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Paramagnetic resonance in copper sulphate

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Paramagnetic resonance absorption in single crystals of copper sulphate pentahydrate has been investigated at wave-lengths of 3·04, 1·23 and 0·85 cm. Only one absorption line is found at wave-lengths of 3·04 and 1·23 cm., and the position agrees with that calculated from susceptibility data. Two lines would be expected theoretically for many orientations of the crystal in the magnetic field, corresponding to the two inequivalent Cu^{++} ions in unit cell. At 0·85 cm. wave-length two lines are found under the appropriate conditions but not at longer wave-lengths. This is interpreted in terms of exchange interaction between dissimilar ions, and the exchange frequency is estimated at 0·15 cm.$^{-1}$. Other effects of exchange interaction in this salt are discussed.

1. INTRODUCTION

The resonant absorption of microwave radiation in paramagnetic salts placed in a magnetic field was first reported by Zavoisky (1945, 1946), who observed the absorption in powdered samples of $MnSO_4$, etc. Further work has been done on powders, but it is by the use of single crystals that it is possible to obtain detailed information about the lowest energy levels of the paramagnetic ion by this method. The chrome alums, in particular, have been investigated in some detail (Bagguley & Griffiths 1947; Bleaney 1949; Halliday & Wheatley 1948; Whitmer, Weidner, Hsiang & Weiss 1948). In general, there are two points of interest which may be investigated, the separations of the lowest energy levels, which may be correlated with the crystalline field theory for the particular ion, and the width of the absorption line. This latter may give information about the interactions of the ions with each other and with the lattice. A general survey of the results obtained with salts of the iron group of transition elements is given by Bagguley, Bleaney, Griffiths, Penrose & Plumpton (1948).

In this paper are described measurements at room temperature on single crystals of $CuSO_4.5H_2O$ at wave-lengths of 3·04, 1·23 and 0·85 cm. A preliminary account of this work has been given by Bagguley & Griffiths (1948), and some measurements at 3·25 cm. have been reported by Arnold & Kip (1949) and also by Wheatley & Halliday (1949) which agree with the results described here. The results are compared with the crystalline field theory worked out by Polder (1942) for this salt, and with susceptibility measurements. There is general agreement between the results of the absorption measurements and those of the susceptibility measurements, but the absorption measurements show two features of considerable interest. The first is that the line width for certain orientations of the magnetic field is much smaller than would be expected from the normal magnetic interactions of the ions. Secondly, two lines would be expected theoretically for many orientations of the crystal in

[366]

the magnetic field, corresponding to the two inequivalent Cu^{++} ions in unit cell. These are observed at 0·85 cm. wave-length but not at longer wave-lengths.

Gorter & Van Vleck (1947) have suggested that the effect of exchange interaction is to narrow the absorption line, and it appears likely that this effect is observed in $CuSO_4 . 5H_2O$. The appearance of only one line can also be interpreted in terms of exchange interaction, in this case between dissimilar ions. This is discussed further in § 6.

2. EXPERIMENTAL ARRANGEMENT

The apparatus used in these experiments will be described in another paper, which is in course of preparation, and it is sufficient to give only a brief description here, together with such details as are particularly relevant to these investigations.

The oscillators used were of the low-power (12 to 100 mW output) reflexion klystron type; at 3 cm. a CV 87, at 1·23 cm. a VX 302 and at 0·85 cm. a special valve of the same type as the VX 302. The voltage supplies to the oscillator were carefully stabilized, since it was found that frequency or amplitude fluctuations in the valve were the main limitations on the accuracy and sensitivity of the method.

Power from the oscillator was fed through a wave-guide 2 m. long to a cylindrical resonator with at least 7 db. of attenuation inserted between the oscillator and the resonator. This length of guide was found sufficient to make any effect of the magnetic field on the valve negligible. The feed into the resonator was a small hole in the side about a quarter of a cavity wave-length from the end and another hole of the same size opposite the first, fed power out of the resonator into a short length of guide terminated by a silicon crystal detector unit. The resonators used had diameters 22 mm. at 3·04 cm. and 1·23 cm. wave-length and 8·5 mm. at 0·85 cm. wave-length. The resonators were excited in the H_{11} mode at 3·04 and 0·85 cm. wave-length and in the H_{01} mode at 1·23 cm. The top of the resonator was closed by a non-contact tuning plunger supported from a micrometer screw and the bottom by another non-contact plunger which could be rotated and on which the crystal was placed. The resonator was placed between the poles of an electromagnet so that the field was at right angles to the h.f. magnetic field in the resonator.

