Pasadena is at magnetic latitude of 40°N, there should be negligible variation with latitude of the sea-level cosmic-ray intensity between this location and more northerly locations.[15]

In conclusion the author wishes to record his deep appreciation for the invaluable advice and counsel of Dr. H. V. Neher and Dr. W. H. Pickering. He sincerely thanks the Carnegie Institution of Washington for their financial assistance.

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[15] R. A. Millikan and H. V. Neher, Phys. Rev. **50**, 15 (1936).

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Paramagnetic Absorption in Single Crystals of Copper Sulfate Pentahydrate*

John Wheatley and David Halliday
Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania

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We have studied paramagnetic resonance in $CuSO_4 \cdot 5H_2O$, at 9375 mc/sec. Although two absorption peaks were expected, only one was found; Van Vleck has explained this in terms of exchange coupling between Cu^{++} ions. We have found electronic gyromagnetic ratios for a large number of orientations of the crystal (with respect to the external field). Theory agrees with experiment if the gyromagnetic ratios that correspond to the three principal susceptibilities are 2.39, 2.39, and 2.07. We also find a variation in absorption line width with orientation. The shapes of the absorption lines agree with a theory of exchange coupling advanced by Gorter and Van Vleck.

I. INTRODUCTION

THE paramagnetic anisotropy of $CuSO_4 \cdot 5H_2O$ has been studied, both experimentally by Krishnan and Mookherji[1] and theoretically by Polder.[2] Since the discovery of paramagnetic resonance absorption, further studies of this salt in the form of single crystals have been made by Kip,[3] by us,[4] and by Bagguley and Griffiths.[5] In microwave resonance experiments, the measured quantity is usually the electronic gyromagnetic ratio (g factor).

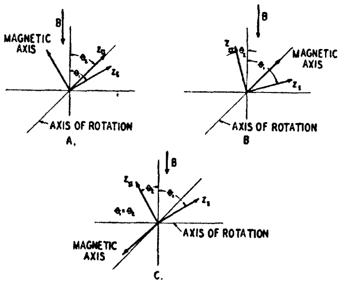

FIG. 1. Geometry of the measurements.

II. CRYSTAL STRUCTURE

Beevers and Lipsom[6] have worked out the structure of copper sulfate. The unit cell contains two Cu^{++} ions. Each ion is surrounded by four negatively charged oxygens (parts of water molecules) in an approximate square, 2.8A on a side; there are also two other oxygens (parts of sulfate groups), each of which is 3.1A from any one of the oxygens in the square. These six oxygens form an octahedron about the cupric ion; the body diagonal perpendicular to the square is the longest. Polder[2] has calculated that this arrangement produces an electric field of nearly tetragonal symmetry at each Cu^{++} ion. The x-ray measurements show that the configuration about each ion is nearly the same and that the angle between the two tetragonal axes is 98°. Magnetic measurements show that this angle is close to a right angle.

III. PREVIOUS MAGNETIC MEASUREMENTS

Krishnan and Mookherji[1] found that two of the principal susceptibilities of the crystal—those along the bisectors of the angles between the tetragonal axes—are nearly equal. They are greater than the third—which is taken normal to the plane formed by the two tetragonal axes. We shall call these tetragonal axes Z_I and Z_{II} following KM.[1] The direction of lowest susceptibility is an axis of magnetic symmetry; we will call it the magnetic axis. From their measurements of the principal susceptibilities of the crystal, KM were able to calculate susceptibilities for directions both parallel

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* Publication number 8p-48. Assisted by the Joint Program of the ONR and the AEC.

[1] K. S. Krishnan and A. Mookherji, Phys. Rev. **50**, 860 (1936); **54**, 533 (1938); **54**, 841 (1938). KM will be used hereinafter when referring to these papers.

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

[3] R. D. Arnold and A. F. Kip, Phys. Rev. **73**, 1247(A) (1948).

[4] J. Wheatley, D. Halliday, and J. H. Van Vleck, Phys. Rev. **74**, 1211(A) (1948).

[5] D. M. S. Bagguley and H. E. Griffiths, Nature **162**, 538 (1948).

[6] C. A. Beevers and H. Lipsom, Proc. Roy. Soc. London **A146**, 570 (1934).

