proximates the Doppler distribution, e^{-x^2}, up to a value x_1 such that

$$x_1 \sim (\log(k_0L/2))^{\frac{1}{2}}.$$

For $x > x_1$ the Doppler distribution is to be multiplied by a factor roughly of the form x_1/x.

These results may now be introduced into (2.3) to calculate, e.g., $T(L/2)$; it is then found that the new value is smaller than the text value

$$T_1(L/2) = \frac{1}{k_0\rho(\pi \log(k_0L/2))^{\frac{1}{2}}},$$

by an amount

$$\Delta T \sim \frac{T_1(L/2)}{2\log(k_0L/2)},$$

which, for $k_0L \sim 200$, is of the order of 10 percent.

We may thus expect that the error in β arising from the use of (1A) is less than, say, 20 percent. On the other hand, the error in the functional form of $N(\mathbf{r}, \mathbf{v})$, or even of $N(\mathbf{r})$, is undoubtedly much greater; in particular, for these quantities the contrast between the central region and the periphery of the enclosure is more significant.

PHYSICAL REVIEW VOLUME 72, NUMBER 12 DECEMBER 15, 1947

Paramagnetic Resonance Absorption in Salts of the Iron Group[*]

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(Received August 29, 1947)

When a paramagnetic salt is placed in a high frequency alternating magnetic field which is perpendicular to a static magnetic field, energy may be absorbed by the salt in a resonant fashion for a range of values of the steady field. These paramagnetic losses have been investigated for three manganous, two cupric, and one chromic salt at a frequency of 9375 mc/sec. Well-defined absorption maxima were obtained in all cases, and absolute values of χ'', the imaginary part of the high frequency magnetic susceptibility, are presented.

I. INTRODUCTION

ABSORPTION of energy from a high frequency alternating magnetic field by a paramagnetic salt placed in the field was first demonstrated by Gorter[1] in 1936. He found that this absorption can be influenced by the application of a static magnetic field either parallel or perpendicular to the alternating field. He and his colleagues have carried on an extensive investigation of both types of absorption during the last decade.[2,3] The perpendicular field case has been further investigated by Zavoisky[4,5] and by two of the present authors.[6]

Purcell and co-workers[7] have recently demonstrated that when paraffin is put into a cavity resonator and a static magnetic field of the correct magnitude is applied perpendicularly to the high frequency magnetic field in the paraffin-filled cavity, energy is absorbed from the alternating field. This absorption shows sharp resonance characteristics and is associated with reorientations of the magnetic moments of the protons in the paraffin. Such nuclear absorptions are several orders of magnitude smaller than the absorptions referred to above, which are ionic in character.

In the earlier experiments[2–4] which were limited by the unavailability of oscillators of sufficiently high frequency,[***] the strength of the static magnetic field corresponding to the maximum absorption was less than the absorption half-width, so that the maxima were not very clearly

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[*] This work was supported in part by the Office of Naval Research under Contract N6ori-43 Task Order III and in part by the Army Air Forces, Air Materiel Command, under Contract W28-099-ac-238.

[**] Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pittsburgh.

[1] C. J. Gorter, Physica 3, 503 (1936).

[2] C. J. Gorter, Physica 3, 1006 (1936).

[3] F. Brons and C. J. Gorter, Physica 5, 999 (1938).

[4] E. Zavoisky, J. Phys. U.S.S.R. 9, 211 (1945).

[5] E. Zavoisky, J. Phys. U.S.S.R. 10, 197 (1946).

[6] R. L. Cummerow and D. Halliday, Phys. Rev. 70, 433 (1946).

[7] E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev. 69, 37 (1946).

[***] Zavoisky's most recent work,[5] carried out at 3000 mc/sec., has only recently been available to us.

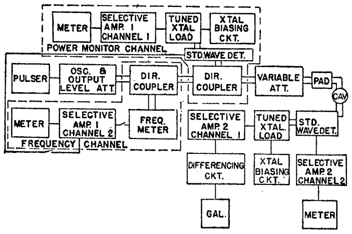

FIG. 1. A block diagram of the apparatus.

defined. In the present experiments, conducted at 9375 mc/sec., the maxima are well defined. Absolute values of χ'' (an absorption parameter to be defined later) are reported in all cases but one. We have adopted the technique of Purcell *et al.* of using a resonant cavity.

