\, b/C. \tag{7.2}$$

Van den Broek's value of b/C is 19.5 (kOe)^2. Miss Voorhoeve and Dokoupil [66]) derive from heat capacity measurements $b/C = 17.5$ (kOe)^2.

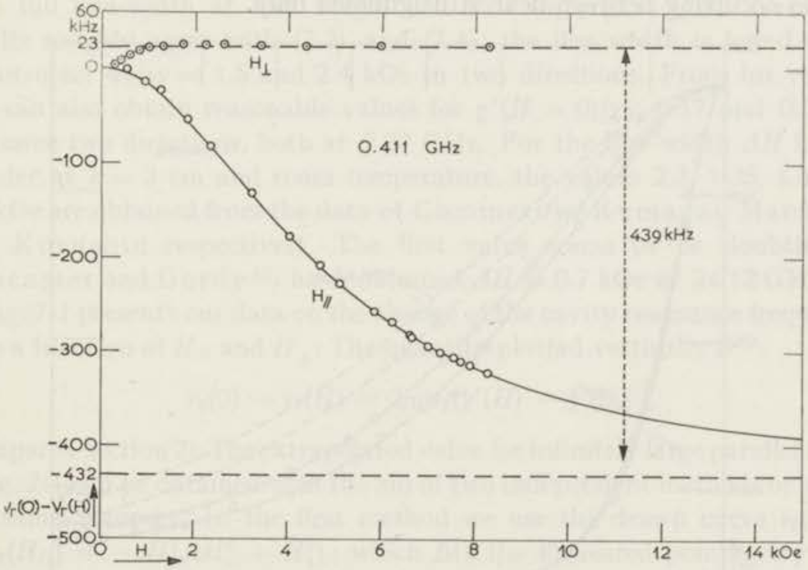

Fig. 7-1. The change $\nu_{\mathrm{r}}(0) - \nu_{\mathrm{r}}(H)$ of the cavity resonance frequency (which is proportional to $\chi'(H) - \chi'(0)$) at 20.4°K and 0.411 GHz in powdered $\mathrm{MnCl_2.4H_2O}$, as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$. The dashed horizontal lines give the extrapolated values for $H_\perp = \infty$ and $H_{//} = \infty$, the latter extrapolation having been made with the aid of the calculated curve (solid line in the figure) $\nu_{\mathrm{r}}(0) - \nu_{\mathrm{r}}(H_{//}) = -cH_{//}^2/(H_{//}^2 + H_1^2)$ with $c = 432$ kHz and $H_1^2 = 23.1$ (kOe)^2. The quantity $\nu_{\mathrm{r}}(H_{//} = \infty) - \nu_{\mathrm{r}}(H_\perp = \infty) = 439$ kHz, derived from other data, has also been indicated in the figure.

The early data of Teunissen and Gorter [54]) and of Starr [53]) are at 77°K: $H_{\mathrm{h}}^2 = 19.5$ and 19.8 (kOe)^2 respectively. Using formula (7.2) this gives $b/C = 18.0$ and 18.3 (kOe)^2 respectively. We shall use an average value $b/C = 18.0$ (kOe)^2. The dashed lines in fig. 7-2 have been computed using this value and the formulae (7.1) and (7.2).

From extrapolation of the data on spin-lattice relaxation of Teunissen and Gorter *l.c.*, the spin-lattice absorption χ'' at 0.411 GHz and 77°K is expected to be at most $0.001\chi_0$ and thus our absorptions certainly are pure spin-spin absorptions.

Taking the lattice sum of a simple cubic lattice of the same density, the dipole-dipole field is found to be $H_1 = 1.37$ kOe and correspondingly $\nu_{\rm dd} = 3.85$ GHz and $b_{\rm dd}/C = 0.94\,({\rm kOe})^2$. The value of $(b_{\rm el} + b_{\rm hfs})/C$ is not known, but it is expected to be relatively small since it amounts only to 0.25 $({\rm kOe})^2$ in $Mn(NH_4)_2(SO_4)_2 . 6H_2O$. The main part of the heat capacity of the spin system should therefore be due to exchange interaction which, as a result, can be estimated to be $H_{\rm ex} \equiv (2b_{\rm ex}/C)^{\frac{1}{2}} = 6$ kOe. Approximately the same value would result from the Curie-Weiss temperature $\Theta = -2.0$°K if the salt would be considered as a simple cubic lattice, exchange interaction occurring between nearest neighbours only.

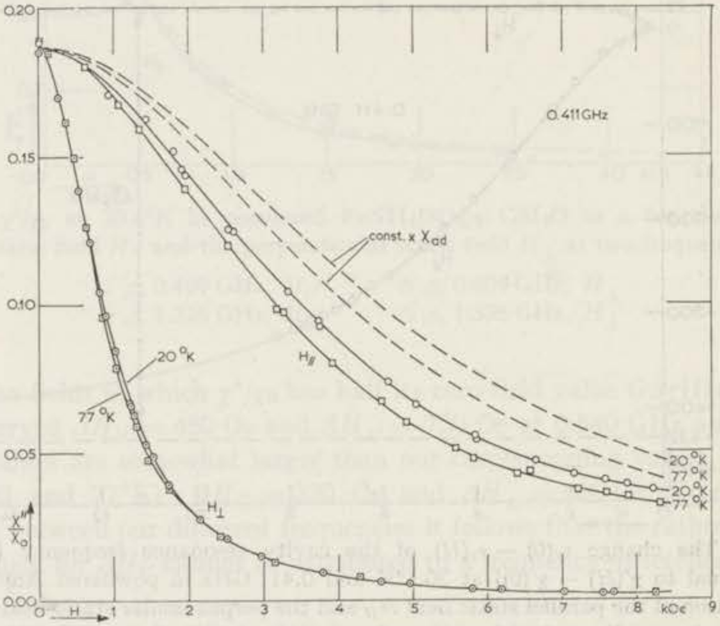

Fig. 7-2. χ''/χ_0 at 20°K and 77°K in powdered $MnCl_2 . 4H_2O$ as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$ at the frequency 0.411 GHz. The dashed lines give $0.187\chi_{\rm ad}/\chi_0$ according to the formulae (7.1) and (7.2) with $(b/C)^{\frac{1}{2}} = 4.24$ kOe and $\Theta = -2.0$°K. The solid lines have been drawn through the measured points.

