

Paramagnetic Dispersion Measurements at 77.3°K*

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The dispersion of the magnetic susceptibility of some paramagnetic compounds of Fe, Mn, and Cr, was studied at 77.3°K over a frequency range of 2 to 10 megacycles/sec. with magnetic fields up to 60,000 gauss. The results substantiate the theory of Casimir and du Pre, which is based upon the thermal coupling between the magnetic spin system and the lattice vibrations. The magnitude of the crystalline field splitting of the energy levels of the ground state was determined from the experimental results, for an assumed type of crystalline field and ionic arrangement. The splitting of chromic ammonium alum was found to differ from that of chromic potassium alum. The relaxation time for ferric ammonium alum was studied as a function of the magnetic field, and was found to fit an empirical formula which is based upon the theoretical conclusions of Van Vleck.

INTRODUCTION

THE dispersion of the magnetic susceptibility of some paramagnetic compounds in an alternating magnetic field was discovered by Gorter in 1936. Subsequent experimental work by Gorter, Brons, Teunissen, and others,^{1,2} on the frequency dependence of the susceptibility, and the associated energy absorption has clarified the nature of the phenomenon. They have shown that the dynamic susceptibility of paramagnetic compounds in an alternating magnetic field can be approximately described as a function of frequency by a simple dispersion formula, characterized by a relaxation time which is increased by a decrease of temperature or by the application of a constant parallel magnetic field. When a constant magnetic field is not present, the dispersion apparently disappears, and the dynamic susceptibility is the same as the static susceptibility determined by the customary static force methods. At the temperature of boiling N₂ (77.3°K) and above, the dispersion has been found in the radiofrequency range. Because the volume susceptibility of paramagnetics at these temperatures is small ($<10^{-3}$) a beat frequency method was used to study the dispersion. The energy absorption was determined by calorimetric methods. At the temperature of liquid helium

(1°–4°K), the phenomenon has been studied by de Haas and du Pre^{3,4} and the dispersion range was found to be less than 60 cycles/sec. Since the volume susceptibility at liquid-helium temperatures is quite large, a.c. bridge technique was used. The frequency dependence of the susceptibility and the energy absorption was determined directly from the bridge balance.

A thermodynamic explanation of paramagnetic dispersion has been presented by Casimir and du Pre⁵ and has been generalized by others.⁶ A thermal coupling between the magnetic spin system and the crystal lattice is assumed to exist. An applied magnetic field directly influences the energy (and thus the temperature) of the spin system only. In an alternating magnetic field the energy flows into and out of the spin system in a manner determined by the specific heats of the spin system and the crystal lattice, and the thermal conductance between the two. At temperatures where the lattice specific heat is large, the dynamic susceptibility at very high frequencies is effectively that of an adiabatic spin system, and at very low frequencies is that of an isothermal spin system. The nature of the thermal conductance mechanism between the spins and lattice has been the subject of detailed

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¹ C. J. Gorter, *Physik. Zeits.* **39**, 815 (1938), a review of the early work.

² P. Teunissen and C. J. Gorter, *Physica* **7**, 33 (1940).

³ W. J. de Haas and F. K. du Pre, *Physica* **5**, 501, 969 (1938); **6**, 705 (1939).

⁴ F. K. du Pre, *Physica* **7**, 79 (1940).

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

⁶ H. B. G. Casimir, *Physica* **6**, 156 (1939); R. de L. Kronig, *Physik. Zeits.* **39**, 823 (1938); P. Debye, *Physik. Zeits.* **39**, 616 (1938).

theoretical investigation, chiefly by Kronig⁷ and by Van Vleck.⁸

The susceptibility of most paramagnetic compounds is primarily due to the electron spin magnetic moment of the paramagnetic ions involved.⁹ The lowest energy states of these ions are degenerate, but in solids the degeneracy is completely or partially removed by the electrostatic field of the crystal lattice and by weak magnetic interaction. The resulting distribution of energy levels gives rise to a specific heat of atomic excitation (Schottky anomaly) for the magnetic spin system. In the case of the paramagnetic alums used for the adiabatic demagnetization cooling process, this anomaly reaches its maximum below 1°K. The determination of the absolute temperature from susceptibility measurements, below 1°K, requires a knowledge of the anomaly in the specific heat. Direct calorimetric measurements below liquid-helium temperatures involve major experimental difficulties, and at higher temperatures the anomalies are masked by the lattice specific heat. The paramagnetic dispersion in these compounds permits the separation of the spin specific heat from the lattice specific heat at temperatures very much higher than 1°K, since the high frequency susceptibility involves the adiabatic properties of the spin system. It is, therefore, possible to determine from dispersion measurements the constants involved in the spin specific heat anomalies (to a first approximation), and thus to aid in the establishment of the absolute temperature scale below 1°K. The present work was intended to verify the validity of the thermodynamic theory and to determine the constants of the spin specific heat for several compounds.