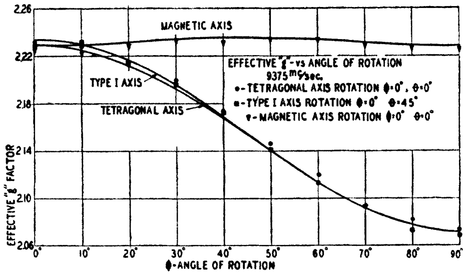

FIG. 2. Variation of g factor with angle of rotation for $CuSO_4 \cdot 5H_2O$ at 9375 mc/sec.

and perpendicular to each of the tetragonal axes. From these values they found effective Bohr magneton numbers for these same directions. The effective Bohr magneton number, n, for any direction is given by

$$n=(3kT\chi_0)^{\frac{1}{2}}/N\beta^2, \qquad (1)$$

where k is Boltzmann's Constant, T is the absolute temperature, χ_0 is the static susceptibility of the crystal in the direction in question, N is Avogadro's number, and β is the Bohr magneton. KM found $n_{\parallel}=2.13$ and $n_{\perp}=1.80$. Also

$$g=n[J(J+1)]^{\frac{1}{2}}, \qquad (2)$$

where J is the total angular momentum quantum number, and "g" is the g factor for the direction in question. If the electric fields acting on the ion are asymmetrical enough to quench the orbital part of the angular momentum, we have instead[7]

$$g=n[S(S+1)]^{\frac{1}{2}}, \qquad (3)$$

where S is the spin quantum number. Polder's work suggests that in $CuSO_4 \cdot 5H_2O$ the orbital angular momentum is quenched and the spin is free. Assuming the spin ($S=\frac{1}{2}$) to be free, KM's results predict $g_{\parallel}=2.46$ and $g_{\perp}=2.08$.

IV. PARAMAGNETIC ANISOTROPY—DISCUSSION

Paramagnetic resonance absorption is a useful tool[8] for studying magnetic properties of copper sulfate single crystals. In microwave absorption experiments, the crystal is subjected to an oscillating magnetic field of microwave frequency, and a static magnetic field, normal to the oscillating field. The microwave frequency, ν, is constant and the magnetic field is varied. An absorption maximum occurs at the value of magnetic induction, $\mathbf{B}$, that satisfies the resonance relation

$$h\nu=g\beta B. \qquad (4)$$

For a given crystal orientation it would seem that Eq. (4) would be satisfied for two different $\mathbf{B}$ values; this is because there are two different orientations of Cu^{++} ions, each with its own g value.

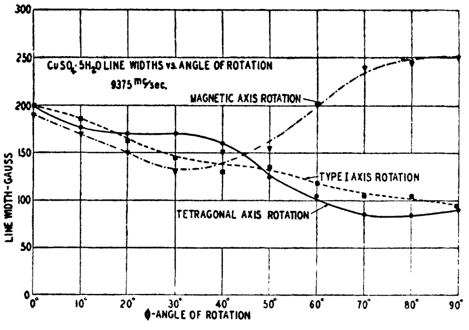

FIG. 3. Variation of absorption line width with angle of rotation for $CuSO_4 \cdot 5H_2O$ at 9375 mc/sec.

The g factor for any direction with respect to a tetragonal axis may be calculated simply by finding the static susceptibility in that direction and substituting in Eq. (1) and Eq. (3). The static susceptibility in any direction in terms of $\chi_{\parallel}$ and $\chi_{\perp}$ (the static susceptibilities parallel and perpendicular to a tetragonal axis) can be calculated from simple geometrical considerations. The result is

$$\chi_\theta=\chi_{\parallel}\cos^2\theta+\chi_{\perp}\sin^2\theta, \qquad (5)$$

where θ is the angle between the direction specified and a tetragonal axis.

The g factor for any direction with respect to a tetragonal axis is then evidently given by

$$g=(g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{\frac{1}{2}}, \qquad (6)$$

where θ is the angle between the direction specified and a tetragonal axis.

It follows that for the two ions in the unit cell the values of g will be given by

$$g_1=(g_{\parallel}^2\cos^2\theta_1+g_{\perp}^2\sin^2\theta_1)^{\frac{1}{2}}$$

and

$$g_2=(g_{\parallel}^2\cos^2\theta_2+g_{\perp}^2\sin^2\theta_2)^{\frac{1}{2}}, \qquad (7)$$

where θ_1 and θ_2 are the angles which the direction of the external field makes with Z_I and Z_{II}, respectively. In an absorption experiment, then, we expect to find two absorption maxima, those corresponding to g_1 and g_2 in Eq. (7). At 3.2 cm, however, we find only one peak. Van Vleck[9] attributes this to a strong exchange coupling between the cupric ions; the single effective "g" is the arithmetic mean of g_1 and g_2,

$$g_{\text{eff.}}=(g_1+g_2)/2. \qquad (8)$$

V. EXPERIMENTAL ARRANGEMENT

The experimental arrangement is like that used in previous work.[8] The output of a square-wave

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[7] J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Chapter XI (Clarendon Press, Oxford, 1932).

[8] R. L. Cummerow, D. Halliday, and G. E. Moore, Phys. Rev. **72**, 1233 (1947).