Measurements were made at constant frequency by tuning the resonator to resonance with the copper sulphate crystal in position and taking readings of the detector current at different magnetic field strengths, the resonator being tuned before each reading. Since the detector current did not exceed 2 μA the rectification law can be assumed to be a square law, and in this case the increased absorption in the sample due to the paramagnetic resonance is proportional to

$$\left(\frac{Q_0}{Q_H} - 1\right) = \left(\sqrt{\left(\frac{\theta_0}{\theta}\right)} - 1\right),$$

where Q_0 and θ_0 are the magnification factor of the resonator and the galvanometer reading, respectively, at zero magnetic field and Q_H and θ are these quantities at a magnetic field H. In all results given in this paper the absorption is expressed in arbitrary units, and no attempt has been made to measure the absolute value.

The magnetic field was measured by a search coil calibrated by the N.P.L. and a fluxmeter which was checked against a ballistic galvanometer using a substandard

ammeter and mutual inductance. The accuracy of the measurement of magnetic field was from $\frac{1}{2}$ to 1 %. For the very narrow lines this accuracy was not sufficient to obtain the shape of the line and another procedure was used. The magnetic field was adjusted to be at the centre of the absorption line at the start of each measurement. A small change in the magnetic field was then made and this change was measured by a ballistic galvanometer connected to a coil permanently in the field. This procedure was repeated for different changes in the field until the line had been delineated. An example of a curve obtained in this way is shown in figure 6.

3. Crystallographic and susceptibility data

The analysis of the crystal structure of $CuSO_4 . 5H_2O$ given by Beevers & Lipson (1934) shows that there are two inequivalent Cu^{++} ions in a unit cell, with parameters (000), and $(\frac{1}{2}\frac{1}{2}0)$. Each ion is surrounded by a nearly octahedral arrangement consisting of four water molecules and two oxygen atoms; the angle between the planes of water molecules of the two ions is 82°. Using these data Polder (1942) has calculated the effect of the crystalline electric field on the Cu^{++} ions. He takes an electric field of cubic symmetry with a strong component of tetragonal symmetry, the tetragonal axis being normal to the plane of the water molecules. The Cu^{++} ion is in a D state which is split by the cubic field into a triplet and a doublet, the doublet lying lowest. The tetragonal field removes the orbital degeneracy, giving a separation between the two components of the doublet of the order of 12,000 cm.$^{-1}$. Thus the lowest orbital level is well removed from the next level.

The spin degeneracy is removed by a magnetic field, giving a doublet whose separation is $g\beta H$, where H is the magnetic field, β the Bohr magneton and g depends on the orientation of the tetragonal axis with respect to the magnetic field. For a completely free spin g would be 2, and the effect of the spin-orbit coupling is to increase g to a value of 2·47 when H is along the tetragonal axis and 2·06 when H is at right angles to this axis. When account is taken of the two Cu^{++} ions, this gives good agreement with the results of the susceptibility measurements of Krishnan & Mookherji (1936, 1938). They find that the crystal is magnetically uniaxal, with the principal axis parallel to the intersection of the planes of the water molecules of the two ions, and that in this direction the susceptibility is a minimum. The values of the susceptibilities given by these authors parallel and perpendicular to the magnetic axis are $\chi_\| = \dfrac{0 \cdot 399}{(T - 2 \cdot 0)}$ and $\chi_\perp = \dfrac{0 \cdot 486}{(T + 1 \cdot 8)}$, giving effective g values of 2·07 and 2·26.

Paramagnetic resonance occurs when the radiation energy $h\nu$ is equal to the energy difference between the spin levels, i.e. in this case when $h\nu = g\beta H$. Thus since g is dependent on the orientation of the magnetic field, one would expect the position of the absorption line to be similarly dependent and also for there to be two lines corresponding to the two Cu^{++} ions except when the g values of the two ions are equal or are not sufficiently different for the two lines to be resolved.