THEORY

The theory of Casimir and du Pre is based upon the thermodynamics of two coupled systems, the magnetic spin system and the lattice vibration system. The time required to establish temperature equilibrium within each system is assumed to be very small compared to the time required for equilibrium between the two sys-

tems. Since the theory is concerned with the latter time interval, each system is considered as internally in equilibrium, the spin system at a temperature T_S and the lattice system at a temperature T_L . Designate $\Theta = T_L - T_S$; α the thermal conductance between the spin system and the lattice; L the specific heat of the lattice; C_σ and C_H the spin specific heat at constant magnetization and constant field, respectively. The magnetic field H is the internal applied field (equal to the external applied field plus the demagnetizing field), and σ is the magnetization per unit quantity of the spin system. The case of interest is that of a constant field H_0 plus a parallel alternating field of amplitude h and frequency ν , so that $H = H_0 + he^{i\omega t}$ where $\omega = 2\pi\nu$ and t is the time.

The heat content of the spin system changes according to the equation

$$dq = dU - Hd\sigma = -\alpha\Theta dt,$$

where U is the internal energy of the spin system. With the assumption of adiabatic conditions for the paramagnetic compound as a whole, the resulting change of the spin system temperature $dT = d\Theta + \alpha\Theta L^{-1}dt$. Application of the fundamental thermodynamic relations of magnetization¹⁰ (T and H independent variables) gives the solution for the above field suddenly applied:

$$\Theta = \Theta_0 e^{-t/\tau} - T_S \left(\frac{\partial \sigma}{\partial T} \right)_H \frac{he^{i\omega t}}{C_H} \frac{i\omega\tau}{1+i\omega\tau},$$

where the relaxation time $\tau = C_H/\alpha(1+C_H L^{-1})$. The first term of this equation represents a transient temperature change due to the sudden application of H_0 , causing the spin temperature to increase isentropically¹¹ by an amount Θ_0 . The second term is the steady-state condition, and shows the frequency dispersion.

The dynamic susceptibility (measured by the change in inductance of the coil producing the alternating field in the specimen) at any frequency of the alternating field is found from the

¹⁰ P. S. Epstein, *Thermodynamics* (John Wiley and Sons, 1937), p. 346.

¹¹ The isentropic temperature rise may be computed from the equation $T_2 = T_1(1+cH^2/a)^3$, where T_1 and T_2 are spin temperatures before and after application of a field H , and a, c are constants defined later in the paper.

⁷ R. de L. Kronig, *Physica* **6**, 33 (1939).

⁸ J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

⁹ E. C. Stoner, *Magnetism and Matter* (Methuen, 1934), p. 310.

relation

$$\frac{d\sigma}{dH} = \left(\frac{\partial\sigma}{\partial H}\right)_T + \left(\frac{\partial\sigma}{\partial T}\right)_H \frac{dT_s}{dH}$$

The steady-state condition is then

$$\frac{\chi_\omega}{\chi_0} = 1 - \frac{C_H - C_\sigma}{C_H} \left(\frac{i\omega\tau}{1 + i\omega\tau} \right) - \frac{C_H - C_\sigma}{C_H + L} \left(\frac{1}{1 + i\omega\tau} \right), \quad (1)$$

where $\chi_\omega = d\sigma/dH$ is the dynamic susceptibility and $\chi_0 = (\partial\sigma/\partial H)_T$ is the isothermal susceptibility. The dynamic susceptibility is the adiabatic susceptibility of the specimen as a whole, but only at very high frequencies is it the adiabatic susceptibility of the spin system.

The lattice specific heat L follows the Debye T^3 law at low temperatures. At liquid-hydrogen temperatures ($\sim 20^\circ\text{K}$) or above, the value of L for most paramagnetics is so much greater than the magnetic specific heats that Eq. (1) reduces to

$$\frac{\chi_\omega}{\chi_0} = 1 - \frac{C_H - C_\sigma}{C_H} \left(\frac{\omega^2\tau^2 + i\omega\tau}{1 + \omega^2\tau^2} \right). \quad (2)$$

Below liquid-helium temperatures L becomes negligible, and Eq. (1) gives as the ratio of the adiabatic to isothermal susceptibilities $\chi_\omega/\chi_0 = C_\sigma/C_H$ at all frequencies. At liquid-helium temperatures it is possible to increase the effective L by placing the crystals of the specimen in direct contact with the liquid helium. The effectiveness of this procedure depends upon the thermal conductance from all parts of the crystal lattice to the liquid helium, and this is as yet an uncertain quantity. For the remainder of this paper, only high temperatures will be considered and Eq. (2) will be used.