Paramagnetic resonance at about 9 GHz and room temperature has been observed by Cummerow *e.a.* (1947) 24), Kumagai *e.a.* (1952) 36), Lacroix (1954) 41), MacLean *e.a.* (1955) 45) and Kurushin (1959) 39). The latter author also gives the absorption in parallel fields. The data of Teunissen and Gorter *l.c.* indicate that spin-lattice relaxation plays no rôle at 9 GHz, not even at room temperature. Lacroix has measured both $\chi''(H_\perp)$ and $\chi'(H_\perp)$ and has compared his results with rather artificial Lorentzian line-shape functions. Comparison with the well-known formulae of Kronig, Van Vleck, Weisskopf and Fröhlich for a Lorentzian line shape:

$$\frac{\chi''}{\chi_0 \nu} = \frac{\rho}{2}\left[\frac{1}{1+\rho^2(\nu-\nu_L)^2} + \frac{1}{1+\rho^2(\nu+\nu_L)^2}\right] \tag{7.3}$$

and

$$\frac{\chi'}{\chi_0} = 1 - \frac{\rho\nu}{2}\left[\frac{\rho(\nu-\nu_L)}{1+\rho^2(\nu-\nu_L)^2} + \frac{\rho(\nu+\nu_L)}{1+\rho^2(\nu+\nu_L)^2}\right], \tag{7.4}$$

in which $\nu_L = g\beta H_\perp/h$, might have been preferable. If $\rho\nu \gg 1$, the left hand term in formula (7.3) is dominating near the centre of the line and leeds to a full line-width at half height of $\Delta H = 4\pi/\rho\gamma$ ($\gamma = g\beta/\hbar$). Lacroix' results roughly agree with (7.3) and (7.4); the line width is found to be anisotropic: $4\pi/\rho\gamma = 1.5$ and 2.4 kOe in two directions. From his results one can also obtain reasonable values for $\chi''(H = 0)/\chi_0$: 0.17 and 0.34 in the same two directions, both at 9.39 GHz. For the line width ΔH in the powder at $\lambda = 3$ cm and room temperature, the values 2.3, 1.35, 1.4 and 1.9 kOe are obtained from the data of Cummerow, Kumagai, MacLean and Kurushin respectively. The first value seems to be doubtful⁴⁵). Lancaster and Gordy⁴²) have obtained $\Delta H = 0.7$ kOe at 24.12 GHz.

Fig. 7-1 presents our data on the change of the cavity resonance frequency ν_r as a function of $H_{//}$ and $H_\perp$. The quantity plotted vertically is:

$$\nu_r(0) - \nu_r(H) = 2\pi q \nu_r \{\chi'(H) - \chi'(0)\} \tag{7.5}$$

(compare I section 2). The extrapolated value for infinitely large parallel fields in fig. 7-1 can be obtained with the aid of two independent methods of about the same accuracy. In the first method we use the drawn curve $\nu_r(0) - \nu_r(H_{//}) = -cH_{//}^2/(H_{//}^2 + H_1^2)$ which fits the measured points very well if we choose $c = 432$ kHz and $H_1^2 = 23.1$ (kOe)² (solid line in fig. 7-1). Although deviations from this curve should be expected to occur at high fields (about 15 to 20 kOe) in view of the theoretical value of $\chi'_{\mathrm{bet}}/\chi_{\mathrm{ad}}$ (see below), $\nu_r(0) - \nu_r(H_{//} = \infty)$ may be expected to differ from $-c$ by only a few percent. In the second method we use the relation $\nu_r(H_{//} = \infty) - \nu_r(H_\perp = \infty) = 2\pi q \chi_0 \nu_r$, in which the filling factor q can be obtained by comparison with samples of a number of other salts (compare I section 2h: check about the relative values of q). The result is $\nu_r(H_{//} = \infty) - \nu_r(H_\perp = \infty) = 439$ kHz (see fig. 7-1). This would give $\nu_r(0) - \nu_r(H_{//} = \infty) = -439 + 23 = -416$ kHz. Using the average value $\nu_r(0) - \nu_r(H_{//} = \infty) = -424 \pm 8$ kHz we obtain $\chi'(H = 0)/\chi_0 = 0.948 \pm 0.002$ and $\chi'(H_{//} = 8\ \mathrm{kOe})/\chi_0 = 0.238 \pm 0.014$. This latter result can also be written as $\chi'(H_{//} = 8\ \mathrm{kOe})/\chi_{\mathrm{ad}} = 0.88 \pm 0.08$, if χ_{ad} is taken from the formulae (7.1) and (7.2) with $b/C = 18 \pm 1$ (kOe)² ($H_h^2 = 23.8 \pm 1$ (kOe)² at 20.4°K).

If one tries to fit the measured perpendicular-field absorption in fig. 7-2 with formula (7.3), the best agreement is obtained with $\rho \approx 0.4_5$ (GHz)$^{-1}$ or $4\pi/\rho\gamma \approx 1.6$ kOe, but then the deviations still amount to 10% which is above the estimated inaccuracy of 5%.

At $\nu = 1.327$ GHz we obtained the following results. $\chi'(H = 0)/\chi_0 = 0.75 \pm 0.05$. The absorption $\chi''/\chi_{\mathrm{ad}}$ is in low parallel fields approximately constant and decreases slowly in higher fields to the value $(\chi''/\chi_{\mathrm{ad}})(H_{//} = 8\,\mathrm{kOe}) = 0.8 \times (\chi''/\chi_{\mathrm{ad}})(H = 0)$. The value of $(\chi''/\chi_{\mathrm{ad}})(H = 0) \equiv (\chi''/\chi_0)(H = 0)$ is $0.4_7 \pm 0.1$. The absorption in perpendicular fields is approximately constant from 0 to 0.5 kOe and then decreases in higher fields; at $H_{\perp} = 1.4$ kOe the absorption has decreased to half the zero-field value.