Another theoretical treatment of the susceptibility of $CuSO_4 . 5H_2O$ was given by Jordahl (1934) in an earlier paper and with less accurate data available. He considered only one ion per unit cell and obtained a very much smaller splitting (about

200 cm.$^{-1}$) for the basic orbital doublet, so that both levels would be occupied at room temperature. Since there are a number of discrepancies between the results of this treatment and both the susceptibility and the absorption data it will not be considered further in this paper.

4. RESULTS

Most of the measurements were made at three different orientations of the crystal in the magnetic field. The first, denoted by L_1, is with the field parallel to the principal axis of magnetic susceptibility. This is at right angles to the tetragonal axes of both ions and makes angles of (154°, 64°, 51°) with the axes of unit cell. The second, L_2 (78°, 130°, 52°), is along the tetragonal axis of the ion at (000) and the third L_3 is the internal bisector of the two tetragonal axes L_2 and L_4 (70°, 41°, 69°).

Plane sections of from 1 to 2 mm. thick were ground from a crystal, the plane of section I containing L_1 and L_2 and of section II containing L_2, L_3 and L_4. The results for the field parallel to the directions L_1, L_2 and L_3 are given in table 1. Here g is obtained from the relation $g\beta H = \mathbf{h}\nu$, and the values of g (susceptibility) given for comparison are taken from Krishnan & Mookherji (1936), except the values for L_2 at 0·85 cm. which are referred to later. $\Delta H_{\frac{1}{2}}$ is the difference in magnetic field between the position of maximum absorption and that at which the absorption is half its maximum value.

The accuracy of the g values is about $\pm \frac{1}{2}$% except for the very wide lines where it is somewhat less.

TABLE 1

direction of H	L_1 (154°, 64°, 51°)			L_2 (78°, 130°, 52°)				L_3 (70°, 41°, 69°)		
wave-length (cm.)	3·04	1·23	0·85	3·04	1·23	0·85		3·04	1·23	0·85
H at resonance (kG)	3·36	8·36	12·1	3·11	7·64	10·6	11·9	3·10	7·70	11·2
g	2·09	2·08	2·08	2·26	2·27	2·37	2·12	2·27	2·26	2·25
g (susceptibility)	2·06	2·06	2·06	2·27	2·27	2·47	2·06	2·27	2·27	2·27
width $\Delta H_{\frac{1}{2}}$ (gauss)	28	24	25	115	640	$\simeq 450$		58	50	—

5. DISCUSSION OF RESULTS

(a) g values

The agreement between the g values obtained by this method and those obtained from susceptibility measurements is within the experimental errors. In the case of L_2 at 0·85 cm. the mean of the two g values is 2·25, again in agreement with the susceptibility value. On the theory outlined in §3, two lines should be observed in this direction and the g values should be 2·06 for the ion whose tetragonal axis is at right angles to the magnetic field, since this is the same as when H is along L_1, and 2·47 for the other ion to give a mean value of 2·27. These are the values given in table 1.

At 3·04 cm., only one line is observed with H along L_2. The experimental curve for this case is shown in figure 1 and the expected positions of the two lines are marked at 2·86 and 3·42 kG. From this it is clear that it is not because of lack of

resolution that the two lines are not observed. Figure 2 shows the two lines resolved at 0·85 cm. The greater scatter of the experimental points in this case is due to the fact that the valve used at this wave-length was not as steady as the other valves.

A number of measurements were made at 3·04 cm. wave-length at various directions in the plane $L_2 L_3 L_4$ which contains the tetragonal axes of the two ions.
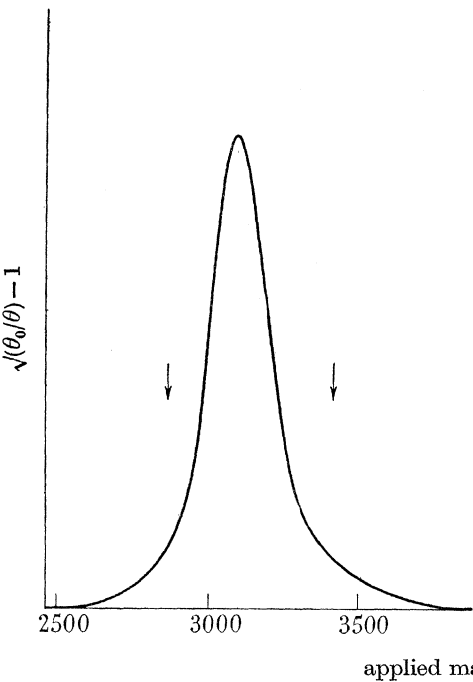

