

However, [37] is in disagreement with (37) and (41); in particular, the exponent in the former is half that in the latter. The numerical solutions to Eqs. (32)–(34) support (37) and (41) rather than [37].

Ledinegg and Urban obtain their asymptotic estimate as follows. The function $f(\xi)$ in (32) (their Eq. [23]) is set equal to

$$f(\xi) = f_0(\xi) + \phi(\xi), \quad [24a]$$

where $f_0(\xi)$ is the solution of (19) given by (23). They assume that

$$|\phi(\xi)|/f_0(\xi) \ll 1, \quad [24c]$$

stating that this inequality will be justified through an explicit calculation of the function ϕ . The justification for [24c] is contained in their Eq. [33a] which indicates that [24c] is correct, but *only* for $|\xi| < \alpha$. But they have already used [24c] for $|\xi|$ greater than α in order to deduce an approximate integral equation for ϕ , [26b]. Thus their treatment is not internally consistent.

On the basis of our results it may be shown that $f(\xi)$ decreases as ξ^{-2} for large ξ ; on the other hand, $f_0(\xi)$ decreases exponentially. Hence, in fact, [24c] does not hold for $\xi > \alpha$, and the integral equation [26b] is not correct.

Zero-Field Spin Absorption in Paramagnetic Salts*

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The spin absorption spectrum in the absence of a static magnetic field has been observed in several paramagnetic salts at liquid-helium temperatures. The absorptive component of the complex susceptibility χ'' was measured as a continuous function of frequency over the range 130–4000 Mc/sec by observing the influence of powdered samples on the transmission of a tunable coaxial resonant cavity. Exchange narrowing in qualitative agreement with the theory of Wright was observed in cupric salts. Moments of the shape functions obtained by expressing the results in terms of an empirical, fitted function yield, on the basis of the theories of Wright and Caspers, values of the exchange constant A of 3.3 and 3.7 for the cupric potassium and cupric ammonium Tutton salts, respectively. The cupric salt experimental curves are lower and broader than the curves proposed by Locher and Gorter. The absorption band in chromic potassium alum has a “flat-topped” appearance, and a width approximately three times the dipolar relaxation frequency ν_0 . No temperature dependence of the shape functions was observed.

I. INTRODUCTION

SPIN absorption refers to the absorption of energy from an oscillating magnetic field by a system of mutually interacting magnetic spins which occurs whenever the frequency of oscillation is sufficiently high to compete with the relaxation processes tending to maintain the internal statistical equilibrium of the system. Two classes of spin systems have been investigated: assemblies of atoms having nuclear magnetic dipole moments and crystalline compounds containing magnetic ions. The nuclear magnetic case, for which the spin absorption frequencies are of the order 10^4 cps, has been discussed by Anderson.¹ Magnetic ions in concentrated magnetic salts have spin absorption frequencies of the order 10^9 cps, and have been the subject of a large number of investigations,^{2–7} including the experiments reported in the present paper.

In paramagnetic salts, for the case of small or zero static magnetic fields, and at frequencies much higher than the reciprocal of the spin-lattice relaxation time ($\tau_L^{-1} < 10^8$ cps at liquid-helium temperatures), the absorption of energy from the oscillating field is a manifestation of the spin-spin relaxation processes. Even a weak spin-lattice interaction is sufficient to maintain the spin system in good thermal contact with the lattice, but slight departures from equilibrium completely internal to the spin system give rise to a quadrature component of the magnetization χ'' . The resulting spin absorption, proportional to χ'' , may be thought of as arising from transitions among energy levels each of which corresponds to a stationary state of the crystal as a whole. The frequency dependence of χ'' is expressed in the form

$$\chi'' = \frac{1}{2}\pi[\nu f(\nu)/kT], \quad (1)$$

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¹ A. G. Anderson, Phys. Rev. **125**, 1517 (1962).

² For a review of early work, see C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, New York, 1947); C. J. Gorter, *Progress in Low Temperature Physics* (Interscience Publishers, Inc., New York, 1957), Vol. II, p. 267.

³ L. J. Smits, H. E. Derksen, J. C. Verstelle, and C. J. Gorter, *Physica* **22**, 773 (1956).

⁴ J. C. Verstelle, G. W. J. Drewes, and C. J. Gorter, *Physica* **24**, 632 (1958).

⁵ H. Hadders, P. R. Locher, and C. J. Gorter, *Physica* **24**, 839 (1958).

⁶ P. R. Locher and C. J. Gorter, *Physica* **27**, 997 (1961).

⁷ P. R. Locher and C. J. Gorter, *Physica* **28**, 797 (1962); P. R. Locher, thesis, Leiden, 1962 (unpublished).

where the possible temperature dependence of the shape function $f(\nu)$ is usually not explicitly expressed. An "apparent" spin-spin relaxation time τ_S is defined in terms of the shape function by

$$\tau_S = f(0)/4\chi_0 kT, \quad (2)$$

where $f(0)$ refers to $f(\nu)$ evaluated at frequencies for which $\nu\tau_S \ll 1$, and χ_0 is the static susceptibility. In the absence of a static magnetic field, the spin absorption takes place in a region near zero frequency whose mean width is of the order of τ_S^{-1} , or about 1000 Mc/sec. When a static field H_0 is present, in addition to the absorption in the so-called zero-frequency band, there is also absorption in regions centered on the Larmor frequency γH_0 and multiples of γH_0 . Crystalline Stark effects complicate the situation by causing additional absorptions at frequencies corresponding to the low-lying electrical splittings, as well as cross-relaxation effects.⁸

We are concerned in this paper with the absorption in the zero-frequency band. Broer,⁹ following a method pioneered by Waller,¹⁰ was able to compute values for the first two nonvanishing (even order) moments of the shape function describing this band, assuming magnetic dipole interactions only. Computation of higher order moments is exceedingly complicated; Broer instead postulated an analytical form for the shape function. His choice was a Gaussian expression, normalized to fit his computed low-order moments; he used this function to derive theoretical values of the spin-spin relaxation time. Wright¹¹ included the effects of exchange interactions, and in approximate form extended the moment computations to higher order. She showed that a nonvanishing exchange constant A causes a broadening of the zero-frequency band in the presence of large static magnetic fields, whereas there is an exchange narrowing in the zero-field case. Caspers,¹² in a recent paper, considered the effects of hfs. All of the above studies have been restricted to cases where either $H_0 = 0$, or H_0 is very much greater than the internal fields H_i . The theoretical situation for the intermediate case, in which H_0 is comparable to H_i , is not well understood.