Thermodynamics contributes the additional relation

$$C_H - C_\sigma = T \left(\frac{\partial\sigma}{\partial T} \right)_H^2 / \left(\frac{\partial\sigma}{\partial H} \right)_T. \quad (3)$$

The value of C_σ is the same as that of C_0 (specific heat at zero field) for the spin system, since, when σ is constant, no magnetic work is involved

and C_σ is thus independent of the field strength. (This is true only of perfect magnetics where σ is a function of H/T , and U is therefore independent of H .) The value of C_0 may be computed from the partition function for the lowest energy state of the paramagnetic ion, when split by the crystalline field and magnetic interaction. This has been done by Van Vleck,¹² and by Hebb and Purcell.¹³ At temperatures where kT is large compared to the energy difference between the split levels, the specific heat anomaly has the customary form $C_0 = a/T^2$ where the constant a involves the magnitude of the splitting. The alums and most of the other compounds investigated behave as ideal paramagnetics at liquid-helium temperatures and above, i.e., the magnetization $\sigma = cH/T$ where c is the Curie constant for the paramagnetic ions involved. Substitution of these relations into Eq. (3) gives

$$C_H T^2 = a + cH^2. \quad (4)$$

For the purpose of dispersion studies, the only part of the applied field that need be considered in Eq. (4) is the constant field H_0 (henceforth used without the subscript). The effect of the alternating field may be neglected because of its relatively small magnitude. The alternating field also modulates χ_ω at a frequency double that of the applied frequency, but this is not detectable by the usual measurements.

The magnetic work $Hd\sigma$ used in the above thermodynamic treatment is more precisely the scalar product $(\mathbf{H} \cdot d\boldsymbol{\sigma})$. Since the change of magnetization is produced by the alternating field, only that component of the alternating field parallel to the constant field is involved in the dispersion. This conclusion has been experimentally investigated by Teunissen and Gorter,¹⁴ and they found it to be correct.

METHOD OF MEASUREMENT

A schematic diagram of the apparatus used in the present research is shown in Fig. 1. The constant magnetic field was created by a solenoid electromagnet (No. 4 of the M.I.T. magnet

¹² J. H. Van Vleck, *J. Chem. Phys.* **5**, 320 (1937).

¹³ M. H. Hebb and E. M. Purcell, *J. Chem. Phys.* **5**, 338 (1937).

¹⁴ P. Teunissen and C. J. Gorter, *Physica* **5**, 486 (1938).

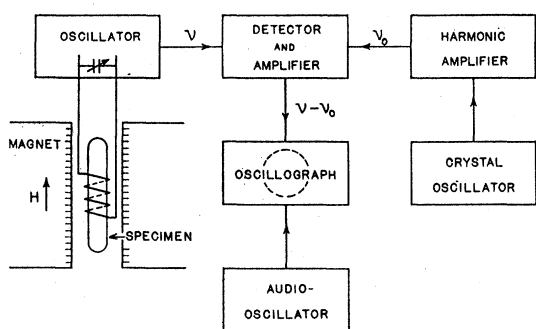


FIG. 1. Schematic diagram of the apparatus.

laboratory)¹⁵ which permitted investigations up to 60,000 gauss. The coil in which the specimen was placed was connected in parallel with a capacitance, and the resulting resonant circuit determined the frequency of a stable oscillator.¹⁶ The output of this specimen oscillator was beat with the output of a crystal controlled oscillator. The crystal had a fundamental frequency of 100 kc/sec. and by means of a harmonic amplifier any multiple of this frequency could be selected. The two signals were fed into an ordinary radio receiver and the audiofrequency beat note was amplified and appeared across one set of plates of a cathode-ray oscillograph. The output of a calibrated audiofrequency oscillator was connected to the other set of plates, and the frequency of this oscillator was adjusted to maintain a standing pattern on the oscillograph. In this manner any change of frequency of the specimen oscillator could be followed by the audio-oscillator. Since the inductance of the coil surrounding the specimen was a function of the dynamic susceptibility of the specimen, the effect of the applied constant magnetic field could be determined from the resulting frequency change of the specimen oscillator.

The electromagnet had a cylindrical core 4 inches in diameter into which was placed a Dewar flask containing the specimen and coil.