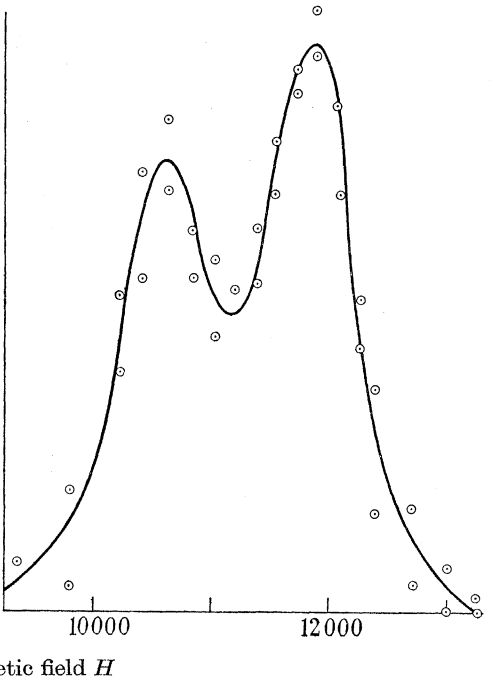FIGURE 1. Absorption curves for H along L_2 at $\lambda = 3\cdot04$ cm.

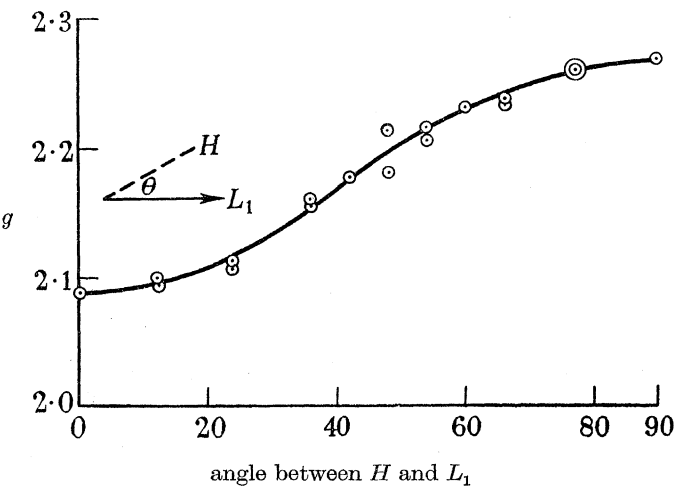FIGURE 2. Absorption curve for H along L_2 at $\lambda = 0\cdot85$ cm.

FIGURE 3. Variation of g with orientation for H in the plane $L_1 L_2$ at $\lambda = 3\cdot04$ cm.

If the angle between these axes is $(90 - \alpha)$ and θ is the angle between H and one of the axes, the mean g value measured will be given by

$$g^2 = \tfrac{1}{2}(g_\parallel^2 + g_\perp^2) + \tfrac{1}{4}(g_\parallel^2 - g_\perp^2)\sin 2\alpha \sin 2\theta,$$

where $g_\parallel$ and $g_\perp$ are the g values of an ion when H is respectively parallel and perpendicular to the tetragonal axis. No variation of the g value greater than $\tfrac{1}{2}\%$ (the experimental error) was found, which shows that α is less than $2°$. This agrees with the susceptibility measurements of Krishnan and shows that the tetragonal axes of the electric field are more nearly at right angles to each other than is suggested by the crystallographic data.

Measurements were also made in the $L_1 L_2$ plane at $3 \cdot 04$ cm. wave-length, and the results are shown in figure 3 in which the points are the experimental results and the full curve the theoretical values given by the expression $g = g_\parallel + (g_\perp - g_\parallel)\sin^2\theta$, where it is assumed that $(g_\perp - g_\parallel)$ is small. Again the agreement is within the experimental error.

(b) Width of lines

Great variation of the width of the line was found both with orientation and with wave-length. For H parallel to L_1, the width is very small and appears to be independent of wave-length over the range investigated. Similarly, when H is parallel to L_3 there is no very marked change of width with wave-length. For both these directions the magnetic field is equally inclined to the tetragonal axes of the two Cu^{++} ions and therefore the effective g value is the same for each ion.