Both our data and the data at about 9 GHz on powdered $MnCl_2.4H_2O$ in zero and perpendicular fields can roughly be described by the formulae (7.3) and (7.4) with $\rho \approx 0.4_5$ (GHz)$^{-1}$ or $\Delta H \equiv 4\pi/\rho\gamma \approx 1.6$ kOe. It is interesting to compare this result with the model of exchange narrowing of Anderson and Weiss[2]) or with the model of the "mixed" curve given by formula (8) in I. Starting from fixed values of the second and fourth moments, our model and that of Anderson and Weiss are found to predict equal results for the width of the approximately Lorentzian line in cases of relatively strong exchange interaction. In the usual notation of Anderson and Weiss, the full line-width at half height is

$$\Delta H = 2 \times (10/3)\, H_{\mathrm{p}}^2/H_{\mathrm{e}} = 2H_{\mathrm{i}}^2/H_{\mathrm{e}} \tag{7.6}$$

if $H_{\mathrm{L}} \ll H_{\mathrm{e}}$. The parameter $H_{\mathrm{e}}(= \omega_{\mathrm{e}}/\gamma)$ is obtained from the relation $\langle(\Delta\omega)^4\rangle/\langle(\Delta\omega)^2\rangle = 3\langle(\Delta\omega)^2\rangle + (\pi/2)\,\omega_{\mathrm{e}}^2$. Using Van Vleck's expressions for the fourth and second moments [56]) in the case of a simple cubic lattice (calculated with the truncated Hamiltonian) one obtains*).

$$H_{\mathrm{e}} = \{2.83\, S(S + 1)\}^{\frac{1}{2}}\, 2J/g\beta, \tag{7.7}$$

and from this the relation

$$H_{\mathrm{ex}} = 1.46\, H_{\mathrm{e}} \tag{7.8}$$

can be derived for this lattice. Miss Wright[70]) calculated the moments for the case of zero field and correspondingly she uses the total instead of the truncated Hamiltonian. Her result for the same simple cubic lattice leads to the relation

$$H_{\mathrm{ex}} = 1.14\, H_{\mathrm{e}}. \tag{7.9}$$

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*) Anderson and Weiss apparently erroneously identified their constant J with Van Vleck's constant $\tilde{A}$. The correct relation is, however, $2J = \tilde{A}$ since the exchange energy between neighbouring spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ is respectively given by $2J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ and $\tilde{A}\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$. All the values of H_{e} in the paper of Anderson and Weiss ought therefore to be multiplied by a factor of 2, which would spoil to a certain extent the agreement between the calculated and the observed line widths.

If both Van Vleck's and Miss Wright's calculations are accurate, the difference between (7.8) and (7.9) indicates that $\langle(\Delta\omega)^4\rangle/\langle(\Delta\omega)^2\rangle - 3\langle(\Delta\omega)^2\rangle$ depends on truncation and a corresponding difference between the Lorentzian line width $\Delta\omega$ at $H = 0$ and at $H_i \ll H \ll H_e$ should occur. In other words: the parameter ρ in the formulae (7.3) and (7.4) would not be accurately constant from $H = 0$ to $H_i \ll H \ll H_e$. Experimentally there are no indications for such a field-dependence of ρ, but one should remember that in practice there are complicating factors, such as the lattice not being simple cubic, the unknown influence of electric splittings and hyperfine structures, anisotropy, and in some cases the line broadening due to the heat contact with the lattice. We shall use here and in the next two sections the average relation

$$H_{\mathrm{ex}} = 1.3\, H_e. \tag{7.10}$$

Using the values $H_{\mathrm{ex}} = 6$ kOe and $H_i = 1.37$ kOe, mentioned at the beginning of this section, we obtain from (7.10) and (7.6) $\Delta H = 0.8$ kOe, which is smaller by a factor 2 than the experimental value. This factor might perhaps be explained by the thus far neglected electric splittings and the hyperfine structure[2]).

Finally, we shall discuss our data in parallel fields. From fig. 7-2 it can be seen that the values $\chi''/\chi_{\mathrm{ad}}$ are little if at all dependent upon the temperature. The absorption band in a $\chi''/\chi_{\mathrm{ad}}$ *versus* log ν graph appears to shift slightly towards higher frequencies when the field is increased from $H = 0$ to $H_{//} = 8$ kOe. The same effect may be derived from Kurushin's data. We do not know an explanation of this effect. It should be expected that in higher fields (> 8 kOe) a relatively strong Kronig-Bouwkamp absorption band moves towards lower frequencies. At 0.411 GHz and 20°K (fig. 7-2) $\chi''/\chi_{\mathrm{ad}}$ seems to increase again from the value 0.13_3 at 6 kOe to the value 0.14 at 8 kOe and this might indicate the beginning of the Kronig-Bouwkamp absorption. Of course χ'/χ_{ad} has not at all reached the value $\chi'_{\mathrm{bet}}/\chi_{\mathrm{ad}}$ at $H_{//} = 8$ kOe. In view of the strong exchange interaction $\chi'_{\mathrm{bet}}/\chi_{\mathrm{ad}}$ should be small, probably of the order 0.2 or 0.1. It would be interesting to perform measurements in fields up to at least 20 kOe.

8. $CuSO_4\,5H_2O$. *Results and discussion.* We have investigated $CuSO_4.5H_2O$ at 0.409 and 1.329 GHz. The results are given in the figures 8-1, 8-2 and 8-3. We shall only give a provisional discussion of these data, postponing a more complete discussion until more data are available.

In contrast with the salts of the preceding sections, it is not known whether at about 20°K the spin-lattice relaxation occurs at frequencies low compared with our frequencies. De Vrijer's observation[67]) that at 11 MHz and 20°K χ' equals χ_0 within 2% in parallel fields up to 4 kOe indicates that this is not so, because it follows from heat capacity data[25]) that

$(b/C)^{\frac{1}{2}} \approx 13$ kOe*) and thus $\chi'(H_{//} = 4\ \text{kOe})$ should have been $0.9\chi_0$ if the spin-lattice relaxation would have occurred below 11 MHz.

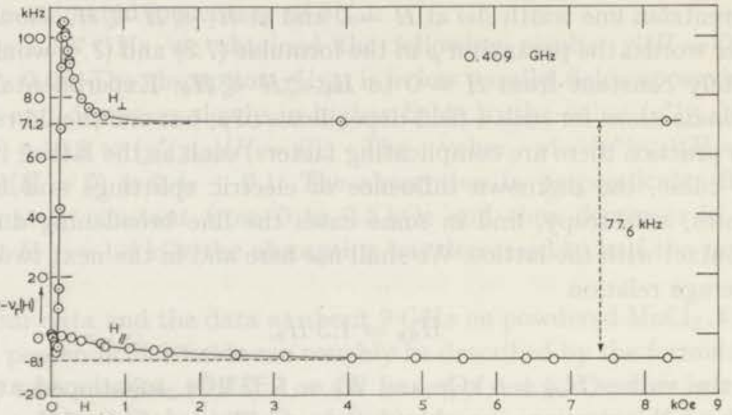

Fig. 8-1. The change $\nu_r(0) - \nu_r(H)$ of the cavity resonance frequency (which is proportional to $\chi'(H) - \chi'(0)$) at 20.4°K and 0.409 GHz in powdered $CuSO_4.5H_2O$ as a function of the parallel static field $H_{//}$ and the perpendicular static field $H_\perp$. The dashed horizontal lines give the extrapolated values for $H_\perp = \infty$ and $H_{//} = \infty$. The solid lines have been drawn through the measured points. The quantity $\nu_r(H_{//} = \infty) - \nu_r(H_\perp = \infty) = 77._6$ kHz, derived from other data, has also been indicated in the figure.