¹⁵ F. Bitter, *Rev. Sci. Inst.* **10**, 373 (1939).

¹⁶ The oscillator was designed for maximum frequency stability, and used a push-pull circuit which required only two coil leads. Since varying load on the oscillator causes frequency variation by changing the grid current, and thus the input capacitance of the vacuum tubes, the circuit was designed to compensate automatically for this effect. At 10 megacycles/sec. the frequency did not wander more than 1 cycle/sec. during the time required for a set of measurements (about 15 minutes).

The paramagnetic compounds were sealed off with helium gas in Pyrex specimen tubes 6 cm long and 1.3 cm in diameter. By means of a string the specimens could be lowered into another Pyrex tube of slightly greater diameter, upon which was wound the coil. The tube with the coil fitted into another Pyrex tube sealed off at the bottom, and the whole assembly was then placed in the Dewar. The purpose of this last tube was to separate the coil from the liquids in the Dewar. It was found that, without this protection, the gas bubbles of the boiling liquid caused transient disturbances of the distributed capacitance of the coil. The coil used for investigations over the frequency range of 2–10 megacycles/sec. was about 4 mm wide and consisted of 10 turns of No. 28 copper wire. The apparatus was arranged so that the coil was in the center of the magnet and was also at the center of the specimens inserted in it. When liquid nitrogen was used in the Dewar, the tubes contained hydrogen gas to provide thermal contact between the specimen and the liquid nitrogen. A specimen originally at room temperature required about 2 minutes to reach thermal equilibrium with the bath.

The dynamic susceptibility, as given by Eq. (2), consists of a real and imaginary component,

$$\chi_{\omega} = \chi' - i\chi'',$$

$$\frac{\chi'}{\chi_0} = 1 - F \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2},$$

$$\frac{\chi''}{\chi_0} = F \frac{\omega \tau}{1 + \omega^2 \tau^2},$$

where

$$F = (C_H - C_0) / C_H = [1 + (a/cH^2)]^{-1}. \quad (5)$$

The inductance of the coil surrounding the specimen is $L = L_0 + A\chi'$, where L_0 is the inductance when no specimen is present, and A is a constant (maximum value = $4\pi L_0$) depending upon the volume of the coil field filled by the specimen. The frequency of the specimen oscillator is given by the equation $\omega^2 LC = 1 - (CR^2/L)$, where R is the effective radiofrequency resistance of the coil. The resistance term of this equation is generally negligible, although it may produce a second-order effect at very low temperatures.

If this term is neglected, the fractional change of frequency due to the specimen is given by $2d\nu/\nu = -dL/L$, where $dL = A\chi'$ and $L \approx L_0$, since the specimen susceptibility is very small. At liquid-nitrogen temperatures the value of $d\nu/\nu$ for most of the paramagnetics was approximately 10^{-4} to 10^{-5} .

The energy absorption accompanying the frequency dispersion is represented by the out-of-phase component of the susceptibility, χ'' . This results in an increase of the effective radio-frequency resistance of the coil equal to $A\omega\chi''$. A simple calculation shows that the energy absorbed per second is $W = \frac{1}{2}h^2\omega\chi''$, (per unit volume if χ is the volume susceptibility). It is apparent that, as a function of increasing frequency, R and W increase rapidly in the dispersion region and reach a constant value at high frequencies. The energy absorbed per cycle (W/ν) is a maximum when $\omega = \tau$. The increase of the coil resistance has two effects on the frequency of the oscillator. The first is that due to the resistance term in the frequency formula, and this is usually negligible. The second is that due to the increased load on the oscillator, and this may be appreciable. As mentioned in footnote 16 the present oscillator compensated for this effect.

The procedure used for a set of measurements was as follows. The variable capacitance of the specimen oscillator was adjusted to give a suitable beat note with the desired crystal harmonic. The frequency of the beat note as a function of the applied constant field was then measured. Inasmuch as the maximum field (60,000 gauss) was more than sufficient to make χ_ω negligible at the high frequencies, the total change of the beat frequency from zero field to the maximum field was assumed to represent the total effect of χ_0 . The value of χ_ω/χ_0 for any intermediate field was then the ratio of the frequency change from the maximum field to the intermediate field, to the total frequency change to zero field. This method was used because when the specimen is inserted into the coil a very large frequency change results from the effect of the dielectric constant of the specimen upon the distributed capacity of the coil. This capacitance change is, of course, independent of the applied

field, and may be approximately evaluated by the use of a non-magnetic dummy specimen with similar dielectric properties (such as aluminum alum). The dummy method has been used in all previous researches,^{1,2} but has the serious objection that the dielectric behavior of the specimen depends not only on chemical similarity but also on geometric similarity. Since the compounds are either powders or small crystals, the packing density would be a variable of major importance and uncertainty. A Faraday screen would help to reduce the capacitance effect, but this was not used since the method described at the beginning of the paragraph appeared to be adequate, and there is no evidence to raise any doubts concerning it.