The older measurements of spin absorption²⁻⁴ were primarily of the calorimetric type, and were restricted to frequencies below 100 Mc/sec. The principal results were relaxation times as a function of the magnitude of the static magnetic fields. Only the recent work of Locher and Gorter at the University of Leiden,^{6,7} having been conducted at frequencies comparable to τ_S^{-1} , of the experiments so far reported has yielded direct information regarding the analytical form of the shape function in paramagnetic salts. Their method, though

⁸ N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, *Phys. Rev.* **114**, 445 (1959).

⁹ L. J. F. Broer, *Physica* **10**, 801 (1943).

¹⁰ J. Waller, *Z. Physik* **79**, 370 (1932).

¹¹ A. Wright, *Phys. Rev.* **76**, 1826 (1949).

¹² W. J. Caspers, *Physica* **27**, 1023 (1961)

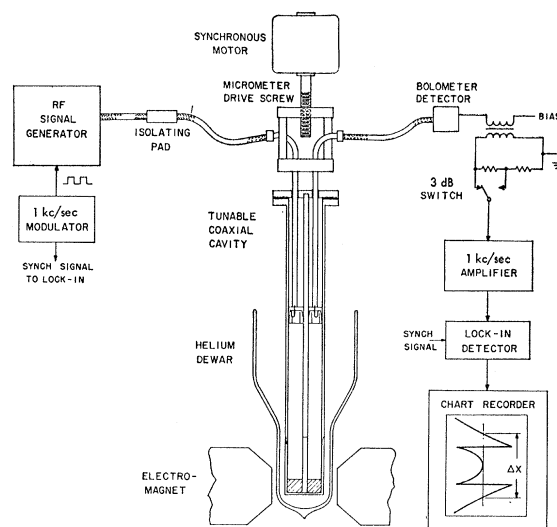


FIG. 1. Schematic drawing of system for measuring cavity resonance widths.

restricted to measurements at several discrete frequencies, is sensitive and versatile: Small effects can be measured under a variety of static magnetic field conditions. In the experiments reported in this present paper we have been able to measure spin absorption as a *continuous* function of frequency in the range 130–4000 Mc/sec, though we have limited our investigations to the zero-field case. Whereas the Leiden experiments were done at the temperatures of liquid hydrogen and liquid nitrogen, our work was conducted in the liquid-helium range.

A primary problem posed by the theory of zero-field spin absorption in paramagnetic salts regards the influence of exchange interaction. The calculations of Wright show that in general $f(\nu)$ cannot be the Gaussian function hypothesized by Broer for the zero-exchange case, but the actual shape is not given by the theory. For this reason we have investigated the frequency dependence of the absorption in several salts which differ from one another in the value of the exchange constant A . Since Wright's work assumed the absence of low-lying Stark levels ($S = \frac{1}{2}$), most of the studies were made on cupric salts, for which this condition obtains. The contrasting case, in which there are small electrical splittings of the ground level, was briefly investigated by means of measurements on chromic potassium alum ($S = \frac{3}{2}$). Possible temperature dependence of the shape functions was looked for in several cases.

II. EXPERIMENTAL METHOD

The essence of the experimental method is to measure the transmission properties of a tunable coaxial resonant cavity containing a powdered sample of the paramagnetic salt. The cavity is shown schematically (and not to scale) in Fig. 1. The lower end, where the sample is located, is immersed in liquid helium; the upper end is

formed by a sliding tuning plunger which contains the input and output coupling loops. As the length of the cavity is varied through a resonance value at constant frequency, the output signal varies according to a resonance curve for which the width measured between half-power points is proportional to the sum of the rf losses (spin absorption in the sample, losses coupled in from external circuits, copper losses, etc.). An additional so-called "field-on" measurement of the resonance width is made with a large static magnetic field (approximately 7500 G) applied to the sample. The only appreciable effect of the static field is to suppress the spin absorption losses¹³; the difference of the "field-off" and "field-on" width measurements yields, apart from geometrical factors, a value of χ'' .

The cavity, which is constructed of gold-plated stainless steel and precision brass tubing, has the following dimensions: outer conductor i.d., 1.00 in.; inner conductor o.d., 0.25 in.; length, variable from 29 to 51 in. The lower three inches, which makes spring finger contact with the remainder of the cavity, can be removed for insertion of a sample of length d . The sliding plunger also makes electrical contact through spring fingers. It is pushed and pulled in the vertical direction by two small brass tubes which also contain the input and output signal cables. In performing an individual measurement of half-power width the plunger is set near a resonance position; it is then slowly driven through the resonance position by a synchronous-motor operated micrometer screw. The cryogenic system is conventional. Temperatures between 1.5 and 4.2°K are obtained by pumping on the helium vapor.

Figure 1 also illustrates in block form the system for obtaining half-power widths of the cavity transmission curves. A stable, square-wave-modulated signal gener-

ator, suitably isolated, excites the rf fields in the cavity. In the frequency range of the experiment only TEM modes are possible. The rf signal from the output loop is detected in a matched bolometer; the variation in amplitude appears ultimately on a synchronously driven chart recorder. As the resonance curve is passing through its maximum, the bolometer output signal is reduced by a factor of 2 using a calibrated attenuator ("3-dB switch"). Thus, since the bolometer is accurately a square-law device, the height of the recording at the peak of the curve indicates the level of the half-power points independently of the gain or linearity of the amplifiers. The measurement of the separation on the recorder tracing of the half-power points Δx is enhanced by recording only an expanded portion of the resonance curve in the vicinity of the half-power level. The value of χ'' is given by

$$\chi'' \left(\frac{\text{emu}}{g} \right) = \frac{1}{4\pi} (\Delta x_1 - \Delta x_2) G \frac{FA}{M}, \quad (3)$$

where Δx_1 and Δx_2 are the values of Δx for the "field-off" and "field-on" conditions, respectively, F is a factor relating the speed of the sliding tuning plunger to the speed of the recorder chart, A is the cross-sectional area and M is the mass of the sample, and G is a geometrical factor given by

$$G = \frac{1 + K^{-1} \tan^2 \beta d}{1 + \tan^2 \beta d + \tan \beta d / \beta d}. \quad (4)$$

In Eq. (4) K is the dielectric constant and βd is the electrical length of the sample. In deriving Eq. (3) and in determining βd , the assumption is made that the refraction in the sample depends only upon its dielectric properties. Dielectric constants at low temperatures were determined by cavity and slotted line methods.¹⁴ Direct coupling between input and output loops cause small asymmetries in the resonance curves at low frequencies, but tests involving other coupling arrangements prove this to have a negligible effect on the final results.