The good fit obtained at 0.409 GHz with formula (7.3) where $\rho = 6.5$ $(\text{GHz})^{-1}$ ($g = 2.2$; $4\pi/\rho\gamma = 100$ Oe) (fig. 8-2) suggests that the zero-field absorption is likely to follow a Debije curve ($\nu_L = 0$ in formula (7.3)) with the same ρ-value. At 77°K the absorption has been found not to differ from that at 20°K (fig. 8-2). The absorption at 1.329 GHz can also approximately be described by formula (7.3), $\Delta H = 4\pi/\rho\gamma$ being about 10% larger, which difference might well be attributed to the anisotropy of g. Volger's 62) 61) perpendicular-field absorptions at 6 to 78 MHz (77 and 90°K) approximately fit formula (7.3) with $4\pi/\rho\gamma = 100$ Oe, apart from the absolute values which are lower by a constant factor 0.65. The absolute values of De Vrijer's 67) zero-field absorption data at 1 to 10 MHz and 20°K are even lower by a factor 0.23 than would be expected from formula (7.3) with $\rho = 6.5\ (\text{GHz})^{-1}$.

Fig. 8-1 is analogous to fig. 7-1. The extrapolated value for $\nu_r(H_{//} = \infty) - \nu_r(0)$ is 8.1 kHz or slightly larger. A smaller value would give a negative sign for χ' at $H_{//} = 5$ to 8 kOe while a considerably larger value would conflict with $\nu_r(H_{//} = \infty) - \nu_r(H_\perp = \infty) = 77._6 \pm 3$ kHz, obtained from a comparison with the samples of a number of other salts (I section 2h). The measured points χ'/χ_0 in perpendicular fields, derived from fig. 8-1,

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*) Volokhova 65) has derived $(b/C)^{\frac{1}{2}} \approx 0.7$ kOe from $\chi''(H_{//})$ at 0.6 GHz, but the method used is subject to serious doubt (see below and section 10; note that $\rho'\nu > 1$ for $\nu = 0.6$ GHz).

approximately fit formula (7.4) with $\rho = 6.1$ (GHz)$^{-1}$, apart from small but distinct deviations below about 100 Oe. For instance, the experimental value in zero field is $\chi'(H=0)/\chi_0 = 0.10 \pm 0.01$, while $1/(1+\rho^2\nu^2)$ equals 0.138 and 0.124 for $\rho = 6.1$ and 6.5 (GHz)$^{-1}$ respectively. A "mixed" curve, according to formula (9) in I, gives a slightly better agreement, if a reasonable value for the exchange parameter α is chosen (0.01).

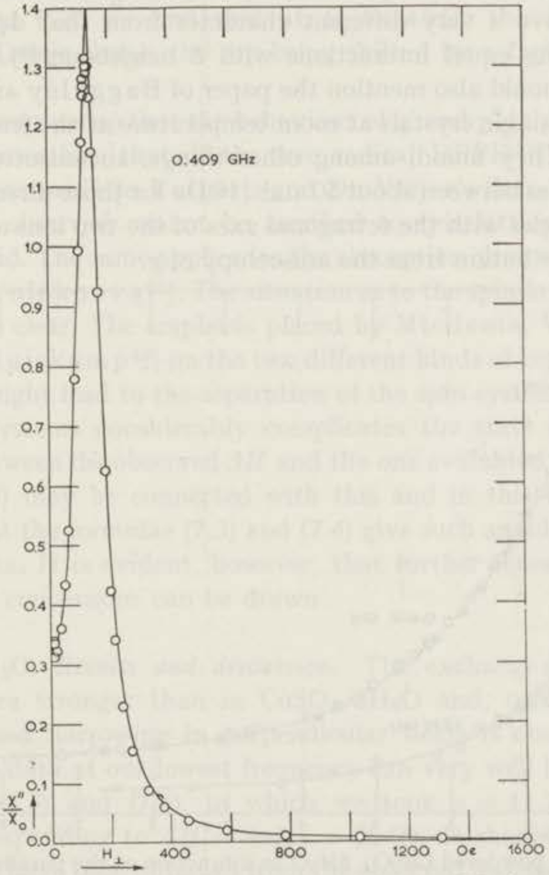

Fig. 8-2. The measured points χ''/χ_0 at 20.4°K and 0.409 GHz in powdered $CuSO_4 . 5H_2O$ as a function of the perpendicular static field $H_\perp$. The line gives the Lorentzian line shape calculated according to formula (7.3) with $g = 2.2$ and $\rho = 6.5$ (GHz)$^{-1}$ (full line-width at half height $\Delta H = 4\pi/\rho\gamma = 100$ Oe).

Supposing the heat contact with the lattice not to contribute to the line width, one may compare the experimental line width $\Delta H = 100$ Oe with the prediction of ΔH obtained from the formulae (7.6) and (7.10) for exchange-narrowing in a simple cubic lattice. Taking the lattice-sum of a s.c. lattice of the same density, the dipole-dipole field is found to be $H_i = 0.40$ kOe. Using further the value $2^{-\frac{1}{2}}H_{ex} \equiv (b_{ex}/C)^{\frac{1}{2}} = 13$ kOe (see above) the calculated line width is $\Delta H = 22$ Oe, which is 4.5 times smaller than the observed value. If the value of the Weiss constant $\Theta = -0.60$°K⁵) is used for estimating the magnitude of the exchange interaction (still using the s.c. lattice model with 6 nearest neighbours), the calculated line width is $\Delta H = 73$ Oe. It is remarkable that this second evaluation gives a much more satisfactory result than that making use of the b/C-value. But it must be kept in mind that in the present case the exchange interactions have a very different character from that described by the model supposing equal interactions with 6 neighbours⁴⁹). In connection herewith, we should also mention the paper of Bagguley and Griffiths³) who measured single crystals at room temperature at the frequencies 10, 24 and 35 GHz. They found, among other things, an anisotropy of the line width: ΔH varies between about 50 and 110 Oe for those directions of $\boldsymbol{H}$ that make equal angles with the tetragonal axes of the two ions and where there is thus no contribution from the anisotropy of g.

