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Spin-Spin Relaxation at Very Low Temperatures in Chromic Methylammonium Alum

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We have measured the absorption due to spin-spin relaxation in chromic methylammonium alum at frequencies from 0.1 to 10 Mc/sec and at temperatures from 0.06° to 1°K. At 1°K the spin-spin relaxation time, τ_s, is found to be 4.2×10^{-10} sec and to be decreasing slowly with increasing temperature. Below 1°K., τ_s increases rapidly. The absorption of energy is found to be proportional to the square of the frequency, ν, at the higher temperatures, but varies less rapidly at lower temperatures, being proportional to $\nu^{1.83}$ at 0.06°K. The results are analyzed in terms of Broer's theory of spin-spin relaxation, and, not surprisingly, the theory is found to need refinement in order to be applicable at temperatures where Curie's law is not obeyed. It is concluded that measurements of this type, which give essentially the same kind of information as is obtained from resonance line shapes, should be able to throw light upon the behavior of substances near their antiferromagnetic transition points.

I. INTRODUCTION

RELAXATION effects in paramagnetic salts have been investigated fairly extensively, primarily by Dutch workers, and Gorter's[1] monograph on the subject contains an account of both experimental and theoretical work. Two effects can be distinguished, one associated with the time required for transfer of energy between the spin system and the lattice,[2] and the other with the time required for establishment of thermal equilibrium within the spin system. It is found that while the spin-lattice relaxation time depends strongly upon temperature, the spin-spin relaxation time is temperature-independent and has a value $\sim10^{-10}$ sec. Although interest has centered mainly on spin-lattice relaxation,[3] a significant amount of work has been done on spin-spin relaxation, and the theory of Waller,[4] as developed by Broer[5] has generally been confirmed.

When one is interested only in spin-spin relaxation, experiments are conducted with external magnetic fields which are chosen to be small compared with the internal magnetic fields arising from the mutual interaction between the magnetic ions. In this case the process of magnetization does not take place by a change in energy and a change in population of various Zeeman levels (spin-flips), but by polarization. If we consider the paramagnetic crystal as a whole, it possesses a very large number of energy states, which, in the absence of an external field are states of zero magnetic moment. The magnetization produced by a small external field then can only be described in terms of the off-diagonal elements of the magnetic moment matrix, i.e., by a polarization of the energy levels of the crystal.[6] The adiabatic and isothermal susceptibilities are equal, Curie's law is obeyed, and magnetization in an alternating field is reversible provided the frequency is not too high. At higher frequencies, when the period of the field becomes comparable to the time taken for polarization to occur, i.e., to the time for equilibrium to be set up *within* the spin system, magnetization becomes irreversible and the spin-spin relaxation phenomenon occurs.

Experiments on spin-spin relaxation heretofore have been confined mainly to relatively high temperatures (usually in the liquid air region) and only a few measuring frequencies have been employed. No experiments seem to have been carried out to link up these measurements with those made at extremely low temperatures near the Néel (or Curie) point of the salt, where conconsiderable absorption is found at low audio-frequencies.[7–10] It is usually supposed that the two phenomena are more or less distinct, the latter being associated with cooperative effects, like magnetic hysteresis, which are observed below the transition point. There is some disagreement, however, as to whether the absorption can be described by hysteresis[9,11] or not.[8]

In any event, both types of relaxation have their origin entirely within the spin system, one taking place in a region of temperature where the salt behaves ideally, and the other in a region of temperature where departures from ideality are considerable. We may consider them both from the purely phenomenological point of view by writing the susceptibility $\chi=\chi'-i\chi''$. In the present experiments we have tried to link up these two effects. The choice of salt was governed by the fact that it should have rather well-known thermal properties. The measurements were actually occasioned

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[1] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Amsterdam, 1947).

[2] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507 (1938).

[3] A. H. Cooke, Repts. Progr. in Phys. **13**, 276 (1950).

[4] I. Waller, Z. Physik. **79**, (1932).