For L_2 where the g values of the two ions should be different the width increases rapidly with decreasing wave-length until the two lines are separated. Even at
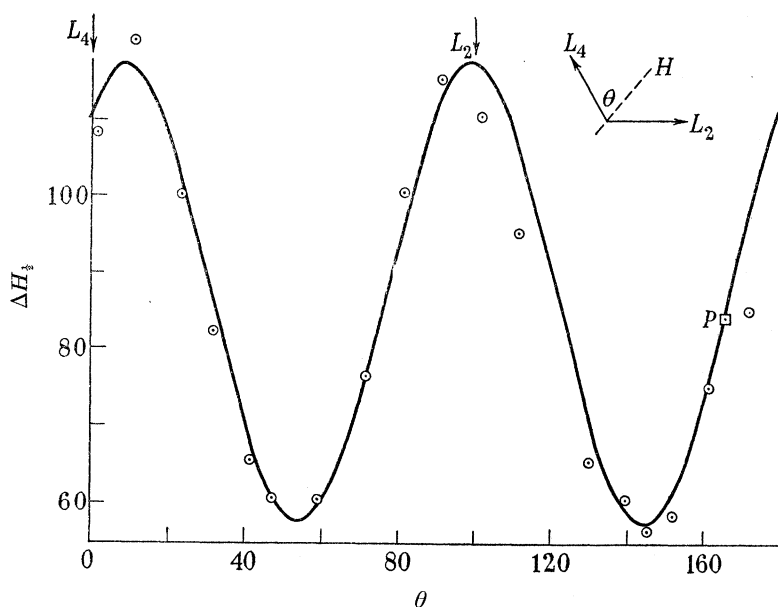

FIGURE 4. Variation of width with orientation for H in the plane $L_2 L_4$ at $\lambda = 3 \cdot 04$ cm.

1·23 cm. wave-length there is some indication of the two lines, since the top of the absorption curve is very flat.

The variation of width with orientation in the plane $L_2 L_4$ is shown in figure 4 and in the plane $L_1 L_2$ in figure 5. The measurements of figure 4 were made at 3·04 cm. and those of figure 5 at 1·23 cm. It was suspected that small errors in the grinding and marking of the crystal section used for the measurements of figure 4 might lead to an appreciable error in the final orientation of the crystal. A check was therefore made with an uncut crystal oriented with H at 13·5° to L_4 (point P of figure 4). The choice of this orientation was made because the width is sensitive to change of orientation in this region, and, secondly, it is easy to set an uncut crystal accurately in this direction, since it is the intersection of the plane $L_2 L_4$ with the plane of the crystal face μ and lies at 79° from the c axis of the crystal.

This measurement showed that there was an error of 8° in the original set of measurements and the curve of figure 4 has been adjusted accordingly. This error was found to be mostly in the marking of the line L_2 in the plane $L_2 L_4$ and not in the cutting of the plane.

The shape of the resonance line with H along L_1 measured at 1·23 cm. is shown in figure 6. Comparison with a Gaussian curve shows that the wings of the absorption line have a considerably greater intensity than in the case of the Gaussian curve.
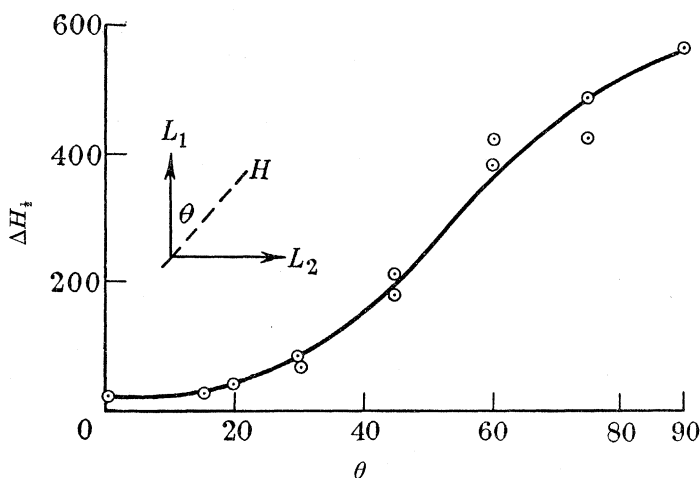

FIGURE 5. Variation of width with orientation for H in the plane $L_1 L_2$ at $\lambda = 1·23$ cm.