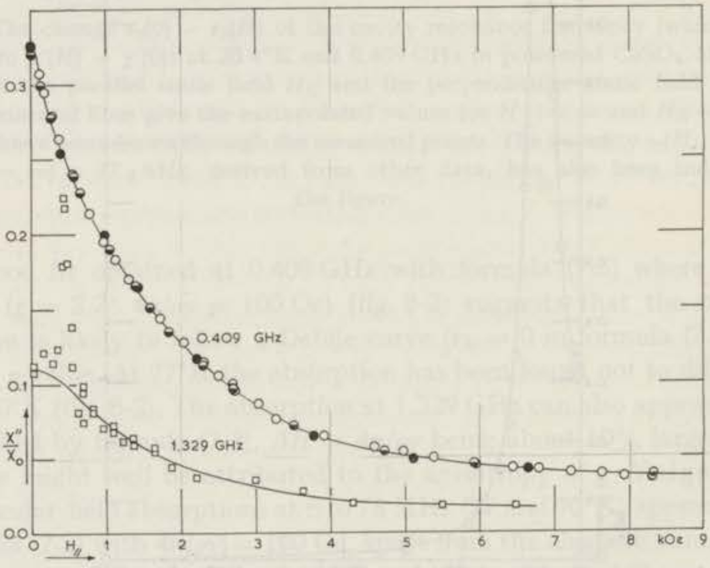

Fig. 8-3. χ''/χ_0 in powdered $CuSO_4.5H_2O$ as a function of the parallel static field $H_{//}$.

● ≙ 0.409 GHz, 77.3°K □ ≙ 1.329 GHz, 20.4°K
○ ≙ 0.409 GHz, 20.4°K
◒ ≙ 0.409 GHz, 14.3°K

The lines have been drawn through the points, neglecting the excess of the points at 350 to 550 Oe in the 1.329 GHz measurement, which is due to deviations from the parallelism of $H_{//}$ and the high frequency field in this early measurement.

Finally we consider the absorption in parallel fields (fig. 8-3). Our result at 0.409 GHz can be compared with those of Volokhova⁶⁵) obtained at 0.6 GHz and 290°K. There seems to be a strong discrepancy but in fig. 1 of Volokhova $\chi''(H_{//} = 2\text{ kOe})$ is assumed to be zero which is certainly not true as can be seen in our fig. 8-3, in which the zero level of the absorption has been derived from χ'' in large perpendicular fields. It was mentioned already that at zero field a Debije-shape absorption may be supposed to occur with a peak at about 160 MHz. In a χ'' *versus* log ν diagram the absorption curve appears to shift towards lower frequencies under the influence of a parallel field. If we correct the absolute values of the absorptions found by Volger[62)][61)] and De Vrijer[67)] upwards according to the mentioned factors 0.65 and 0.23 we find that at $H_{//} = 4$ kOe the absorption still roughly has a Debije shape, the top being shifted by a factor 4.5 towards 35 MHz.

One gets the impression that the behaviour of χ' and χ'' in parallel fields in $CuSO_4.5H_2O$ resembles that of the free radical DPPH[58)][59)]. Regardless of the corrections made to Volger's and De Vrijer's data, it is clear that the absorption observed cannot be ascribed to spin-lattice absorption as these authors did. The same applies for the absorption observed at 10.5 MHz and 290°K by Volokhova[65)]. The situation as to the spin-lattice relaxation is, however, not clear. The emphasis placed by Miedema, Van Kempen, Haseda and Huiskamp[49)] on the two different kinds of copper ions in the lattice which might lead to the separation of the spin system into two very different sub-systems considerably complicates the state of affairs. The discrepancy between the observed ΔH and the one evaluated with the aid of (7.6) and (7.10) may be connected with this and in this light it is even remarkable that the formulae (7.3) and (7.4) give such an adequate description of our data. It is evident, however, that further research is required before definite conclusions can be drawn.

9. $CuCl_2.2H_2O$. *Results and discussion.* The exchange interactions in $CuCl_2.2H_2O$ are stronger than in $CuSO_4.5H_2O$ and, correspondingly, a more pronounced narrowing in perpendicular fields is observed. Fig. 9-1 shows that the data at our lowest frequency can very well be described by the formulae (7.3) and (7.4), in which we took $\rho = 11.7$ $(\mathrm{GHz})^{-1}$ and $g = 2.16$, corresponding to $\Delta H \equiv 4\pi/\rho\gamma = 56$ Oe. It should be noted that the points χ'/χ_0 have been obtained from the observed values $\nu_r(0) - \nu_r(H_\perp)$ by adding such an amount for $\nu_r(H_{//} = \infty) - \nu_r(0)$, and then dividing by $\nu_r(H_{//} = \infty) - \nu_r(H_\perp = \infty)$, that the resulting value for $\chi'(H = 0)/\chi_0$ fits with formula (7.4). It was not possible to measure $\nu_r(H_{//} = \infty) - \nu_r(0)$ because the highest field (8 kOe) remains small compared with the exchange field. Our ρ-value is in good agreement with Verstelle's[59)] value $\rho = 12.0$ $(\mathrm{GHz})^{-1}$, obtained from absorption data at the frequencies 12 to 90 MHz. Verstelle has already remarked (using some of our data) that the zero-field absorption is very close to a Debije curve in the interval 12 to 1800 MHz.

The line width is found to increase with increasing frequency: 58 Oe at 0.415 GHz (at both 20, 77 and 290°K), 70 Oe at 1.326 GHz and 107 Oe at

3.18 GHz. This effect is certainly due to the anisotropy of g. The zero-field absorption still follows a Debije curve with $\rho = 12$ (GHz)$^{-1}$ at 1.77 GHz. For 3.18 GHz a value of $\chi''(H = 0)/\chi_0 = 0.026$ is expected from the Debije curve, whereas we observed (at 20°K) $\chi''(H = 0)/\chi_0 \leq 0.01$. This observation should be repeated.