[9] J. H. Van Vleck, private communication.

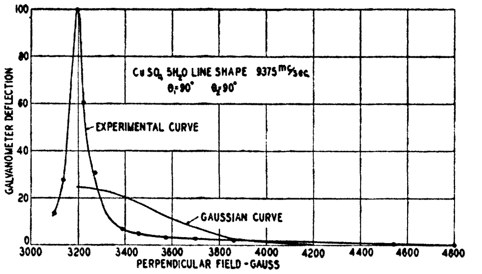

FIG. 4. Comparison of the line shape of an experimental $CuSO_4 \cdot 5H_2O$ absorption line at 9375 mc/sec. with a Gaussian curve having the same area and second moment.

modulated low power oscillator passed through a resonant cavity that contained the copper sulfate crystal. The power was detected by a crystal rectifier. The voltage output of the crystal rectifier was amplified, rectified, and then compared with a stable d.c. battery voltage; the difference between the two was displayed as a galvanometer deflection. If the crystal in the cavity absorbs power, there will be a galvanometer deflection; it can be shown that the galvanometer deflection is proportional to χ'', the imaginary part of the high frequency susceptibility of the salt. The magnetic field was calibrated using the proton moment; we think it is correct to ±6 gauss. The absorption peaks are reproducible to within ±10 gauss.

In order to study the anisotropy, the crystal specimen was mounted on the end of a shaft that protruded slightly into the resonant cavity. The shaft was normal to the steady field. We could measure relative shaft rotation angles. Three orientations of the crystal with respect to the axis of rotation were studied. They are shown in Fig. 1. The drawings (and all later discussion) are based on the assumption that the angle between Z_I and Z_{II} is a right angle. Figure 1A shows rotation of the crystal about an axis parallel to one of the *tetragonal axes* of the unit cell, the angle of rotation, φ, being equal to θ_1 plus a constant. In Fig. 1B the crystal is rotated about an axis parallel to the *magnetic axis* of the crystal; the angle of rotation again is equal to θ_1 plus a constant. Figure 1C shows rotation about such an axis that the angle between the axis of rotation and the magnetic axis is constant and a right angle; further, the direction of the field makes equal angles with Z_I and Z_{II}. We will call this last type of rotation axis a "*Type I*" *axis*. The angles that Z_I, Z_{II}, and the magnetic axis make with the crystallographic axes of the crystal are given by KM. The crystals were carefully ground into small cylinders, the cylinder axis being the rotation axes of Fig. 1.

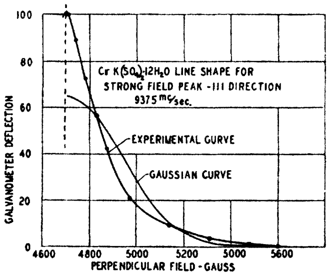

FIG. 5. Comparison of the line shape of the strong field absorption line of $KCr(SO_4)_2 \cdot 12H_2O$ (for the field oriented along the 111 direction) with a Gaussian curve having the same area and second moment.

VI. RESULTS

The experimental data for all three axes are shown in Fig. 2. The values of g for the tetragonal and Type I axis rotations should repeat every 90°; the values of g for the magnetic axis rotation should repeat every 45°. This comes about because the angle between Z_I and Z_{II} is nearly a right angle.

The theoretical curves that best fit the experimental data are shown as full lines in Fig. 2. They are found in the following way from Eq. (7) and Fig. 1: for the tetragonal axis rotation $\theta_1=\phi$ and $\theta_2=90°$. Thus, Eq. (7) reduces to

$$g_1=(g_{\parallel}^2\cos^2\varphi+g_{\perp}^2\sin^2\phi)^{\frac{1}{2}},\quad g_2=g_{\perp}. \tag{9}$$

Finally, according to Van Vleck, the measured g is given by

$$g=(g_1+g_2)/2. \tag{10}$$

From the indicated geometry (and with a similar procedure) we may compute curves for the magnetic axis rotation and Type I axis rotation. For the magnetic axis rotation, $\varphi=0°$, $\theta_1=0°$; for the type I axis rotation, when $\varphi=0°$, $\theta_1=45°$. The theoretical curves depend on $g_{\parallel}$ and $g_{\perp}$; $g_{\parallel}$ and $g_{\perp}$ are chosen so as to best fit the data at the ends of the experimental curves. These values are $g_{\parallel}=2.39$ and $g_{\perp}=2.07$.

VII. ABSORPTION LINE WIDTHS

Besides the anisotropy in the g factors, we found that the widths (at half-amplitude) of the absorption lines varied with the orientation of the crystal in the steady field. The experimental results for the three axes of rotation are shown in Fig. 3. The relationship between φ and θ for each of the curves is the same as that in Fig. 2. Van Vleck[10] has developed a formula for the variation of the mean square line width with angle of rotation for tetragonal axis rotation; it assumes that the exchange energy is a function only of the total crystalline spin; our results are consistant with this theory.