We are concerned here with the resonance absorption, associated with reorientations of the magnetic moments of the metallic ions of a paramagnetic salt, which occurs when the salt is placed in fields that are mutually perpendicular only. As a first approximation let us assume that the ions are nearly free, as is the case for the proton spins mentioned above. In the absence of an external magnetic field, all the ions will then exist in a common ground state. When a static external magnetic field is applied, they will be distributed among $2J+1$ equally-spaced levels according to the Boltzmann distribution. It is necessary to assume a slight interaction with the lattice to insure that this equilibrium distribution will be reached in a finite time (spin-lattice relaxation time). The difference in energy between any two adjacent levels is given by

$$\Delta E = g\beta B, \tag{1}$$

where g is the gyromagnetic ratio, β is the Bohr magneton, and B is the strength of the applied field. When the high frequency perpendicular magnetic field of frequency ν is introduced, the transition probability of an ion from the level it occupies to an adjacent level is a maximum when

$$h\nu = g\beta B, \tag{2}$$

the familiar magnetic resonance condition. The transition probability to a higher level is identical with that to a lower level, but the Boltzmann distribution insures that the lower levels are slightly more densely populated than the higher, and a net absorption of energy from the alternating field occurs. In order for the rate of energy absorption at resonance to remain constant with time, the amplitude of the high frequency magnetic field must not be so great that the Boltzmann distribution cannot be continually reestablished. Such a condition would lead to the equalization of the level populations and hence to a disappearance of the absorption effect. In this work no such saturation effects were observed.

TABLE I. Results of measurements to test Eq. (9).

$MnSO_4\cdot 4H_2O$ mass percent		χ''_{max} 10^{-25} cm³/ion
100		2.31
80		2.32
63		2.21
37		2.34
20		2.44
	mean	2.34
	mean deviation	0.06

The treatment outlined above is satisfactory for the case of nuclear magnetic moments since here the nuclear magnetic dipolar interaction is relatively small. Expressed differently, the spin-spin relaxation time is relatively great or, still differently, the r.m.s. internal magnetic field at an average nuclear dipole caused by remaining dipoles is much smaller than the applied steady magnetic field at resonance. In the case of magnetic ions in salts, however, internal fields of several hundred gauss are common. This means that resonance-absorption peaks with this order of half-width are to be expected.

The interaction of a magnetic ion with its surroundings is made up of at least two parts: (1) the magnetic-dipolar interaction of the ion with neighboring magnetic ions, mentioned above, and (2), the interaction of the ion with the local electric field in the crystal. Frequently, exchange interactions must also be considered. The magnetic-dipolar interaction is usually treated from the point of view of internal magnetic fields; the distribution of ions-in-internal-field, is generally assumed to be Gaussian. The magnetic interaction alone would thus remove the ground-state degeneracy and would cause the ions to be distributed over numerous closely lying levels, rather than to occupy a single ground level.

The electric fields influence only that component of the ionic magnetic moment caused by

