

The theoretical curves in Fig. 1 were obtained from (1) assuming that H_L^2 is equal to $\frac{1}{3}\langle\Delta H\rangle$, where $\langle\Delta H\rangle$ is the Van Vleck second moment of the unsaturated resonance absorption. Since $\langle\Delta H\rangle$ is dependent on crystal orientation, it is necessary to average over orientation. A precise average is complicated but we have estimated that an error of less than 1% is made in linewidth and peak to peak amplitude if we use (1) with $H_L^2 = \frac{1}{3}\langle\langle\Delta H\rangle\rangle$. Here $\langle\langle\Delta H\rangle\rangle$ is the Van Vleck second moment averaged over crystal orientation and is equal theoretically²⁶ to 5.5 G.² This value was used to obtain the upper two curves in Fig. 2 of reference 26. For $\partial\chi'/\partial H_0$ at resonance the orientation average correction is more complicated, and we estimate that an error of less than 1% will be made if we use (1) to calculate $\partial\chi'/\partial H_0$ at resonance, setting $H_L^2 = (0.97) \times \frac{1}{3}\langle\langle\Delta H\rangle\rangle$. The lower theoretical curve in Fig. 1 was obtained in this way.

DISCUSSION

The agreement between theory and experiment is qualitatively convincing; the theory works well for H_1

²⁶ H. W. Gutowsky and B. R. McGarvey, *J. Chem. Phys.* **20**, 1472 (1962).

as small as $\frac{1}{10}$ of the local field. We estimate the systematic error in the experiment at less than 10% in signal and H_1 , and negligible in H_0 and linewidth. Thus there is a minimum discrepancy of 10% between theory and experiment.

Some possible theoretical factors which might explain the small discrepancies are incorrect assumptions concerning transverse and spin-spin energy relaxation, or quadrupole effects. From an experimental point of view we may have overlooked some defect in our calibration procedure.

The theory embodied in (1) is only supposed to be applicable above saturation; thus the theoretical curves in Fig. 1 are drawn only in this region. Provotorov²⁷ has recently advanced a plausible theory applicable through the entire saturation region assuming only $H_1 \ll H_L$ and $1/T_1 \ll \gamma H_L$. Thus this theory should bridge the gap down to small H_1 in the present experiment. We have not attempted to compare his theory with our data, but there seem to be no striking discrepancies. Above saturation Provotorov's theory agrees with the theory of reference 1.

²⁷ B. N. Provotorov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **41**, 1582 (1961) [translation: *Soviet Phys.—JETP* **14**, 1126 (1962)].

Size-Dependent Spin Relaxation Time

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The increase of the paramagnetic relaxation time due to the increase in size of the crystal of copper Tutton salt reported by Nash is interpreted from a model of Eisenstein.

IN a recent article, Nash reported that a "spin relaxation time" of copper Tutton salt crystal in the helium temperature region was size dependent.¹ This relaxation time is deduced from the recovery curve when the spin system is removed from a saturation magnetic field. In this paper we propose to explain this observation by a model of Eisenstein.² An anomalous dispersion of some paramagnetic salts³ will also be explained.

Eisenstein has modified the thermodynamical approach of Casimir and Du Pré⁴ with two assumptions: there is a finite specific heat of the lattice and a local distribution of the spin temperature. The dispersion function of the complex susceptibility χ^* is then given by,

$$\frac{\chi^* - \chi_\infty}{\chi_0 - \chi_\infty} = \frac{s}{1 + isx} + \frac{3}{R^2} (1-s) \frac{\lambda r_0 \coth \lambda r_0 - 1}{x(1 + isx)^2}, \quad (1)$$

where $s = C_L / (C_H + C_L)$, with C_H and C_L the specific heat of the spin (at constant field) and of the lattice, respectively; $R^2 = r_0^2 C_L d / K s \rho$. K is the thermal conductivity, r_0 is the radius of the (spherically shaped) crystal, d is the molar density, $\rho / 2\pi$ is the spin-lattice relaxation time,

$$\lambda r_0 = R \left(\frac{1 + isx}{1 + ix} \right)^{1/2}, \quad (2)$$

and $x = \nu \rho$, with ν as the measuring frequency. Therefore, the frequency spectrum of the normalized complex susceptibility depends on two parameters, s and R . In the case of classical dispersion of Casimir and Du Pré, $s = 1$ ($C_L = \infty$) and the second term in the right side of Eq. (1) is zero; therefore, there is no R dependence.

Equation (1) has been computed numerically for

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¹ F. R. Nash, *Phys. Rev. Letters* **7**, 59 (1961).

² J. Eisenstein, *Phys. Rev.* **84**, 548 (1951).

³ J. van den Broek, L. C. van der Marel, and C. J. Gorfer, *Physica* **25**, 371 (1959).

⁴ H. B. G. Casimir and F. K. Du Pré, *Physica* **5**, 507 (1938).