[5] L. J. F. Broer, Physica **10**, 801 (1943).

[6] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1931), Chap. VII.

[7] D. P. MacDougall and W. F. Giauque, J. Am. Chem. Soc. **58**, 1032 (1936).

[8] A. H. Cooke and R. A. Hull, Proc. Roy. Soc. (London) **A162**, 404 (1937).

[9] E. S. Shire and H. M. Barkla, Proc. Cambridge Phil. Soc. **35**, 327 (1939).

[10] Casimir, de Klerk, and Polder, Physica **1**, 737 (1940); see also review by E. Ambler and R. P. Hudson, Repts. Progr. in Phys. **18**, 251 (1955).

[11] H. N. V. Temperley, Proc. Cambridge Phil. Soc. **35**, 256 (1938).

by an earlier experiment on nuclear alignment,[12] following a suggestion of Bloembergen and Temmer.[13] The idea of this experiment, briefly, was to determine a resonance due to magnetic hfs in a paramagnetic salt at temperatures below 1°K. It was observed, however, that at frequencies around the one required for resonance (~200 Mc/sec), there was a prohibitively large nonresonant absorption. The absorption increased rapidly with decreasing temperature, but was appreciable even at 1°K.

II. EXPERIMENTAL PROCEDURE

Measurements were made in the frequency range 0.1–10 Mc/sec at temperatures from 0.06–1°K. The principle of the method was the same as that used by Gorter[1] and coworkers, *viz.*, the salt was subjected to an rf magnetic field of known amplitude, h_0, and angular frequency, ω, for a given time. From the measured temperature rise and the known specific heat of the salt the energy absorption rate was determined, and since this is equal to $\frac{1}{2}\omega\chi''h_0^2$, χ'' could be calculated.

In previous work the main difficulties were (a) to measure h_0 accurately, and (b) to make allowance for absorption due to causes other than the one being investigated, in particular for dielectric absorption. In a separate series of experiments[14] it was shown that for our purposes dielectric absorption could be neglected. The main source of error, therefore comes, in the measurement of h_0, details of which are given below.

The apparatus is shown in Fig. 1. Not shown in the figure are the surrounding liquid helium and liquid nitrogen baths. Much of the apparatus follows conventional design of adiabatic demagnetization cryostats and only the specimen support and coil system will be described.

The specimen, S, is a 1-cm-diam compressed powder sphere. It is supported by a 1-mm-diam glass tube, T, on to which is cemented a heat trap, G, a cylindrical compress of ammonium hexafluorochromite.[15] G is cooled by adiabatic demagnetization at the same time time as S and then serves to intercept most of the heat conducted along T. With this arrangement, the heat influx to S was not greater than 10 ergs/min immediately after demagnetization, and then gradually fell to a considerably lower value.

The outer coil C is an astatically wound secondary coil of a mutual inductance, the primary of which is wound on the outside of the helium Dewar (not shown). These are connected to a Hartshorn bridge operating at 270 cps which served to monitor the temperature of S. By suitably winding C and the primary coil, the influence of G on the circuit was reduced to a negligible amount.

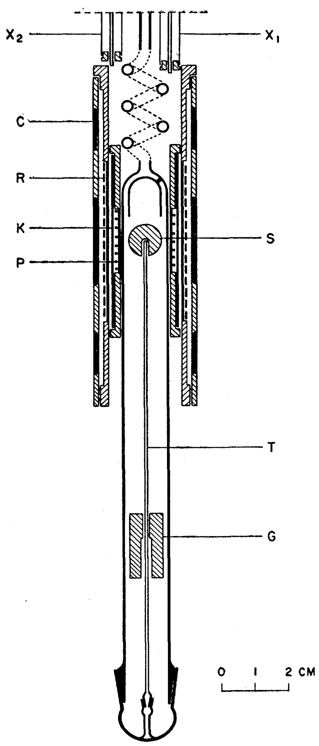

Fig. 1. Apparatus for measuring rf absorption at temperatures below 1°K.