Random errors, arising principally from determinations of cavity resonance widths, depend upon the particular sample and frequency, and range between 1 and 5%. Systematic errors, mostly due to uncertainties in values of βd vary from 1% at low frequencies to 10% at the highest frequencies.

III. EXPERIMENTAL RESULTS

The results for the cupric salt measurements are shown in Figs. 2 through 5. $(\chi''/\chi_0\nu)$, the logarithm of which is plotted versus the frequency ν , is proportional to the shape function $f(\nu)$ as defined in Eq. (1). Extra-

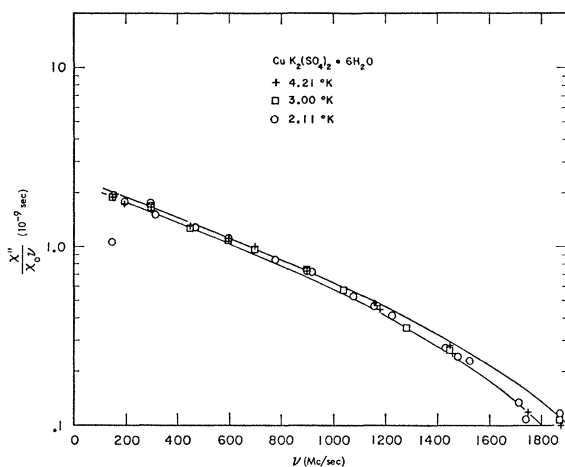


FIG. 2. Experimental results—cupric potassium sulfate.

¹³ In the presence of very large external fields, the pertinent energy levels are single ion levels; the spins are locked into the external field H_0 and energy is absorbed by virtue of spin flips rather than cooperative reordering internal to the spin system.

¹⁴ For instance, see discussions in A. R. Von Hippel, *Dielectric Materials and Applications* (Technology Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1954).

polation to zero-frequency yields, apart from a factor 2π , the apparent spin-spin relaxation time given by Eq. (2). In the Curie law region, temperature dependence of the shape function would be reflected by a systematic shift of the data points as the temperature is varied. The sequence in which the curves are given is according to the strength of the exchange interaction, as determined independently from various specific heat experiments. The smooth lines are drawn to enclose 80–90% of the points.

The chromic potassium alum data are presented in two ways. Figure 6 which plots $\ln(\chi''/\chi_0\nu)$ versus ν , shows the behavior of $f(\nu)$. Figure 7, which gives the frequency dependence of χ'' , emphasizes the “flat-topped” character of these curves, which distinguishes them from similar plots which can be made in the cupric cases.

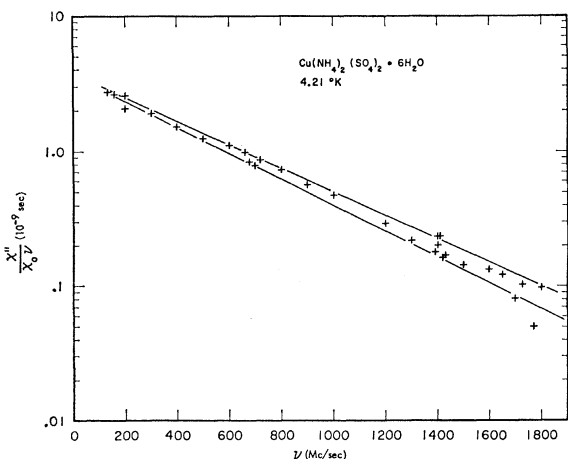


FIG. 3. Experimental results—cupric ammonium sulfate.

IV. ANALYSIS AND DISCUSSION

1. Cupric Salts—General

The exchange narrowing of the zero-frequency band in the absence of external static fields, which is predicted by Wright's theory,¹¹ can be observed in Fig. 8. Here, average curves taken from the cupric salt results, Figs. 2 through 5, have been replotted on a linear scale in terms of a normalized frequency ν/ν_0 . The dipolar relaxation frequency ν_0 , of the order of τ_s^{-1} , is defined in terms of the internal rms dipolar field H_i by

$$\nu_0 = g\beta H_i. \quad (5)$$

According to the theory, these curves should all have the same zeroth moment $\langle \nu^0 \rangle$ (total area) and second moment $\langle \nu^2 \rangle$ (mean-square width), both equalling $\pi/2$; the fourth moment should increase with the exchange constant A . The influence of exchange is thus to require an $f(\nu)\alpha(\chi''\nu_0/\chi_0\nu)$, which tapers off less slowly at higher frequencies, but at the same time is more sharply

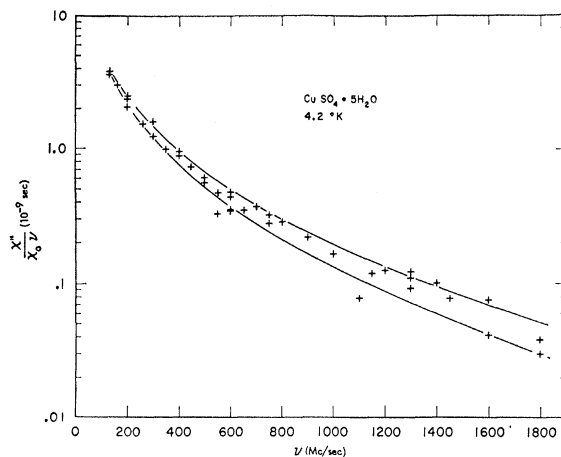


FIG. 4. Experimental results—cupric sulfate pentahydrate.

peaked at the lower end. For smaller values of A the experimental curves seem to approach the Gaussian shape proposed by Broer⁹ (dashed curve, also normalized to give $\langle \nu^0 \rangle = \langle \nu^2 \rangle = \pi/2$).