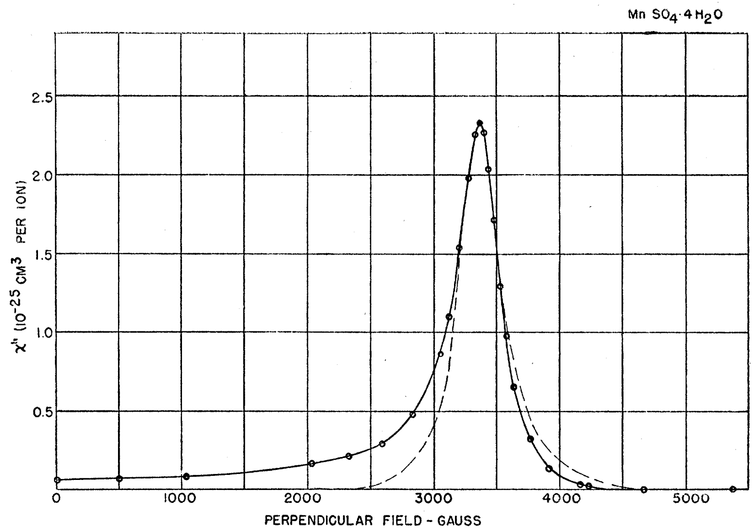

FIG. 2. Paramagnetic absorption in $MnSO_4 \cdot 4H_2O$ at 9375 mc/sec. The dashed curve is Frenkel's theoretical relationship for $\tau = 2.0 \times 10^{-9}$ sec.

orbital electronic motions and do not affect the component caused by spin.[8] The normal space quantization of the magnetic moment of the ion is so altered on this account in the salts of the iron group that the orbital momentum makes almost no contribution to the macroscopic susceptibility, and that part of the ionic magnetic moment is said to be quenched. This quenching action is associated with a splitting of the normal ground level, in a way that depends on the ion and on the symmetry and other characteristics of the electric field.

The manganous (Mn^{++}) ion is in an S state with $J = S = 5/2$, but even so has a second-order resultant orbital angular momentum. The internal electric field is able on this account to split the ground level through spin-orbit coupling.[9] With the application of a sufficiently strong external magnetic field, however, the energy-level structure changes in such a way as to approach that expected for an ion with $J = 5/2$ in a magnetic field alone.

A free cupric (Cu^{++}) ion is in a $^2D_{5/2}$ state. However, in most cupric salts the orbital contribution to the magnetic moment is almost entirely quenched by the electric fields, and the ground level is split in a way that depends on the salt. The degeneracies of these sublevels are removed by internal and externally applied magnetic fields. The case of $CuSO_4 \cdot 5H_2O$ has been described by Polder,[10] who calculates a splitting of the order of 20,000 cm⁻¹.

A free chromic ion is in a $^4F_{3/2}$ state. The splittings caused by the internal electric fields and also by externally applied magnetic fields have been calculated by Broer[11] for the chromic salt investigated by us, namely, chrome alum ($CrK(SO_4)_2 \cdot 12H_2O$).

II. APPARATUS

A block diagram of the microwave and associated measuring apparatus is shown in Fig. 1. There are three microwave channels: the main channel which includes the salt-filled cavity resonator, a channel for monitoring the power output of the microwave oscillator, and a frequency-monitoring channel. The microwave oscillator

TABLE II. Paramagnetic-absorption characteristics of manganous and cupric salts at 9375 mc/sec.

Salt	$\chi''_{\max}$ 10^{-25} cm³/ion	B for $\chi''_{\max}$ gauss	Width for $\chi''_{\frac{1}{2}}$ gauss	Free-ion value of B for $\chi''_{\max}$ gauss
$MnSO_4 \cdot 4H_2O$	2.32	3370	415	3348
$MnC_2O_4 \cdot 2H_2O$	2.24	3353	380	3348
$MnCl_2 \cdot 4H_2O$	0.395	3274	2300	3348
$CuCl_2 \cdot 2(NH_4Cl) \cdot 2H_2O$	0.230	3137	285	—
$CuSO_4 \cdot 5H_2O$	0.287	3039	318	—
$CuSO_4 \cdot 5H_2O$*	0.445	3065	285	—

* Measurement made at 193°K.

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[8] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), p. 294.

[9] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

[10] D. Polder, Physica **9**, 709 (1942).

[11] L. J. F. Broer, Physica **9**, 547 (1942).