The coil R provides the rf magnetic field, h_0, at S. It produces roughly 2 gauss/amp, and is fed through the coaxial line X_2 from a power oscillator. The current flowing into X_2, which is measured by calibrated uhf thermal elements, can be adjusted over a wide range by means of an attenuator. The rf field is calibrated in terms of this current by means of a small pick up coil, P, the emf induced in P being measured on a calibrated vacuum tube voltmeter connected through the coaxial line X_1. In order to eliminate electrostatic coupling between R and P a slotted copper screen, K, connected to the ground side of P, is interposed. Since the presence of P and K will have an effect on the rf magnetic field at S, they are left permanently in place after calibration of R. The accurate measurement of rf magnetic fields, especially at the highest frequencies we used, is known to be very difficult, mainly because of a lack of knowledge of the equivalent circuit elements. In our arrangement the presence of the coaxial lines X_1 and X_2 (100 cm long) are unavoidably bad features, since it is possible for them to resonate with the inductances P and R. In fact R and X_2 were found to be resonant at about 20 Mc/sec and this did result at the highest frequencies in an increase in the field at S for a given current. By making various measurements with X_1 and X_2 in place and then with shorter lines, however,

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[12] Ambler, Hudson, and Temmer (unpublished).

[13] N. Bloembergen and G. M. Temmer, Phys. Rev. **89**, 883 (1953).

[14] E. Ambler and R. P. Hudson (to be published). While a very large peak in both the real and imaginary parts of the dielectric constant was observed at 170°K [this is now known to be due to a ferroelectric transition, R. Pepinsky *et al.*, Phys. Rev. **102**, 1181 (1956)], the absorption decreased strongly with decreasing temperature.

[15] E. Ambler and R. P. Hudson, Phys. Rev. **102**, 916 (1956).