RESULTS

The present investigation was confined to the frequency range of 2–10 megacycles/sec. and to room temperature and liquid-nitrogen temperature (77.3°K). The compounds studied were all of analytical reagent purity, some commercial and some prepared in the laboratory. In addition to those listed in Table I, the following substances were investigated and showed no dispersion; FeCl_3 (anhydrous sublimed), MnCO_3 , and MnF_2 . These three compounds and the $\text{CrNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ have not been studied before. The isothermal susceptibilities of all the substances that have shown dispersion follow the Curie law at the temperatures used.

A detailed comparison between the present results and those of Teunissen and Gorter² will not be made, although there is general qualitative agreement. Their frequency range did not go higher than 4 megacycles/sec. (except for one instance where the frequency was 7 Mc),¹⁷ and

TABLE I. *Spin system data determined from dispersion measurements.*

	$10^{-6}a/c$			$10^{-6}a$	η	δ
	STARR 77°	TEU- NISSEN AND GORTER 77°	DU PRE 1°-4°			
$\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.263	0.248	0.256	1.14	0.0472°	0.193°
$\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	0.64	0.7	0.80	1.19	0.0204	0.231
$\text{CrNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	2.68			4.99	0.0200	0.486
$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	4.2	6.2		18.2	0.126	0.903
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	19.8	19.5		85.9	0.135	2.11

¹⁷ P. Teunissen and C. J. Gorter, *Physica* **6**, 1113 (1939).

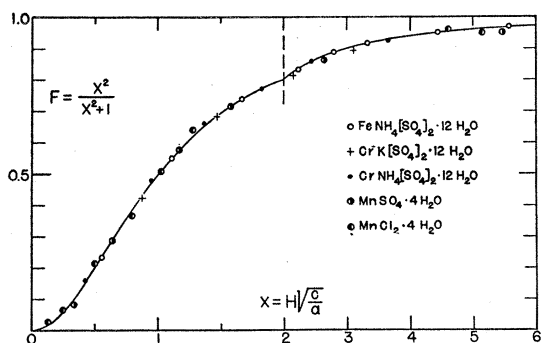


FIG. 2. The factor $F = (C_H - C_\sigma) / C_H$ as a function of the parameter $X = H / (c/a)^{1/2}$. The solid line represents the formula $F = [1 + (a/cH^2)]^{-1}$. The second half of the graph has a condensed scale.

their maximum field was 3200 gauss. Most of their data involve extrapolation and approximation. Their early results are based upon a combination of absorption and dispersion measurements, and apparently contain some undetermined experimental error;¹⁷ only their very latest data² are free from this error. A detailed comparison is also made difficult by the fact that Teunissen and Gorter found that specimens from different sources gave different quantitative results. This was probably due to variations in the water of hydration, since many of the compounds are unstable in this respect. The results of the present work are more precise and reliable than those of Teunissen and Gorter, for the following reasons. First, the use of higher frequencies enabled the determination of the F values without extrapolation. Second, as explained in the section on measurement, the strong magnetic fields available permitted the author to dispense with the correction for the dielectric constant effect, and therefore the large errors involved in the use of the non-magnetic dummy do not enter into the present results.

The general formula for dispersion effects, resulting from systems with a relaxation time, has the frequency dependence given by Eq. (2).¹⁸ However, the model assumed by Casimir and du Pre is uniquely responsible for the factor $F = (C_H - C_\sigma) / C_H$. The validity of their theory would be proven if the paramagnetic dispersion

¹⁸ The electrical system consisting of an inductance connected in parallel with a resistance has a resulting impedance which exhibits the frequency dependence given by the frequency term of Eq. (2).

followed Eqs. (2) and (5). The dependence of F upon the applied field is given by Eq. (5), and, since a and c are constants independent of field and temperature (except for very low temperatures), F should be independent of temperature.