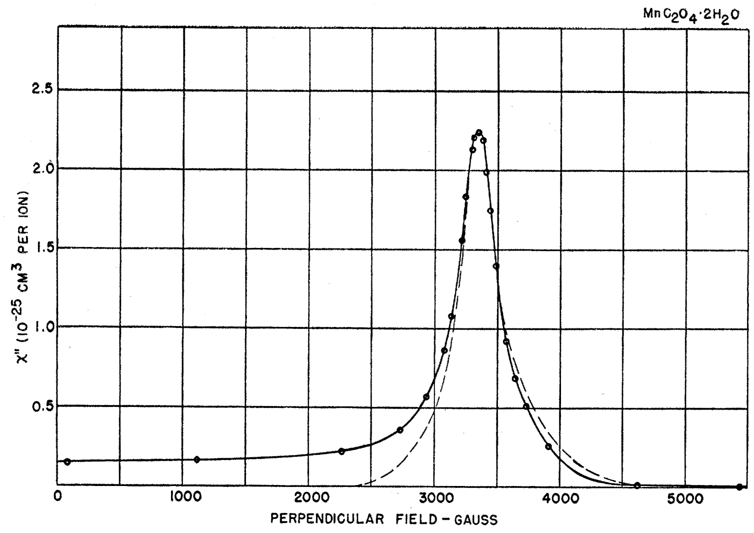

FIG. 3. Paramagnetic absorption in $MnC_2O_4 \cdot 2H_2O$ at 9375 mc/sec. The dashed curve is Frenkel's theoretical relationship for $\tau = 1.9 \times 10^{-9}$ sec.

was a navy 3-cm test set, type AN/APM-3A, modified so that the reflector electrode of the 723 A/B oscillator tube could be pulsed. The applied wave form was a 1300 c/sec. symmetrical square wave, which provided an a. c. output from the crystal detectors in the various channels. This a. c. output was easily amplified and, further, permitted d. c. biasing of the crystal detectors in the main channel and the power-monitoring channel in order to help match the impedance of each crystal and its holder closely to that of the connecting wave guide. The crystal holders for these two channels were mechanically tunable in order to further insure a satisfactory match. Standing-wave detectors were placed ahead of each of these crystal holders to check the impedance match. The crystals in the standing-wave detectors and the frequency-monitoring channel were not biased, since a good termination is not necessary in these channels.

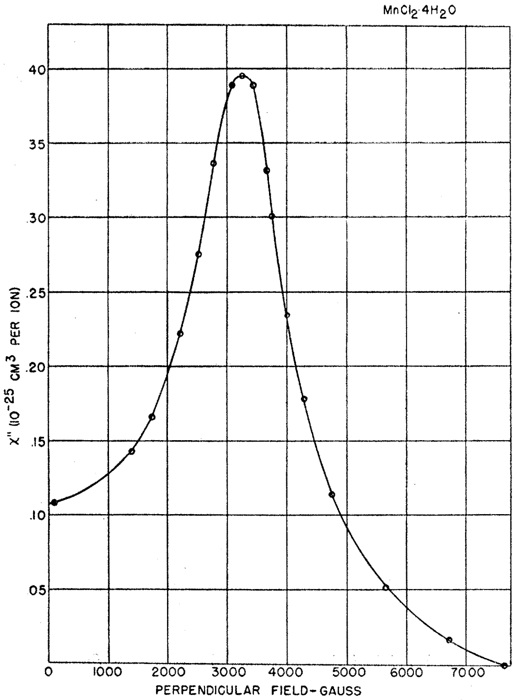

FIG. 4. Paramagnetic absorption in $MnCl_2 \cdot 4H_2O$ at 9375 mc/sec.

The outputs of all crystals were amplified by means of double-channel selective amplifiers tuned to the square-wave fundamental frequency. The rectified output, corresponding to the signal from the main channel, was fed to a differencing circuit in which a comparison was made with a stable variable d. c. voltage obtained from a battery-potentiometer system. The difference signal was then led to a galvanometer. Thus small changes in the power output of the cavity could easily be detected. The measuring system was calibrated by introducing known absorptions by means of a calibrated variable attenuator in the main r-f channel.