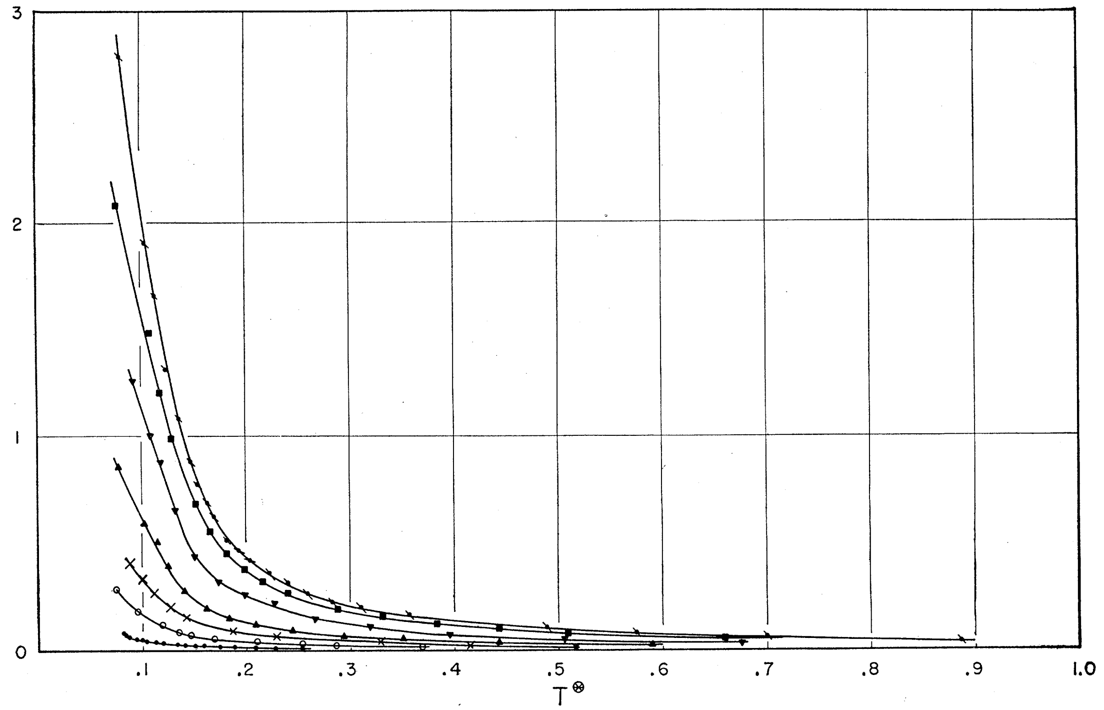

FIG. 2. Complex part of the magnetic susceptibility, χ'', (emu/g ion) plotted against "magnetic temperature," T^*, for various frequencies. ●, 0.1; ○, 0.5; ×, 1; ▲, 2; ▼, 4; ■, 6; and ⧸ 10 Mc/sec.

it was shown that the results were not affected by resonance between P and X_1. It was estimated, moreover, that the relative accuracy of measurement of h_0 over the frequency range used was about 5%, which would give a possible error of 10% in χ''. This figure seems to be supported by a close analysis of the final results.

The actual values of h_0 used in the experiments varied over a wide range and were preadjusted for the different frequencies and temperatures so that with a heating period of 10 to 60 seconds a convenient temperature rise was obtained. In practically all cases corrections for the background heating were entirely negligible.

III. RESULTS

Measurements were made at 0.1, 0.5, 1, 2, 4, 6, 8, and 10 Mc/sec over the entire temperature range, and the derived values of χ'' (emu per g ion) are plotted against the "magnetic temperature," T^*,[16] in Fig. 2. [To avoid overcrowding, the results for 8 Mc/sec have been omitted.] It is interesting to note that from a "practical" point of view the losses are extremely high. For example, at $T^*=0.1$ degree, $\chi''\simeq 2$ at 10 Mc/sec, while χ' would be ~ 20, so $\tan\delta=\chi''/\chi'=0.1$.

In Fig. 3, the values of χ'' are shown on a semilogarithmic plot as a function of frequency for the four temperatures 0.1, 0.15, 0.2, and 0.4 degree T^*. The most striking feature is the rapid increase in absorption with falling temperature, in contrast to the temperature-independent behavior found in earlier measurements in the region of 80°K.[1,3] Qualitatively the same behavior has been observed in experiments made at low audio-frequencies below 1°K.[8–10] In fact, the absorption is so large over a wide temperature region that the possibility occurs of using the effect in calorimetry and thermometry below 1°K (an extension of the "Leiden χ'' method"[10]). The rapid variation with temperature, however, undoubtedly presents a severe difficulty.

When absorption can be described by a relaxation time, τ_s, and the frequency is small compared with $1/\tau_s$, we can write $\chi''/\omega=\tau_s\chi$, where χ is the susceptibility of the spin system. In Fig. 4 we have plotted χ''/ω against T^* for the four frequencies 0.1, 0.5, 6, and 10 Mc/sec; values for the other frequencies have been omitted to avoid overcrowding. The rapid rise at low temperatures shows that a considerable increase in τ_s takes place. At high temperatures, i.e., above about 0.8°K, values of χ''/ω for different frequencies coincide within experimental error but this quantity is still decreasing as the temperature increases. At 1°K, for example, we find $\tau_s=4.2\times10^{-10}$ sec; this may be compared to the value 2.5×10^{-10} sec obtained at liquid air temperatures by Volger[17] for chromic potassium alum. At the lowest temperatures χ'' increases more slowly than ω, as can be seen from Fig. 4, but the deviation is

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[16] The correlation between T^* and T has been given by W. E. Gardner and N. Kurti, Proc. Roy. Soc. (London) **A223**, 542 (1954).

[17] Volger, de Vrijer, and Gorter, Physica **13**, 635 (1947).

not large. For example, at $T^*=0.1$ ($T=0.06$°K), χ'' is roughly proportional to $\omega^{0.83}$, which may be compared to the results of de Klerk[18] ($\propto\omega^{0.7}$) obtained at low audio-frequencies, again for chromic potassium alum. The situation appears, however, to be far too complicated to be described by a simple power-law relation.