6. EFFECT OF EXCHANGE

The width of the absorption line should be due either to spin-lattice interaction or spin-spin interaction or a combination of both effects (Bagguley et al. 1948). In this case the spin-lattice relaxation time is difficult to estimate. Paramagnetic dispersion experiments (Gorter 1947) give a relaxation time of the order of 3×10^{-8} sec. at liquid-air temperature, which would give a line breadth of about 10 G. If this relaxation time decreases rapidly with increase of temperature, as in some substances, it would lead to a very considerable broadening of the line at room tem-

peratures. However, since the narrowest line measured here is only 25 G and preliminary experiments show no great change of width with temperature, it does not seem likely that spin-lattice interaction is affecting the width to any marked extent.

The spin-spin interaction has been investigated theoretically by Van Vleck (1948) and by Pryce & Stevens (1950) and, for the case of nuclear spins, by Bloembergen, Purcell & Pound (1948). They considered the effect of magnetic interaction between the ions, which results in a broadening of the absorption line. This effect can be represented as a fluctuating internal magnetic field whose root-mean-square value in the case of copper sulphate is calculated to be about 240 G. The width of the absorption line should be of this order, whereas in fact very much smaller widths are measured, down to 25 G.

There are therefore two main features of these results which are not in agreement with existing theory, namely, the occurrence of narrow lines and the failure to observe two lines at the longer wave-lengths. Gorter & Van Vleck (1947) have suggested that the narrowing of the line may be due to the effect of exchange inter-action between the Cu^{++} ions. A rapid exchange of electrons between the ions will have the effect of smoothing the fluctuations in the magnetic field, an effect which is similar to the narrowing of the nuclear resonance line in a liquid due to the motion of the molecules (Bloembergen *et al.* 1948). This applies to similar ions, i.e. ions with the same energy in the magnetic field, but for dissimilar ions another effect will be introduced. In this case the precessional frequencies of the two ions are different, and if there is exchange, the type of absorption curve obtained will depend on whether the exchange frequency is greater or smaller than the difference in pre-cessional frequencies. When it is greater, a mean value of the precessional frequencies should be measured, whereas when it is smaller, each ion should be observed separately and two lines should appear.

This qualitative description seems to cover the main facts. Thus with H along L_1, all ions are similar and a narrow line results. With H along L_3 the precessional frequencies of the two types of ions are the same, but the precessional axes are slightly different, which may account for the rather greater width. The greatest difference between the ions is when H is along L_2 and this gives the greatest width. A very rough estimate of the exchange frequency can be made if it is assumed that the two lines are just not resolved when the exchange frequency is equal to the difference in the precessional frequencies. The measurement at 1·23 cm. wave-length shows some indication of the two lines and this may be taken as the appro-priate wave-length. At this wave-length the maximum absorption with H along L_2 occurs at 7640 G, and in this field the difference in the resonance frequencies of the two ions is 0·15 cm.$^{-1}$. This is therefore the order of the exchange frequency.

A quantitative theory of the broadening due to exchange of dissimilar ions has been given by Pryce (1948), who gives an expression for the broadening due to this cause in terms of the g values and the orientation of the magnetic field. This ex-pression contains two undetermined constants A and B which depend on the frequency but are independent of angle and temperature. So far it has not been possible to check this expression in any detail, and in fact this is somewhat difficult

to do, as it only applies at wave-lengths long compared with the resolving wave-length and then the variation in width is small. However, it does give the right form of variation, and with the empirical values $A = -0.91$, $B = 0.74$ gives a good fit with the experimental points of figure 4, although a $\cos^2\theta$ curve gives an equally good fit. It is interesting to note that the variation of width with orientation in this plane $(L_2 L_3)$ approximates to a $\cos^2\theta$ form even at 1.23 cm. wave-length where the lines are very nearly resolved.

The behaviour of $CuSO_4.5H_2O$ may be contrasted with that of the Tutton salts such as $CuSO_4.K_2SO_46H_2O$ (Bleaney, Penrose & Plumpton 1949). In these salts the exchange frequency seems to be small, since the two lines are observed in the appropriate direction at 3 cm. wave-length giving g values in close agreement with theory.