III. MEASUREMENTS

In characterizing the absorption of a paramagnetic salt it is desirable to use a quantity which is dependent only on the kind of salt and the independent variables, such as the frequency ν of the high frequency magnetic field, the strength of the static perpendicular magnetic field, etc. The imaginary part of the complex high frequency susceptibility, χ'', is such a quantity. It is related to the magnetic power absorption in a particular specimen of salt by

$$M=2\pi N\chi''\nu\langle B_0^2\rangle_{\mathrm{Av}}, \tag{3}$$

when N is the number of magnetic ions in the sample, and $\langle B_0^2\rangle_{\mathrm{Av}}$ is the average over the volume of the sample of the mean-squared magnetic field.† The measurement of magnetic losses is further complicated by the electric losses which are unavoidably present in the cavity walls and in the salt itself. The magnitude of the electric loss is not constant but depends on the value of the magnetic loss.

Of the quantities in Eq. (3), $\langle B_0^2\rangle_{\mathrm{Av}}$ and M are not readily measurable so that we must obtain expressions for them in terms of measurable quantities. We now define a Q associated *only* with the energy dissipated magnetically in the cavity

$$Q_m'=\frac{2\pi\text{ (mean-stored energy in cavity)}}{\text{energy dissipated per cycle magnetically}}. \tag{4}$$

Then

$$Q_m'=\omega(\mathrm{mse})/M. \tag{5}$$

The mean-stored energy is given by

$$\mathrm{mse}=\langle B_0^2\rangle_{\mathrm{Av}}V/4\pi, \tag{6}$$

where V is the volume of the cavity (and of the salt). Then

$$Q_m'=V/4\pi N\chi''. \tag{7}$$

By an extension of methods developed by Holstein,[12] one can show that

$$Q_m'=\frac{Q_e}{(P_e/P_{em})^{\frac{1}{2}}-1}, \tag{8}$$

where Q_e is the loaded Q of the cavity measured with *only electric* losses occurring, and P_e/P_{em} is the ratio of the power output of the cavity with *only electric* losses occurring to that with *both* electric and magnetic losses occurring. Combining Eqs. (7) and (8), one obtains an expression for χ'' in terms of measurable quantities

$$\chi''=\frac{V[(P_e/P_{em})^{\frac{1}{2}}-1]}{4\pi NQ_e}. \tag{9}$$

The measurement of Q_e was made with an externally applied field large compared to the field for maximum absorption. This was to insure that there were no transitions of magnetic ions and hence no magnetic absorption. Q_e values of about

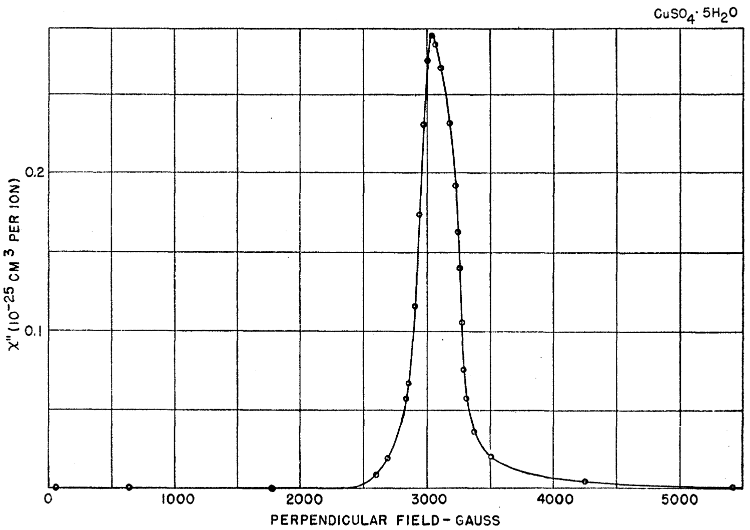

FIG. 5. Paramagnetic absorption in $CuSO_4\cdot 5H_2O$ at 9375 mc/sec.

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† Throughout the following discussion we assume the high frequency permeability to be unity, a good approximation for paramagnetic salts.

[12] T. Holstein, Westinghouse Research Report No. R-94318-F.