IV. DISCUSSION

A description of the phenomenon in terms of hysteresis does not seem to be appropriate since this predicts χ'' to be independent of ω. It should be mentioned, however, that very small hysteresis effects have been observed in this salt[19] [as in most salts used in magnetic cooling], although at a temperature lower by a factor three than the lowest temperature of the present measurements, and by a factor fifty lower than the highest temperature. No definite explanation seems to have been put forward explicitly to account for the hysteresis, but it seems likely that one could be found along the lines proposed by Néel[20] in which the antiferromagnetic domain walls, which possess a net moment, are responsible. It would not be valid to use such a model to explain the present results, although a small amount of short-range order will exist and this, apparently, does affect relaxation times. Since our value of τ_s at 1°K is not flagrantly different from that predicted by Broer's theory, however, it seems preferable to discuss our results in terms of his theory, bearing in mind that it will probably need considerable refinement before it can be strictly applicable at such low temperatures. The problem, which has also been considered by Wright,[21] is in many ways similar to that connected with resonance line shapes.[22,23]

The absorption of energy is determined by the off-diagonal elements of the magnetic moment operator $M=g\beta\sum_i S_{zi}$, where the z axis is the direction of h_0, g the gyromagnetic ratio, and S the spin of a single ion, and the sum extends over all ions in the crystal. A quantity $f(\nu)$ is defined:

$$f(\nu)\Delta\nu=\sum_{\nu-\Delta\nu/2}^{\nu+\Delta\nu/2}|M_{kl}|^2, \tag{1}$$

where the sum contains the squares of all matrix elements for which the energy difference for the states k and l lies in the range $h(\nu-\frac{1}{2}\Delta\nu)$ to $h(\nu+\frac{1}{2}\Delta\nu)$. The power absorbed at frequency ν, $A(\nu)$, obtained using the standard formula for a first-order time-dependent perturbation, is then given by

$$A(\nu)=h_0\,(\pi^2/2)(\nu^2/kT)f(\nu), \tag{2}$$

provided $h\nu\ll kT$ (an assumption valid for our results). Thus we find

$$\chi''=(\omega/4kT)f(\nu). \tag{3}$$

Unfortunately it is not possible to compute $f(\nu)$ directly on account of the enormous number of energy levels involved, and what information is known has been obtained by the method of moments. The zeroth and second moments of $f(\nu)$ are found to be kC and $kC\nu_0^2$ respectively, where C is the Curie constant and $h\nu_0=g\beta H_i$, H_i being the rms value of the "internal" magnetic field. The value of H_i follows from Van Vleck's work[24] and has been quoted explicitly by Wright.[21] For a bcc lattice it is equal to

$$\{g^2\beta^2S(S+1)14.4N^2\}^{\frac{1}{2}},$$

and for chromic methylamine alum one finds $H_i=275$ gauss and hence $\nu_0=770$ Mc/sec. Since the calculation of higher moments is prohibitively lengthy, the procedure next followed is to choose a suitable analytical curve which fits the first two moments. It is not permissible to choose a Debye-type expression since this does not give a finite value for the second moment. Broer chooses a Gaussian expression, and we may write the final result:

$$\chi''=\frac{C}{T}\left(\frac{1}{8\pi}\right)^{\frac{1}{2}}\frac{\omega}{\nu_0}\exp(-\nu^2/2\nu_0^2). \tag{4}$$