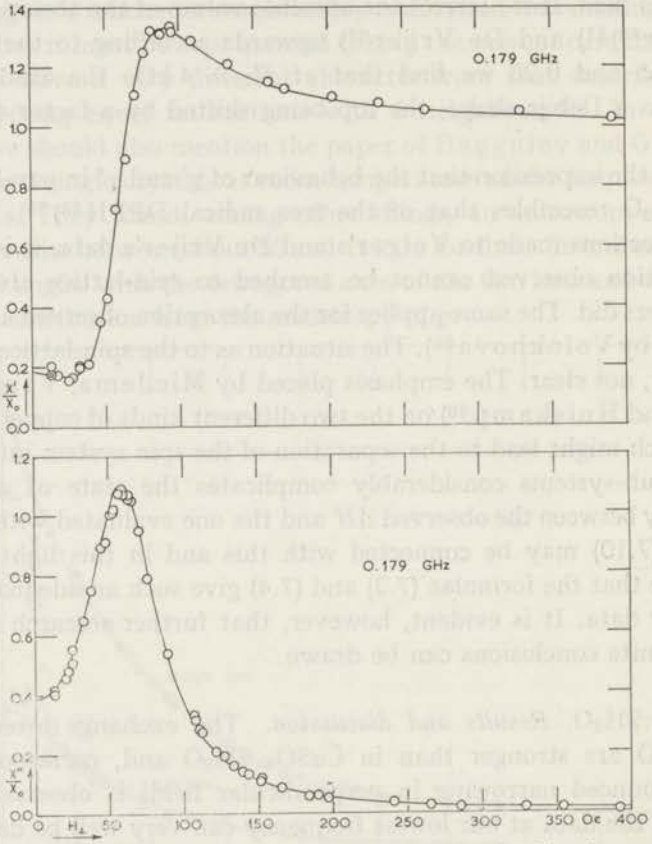

Fig. 9-1. The measured points χ'/χ_0 (upper diagram) and χ''/χ_0 (lower diagram) at 20.4°K and 0.179 GHz in powdered $CuCl_2.2H_2O$ as a function of the perpendicular static field $H_\perp$. The lines give the Lorentzian curves, calculated according to the formulae (7.3) and (7.4) with $g = 2.16$ and $\rho = 11.7$ (GHz)$^{-1}$ ($\Delta H \equiv 4\pi/\rho\gamma = 56$ Oe). The points χ'/χ_0 have been derived from the observations by adding an appropriate amount for $\nu_r(H_{//} = \infty) - \nu_r(0)$ to the observed values $\nu_r(0) - \nu_r(H_\perp)$ (see the text).

In parallel fields up to 8 kOe both χ'' and χ' did not differ from their values at $H = 0$ within the experimental error $\pm 0.01\chi_0$, with the exception of χ'' at 0.179 GHz which seemed to increase roughly linearly with the field $H_{//}$ by an amount $0.03\chi_0$ from 0 to 8 kOe. A decrease rather than an increase would be expected from a comparison with $CuSO_4.5H_2O$ and DPPH[58][59].

Just as in $CuSO_4.5H_2O$ the quantity b/C is known only from specific heat data[28]): $(b/C)^{\frac{1}{2}} = 44$ kOe. It is striking that at a fixed frequency above ρ^{-1} the absorption χ''/χ_0 decreases considerably when going from $H = 0$ to $H_{//} = \frac{1}{5}(b/C)^{\frac{1}{2}}$ in $CuSO_4.5H_2O$ and that also a decrease is observed in DPPH, whereas χ''/χ_0 is approximately constant in $CuCl_2.2H_2O$.

We have calculated the lattice-sum $\sum_i r_{ij}^{-6}$ for $CuCl_2.2H_2O$ ($a:b:c = 0.918 : 1 : 0.463$), obtaining the value $13.4_5 n^2$ (compare I section 4; in a simple cubic lattice this value is $8.4\, n^2$). With the molar volume 67 cm^3 and $g = 2.16$, we arrive for the powder at $H_i = 0.81$ kOe, which is approximately the same value as was calculated by Verstelle[59]).

The line width ΔH calculated in the same way as was done for $CuSO_4.5H_2O$ is 28 or 35 Oe if the exchange is estimated from $(b_{ex}/C)^{\frac{1}{2}} = 44$ kOe or from the Weiss constant $\Theta = -5.0$°K (and 6 nearest neighbours) respectively. The rough agreement with the observed value $\Delta H = 56$ Oe is not unsatisfactory.

10. *Some concluding remarks.* In the sections 7, 8 and 9 (strong exchange interaction) Lorentzian line shapes have been found in perpendicular fields. In the sections 3, 4 and 5 a zero-frequency satellite line has been found in perpendicular fields[22]) that are large compared with $(b/C)^{\frac{1}{2}}$. The intensity $\int (\chi''/\chi_0\nu)\, d\nu$ of this line is of the same order of magnitude as the intensity of the Kronig-Bouwkamp relaxation band in parallel fields, but its width in a graph of $\chi''/\chi_0\nu$ *versus* ν is, in contradistinction to that of the latter band, only slightly field-dependent.

In the sections 7, 8 and 9 no explanation has been offered for the behaviour of χ' and χ'' in parallel fields which are smaller than about $(b/C)^{\frac{1}{2}}$.

In the sections 3 to 6 the general behaviour of $\chi''(\nu)$ and $\chi'(\nu)$ in parallel fields that are large compared with $(b/C)^{\frac{1}{2}}$ agrees with the theoretical predictions[18]) [19]). In parallel fields of the order of $(b/C)^{\frac{1}{2}}$ no rigorous theoretical predictions have been given for cases of small exchange interaction. In $Gd_2(SO_4)_3.8H_2O$, $Mn(NH_4)_2(SO_4)_2.6H_2O$ and $FeNH_4(SO_4)_2.12H_2O$ one observes that the low-frequency part ($\rho'\nu < 1$) of χ''/χ_{ad} shifts towards higher frequencies when $H_{//}$ increases from zero to about one or two times $(b/C)^{\frac{1}{2}}$ (figs. 3-4 and 5-4). This might be due to a general increase of the resonance frequencies, part of which will ultimately go over into the parallel-field resonance lines, concentrated near ν_L and $2\nu_L$. Shaposhnikov[50]) has proposed to describe the resulting rapid decrease of χ'' at low frequencies by

$$\chi''/\chi_0 = \rho'\nu(1 - F)^2 \qquad (10.1)$$

in which $1 - F \equiv \chi_{ad}/\chi_0$. It cannot be denied that (10.1) gives a reasonably good description of the experimental data with a constant value for ρ' in $Gd_2(SO_4)_3.8H_2O$, $Mn(NH_4)_2(SO_4)_2.6H_2O$, $FeNH_4(SO_4)_2.12H_2O$ and $CuCs_2(SO_4)_2.6H_2O$ at frequencies smaller than or equal to about $0.3/\rho'$ if the fields are not too large. In large fields the Kronig-Bouwkamp absorption gives rise to complications, especially at low frequencies ($\rho'\nu < 0.1$). This Kronig-Bouwkamp absorption is of the order $\chi'' = 0.1\,\chi_{ad}$, which is not more than $0.01\chi_0$ for $H_{//} = 3(b/C)^{\frac{1}{2}}$ and which therefore is easily overlooked or may be swamped by the spin-lattice absorption at liquid air or higher temperatures. The formula (10.1) is not at all satisfied in $CrK(SO_4)_2 . 12H_2O$ at 20°K (third relaxation) and in the salts with rather strong exchange interaction. This sheds doubt on the sometimes-followed procedure deriving b/C from the data on χ'' making use of the formula mentioned[65][51][31].