There is no effect of variations of temperature in the liquid-helium range upon the shape of the band for the one cupric case in which this was investigated, i.e., for the cupric potassium Tutton salt, Fig. 2. This result is to be expected at temperatures for which Curie's law holds ($T \gg 0.05^\circ\text{K}$) in view of the high-temperature approximations involved in the theories of the shape functions.^{9–11}

In obtaining quantitative comparisons with the theoretically derived values of the moments and relaxation times, two approaches have been taken to the problem of choosing analytical expressions to represent the data. The first of these, a strictly empirical approach, is suggested by the observation that the curves in the semilog plots, Figs. 2 through 5, do not depart radically from straight lines. The cupric data can be fitted to an

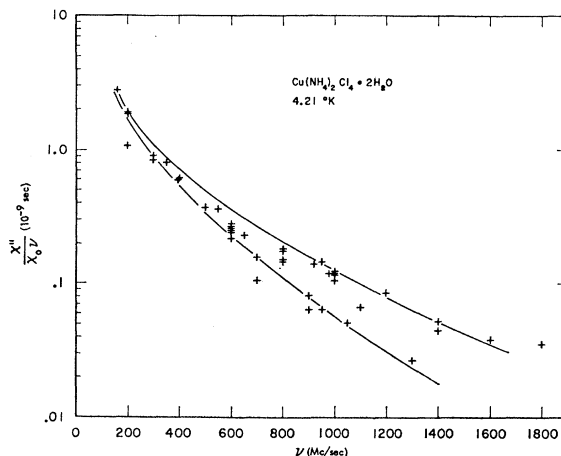


FIG. 5. Experimental results—cupric ammonium chloride.

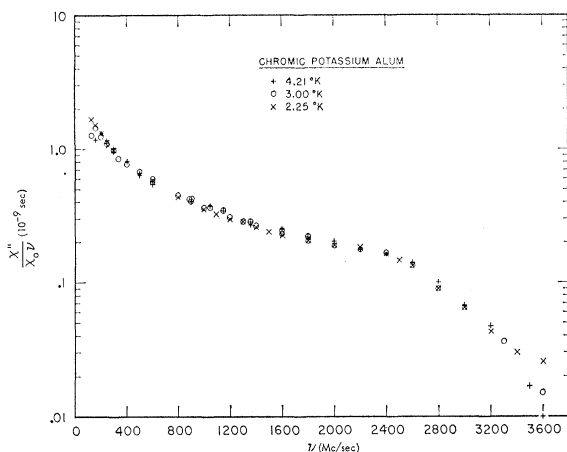


FIG. 6. Experimental results—chromic potassium alum.

expression of the form

$$\chi''/\chi_0\nu = C_0 \exp(-C_1\nu^n), \quad (6)$$

which we shall refer to as the “empirical, fitted function.” The intercept C_0 has, from Eq. (2), the value $2\pi\tau S$, providing (6) is valid in the limit $\nu=0$. A Gaussian (Broer) curve would appear parabolic ($n=2$), but in all our observations the parameter n seems to be significantly smaller than 2. Although Eq. (6) must be accepted with reservations, especially in cases of large exchange where higher order moments are important,

the use of the empirical, fitted function has the advantage that in all cases a good fit can be obtained over the whole frequency range of the observations, i.e., over a large portion of the absorption band. Results obtained from an analysis based upon the use of the empirical, fitted function are given in part 2 of this section.

The second approach to the problem of fitting the experimental curves to an analytical expression, is that suggested by Locher and Gorter,⁶ in analogy to a method which has been used by Lacroix¹⁵ to describe the shape of exchange narrowed resonance lines. An attempt is made to fit the data by an expression which combines a Gaussian and Debye dependence, viz.,

$$\frac{\chi''}{\chi_0\nu} = \frac{\rho'}{(1+\rho^2\nu^2)} \exp(-\alpha^2\rho^2\nu^2), \quad (7)$$

in which $\rho = \rho' \exp\alpha^2 \operatorname{erfc}\alpha$, and erfc stands for the complimentary error function. The shape is completely determined by the two parameters α and ρ' . α is a measure of the relative Gaussian-Debye character of the curves: For $\alpha=0$ a simple Debye shape is obtained, whereas in the limit $\alpha \rightarrow \infty$ (keeping $\alpha\rho$ fixed) the curve is Gaussian. The parameters are evaluated by graphically fitting the experimental curves to families of functions based on Eq. (7) (light lines, Fig. 9). Although the use of this method is appealing in that it has a physical basis in the related and much investigated theory of

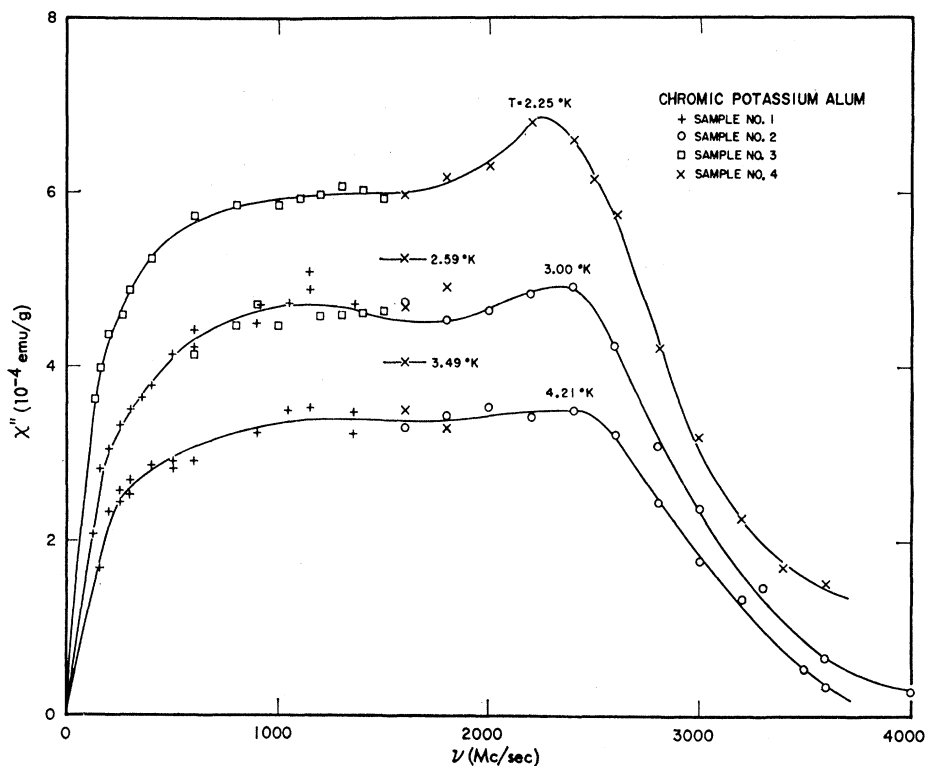


FIG. 7. Experimental results (χ'' plot)—chromic potassium alum.