7. DISCUSSION

It has been shown above that the g values obtained by experiments on para-magnetic resonance in $CuSO_4.5H_2O$ are in agreement with the susceptibility measurements of Krishnan & Mookherji (1936), and also that their interpretation in terms of two inequivalent ions per unit cell is consistent with these results if it is assumed that there is an exchange interaction between these ions. Van Vleck (1948) has considered the case of exchange between similar ions. The quantities he calculates are (in his notation) $\langle\Delta\nu^2\rangle_{av.}$ and $\langle\Delta\nu^4\rangle_{av.}$ which can be defined by the relation

$$\langle\Delta\nu^n\rangle_{av.} = \frac{\int_{-\infty}^{\infty} A(\nu)\,(\nu - \nu_0)^n\,d\nu}{\int_{-\infty}^{\infty} A(\nu)\,d\nu},$$

where $A(\nu)$ is the intensity of absorption at frequency ν and ν_0 is the frequency of maximum absorption. He shows that $\langle\Delta\nu^2\rangle_{av.}$ is not affected by exchange inter-action, whereas there is a positive contribution to $\langle\Delta\nu^4\rangle_{av.}$, which means that the half-width of the absorption line is decreased by exchange. For dissimilar ions, however, exchange does contribute to $\langle\Delta\nu^2\rangle_{av.}$, and the half-width of the line is now increased. The effect of exchange on the width of the absorption lines is therefore twofold: a broadening when the ions are dissimilar and a narrowing when the ions are similar. The case of dissimilar ions has been considered above, and it was shown that an estimate of 0.15 cm.$^{-1}$ can be made for the exchange frequency in that case.

Unfortunately, it has not been possible to estimate experimentally $\langle\Delta\nu^2\rangle_{av.}$ and $\langle\Delta\nu^4\rangle_{av.}$ for those orientations of the crystal in which all the ions are similar. The observations at present suggest a line shape of the form

$$A = 1/(1 + x^2),$$

where x is the distance from resonance measured in units of the half width, so that the contribution from the wings of the absorption line is sufficient to make $\langle\Delta\nu^2\rangle_{av.}$ and $\langle\Delta\nu^4\rangle_{av.}$ infinite. It is necessary, therefore, for more sensitive experiments to be carried out in the wings of the line to determine the true values of these quantities. However, as stated above, this exchange narrowing is analogous to the narrowing

of the nuclear resonance line in liquids due to the motion of the magnetic dipoles, which has been treated by Bloembergen *et al.* (1948). Using this analogy, Van Vleck suggests that the half-width $\Delta\nu_{\frac{1}{2}}$ of the line should be of the order of $\tau_c\langle\Delta\nu^2\rangle_{\mathrm{av.}}$, where τ_c is the relaxation time for the process. The calculated value of $[\langle\Delta\nu^2\rangle_{\mathrm{av.}}]^{\frac{1}{2}}$ for copper sulphate taken from Van Vleck's paper is $0\cdot02$ cm.$^{-1}$, and the measured value of the width of the narrowest absorption line expressed as $\Delta\nu_{\frac{1}{2}}$ is $5\cdot10^{-3}$ cm.$^{-1}$ which gives a value for $1/\tau_c$ of $0\cdot08$ cm.$^{-1}$. If this is interpreted as the exchange frequency it is seen to be rather smaller than the value of $0\cdot15$ cm.$^{-1}$ obtained above, although in view of the very rough approximation made, the discrepancy is not significant.
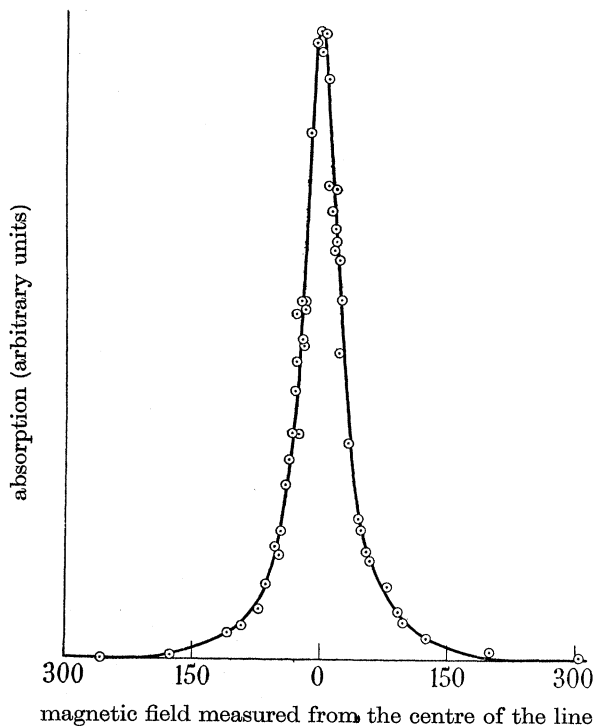

FIGURE 6. Absorption curve for H along L_1 at $\lambda = 1\cdot23$ cm.