Note added in the proof. Quite recently, Dr. A. D. Pickar has performed (thesis, University of Maryland, U.S.A., 1962) zero-field absorption measurements at a large number of frequencies between 0.13 and 4.0 GHz, using a long tunable coaxial resonant cavity. A series of powdered paramagnetic crystals have been investigated and nearly all measurements have been performed at liquid helium temperatures. Some of the interesting results do not quite agree with our results. The differences require further study.

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SAMENVATTING

In dit proefschrift worden resultaten en discussies gegeven van metingen der susceptibiliteitscomponenten χ' en χ'' van paramagnetische kristallenpoeders die in goede benadering voldoen aan de wet van Curie en waarin slechts de electronenspins bijdragen tot de magnetisatie. De metingen werden uitgevoerd bij een aantal vaste frequenties ν in het decimetergolvengebied (200 tot 3000 MHz) bij een temperatuur van 20°K en in enkele gevallen ter controle ook bij 14, 77 of 290°K. Bij een meting bevindt het preparaat zich op een vaste plaats in het hoogfrequente magnetische veld (orde van grootte 0,1 Oe) van een resonerende trilholte, terwijl bovendien een tussen 0 en ruim 8000 Oe te variëren statisch magneetveld $\boldsymbol{H}$ kan worden aangelegd, evenwijdig aan $(H_{//})$ of loodrecht op $(H_{\perp})$ het hoogfrequente veld. In de paragrafen 2 van de beide hoofdstukken van dit proefschrift wordt een beschrijving gegeven van de meetmethoden die veel verwantschap vertonen met gebruikelijke methoden voor centimetergolven. Uit de waarnemingen worden χ' en χ'' berekend als fracties van χ_0, de statische susceptibiliteit bij de heersende temperatuur.

Het onderzoek beweegt zich nabij de grens tussen de terreinen paramagnetische spin-spinrelaxatie en paramagnetische resonantie. Spinroosterrelaxatie speelt bij de gebruikte frequenties en temperaturen vrijwel geen rol.

In hoofdstuk I worden de meetresultaten χ'/χ_0 en χ''/χ_0 van $CuCs_2(SO_4)_2.6H_2O$ en $Cu(NH_4)_2(SO_4)_2.6H_2O$ gegeven. Bij de discussies worden de volgende gevallen onderscheiden.

a) $H = 0$. In het Cs-zout, waarin de exchangewisselwerking (d.i. plaatsruilwisselwerking) zwak is, blijkt $\chi''/\chi_0\nu$ vrij goed overeen te stemmen met een Gauss-functie. In het NH_4-zout treedt een "exchange narrowing" op, die behoorlijk beschreven kan worden met het product van een Debije- en een Gauss-functie. De resulterende momenten worden vergeleken met de formules van Broer en Miss Wright, die door Caspers zijn uitgebreid door ook de zogenaamde hyperfijnwisselwerking (hfs) met de koperkernen in rekening te brengen. Hierbij wordt gebruik gemaakt van de sterkte van de dipool-dipool-, hfs- en exchangewisselwerking volgens de analyse van de soortelijke warmte van het spinsysteem door Benzie en Cooke. De overeenstemming is goed.

b) $H_\perp \gg H_i$ (H_i is het middelbare dipool-dipoolveld). In het Cs-zout wordt, naast de normale absorptielijn bij het Larmorveld, een satelliet-lijn bij het halve Larmorveld gevonden. Voor de breedte van de normale lijn wordt kwalitatieve overeenstemming gevonden met de in het Cs- en het NH_4-zout op verschillende wijze te verwachten invloed van het wel of niet ("truncation") meetellen van het niet-seculaire gedeelte van de dipool-dipoolwisselwerkingshamiltoniaan.

c) $H_{//} \gg H_i$. In het Cs-zout worden bij de hoogste frequenties twee resonantielijnen gevonden bij het Larmorveld en het halve Larmorveld. In het NH_4-zout zijn de overeenkomstige lijnen zwakker, breder en niet van elkaar gescheiden. De intensiteiten stemmen goed overeen met de verwachtingen volgens Caspers, rekening houdend met de onder a) genoemde sterkte van de verschillende wisselwerkingen. Ook de gegevens over χ'_{bet} ($\equiv \chi_{\mathrm{is}}^{\mathrm{sm}}$), die echter niet zo nauwkeurig zijn, stemmen overeen met de theorie van Caspers. De door Verstelle gemeten Kronig-Bouwkamp-absorptie wordt mede in de analyse van de intensiteiten betrokken. De breedte van de twee resonantielijnen komt, wat de orde van grootte betreft, overeen met de voor eenvoudige modellen berekende waarden van Hung Cheng.