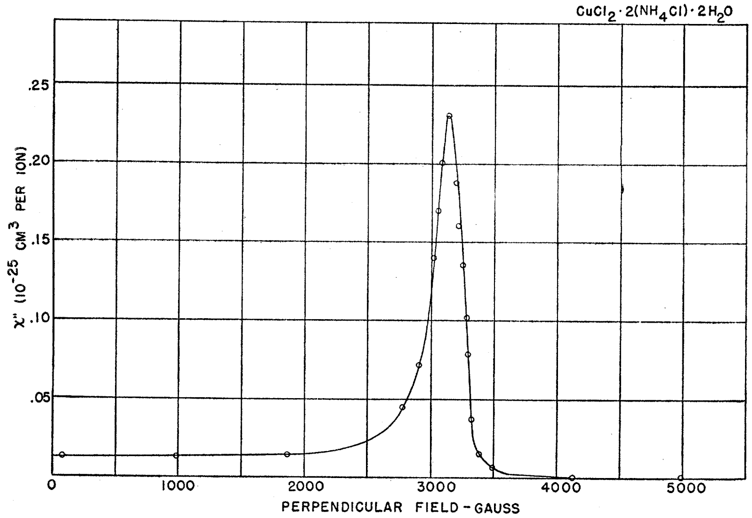

FIG. 6. Paramagnetic absorption in $CuCl_2 \cdot 2(NH_4Cl) \cdot 2H_2O$ at 9375 mc/sec.

140 were obtained, the cavity being singly reentrant, about 0.83/cm^3 in volume, and filled completely with salt. The quantity P_e/P_{em} is, then, the ratio of the power output at large externally applied fields to the power output at any other value of static field where both magnetic and electric losses occur. For $MnSO_4 \cdot 4H_2O$, for example, the value of P_e/P_{em} at the absorption maximum was about 4.5. Knowing these two data and V and N of Eq. (9), one may compute χ'' as a function of the value of the applied external field.

Equation (9) was tested by preparing five mixed powdered samples of $MnSO_4 \cdot 4H_2O$ and the non-paramagnetic $BaSO_4$, with the relative masses of the former varying from 20 to 100 percent of the total. These samples were placed in the cavity and χ''_{max} was measured, with the results given in Table I. For comparison, four separate measurements on powdered samples of pure $MnSO_4 \cdot 4H_2O$ yielded a mean χ''_{max} of 2.32×10^{-25} cm^3/ion with a mean deviation of 0.04×10^{-25} cm^3/ion. The good agreement of all these results, considering that the measurements were made under different conditions as to Q_e, P_e/P_{em}, and N, allows some confidence to be placed in the measuring procedure.

The magnetic field was determined by measuring the commutated output voltage of a small spinning coil placed in the field. The size of this coil was adjusted so that for the range of fields used a type-K potentiometer and standard cell could be conveniently employed to measure the voltage. The spinning coil was calibrated by using

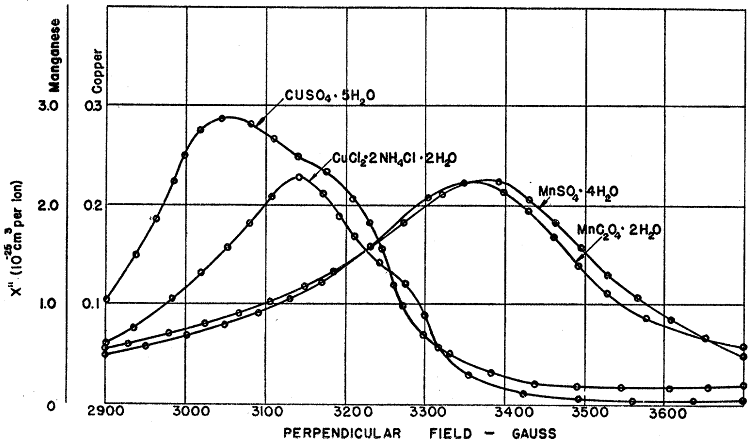

FIG. 7. Paramagnetic absorption for two manganous and two cupric salts at 9375 mc/sec.