¹⁵ R. Lacroix, *Helv. Phys. Acta* **27**, 283 (1954).

TABLE I. Parameters used in cupric salt analysis.

	<i>A</i>	ν_0 (Mc/sec)	<i>n</i>	Parameters Eq. (6)		Parameters Eq. (7)	
				$C_0 \times 10^9$	C_1	α	$\rho' \times 10^9$ (sec)
Cu K ₂ (SO ₄) ₂ ·6H ₂ O (Tutton salt)	2.3–3.3 ^a	700	1.1	2.3	17.2 × 10 ⁻¹⁰	1.0	1.7–2.0
Cu(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O (Tutton salt)	3.5–4.5 ^a	670	1.0	3.7	2.10 × 10 ⁻⁹	0.4	2.2–3.1
Cu SO ₄ ·5H ₂ O	21–25 ^a	1030	0.3	170	14.0 × 10 ⁻⁸	0.05	5.3–9.5
Cu(NH ₄) ₂ Cl ₄ ·2H ₂ O	58 ^b	812 ^b	0.4	210	1.74 × 10 ⁻⁸

^a Based on data of L. J. F. Broer and J. Kemperman, *Physica* **13**, 465 (1947); J. Volger, F. W. de Vrijer, and C. J. Gorter, *Physica* **13**, 621 (1947); and R. J. Benzie, A. H. Cooke, and S. Whitley, *Proc. Phys. Soc. (London)* **A63**, 213 (1950), assuming an sc lattice.

^b Scaled from data on the potassium chloride of J. van den Broek, L. C. van der Marel, and C. J. Gorter, *Physica* **27**, 661 (1961), assuming a bcc lattice.

resonance line shapes, it has the drawback that an exact fit cannot always be made. In Fig. 9, χ''/χ_0 given by Eq. (7) is plotted versus $\rho'\nu$ for various values of α . Experimental results (bold lines) are superimposed, the values of ρ' being chosen to provide the best possible fit to the theoretical curves. (A change in ρ' shifts all the data points by a uniform amount along the horizontal axis.) The value of α is found from the matching theoretical curve. Two values of ρ' are indicated in Fig. 9, one appropriate to a fitting at low frequencies, and another appropriate to a fitting at high frequencies. Results of this type of analysis of our data are discussed in part 3.

Table I summarizes the parameters which have been used in analyzing the cupric salt data. Values of the exchange constant *A* (column 1) were derived from various measurements of the exchange contribution to the magnetic specific heats, assuming nearest-neighbor interactions and cubic crystal structures. Dipolar relaxation frequencies ν_0 (column 2), defined by Eq. (5), were obtained by appropriate lattice sum computations along lines suggested by Van Vleck.¹⁶ (Besides *A* and

ν_0 , Caspers modified theory¹² requires values of the hfs contributions to the specific heats. These have been experimentally determined for cupric Tutton salts by Benzie and Cooke,¹⁷ and have been used in the analysis of the appropriate portions of our data. However, approximately the same hfs specific heat values were also assumed for the remaining cupric salt cases, because no actual experimental values were available. Errors brought about by this assumption are not expected to be large, because the dominating specific heat contribution in these cases is that due to exchange.) Columns 3, 4, and 5 tabulate the particular values of the fitting parameters which have been used in the empirical function Eq. (6). Columns 6 and 7 list the values of the parameters obtained from fitting the data with the Gaussian-Debye function Eq. (7), as illustrated in Fig. 9. (In the copper sulfate case, the experiment did not include frequencies much below the peak in the χ''/χ_0 curve, so that fitting of the data to Eq. (7) at low frequencies must be considered tentative. This difficulty was even more serious in the ammonium chloride case, and this type of analysis could not be applied to this salt.)

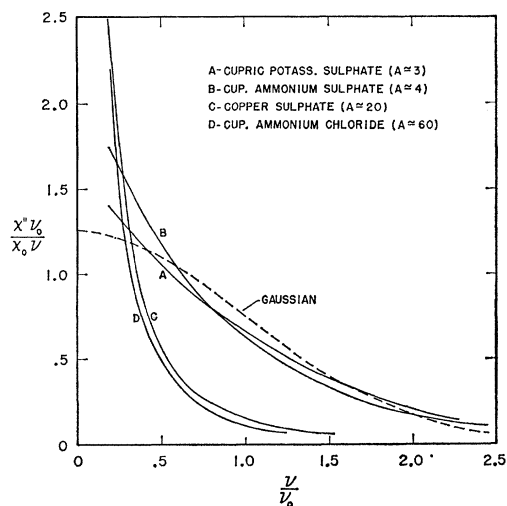


FIG. 8. Normalized experimental shape functions—cupric salts.

¹⁶ J. H. Van Vleck, *J. Chem. Phys.* **5**, 320 (1937).

2. Cupric Salts—Analysis Using Empirical, Fitted Function

Quantitative results obtained from the use of the empirical, fitted function Eq. (6) are compared with theory and some other experiments in Table II. Theoretical values of the reciprocal relaxation time are, according to the theories of Wright and Caspers, given by

$$\tau_S^{-1} = \frac{(8\pi)^{1/2}\nu_0}{1+0.054A^2} \left[1 + \frac{1}{3} \frac{C(\text{hfs})}{C(d)} \right]^{1/2}, \quad A \ll 7, \quad (8)$$

where $C(\text{hfs})$ and $C(d)$ are the specific heats due to nuclear and dipolar magnetic interactions, respectively. Equation (8) has been evaluated for each cupric compound (column 1), although the restriction on the magnitude of *A* is satisfied only by the two Tutton salts. Column 2 lists experimental values of τ_S^{-1} obtained by

¹⁷ R. J. Benzie and A. H. Cooke, *Nature* **164**, 837 (1949).

TABLE II. Cupric salts—analysis using empirical, fitted function.