In order to study the F values, the present measurements were made at 10 megacycles/sec. At 77°, for the compounds investigated, this frequency results in a value of $\omega \gg \tau$. In those cases where there was a dependence of χ' upon frequency in the range studied, this could be corrected by calculation of the relaxation time. In no case did this correction amount to more than a few percent. The author's experimental results are shown in Fig. 2. The experimental curve of F vs. H has been replotted for each compound in terms of the parameter $X = H / (c/a)^{1/2}$. The value of a/c is chosen so that when $F = 0.5$, $X = 1$. The a/c values found this way are given in Table I. The solid curve of Fig. 2 represents the plot of Eq. (5). It is apparent that, within the experimental error (about 2 percent), the field dependence of F is the same for all the compounds and is that theoretically predicted. The effect of temperature on F is not very certain. The comparison of the results of different investigators in Table I is not very conclusive because of the reasons discussed above. In the case of the most investigated compound, $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, the a/c value appears to be reasonably independent of temperature. Teunissen and Gorter¹⁷ made a detailed study of this point and also came to the same conclusion. An investigation of paramagnetic absorption and dispersion in $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ at 64°, 77°, and 90°K has recently been made by Gorter, Dijkstra, and Groendijk.¹⁹ Their dispersion results gave the same value of $a/c = 0.76 \times 10^6$ at all the temperatures, but their absorption measurements are not easily interpreted. Both $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ show dispersion at room temperature, and the present work showed that the a/c value at this temperature is the same as that at 77°. In general, the evidence seems to indicate that the F function is independent of temperature and that the model of paramagnetic dispersion assumed by Casimir and du Pre is correct.

¹⁹ C. J. Gorter, L. J. Dijkstra, and H. Groendijk, *Physica* 7 (July, 1940).

The specific heat constant a consists of two terms, one due to the crystalline field splitting and the other due to the splitting caused by the magnetic spin-spin interaction. Waller,²⁰ Van Vleck,¹² and Hebb and Purcell¹³ have theoretically evaluated these terms. At the comparatively high temperatures involved in these dispersion measurements, the value of a for the Cr^{+++} compounds is

$$a = 0.250R\delta^2 + 2.40R\eta^2 \text{ ergs deg. mole}^{-1},$$

where R is the gas constant per mole, δ is the crystalline field splitting in degrees, and η is the characteristic temperature of the magnetic spin-spin interaction (approximately the ferromagnetic Curie temperature). For the Cr^{+++} compounds, the Curie constant is $c = 1.86 \text{ erg deg. gauss}^{-2} \text{ mole}^{-1}$. The value of a for the Fe^{+++} and Mn^{++} compounds, for the case of a cubic crystalline field and a face-centered arrangement of the paramagnetic ions, is

$$a = 0.222R\delta^2 + 2.40R\eta^2,$$

and the Curie constant is $c = 4.34$. The structure of the ferric ammonium alum is such that this formula has been assumed to be applicable. The crystal structures of the Mn^{++} compounds investigated have not been determined. However, the above formula was arbitrarily assumed to hold in this case also, in order to arrive at some estimate of the quantities involved. Table I contains the values of a and δ based upon the a/c values of the present research. The characteristic temperature η was computed from the following definitory formula given by Van Vleck¹² (the τ of his paper), $\eta = Ng^2\beta^2 J(J+1)/k$, where N is the number of magnetic ions per cc, and the remaining symbols have their customary meaning.

Kronig and Bouwkamp²¹ have shown on theoretical grounds that in the case of $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ magnetic fields greater than about 900 gauss should suppress the magnetic interaction between spins, so that only the splitting due to the crystalline field should remain. From the values in Table I, the crystalline splitting specific heat is about 60 percent of the total. According

to Kronig and Bouwkamp the low field value of $F = [1 + (a/cH^2)]^{-1}$ should change at high fields to $F = [1 + (0.53a/cH^2)]^{-1}$. A field of 900 gauss corresponds to an $F = 0.75$, and any marked deviation from the low field F formula should, therefore, be observable. No such deviation was found, as can be seen from Fig. 2. If this effect should occur at a very much higher field, so that $F \approx 1$, it would not be detectable. The conclusion that the effect predicted by Kronig and Bouwkamp does not exist in the experimentally detectable range was also reached by du Pre,⁴ from his measurements at liquid-helium temperatures.