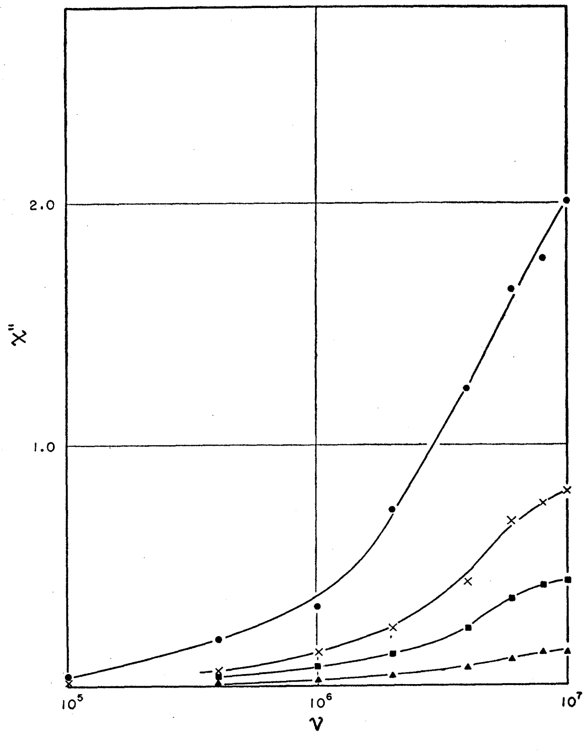

FIG. 3. Complex part of the magnetic susceptibility, χ'' (emu/g ion) plotted as a function of frequency, ν, for different "magnetic temperatures," T^*, ●, 0.1°; ×, 0.15°; ■, 0.2°; and ▲, 0.4° T^*.

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[18] De Klerk, Steenland, and Gorter, Physica **15**, 649 (1948).

[19] R. P. Hudson and C. K. McLane, Phys. Rev. **95**, 932 (1954).

[20] L. Néel (unpublished); see Yin-Yuan Li, Phys. Rev. **101**, 1450 (1956).

[21] A. Wright, Phys. Rev. **76**, 1826 (1949).

[22] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[23] M. H. L. Pryce and K. W. H. Stevens, Proc. Phys. Soc. (London) **A63**, 36 (1950).