	Reciprocal relaxation times τ_S^{-1} (Mc/sec)				Moment ratios (exper./theor.) of:		
	Theory (Wright- Caspers)	(Extrap. to zero freq.)	Experiment (Extrap. to 78 Mc/sec)	(Leiden at 78 Mc/sec)	$\langle \nu^0 \rangle$	$\langle \nu^2 \rangle^{1/2}$	$\frac{\langle \nu^4 \rangle}{\langle \nu^2 \rangle^2}$
Cu K ₂ (SO ₄) ₂ ·6H ₂ O	3400–3200	2500	2900	...	1.07	1.21	1.5–1.0
Cu(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O	2500–2200	1700	2000	880	1.12	0.93	1.1–0.8
Cu SO ₄ ·5H ₂ O	230–160	37	1000	1200	1.50	0.6	0.7–0.5
Cu(NH ₄) ₂ Cl ₄ ·2H ₂ O	23	30	1400	...	3.5	0.6	...

evaluating Eq. (6) in the limit $\nu=0$. There is fair agreement between columns 1 and 2; certainly better than can be obtained assuming a Gaussian shape function. The values of τ_S^{-1} in column 4 are from the calorimetric studies at the University of Leiden¹⁸ which had been made at 78 Mc/sec, a frequency sufficiently high to give a measurable spin absorption, but, hopefully, low compared with the width of the zero-frequency band. It is obvious that this latter condition was not satisfied in the large exchange cases. The Dutch calorimetric results are of the same order of magnitude as the values obtained by evaluating our data at the same frequency (column 3).

The second part of Table II gives a comparison between experimentally determined moments of the shape function [from integration of Eq. (6)], and theoretical values given by the theories of Wright and Caspers. Column 5 gives the ratios of the zeroth moments (total area) to the theoretical value $\chi_0 kT$. Since the theory of the zeroth moment contains no approximations or assumptions (except $kT \gg h\nu$), the deviation of this ratio from unity may be considered as a crude measure of the adequacy of Eq. (6) to describe the entire band. This deviation is most serious for greater exchange narrowing, because Eq. (6) does not account for the expected leveling off of $f(\nu)$ at low frequencies. In column 6, a comparison of the experimental second moment is made to the theoretical values of Wright and Caspers, viz.,

$$\langle \nu^2 \rangle^{1/2} = \nu_0 \left[1 + \frac{1}{3} \frac{C(\text{hfs})}{C(d)} \right]^{1/2} \quad (9)$$

The approximate experimental error in the second moment is $\pm 15\%$ for the Tutton salt cases, based on the uncertainties in the fitting parameters. In column 7, comparisons are made between theoretical and experimental values of the fourth moment, the lowest moment to depend upon the exchange constant A in the Wright-Caspers theories. The approximate theoretical expression is

$$\frac{\langle \nu^4 \rangle}{\langle \nu^2 \rangle^2} = \frac{(0.43A^2 + 2.6)[C(d)]^2 + (2/9)C(\text{ex})C(\text{hfs})}{[C(d) + \frac{1}{3}C(\text{hfs})]^2}, \quad (10)$$

$A \ll 7, \quad C(\text{ex}) \gg C(\text{hfs}),$

¹⁸ J. Volger, F. W. de Vrijer, and C. J. Gorter, *Physica* **13**, 621 (1947).

where $C(\text{ex})$ is the contribution to the specific heat arising from exchange interaction. We have assumed the conditions on the specific heats to be satisfied in the cases of the Tutton salts, as did Locher and Gorter. [$C(\text{ex})/C(\text{hfs})=3.3$ and 4.7 in the potassium sulfate and ammonium sulfate cases, respectively.] The ratios given in column 7 (based on the highest and lowest A listed for each salt in Table I) have an estimated error of $\pm 15\%$ in the Tutton salt cases, when both the uncertainties in the fitting parameters and the quoted uncertainty in the theoretical formula Eq. (10) are taken into account. Theory and experiment agree for the Tutton salt fourth moments; in the case of cupric sulfate the agreement is unexpectedly, perhaps fortuitously good, being no poorer than the results for lower moments, where the extrapolations involved in using Eq. (6) are less important. It can be shown that agreement of the empirical, fitted function moments with the theoretical moments is on the whole improved by our including the hfs corrections of Caspers.

By equating experimental values of the moments (based on the empirical, fitted function) to values derived from the theoretical formula Eq. (10), new experimental values of the exchange constant are obtained. These are $A=3.3$ and 3.7 for the cupric potassium and cupric ammonium sulfates, respectively. The error arising out of the experimental method is $\pm 5\%$, but the uncertainty in the theoretical formula also contributes an error of 5% (of the same magnitude and direction in both salts).

3. Cupric Salts—Analysis Using Gaussian-Debye Curves

Figure 9, which illustrates the correspondence between the experimental results and the Gaussian-Debye function Eq. (7) in the case of the ammonium sulfate, is typical of curves which can be drawn for all the cupric measurements. The experimental curves appear to be wider and lower than the theoretical ones, but a reasonable fit can be obtained in the wings. The appearance of the curves thus suggests a sort of inhomogeneous broadening, i.e., experimental curves which might be considered as a superposition of a number of simple curves of the form Eq. (7). The discrepancy between the experimental and proposed theoretical curves is outside the limits of known experimental error.

Before calculating the broadening to be expected from

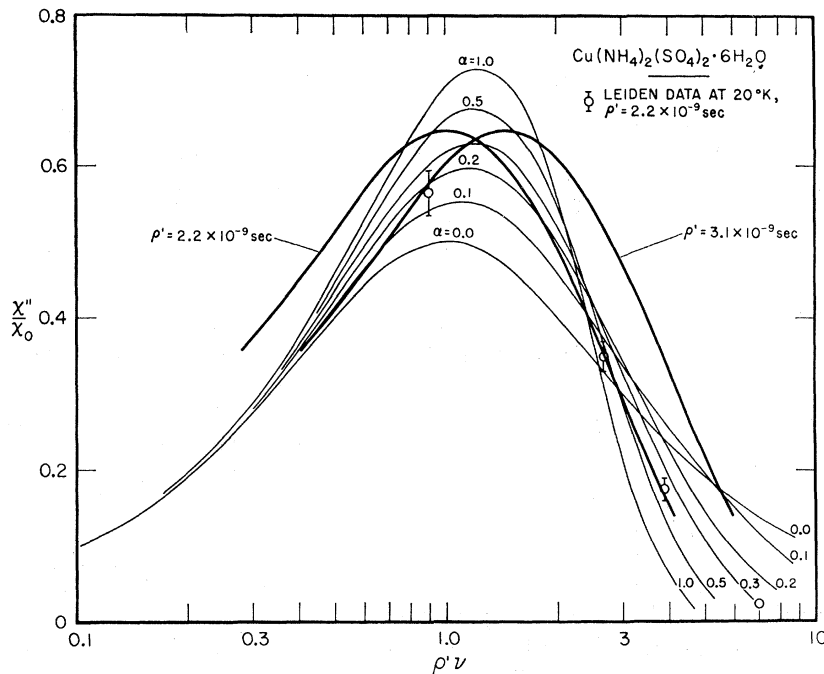


FIG. 9. Comparison of experimental results to Gaussian-Debye curves Eq. (7)—cupric ammonium sulfate.