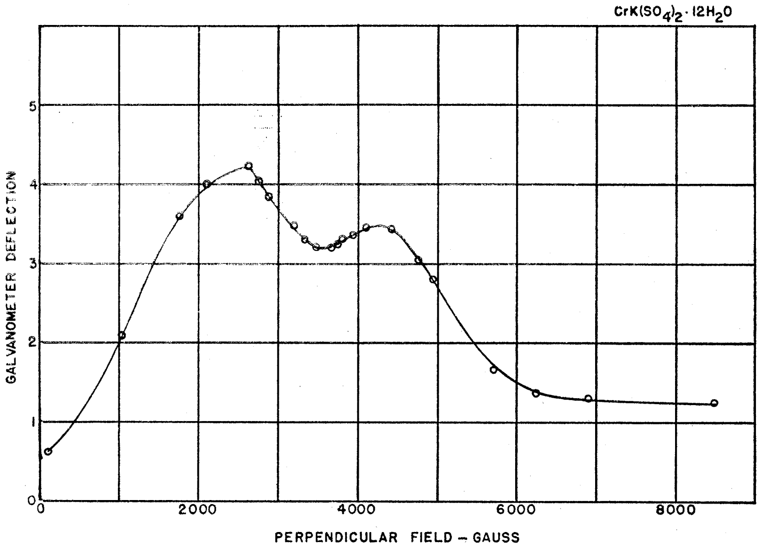

FIG. 8. Paramagnetic absorption in $CrK(SO_4)_2 \cdot 12H_2O$ at 9375 mc/sec. The ordinate is proportional to χ''.

conventional search coil, galvanometer, and standard solenoid techniques. We believe the reported fields to be accurate to about 0.5 percent.

IV. RESULTS AND DISCUSSION

Figures 2 to 6 show χ'' *versus* the perpendicular magnetic field at a frequency of 9375 mc/sec. for three manganous and two cupric salts. Figure 7 shows the curves for four of these salts replotted for better delineation of such characteristics as shape and half-width. Figure 8 shows a curve for chrome alum in which a quantity proportional to χ'' is plotted against B. In Table II some important features of these curves are noted. In addition, data are given for a determination of χ'' of $CuSO_4 \cdot 5H_2O$ made at 193°K (dry-ice temperature). All other determinations were made at room temperature.

A glance at Figs. 2–4 shows that there is a finite amount of magnetic absorption with zero external field. This zero-field absorption indicates, in the usual case, that a certain number of the ions are normally subjected to an internal magnetic field of the correct magnitude to satisfy Eq. (2). At sufficiently high external fields the resultant B for all ions is too great for any transitions to occur, and hence the absorption is zero.

According to Eq. (2), the maximum absorption for almost free manganous ions should occur at 3348 gauss$_4$ that for $MnC_2O_4 \cdot 2H_2O$ occurs at 3353 gauss. The difference between these values is not significant. The value for $MnSO_4 \cdot 4H_2O$, 3370 gauss, does seem to be significantly higher than the free-ion value. The shift of the maximum for the manganous chloride curve is in the opposite direction and much larger (74 gauss). The absorption curve for $MnCl_2 \cdot 4H_2O$ is five times wider than the curves for the oxalate and the sulfate.

Frenkel[13] has proposed a theory of paramagnetic-resonance absorption which gives an explicit relationship between χ'' and B provided the spin-spin relaxation time τ is known. A comparison with experiment, however, is hindered by the fact that the dependence of τ on B is not known. Assuming a constant value of 2.0×10^{-9} sec. for $MnSO_4 \cdot 4H_2O$ and of 1.9×10^{-9} sec. for $MnC_2O_4 \cdot 2H_2O$, we obtain the dashed curves of Figs. 2 and 3, respectively. These relaxation times are of the expected order of magnitude. It should be noted that Frenkel's expression for χ'' vanishes for $B = 0$, that is, no zero-field absorption is permitted. For the broad $MnCl_2 \cdot 4H_2O$ curve no very good fit for a single value of τ seems possible.