[24] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

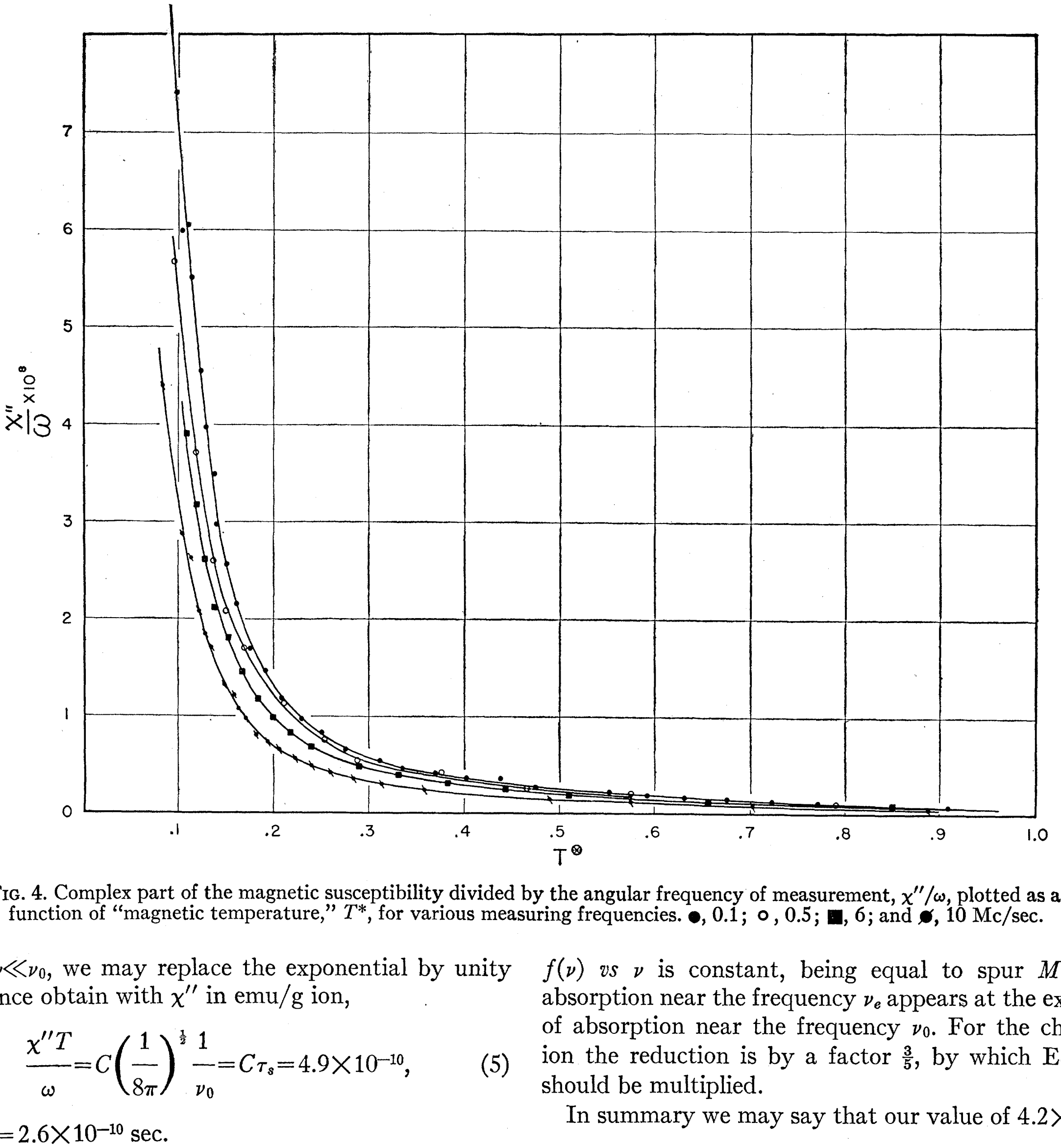

FIG. 4. Complex part of the magnetic susceptibility divided by the angular frequency of measurement, χ''/ω, plotted as a function of "magnetic temperature," T^*, for various measuring frequencies. ●, 0.1; ○, 0.5; ■, 6; and ✱, 10 Mc/sec.

Since $\nu\ll\nu_0$, we may replace the exponential by unity and hence obtain with χ'' in emu/g ion,

$$\frac{\chi''T}{\omega}=C\left(\frac{1}{8\pi}\right)^{\frac{1}{2}}\frac{1}{\nu_0}=C\tau_s=4.9\times10^{-10}, \tag{5}$$

and $\tau_s=2.6\times10^{-10}$ sec.

The experimental values of $\chi''T/\omega$ are plotted against frequency in Fig. 5 for various temperatures; the dotted line shows the value given by Eq. (5). At the highest temperatures the values of $\chi''T/\omega$ are about twice as large as the theory predicts, and decrease by a small amount at the higher frequencies. At the lower temperatures, however, not only are the values much higher but the decrease of $\chi''T/\omega$ with increasing frequency is much more pronounced.

Up to now the effect of the crystalline electric field upon the ions has not been introduced. When it is, the agreement with theory becomes slightly worse, as is the case for the results of Volger at higher temperatures. Broer points out that if the energy levels of the individual ions are split by an amount δ, say, then an absorption peak will occur at frequency $\nu_e=\delta/h$, and since for zero external field, the area under the curve of $f(\nu)$ *vs* ν is constant, being equal to spur M^2, the absorption near the frequency ν_e appears at the expense of absorption near the frequency ν_0. For the chromic ion the reduction is by a factor $\frac{3}{5}$, by which Eq. (5) should be multiplied.