VIII. ABSORPTION LINE SHAPES

We have studied, in detail, the shapes of the absorption lines. The copper sulfate absorption lines

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[10] J. H. Van Vleck, private communication.

are much narrower than one expects on the basis of known internal magnetic fields. Also, we find that the absorption in $CuSO_4 \cdot 5H_2O$ reaches negligible values only after the applied field is about 1500 gauss greater than that at the absorption maximum. This is shown in Fig. 4. A line shape theory has been worked out by Gorter and Van Vleck,[11] and in detail by Van Vleck,[12] on the assumption of exchange interaction between the cupric ions. Their results show that when exchange is important, the usual assumption of a Gaussian curve for the absorption line is a poor one. Instead, they find that the absorption line should be peaked in the center and should have a long tail. To test this, we have drawn a Gaussian curve with the same area and second moment as the absorption line (Fig. 4). The Gaussian curve is a very poor approximation to the experimental curve. In Fig. 5 is shown the strong field side of the upper absorption line of $CrK(SO_4)_2 \cdot 12H_2O$ (steady field oriented along the 111 crystallographic direction). Exchange effects here are probably small. We draw here, too, a Gaussian curve with the same area and second moment as the absorption line. In this case the Gaussian curve is a reasonable approximation to the experimental curve. The difference between the absorption line shapes of the two salts can thus be explained on the basis that there is exchange interaction between the cupric ions.

We wish to acknowledge the continued aid and encouragement of Dr. A. J. Allen.

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[11] C. J. Gorter and J. H. Van Vleck, Phys. Rev. **72**, 1128 (1947).

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

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The Second Viscosity of Liquids*

L. N. LIEBERMANN
University of California, Marine Physical Laboratory, San Diego, California

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The second coefficient of viscosity is concerned with the viscous forces generated by compression (or dilatation). In the absence of knowledge of its magnitude in liquids it has been customary in hydrodynamics to assume that the coefficient of dilatational viscosity, n', could be approximated by the ideal gas value $n' = -2n/3$, where n is the coefficient of shear viscosity. A method has been developed for obtaining values for the dilatational viscosity which is based on Eckart's theory of acoustical streaming; the non-periodic motion of the fluid in the vicinity of a sound source is dependent on the two coefficients of viscosity. Values for the coefficient of dilatational viscosity for a variety of organic liquids and for water are given in the table. The coefficient of dilatational viscosity was found to be positive in sign and greater in magnitude than the shear viscosity. For example, the dilatational viscosity of water was found to be 2.4 centipoise and that for carbon disulfide greater than 200 centipoise. There is no correlation between the magnitude of the shear and dilatational viscosities for the liquids studied. Temperature variation measurements on water show that the temperature dependence of dilatational and shear viscosity in this substance is identical. Introduction of values for the dilatational viscosity into acoustical calculations eliminates the well-known discrepancy between theory and observation of sound absorption in liquids at very high frequencies.

I. INTRODUCTION

THE classical theory of viscosity is closely analogous to the theory of elasticity. In the classical elasticity theory two coefficients of elasticity appear, the Lamé coefficients, λ and μ. In an analogous manner there are two coefficients of viscosity, n and n'. The coefficient, n is familiar; it is simply the coefficient of shear viscosity. Values for this coefficient are determined with the use of a rotating cylinder or a transpirational viscosimeter and are to be found for a variety of substances in handbooks.

The second coefficient of viscosity, n', is less familiar; it might be called the coefficient of dilatational viscosity. It is a measure of the viscous forces which arise when a volume of fluid is compressed or dilated without change in shape. The magnitude of the viscous forces depends on the *rate* of compression or dilatation. A conventional viscosimeter does not measure the dilatational viscosity inasmuch as the dilatation or compression in these instruments is obviously negligible. No dilatational viscosimeter exists nor may values for the dilatational viscosity be found in the literature.

In hydrodynamics it has been customary in dealing with actual liquids to assign for the value of the dilatational viscosity, that calculated for an ideal gas; the dilatational viscosity of an ideal gas may be shown to be equal to $-2n/3$.[1] Most textbooks[2] do not attempt to justify this assumption

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* This work represents one of the results of research carried out under contract with the Bureau of Ships, Navy Department.

[1] Horace Lamb, *Hydrodynamics*, 6th edition (Cambridge University Press, London, 1932), p. 574.

[2] For example: Lord Rayleigh, *Theory of Sound* (Dover Publications, New York, 1945), p. 314.