two obvious sources, viz., magnetic anisotropy and hyperfine splitting, it must be remarked that Locher and Gorter⁶ do not find this effect in their measurements. In addition to their four experimental points on cupric ammonium sulfate also shown in Fig. 9, they relied on some low-frequency ($\rho'\nu < 0.2$) measurements of Volger¹⁹ in choosing the parameters $\rho' = 2.2 \times 10^{-9}$ sec, $\alpha = 0.3$. However, they comment⁶ that their data fit the curves Eq. (7) despite the fact that these were proposed to describe the case of no zero-field splittings (hfs). In any event, a discrepancy, not quite within known experimental limits, does exist between their Tutton salt result and ours at 410 Mc/sec, and possibly at lower frequencies (extrapolating their data to meet the low-frequency work of Volger). No discrepancy exists in the other cupric case in which their measurements overlap ours, viz., two zero-field measurements at 409 and 1330 Mc/sec in copper sulfate.⁷ It seems doubtful that the difference in the measuring temperatures involved in the several experiments could be the cause of the discrepancies in the Tutton salt results.

We take as a measure of the supposed inhomogeneous broadening, the fractional difference in the values of ρ' listed in Table I. These $\Delta\rho'/\rho'$ are given in column 3 of Table III, along with the average value of ρ' (column 2), and the values of α taken from Table I. We also include some values of α and ρ' obtained by Locher and Gorter; these are designated "Leiden." (The "Leiden" values for the ammonium Tutton salt are from the zero-field results shown in Fig. 9, whereas the copper sulfate values are those surmised by Locher and Gorter on the

basis of field dependence studies at 409 Mc/sec and 20.4°K.)

We take as an approximate measure of the magnetic anisotropy the fractional spread in the g -factor values obtained for various directions in electron paramagnetic resonance (EPR) experiments²⁰ (Table III, column 4). The supposed contribution of hfs (column 5) to the fractional broadening is based on Caspers computation of the rms width of the absorption band, i.e., the values listed are $(\langle \nu^2 \rangle^{1/2} - \nu_0)/\nu_0$, where $\langle \nu^2 \rangle^{1/2}$ is given by Eq. (9). The sum of these two effects, listed in column 6, agrees fairly well with the "observed" broadening (column 3) in the cases of the Tutton salts, but not in copper sulfate. In this latter case, however, other sources of anisotropy are probably of great importance, such as the variation in the strength of the exchange interaction in various directions mentioned by Bagguley and Griffiths²¹ in connection with their EPR studies. In any event, the hypothesis of inhomogeneous broadening does not seem unreasonable, and in the following analysis it is assumed that in each salt the α (chosen from fitting the experimental curve in the high-frequency wing) and the ρ' (average value) describe a single one of the superimposed Gaussian-Debye curves which supposedly make up the experimental curve. Thus, we will make comparisons of the moments and relaxation times to values computed on the basis of the simple non-hfs (Wright) theory.

The experimental second moments obtained from an integration of Eq. (7) are compared with the theoretical

²⁰ K. D. Bowers and J. Owens, Rept. Prog. Phys. 18, 304 (1955).

²¹ D. M. S. Bagguley and J. H. E. Griffiths, Proc. Roy. Soc. (London) A201, 366 (1950).

¹⁹ J. Volger, thesis, Leiden, 1946 (unpublished).

TABLE III. Cupric salts—analysis using Gaussian-Debye curves Eq. (7).

	Parameters			Fractional broadening			Moment ratios (exper./theor.) of:		τ_S^{-1} (Mc/sec)	
	α	$\frac{\rho' \text{ av.}}{\times 10^9}$ (sec ⁻¹)	$\frac{\Delta\rho'}{\rho'}$	$\frac{\Delta g}{g}$	hfs	Total	$\frac{\langle\nu^4\rangle}{\langle\nu^2\rangle^2}$	$\frac{\langle\nu^4\rangle}{\langle\nu^2\rangle^2}$	Exper.	Wright
Cu K ₂ (SO ₄) ₂ ·6H ₂ O	1.0	1.8	0.19	0.15	0.12	0.27	1.0	0.7-0.5	3500	2760-2210
Cu(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O										
(1) This paper	0.4	2.7	0.34				0.9	0.6-0.4	2300	
(2) Leiden. (Ref. 6)	0.3	2.2	...	0.19	0.14	0.33	1.2	0.7-0.5	2900	2050-1610
Cu SO ₄ ·5H ₂ O										
(1) This paper.	0.05	7.4	0.57				0.5	0.1-0.1	850	
(2) Leiden-field dependence. (Ref. 7)	0.01	6.5	...	0.17	0.06	0.23	1.3	0.5-0.3	970	210-150

value ν_0 in column 7 of Table III. The correlation is rather good, especially in the case of the Tuttons. Fourth moments are compared with Wright's theory in column 8. The agreement is reasonable, though not as good as had been obtained using the fitted function (Table II). We note that Locher and Gorter's choice of parameters for copper sulfate using the field dependence data, seems to be more reasonable than our own zero-field choice, in that it gives results close to those obtained from the empirical, fitted function method. As we had pointed out, the fitting of the copper sulfate data to Eq. (7) was in our case inexact.

Experimental values of reciprocal relaxation times obtained by extrapolating to zero frequency are shown in column 9, and the theoretical values based on Wright's theory are listed in column 10. The agreement is about as good as that obtained using the empirical, fitted function (Table II).

4. Chromic Potassium Alum

The frequency dependence of the absorption in the chromic alum Cr₂(SO₄)₃·K₂SO₄·24H₂O as shown in Fig. 7 differs markedly from that which characterizes the cupric salts. Instead of a single, distinct peak, χ'' remains more or less constant at its maximum value between 300 and 2500 Mc/sec. The only function which has so far been proposed for the shape of the zero-frequency band in a salt for which there are low-lying Stark levels, is the Gaussian employed by Broer⁹ in estimating relaxation times. Locher and Gorter⁷ realized, on the basis of their recent measurements, that a Gaussian is not at all an adequate description of the absorption in chromic potassium alum. Their zero-field data agree with ours. However, because the highest of their several frequencies was at 1760 Mc/sec, they were not able to detect the rapid drop-off beyond 2500 Mc/sec, which is a major feature of our results. In explaining the shape of the band in this salt, we cannot look towards the same mechanisms involved in the cupric case; the exchange and hyperfine interactions are very small, which accounts for the popularity of this alum in adiabatic demagnetization experiments.