In hoofdstuk II worden de meetresultaten χ'/χ_0 en χ''/χ_0 gegeven van $Gd_2(SO_4)_3.8H_2O$, $CrK(SO_4)_2.12H_2O$, $Mn(NH_4)_2(SO_4)_2.6H_2O$, $FeNH_4(SO_4)_2.12H_2O$, $MnCl_2.4H_2O$, $CuSO_4.5H_2O$ en $CuCl_2.2H_2O$. De discussies worden voor elk zout afzonderlijk gegeven. Ze dragen een meer incidenteel karakter dan die in het eerste hoofdstuk. In de eerste drie zouten wordt in grote velden $H_\perp$ een satelliet-absorptielijn bij de frequentie nul gevonden, waarvan de breedte, in tegenstelling tot de overeenkomstige lijn in velden $H_{//}$ (Kronig-Bouwkamp-absorptie), slechts weinig van de sterkte van het statische veld blijkt af te hangen. In grote velden $H_{//}$ wordt bij de laagste frequenties in $Mn(NH_4)_2(SO_4)_2.6H_2O$ en $Gd_2(SO_4)_3.8H_2O$ Kronig-Bouwkamp-absorptie gevonden. In $MnCl_2.4H_2O$, en beter nog in $CuSO_4.5H_2O$ en $CuCl_2.2H_2O$, voldoet de absorptie in loodrechte velden en veld nul bij benadering aan de Kronig-Van Vleck-Weisskopf-Fröhlich-formules voor respectievelijk een Lorentz- en een Debije-lijnvorm. In paragraaf 7 is in verband hiermee speciale aandacht geschonken aan het verschijnsel "exchange narrowing". Een bevredigende theorie over het gedrag in velden $H_{//}$ ontbreekt nog voor deze zouten.

De blijkbaar slechts beperkte geldigheid van Shaposhnikov's formule voor de spin-spinabsorptie van paramagnetische zouten in parallelle velden wordt besproken in de slotparagraaf 10 van hoofdstuk II.

STELLINGEN

I

De door Anderson en Weiss opgegeven waarden van de exchangevelden H_e in een aantal mangaan- en ijzerzouten zijn een factor 2 te laag als gevolg van een onjuist citeren van Van Vleck's uitdrukking voor het 4de moment; de vergelijking tussen de berekende en de gemeten waarden van de resonantielijnbreedten dient nu te worden herzien.

P. W. Anderson en P. R. Weiss, Rev. mod. Phys. **25** (1953) 269.
J. H. Van Vleck, Phys. Rev. **74** (1948) 1168; Suppl. Nuovo Cimento **6** (1957) 993.
Hoofdstuk II, § 7 van dit proefschrift.

II

Het is niet gerechtvaardigd Shaposhnikov's formule voor de spin-spinabsorptie in parallelle velden, $\chi''(H_{//})/\chi_0 = \rho'\nu(1 - F)^2$, te gebruiken voor een bepaling van de grootheid b/C van een paramagnetisch zout.

Hoofdstuk II, § 10 van dit proefschrift.

III

Voor het verder onderzoek van de spin-spinrelaxatie in $CuSO_4 . 5H_2O$ is het in de eerste plaats nodig de spin-roosterrelaxatie in dit zout nader te onderzoeken.

Hoofdstuk II, § 8 van dit proefschrift.

IV

De door Pickar gebruikte methode ter bepaling van de nul-veldabsorptie in paramagnetische zouten leidt tot systematische fouten indien het exchangeveld in de stof van de orde van grootte is van, of groter is dan, het maximale uitwendige magneetveld.

A. D. Pickar, proefschrift, University of Maryland, U.S.A. (1962).
Hoofdstuk II, § 7, 8 en 9 van dit proefschrift.

V

Op grond van theoretische overwegingen moet men verwachten dat er bij bepaalde paramagnetische kristallen een nauwe relatie bestaat tussen de intensiteit van de Kronig-Bouwkamp-absorptie en het tweede moment van de 1ste Larmorlijn (de normale resonantielijn) in loodrechte magneetvelden, wat betreft de wijze waarop deze grootheden afhangen van de hoeken tussen het statische magneetveld en de kristalassen.

VI

Bij de experimentele bepaling van de momentenverhouding $\langle \Delta H^4 \rangle^{\frac{1}{4}} / \langle \Delta H^2 \rangle^{\frac{1}{2}}$ in een serie mangaanzouten hebben MacLean en Kor vermoedelijk onvoldoende rekening gehouden met de aanzienlijke bijdrage tot deze verhouding, afkomstig van de absorptie in de uiterste flanken van de resonantielijn. Hierdoor kan een door de auteurs niet opgemerkte tegenstrijdigheid tussen theorie en experiment bij $MnCl_2 . 4H_2O$ worden verklaard.

C. MacLean en G. J. W. Kor, Appl. sci. Res. **B4** (1955) 425.

J. H. Van Vleck, Suppl. Nuovo Cimento **6** (1957) 993.

VII

In zijn theorie van de warmtegeleiding in de vaste stof houdt Peierls geen rekening met Heisenberg's onzekerheidsrelatie tussen de normaalcoördinaten en de corresponderende geconjugeerde variabelen bij zijn beschouwing van golfpakketjes.

R. E. Peierls, Quantum theory of solids (Oxford, At the Clarendon Press, 1955).

VIII

Voor het door Makin en Manthorpe gemeten verschijnsel dat de hardheid van Cu, bestraald met neutronen bij —195°C, afneemt tijdens het ontlaten tussen 0 en 20°C, is, naast die van de auteurs, ook een andere verklaring mogelijk.

M. J. Makin en S. A. Manthorpe, Acta met. **9** (1961) 886.

IX

In de correctiefactor bij de uitgebreide wet van Stokes voor de wrijving van kleine vloeistofdruppeltjes, die eenparig door een gas bewegen, geeft het gebruik van de vrije weglengte λ in het gas gemakkelijk aanleiding tot misverstand, en daarmee tot niet te verwaarlozen fouten, door de verschillende definities die er voor λ bestaan. In navolging van Millikan dienen dan ook bij voorkeur de druk en de temperatuur van het gas in plaats van λ te worden gebruikt bij de practicumhandleiding van de proef van Millikan (proef F1).

Handleidingen bij de proeven van het natuurkundig practicum, Leiden, 1936 tot 1962.
R. A. Millikan, The Electron (The University of Chicago Press, Chicago, Illinois, U.S.A., 1924).

X

De bewering van Douglass dat de vernietiging door stroom van de supergeleidende toestand in een dunne laag een thermodynamische overgang van de eerste orde is, is onjuist.

D. H. Douglass Jr., Phys. Rev. **124** (1961) 735.
V. L. Ginzburg en L. D. Landau, Zh. eksp. teor. Fiz. (U.S.S.R.) **20** (1950) 1064; vertaling: Phys. Abh. Sov. Un., Band **13**, Tieftemperaturphysik Folge 1, (1958) 7.

Stellingen behorende bij het
proefschrift van P. R. Locher

VI

Bij de experimentele bepaling van de [illegible] verhouding, afhankelijk van de [illegible]

J. H. Van Vleck, [illegible]

VII

In zijn theorie van de [illegible]

[illegible]

VIII

Voor het door Makin en [illegible]

M. J. Makin en [illegible]

IX

[illegible]