In summary we may say that our value of 4.2×10^{-10}

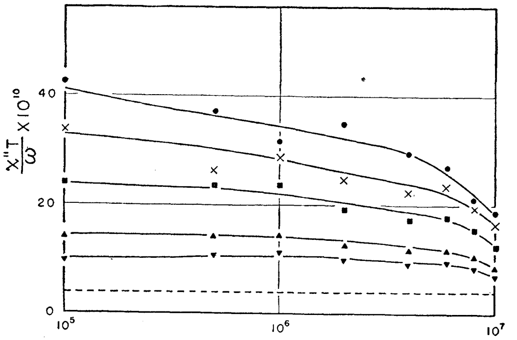

FIG. 5. Complex part of the magnetic susceptibility χ'', times the absolute temperature, T, divided by the angular frequency of measurement, ω, plotted as a function of frequency for various magnetic temperatures, T^*. ●, 0.1°; ×, 0.15°; ■, 0.2°; ▲, 0.4°; and ▼, 0.8° T^*.

sec for τ_s at 1°K, together with the observation that this quantity is still falling with increasing temperature, compares quite well with the measurements at higher temperatures which undoubtedly confirm the essential correctness of Broer's theory. Our results at very low temperatures show that in this temperature range the theory cannot be applied in its present form. This is not surprising for, besides the valid assumption that $h\nu \ll kT$, the further assumptions that $h\nu_0 \ll kT$ and $\delta \ll kT$, which would be invalid, seem to us to be implicit in the treatment. The limitations of the use of a Gaussian function for $f(\nu)$ were realized by Broer himself, and this kind of assumption has been discussed in a somewhat different connection by Van Vleck.[24] The experimental results give χ'' and hence $f(\nu)$ quite accurately in a range of temperature where deviations from Curie's Law are important. Such information should be of interest through the light it can throw on the behavior of substances just above their transition points, although this would only become really apparent if the behavior of $f(\nu)$ could be predicted theoretically. The quantity $f(\nu)$ is closely connected with the shape of resonance lines (compare references 21 and 22).

A different approach to the problem is suggested by the work of Bloembergen, Purcell, and Pound,[25] Anderson and Weiss,[26] Kubo and Tomita,[27] and others on the shapes of resonance lines from the point of view of stochastic processes. In the paramagnetic region the magnitude and direction of the local magnetic field acting upon an ion will be a random function with a "correlation time," $\tau_c \approx \tau_s$; at lower temperatures, when short-range order begins to be appreciable, we may expect an increase in τ_c and it might be possible to relate this to the observed increase in τ_s.

For example, a direct connection with Broer's theory can be established by comparing Eq. (2) above with the expression for the power absorption obtained using the formulas given in reference 27. The latter give for an isotropic substance

$$A(\nu) = \frac{h_0^2 \omega^2}{2kT} \int_0^\infty G(\tau)\, e^{-i\omega\tau} d\tau, \tag{6}$$

where $G(\tau)$ is called the "autocorrelation function" of the fluctuating magnetic moment in the direction of h_0, i.e., the z-axis. Thus

$$G(\tau) = \langle M_z(\tau + t) M_z(t) \rangle_{\text{Av over } t}.$$

Broer's assumption that $f(\nu)$ has a Gaussian distribution is equivalent to assuming that $G(\tau)$ is given by

$$G(\tau) = \tfrac{1}{3} g^2 \beta^2 S(S+1) \exp(-2\pi\nu_0^2 \tau^2).$$

We hope to extend these measurements to higher frequencies and lower temperatures[28] to obtain more complete information about $f(\nu)$. The behavior of $f(\nu)$ as the temperature passes through the Néel point[29] should be of theoretical interest. It would be more profitable, perhaps, to investigate substances which are magnetically anisotropic, in particular single crystals which have a preferred axis of very high susceptibility and which should provide results which would be simpler to analyze theoretically.

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[25] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[26] P. W. Anderson and P. R. Weiss, Revs. Modern Phys. **25**, 260 (1953); P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

[27] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[28] Preliminary measurements at lower temperatures show evidence of a maximum, with $\chi''/\omega > 20 \times 10^{-8}$.

[29] Measurements on $MnCl_2 \cdot 4H_2O$ have been made; E. Ambler and R. P. Hudson, Phys. Rev. **104**, 1506 (1956), following paper.