The properties of $\text{CrNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ differ from those of $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, as shown in Table I. According to Lipson and Beevers²² the crystal structures of these two alums are the same. The Cr^{+++} ion in the alums is surrounded by an octahedron of six water molecules. The distortion of this octahedron, giving rise to a trigonal crystalline field, is responsible for the crystalline splitting. The difference in distortion required to produce the differing fields in the two alums is probably not very large. In this connection, the work of Kraus and Nutting²³ on the absorption spectra of the chrome alums is of interest. They found that the ammonium alum goes through a crystal structure transition at 81°K with a change in the absorption spectrum. The transition is sluggish and the alum is easily

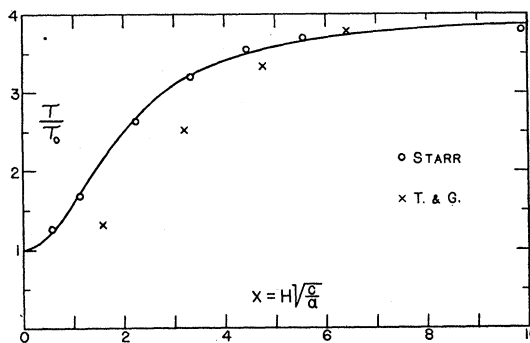


FIG. 3. The relaxation time of $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ as a function of the parameter $H/(c/a)^{1/2}$. The solid line represents the formula $\tau = \tau_0 4(1 + X^2)/(4 + X^2)$.

²⁰ I. Waller, *Zeits. f. Physik* **104**, 132 (1936).

²¹ R. de L. Kronig and C. J. Bouwkamp, *Physica* **5**, 521 (1938); **6**, 290 (1939).

²² H. Lipson and C. A. Beevers, *Proc. Roy. Soc.* **A151**, 347 (1935).

²³ D. L. Kraus and G. C. Nutting, *J. Chem. Phys.* **9**, 133 (1941).

supercooled. The potassium alum does not have this transition. It is possible that this difference in the two alums is related to the difference in the observed crystalline field splittings.

In the frequency range studied, sufficient dispersion was found in $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ at 77° to permit the determination of the relaxation time τ as a function of the applied field. The definition and Eq. (4) give

$$\tau = C_H/\alpha = (a + cH^2)/T^2\alpha.$$

The previous experimental work² (with which the present is in qualitative agreement) has shown that α , the thermal conductance, is a function of the applied field and temperature. The theoretical study of α by Van Vleck⁷ has shown that α should be proportional to $(1 + bH^2)$ where b is a constant. This suggestion has been included in the following empirical equation, which has been found to fit the present results for the ferric alum at 77° .

$$\tau = \tau_0 4(1 + X^2)/(4 + X^2),$$

where $X = H(c/a)^{1/2}$ and $\tau_0 = 4.05 \times 10^{-8}$ seconds. The solid curve shown in Fig. 3 represents this equation, with the a/c value from Table I. The experimentally determined values of τ , also shown, fit this curve within the experimental error (2 percent). The factor 4 in the equation is the ratio of the relaxation times in infinite field and zero field. The value 4 is within the theoretical limits (1.7–4.5) found by Van Vleck⁸ for ferric alum. The relaxation times found by Teunissen and Gorter¹⁷ are also shown in Fig. 3, with an assumed $\tau_0 = 7.0 \times 10^{-8}$ second. There is no possible adjustment of the constants of the above type of formula which will make it fit their data. With the τ_0 found in the present research ($\tau_0 = 4.05 \times 10^{-8}$) the formula

$$\tau = \tau_0 7(1 + X^2)/(7 + X^2)$$

is in very rough agreement with the results of Teunissen and Gorter, but the ratio 7 is much greater than that theoretically permitted by Van Vleck.

The paramagnetic compounds which do not exhibit dispersion (FeCl_3 , MnCO_3 , MnF_2 , and the long list of Teunissen and Gorter²) appear to fall into two classifications. The first includes

ions of the first transition series which are not known to exhibit dispersion in any of their compounds, i.e., all ions except Fe^{+++} , Mn^{++} , Cr^{+++} , and V^{++} . According to Kronig⁷ and Van Vleck⁸ the energy separation of the ground state from the excited states is very small in the ions of this group. This results in a large spin-lattice coupling through the orbital moment of the excited states. As a consequence of the resulting large α , the relaxation time is very small and the dispersion region involves frequencies very much higher than is experimentally practical. The second group which does not exhibit dispersion includes compounds of Fe^{+++} , Mn^{++} , Cr^{+++} , and V^{++} which have little or no water of hydration. It is unlikely that any effect of dehydration in these compounds would cause a sufficient decrease in relaxation time to move the dispersion region outside the experimental range. The absence of dispersion in the second group is probably due to the increased specific heat of the spin system, as a result of the increased crystalline field asymmetry and the increased magnetic spin-spin interaction caused by the dehydration. In the present research, FeCl_3 , MnF_2 , and MnCO_3 were investigated up to 60,000 gauss without any detectable effect upon the dynamic susceptibility. Since a value of $H(c/a)^{1/2} = 0.2$ may be easily detected, the a/c value for these compounds must be greater than 10^{11} for the dispersion effect to be undetectable. This is about 4×10^5 times as large as the value for ferric ammonium alum. Inasmuch as the value of c is approximately independent of the state of hydration, the specific heat of the spin system would have to be responsible for this large ratio ($a = C_0 T^2$). This is not an unreasonable situation. It is known that the unusual magnetic properties of the anhydrous compounds of the iron group²⁴ are probably due to strong magnetic exchange interaction, as in ferromagnetism. In the case of FeCl_3 this produces a Curie point²⁴ of -12° , and in MnF_2 an antiferromagnetic Curie point of 70° has been found.²⁵ Since the specific heat is roughly proportional to the square of the Curie point temperature, the spin