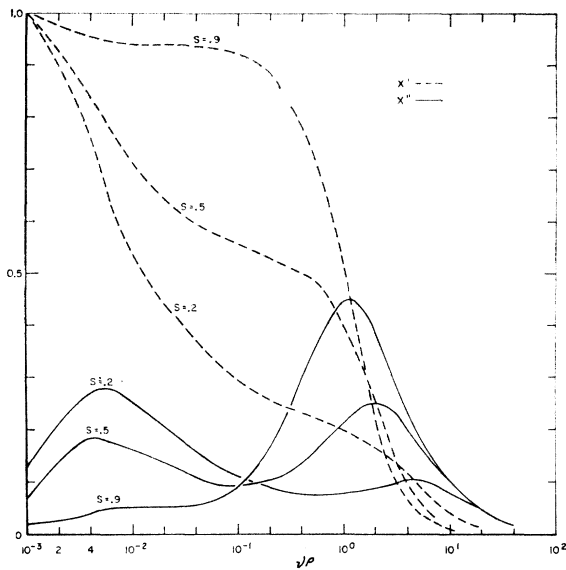


FIG. 1. Frequency spectra of the complex susceptibilities of Eisenstein's model for $R=50$, and different values of s .

various values of R and s . Figure 1 shows, as an illustration, the frequency spectra of the normalized susceptibility for $R=50$ and $s=0.2, 0.5$, and 0.9 . These spectra are considerably different from the spectrum derived from the Casimir and Du Pré dispersion. Particularly, at $s=0.5$, we observed two maxima in the absorption part (χ'') of the susceptibility. The appearance of these two maxima is interesting because it could be the explanation of the anomalous dispersion of some paramagnetic salts observed by Van den Broek *et al.*³ and Weber.⁵ We found the conditions under which these maxima have appreciable heights simultaneously to be $s \ll 1$ and $R \gg 1$. These conditions are in agreement with the actual experience in the experiment.⁶ *Note added in proof.* However, the present result does not explain the magnetic field dependence of the two absorption peaks. This was pointed out to the author by Dr. Van den Broek and Dr. Weber.

The time spectrum, $I(t)$, corresponding to Eq. (1) is its Fourier transform, thus,

$$I(t) = \frac{6(\chi_0 - \chi_\infty)}{\pi^2 \rho} \sum_{n=1}^{\infty} \frac{1}{n^2 s} [x_n^+ - x_n^-]^{-1} \times \{ (s x_n^+ - 1) \exp(-x_n^- t / \rho) + (1 - s x_n^-) \exp(-x_n^+ t / \rho) \}, \quad (3)$$

where

$$x_n^\pm = \frac{1}{2s} \left\{ 1 + \frac{n^2 \pi^2}{R^2} \pm \left[\left(1 + \frac{n^2 \pi^2}{R^2} \right)^2 - 4s \frac{n^2 \pi^2}{R^2} \right]^{1/2} \right\}. \quad (4)$$

⁵ G. Weber, thesis, Institut für Technische Physik, Darmstadt (unpublished).

⁶ J. van den Broek and G. Weber (private communications).

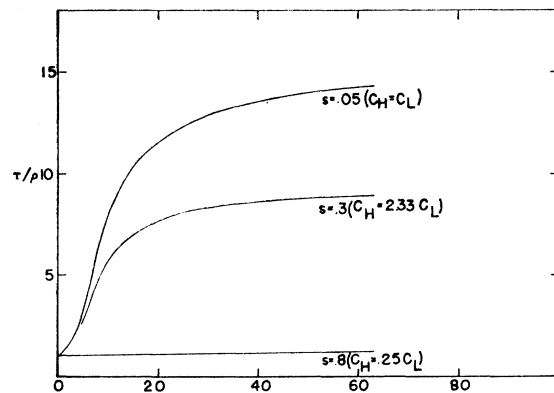


FIG. 2. The dependence of ν_m^{-1} on R and s of Eisenstein's model.

In deriving (3), we have used a partial fractional expansion of the coth function.⁷

Equations (3) and (4) imply that the shape of the time spectrum of Eisenstein is dependent on s and R . When s approaches unity or R approaches zero, the spectrum approaches a single exponential.

Now, we shall interpret the experimental data of Nash by Eisenstein's model. First, when t is very large [the tail of $I(t)$], only the term in Eq. (3) with smallest exponential coefficient (i.e., x_1^-/ρ or x_1^+/ρ , depending on whether $n\pi/R > 1$ or < 1) will dominate; therefore, $I(t)$ approaches asymptotically to a single exponential. Therefore, we can deduce a relaxation time which is close to Nash's $\tau_{1/e}$ by fitting the tail of $I(t)$ with an exponential curve $\exp(-t/\tau)$. In choosing the tail, $I(t)$ would correspond to Nash's region where the temperature of the spin is approximately equal to that of the lattice.

The relaxation time τ then depends on s and R as shown in Fig. 2. Recalling the definitions of R , by taking K , s , and ρ to be independent of the size, r_0 , then R is directly proportional to r_0 , or L in the notation of Nash. Therefore, one can compare Fig. 2 with Nash's figures, keeping in mind that τ and R could have different scales from $\tau_{1/e}$ and L of Nash. We note that the curve of Fig. 2 reproduces the features of Nash's data. The temperature effect in Nash's experiment is also qualitatively consistent with our model if the increasing temperature corresponds to increasing s . This is to be expected since $s = (1 + C_H/C_L)^{-1}$ and C_H/C_L is expected to decrease with increasing temperature.

Nash's results on the effect of crystal growth are also qualitatively compatible with our model. Comparison of his data with our Fig. 2 suggests that r_0/R must be larger for the more quickly grown crystals. Now, recalling $r_0/R \propto K^{-1/2}$, here the thermal conductivity K is very sensitive to impurities and crystal imperfections. Consequently, it could be much lower for the quickly grown crystals, thus accounting for the observed effect.

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⁷ E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1952), p. 136.