The half-widths of all of the absorption peaks for manganous salts are somewhat narrower than might be expected from the known magnitudes of the internal fields involved. Professor C. J. Gorter has suggested in a private discussion that an exchange interaction may be responsible.

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[13] J. Frenkel, J. Phys. U.S.S.R. 9, 299 (1945).

TABLE III. Values of χ in units of 10^{-25} cm^3/ion for iron group salts.

Salt	Direct measurement	Area under absorption curve
$CuSO_4 \cdot 5H_2O$	0.028	0.024
$CuCl_2 \cdot 2(NH_4Cl) \cdot 2H_2O$	0.028	0.024
$MnSO_4 \cdot 4H_2O$	0.24	0.30
$MnC_2O_4 \cdot 2H_2O$	0.24	0.29
$MnCl_2 \cdot 4H_2O$	0.24	0.32

It is not feasible to compare the field for maximum absorption for the cupric salts to that for almost free ions, since the $^2D_{5/2}$ state of the free ion is a very poor approximation to the actual state of the cupric ion in a salt. This is so because of the quenching of the orbital part of the magnetic moment discussed above. It will be noted that both cupric salts give indications of structure in the absorption curves. The reasons for this structure are not known. The calculated splittings of Polder[10] seem to offer no ready explanation. It is hoped that absorption measurements in $CuSO_4 \cdot 5H_2O$ single crystals now in progress will help to explain this phenomenon.

The half-widths for the two copper curves agree fairly well with the known internal fields. However, Professor C. J. Gorter has suggested that this agreement is fortuitous, being associated with the known magnetic anisotropy, and that the half-widths for single crystals would be narrower. This is to be expected because of the narrowing arising from exchange interaction mentioned earlier.

The curve for chrome alum (Fig. 8) can be qualitatively explained by considering the splittings calculated by Broer.[11] In zero external magnetic field the ground level is split into two doubly degenerate levels 0.17 cm^{-1} apart. As the strength of the external magnetic field is increased, the degeneracies are removed in a way that depends on the orientation. By considering Fig. 1 of Broer's paper the existence of two absorption maxima is not surprising since, for a given orientation, transitions between levels in each degenerate set will occur at different external fields, corresponding to a level separation of 0.31 cm^{-1} (9375 mc/sec).

A semiquantitative check on the experimental results can be obtained by computing the normal paramagnetic susceptibility of the various salts from the areas under the absorption curves, using a formula presented by Gorter and Kronig.[14] The special case of this formula that is of interest is

$$\chi = \frac{2}{\pi} \int_0^\infty \frac{\chi'' d\nu}{\nu}. \tag{10}$$

Unfortunately, χ'' is given as a function of B for a fixed ν and not the reverse, so that Eq. (10) cannot be evaluated as it stands. An approximate evaluation, valid for very narrow absorption lines, is possible from the following considerations. Any of the absorption peaks reported may be viewed—if only magnetic interactions be considered—as indicating roughly the nature of the distribution of internal magnetic fields for various external fields. What is wanted, however, is the distribution of internal fields for a fixed external field corresponding to the value B_0 at the absorption maximum. Such a distribution may be approximated by multiplying every ordinate of the absorption curve by the ratio B/B_0. By use of the differential form of Eq. (2), namely,

$$d\nu/\nu = dB/B,$$

we are finally led to

$$\chi = 2A/\pi B_0,$$

where A is the area under the absorption curves of Figs. 2 to 6. Table III shows the results.

Considering the assumptions made in the application of Eq. (10), the agreement is perhaps all that can be expected. Well-known experimental difficulties stand in the way of obtaining data suitable for direct verification by Eq. (10).

The authors are very greatly indebted to Professors C. J. Gorter and J. H. Van Vleck for their many indispensable suggestions in connection with the interpretation of the results. We are also thankful to Dr. A. J. Allen for his active interest and encouragement during the course of this research. We further wish to thank Mr. T. Miller of the Westinghouse Research Laboratories for providing the accurately calibrated attenuator used in this work.

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[14] C. J. Gorter and R. de L. Kronig, Physica 3, 1009 (1936).