²⁴ C. Starr, F. Bitter, and A. R. Kaufmann, *Phys. Rev.* **58**, 977 (1940); C. Starr, *Phys. Rev.* **58**, 984 (1940).

²⁵ W. J. de Haas, B. H. Schultz, and J. Koolhaas, *Physica* **7**, 57 (1940).

system specific heat of FeCl_3 due to magnetic causes alone is about 0.65×10^5 times as great as that of ferric alum ($\eta = 0.047^\circ$), and that of MnF_2 is 22×10^5 times that of ferric alum. As most of the dehydrated compounds have Curie point temperatures of similar magnitudes, the explanation given above for the apparent ab-

sence of dispersion in these compounds is probably correct.

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Remarks on the Volume Magnetostriction of Nickel

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Results of a theory of volume magnetostriction developed in a recent paper and applied there to iron are applied here to the case of nickel, and a correction is made of the data on iron. The molecular field factor N , its dependence on volume, the magnetization at absolute zero I_0 and its dependence on volume are calculated and discussed. Contrary to the results of magnetocaloric effect, and in accord with the expectations based on the dependence of the exchange integral on interatomic distance, N appears to decrease in nickel with increasing volume (for $j=1$). To account for the dependence of the magnetization, at absolute zero, on volume it is necessary to assume a dependence of the number of holes in the $3d$ band on the interatomic distance. This dependence can be understood on the basis of the band structure, which can be obtained by extrapolating Krutter's calculations on copper. Corrected numerical values for iron are given.

IN a recent paper,¹ referred to as I, certain relations were developed between the observed change of volume $(1/V)(\partial V/\partial H) = (\partial\omega/\partial H)$ of magnetized ferromagnetic metals at saturation, the molecular field factor N , and the magnetization at absolute zero I_0 . The formulas were applied to the case of iron and some conclusions relative to specific heat were drawn. The aim of the present paper is twofold. Similar considerations will be made for nickel, and at the same time an error, kindly pointed out to the author by Drs. Primakoff and Holstein, will be corrected. This correction, though not affecting the main conclusions of I, introduces some small changes of the numerical values.

We indicate first the corrections: from the formula²

$$\begin{aligned} (\partial V/\partial H)_{T,p} &= -(\partial VI/\partial p)_{T,H} \\ \text{we have} \quad (\partial I/\partial p)_{T,H} &= -(\partial\omega/\partial H)_{T,p} + I\kappa \end{aligned}$$

and similarly

$$\left(\frac{\partial I}{\partial T}\right)_v = \left(\frac{\partial I}{\partial T}\right)_p - \frac{3\alpha}{\kappa} \left(\frac{\partial\omega}{\partial H}\right)_{T,p} + 3\alpha I. \quad (1)$$

Therefore in formulas (7, I) and (8, I) one has to substitute $(\partial\omega/\partial H)_{T,p} - I\kappa$ for $(\partial\omega/\partial H)_{T,p}$. Similar corrections in (9, I) are necessary but they cancel out finally so that formula (10, I) remains valid.³ The corrected numerical values for iron are given in the last part of this paper. Let us now go over to the case of nickel.

The main difficulty in applying the theory to the case of nickel is the fact that very few data on volume magnetostriction in the saturated state are known. Systematic studies of this effect at various temperatures, such as were made for iron by Kornetzki, are not available. The effect itself is much smaller than in the case of iron and corrections due to magnetocaloric effect are

¹ R. Smoluchowski, *Phys. Rev.* **59**, 309 (1941).

² R. Becker, *Zeits. f. Physik* **87**, 547 (1934).

³ There is a misprint in the formula following formula (9, I): it should be $N(\partial I/\partial T)_v$ instead of $(\partial I/\partial T)_v$; also, on p. 313, in the fifteenth line from the bottom, ρ should read τ .