The zero-field Stark splitting has been investigated

by means of paramagnetic resonance experiments of Bagguley and Griffiths²² and Bleaney.²³ At room temperature there is a single splitting amounting to 0.12 cm⁻¹, but below 160°K, at which a crystalline structural transition occurs, several groups of ions having different splittings exist simultaneously. Proposals regarding the percentage of ions having various values of the splitting which have been made to explain the EPR data, are not consistent with proposals made to explain specific heat data.²⁴ We are led to ask whether we are observing in our experiment absorptions due to transitions among low-lying Stark levels. By making a rough numerical integration of the curve in Fig. 7, we obtain within 15% the zeroth moment that is theoretically predicted if no Stark transitions were being observed. ($\langle\nu^0\rangle$ for the zero-frequency band in chrome alum, on the basis of the calculations of Waller¹⁰ and Broer,⁹ is $\chi_0 kT$ multiplied by a factor of $\frac{3}{2}$ to take into account the absorption appearing at the frequency of the Stark transition ν_e .) To account for the 15% discrepancy on the basis of splittings observed in EPR, viz., $\nu_e = 8100$ and 3100 Mc/sec, would require 75% of the ions to have the higher splitting, and the remainder the lower. However, if we assume Gaussian curves of the appropriate intensities at ν_0 and ν_e , we do not even roughly reproduce the observed χ'' curve; nor would we be successful using an alternative scheme based on a model²³ proposed to explain specific heat results, viz., 15% of the ions having $\nu_e = 8100$ Mc/sec, and 85% having $\nu_e = 4600$ Mc/sec. It seems unlikely that we are observing an anomalously low-lying Stark transition, but measurements on other chromic alums (for instance, the methylammonium alum) would be desirable before drawing final conclusions.

By a simple straight line extrapolation of our $\chi''/\chi_0\nu$ curve Fig. 6 to zero frequency, we obtain a reciprocal spin-spin relaxation time $\tau_S^{-1} = 2900$ Mc/sec, which differs, though not alarmingly, from the value $\tau_S^{-1} = 4000$

²² D. M. S. Bagguley and J. H. E. Griffiths, Proc. Roy. Soc. (London) **A204**, 188 (1950).

²³ B. Bleaney, Proc. Roy. Soc. (London) **A204**, 203 (1950).

²⁴ See, for instance, D. de Klerk, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 15, Sec. 42, p. 105.

Mc/sec obtained by the Leiden group¹⁸ from calorimetric measurements at 78 Mc/sec. On the basis of an extrapolation to $\nu=0$ of their χ''/ν data, Locher and Gorter⁷ confirm the calorimetric value, but it is not clear on what basis they drew their extrapolating curve. The value of τ_S^{-1} obtained by Broer on the basis of a Gaussian shape function of rms width ν_0 , is 7100 Mc/sec.

In the $S=\frac{1}{2}$ case, the width of the zero-frequency band is approximately ν_0 , a frequency which also corresponds to the absorption of a quantum by a single-ion flipping in a field H_i . In reality, of course, the single-ion view is not applicable. For small fields ($H_0 \ll H_i$) pure states exist only for the crystal as a whole. There are no individual spin flips, but a sort of "cooperative flipping." Yet if we adhere to the notion that considering a spin flip in a field H_i provides an estimate of the width of the band, the band which we observe in chrome alum ($S=\frac{3}{2}$, $H_i=310$ G) corresponds to the complete flipping of a dipole (i.e., the transition $-\frac{3}{2} \rightarrow +\frac{3}{2}$ absorbs quanta of frequency $3\nu_0 \approx 2700$ Mc/sec). This rule of thumb might be verified by measurements on suitable systems with various values of S . Magnetic field dependence

studies would also be helpful. For instance, some preliminary studies we have made show the manner in which the flat-topped curve in Fig. 7 evolves continuously into a resonance spectrum as increasingly larger static magnetic fields are applied perpendicular to the rf fields.

Figure 6 indicates that the shape function in chromic potassium alum is independent of temperature at liquid-helium temperatures.

V. CONCLUSIONS

The method which has been developed for measuring spin absorption as a continuous function of frequency enhances the understanding of the zero-frequency band. In cupric salts in zero field the theories of shape function moments and relaxation times are generally confirmed, though there remain theoretical and experimental difficulties for cases of very large exchange interaction. The results for the chromic alum are entirely unexpected, and suggest several avenues of approach for further study.

Spin-Wave Contribution to Low-Temperature Specific Heat of Yttrium Iron Garnet in Zero Applied Fields*

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Recent results of specific heat measurements of yttrium iron garnet in zero applied field have been analyzed previously by using the approximate spin-wave dispersion relation $\hbar\omega = Dk^2$, neglecting the effects of the dipolar interaction and anisotropy. It is shown that this approximation is valid for temperatures above $\sim 0.2^\circ\text{K}$.

I. INTRODUCTION

THE low-temperature specific heat of yttrium iron garnet (YIG) has been measured and analyzed recently in terms of the spin-wave and lattice contributions in order to determine the exchange constant D .¹⁻⁴ In analyzing the data, the spin-wave dispersion relation was approximated by

$$\hbar\omega_k = Dk^2, \quad (1)$$

where the exchange constant D is related to the Landau

exchange constant A by the relation

$$A = DM_s/2g\mu_B.$$

In this paper we examine the effect of this approximation and show that in the temperature range above 1°K in which the experiments were performed the approximation is quite good. At lower temperatures, of the order of 0.2°K in YIG, the approximation is no longer valid. The experimental results of references one through four are summarized in Shinozaki's paper.

II. SPECIFIC HEAT CALCULATION

The spin-wave contribution to the specific heat is

$$C_0 = \frac{d}{dT} \frac{1}{(2\pi)^3} \int d\mathbf{k} \frac{\hbar\omega_k}{\exp(\hbar\omega_k/k_B T) - 1}. \quad (2)$$

In the approximation (1) the integral is easily evalu-

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⁴ J. E. Kuzler, L. R. Walker, and J. K. Galt, Phys. Rev. **119**, 1609 (1960).