Exchange interaction should also have an effect on the specific heat of the salt at low temperatures. Ashmead (1939) found a specific heat anomaly in $CuSO_4.5H_2O$ with a maximum at about 1° K, and Duyckaerts (1942) has measured the specific heat at temperatures just above this. Duyckaert's values lead to an excess specific heat above the Debye term of about $1\cdot5/T^2$ cal./mol. at temperatures reasonably above the temperature of the specific heat maximum. If this is attributed to exchange effects, an approximate relation between the excess specific heat and the exchange energy is given by $\dfrac{C_v}{R} = \dfrac{3}{4}f\left(\dfrac{J}{kT}\right)^2$, where $2f$ is the number of nearest neighbours and $2J$ the exchange energy. Using $C_v = 1\cdot5/T^2$ as above, the exchange frequency becomes $1\cdot4/\sqrt{f}$ cm.$^{-1}$. For any reasonable value of f this is rather larger than the other values given above.

Again, if the static susceptibility of copper sulphate can be expressed as $\chi = \dfrac{C}{T+\theta}$, the Curie temperature θ should be affected by the exchange interaction. Measurements on powdered $CuSO_4 . 5H_2O$ by de Haas & Gorter (1930) down to $14°\,K$ and by Reekie (1939) down to $1.6°\,K$ both give $\theta = 0.7°\,K$. Recent measurements by Benzie & Cooke on a single crystal in the temperature range $10°$ to $1°\,K$ show that the crystal is isotropic so far as the value of θ is concerned. They find a value of $0.6 \pm 0.05°\,K$. If this is entirely attributed to exchange interaction, the approximate relation $k\theta = fJ$ gives an exchange frequency of $0.9/f$ cm.$^{-1}$, again a rather large value.

These estimates of the exchange frequency are not very consistent although they are of the same order of magnitude. The reasons for the differences may lie in one or more of the following considerations:

(1) The estimates are based on approximate relations.

(2) The exchange interaction between similar and dissimilar ions may be different. The value of 0.15 cm.$^{-1}$ is for the exchange between dissimilar ions, and if the interaction between similar ions is greater than this, the average value determined from the specific heat and susceptibility measurements would also be greater.

(3) The width of the narrowest absorption line may be partly due to other causes, such as the spin-lattice relaxation time being short. The estimate of 0.08 cm.$^{-1}$ obtained from this must therefore be regarded as a lower limit.

(4) The exchange interaction may be a function of the temperature.

Thus there appears to be need for further experimental work by all these methods to clear up the many points still outstanding.

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The adsorption of vapours on mercury
IV. Surface potentials and chemisorption

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An apparatus has been constructed to measure the surface potential of adsorbed vapours on mercury. There was shown to be a change in potential of 0·055 V at the phase change associated with the alteration in the orientation of toluene molecules adsorbed on the surface of the mercury.

Carbon tetrachloride, hexachlorethane and chloroform vapours reacted with mercury, and the rate of the reaction was determined by the accompanying change in surface potential which was over 1 V in the case of carbon tetrachloride. The kinetics indicated that the substances were dimerizing under the action of the mercury surface with negligible activation energy. The rate of reaction with carbon tetrachloride was in agreement with the calculated rate, assuming that the activated complex consisted of two physically adsorbed molecules loosely held together and able to move over the surface.

Methyl iodide vapour was found to react with mercury only when illuminated with light from a mercury lamp. There was little change of surface potential associated with this reaction, but the kinetics were determined from the irreversible changes in the surface tension of the mercury. It was found that the rate of reaction depended on the square root of the light intensity, which suggested that the methyl iodide was being dissociated into radicals, which in turn reacted with the mercury.

Introduction

The measurement of surface potentials has proved a useful method of studying insoluble films at liquid surfaces, and it can be extended to the study of the films formed by vapours on metal surfaces as was done by Frost (1942). Two electrodes are necessary to measure the potential, and the vapour will be adsorbed on both, rendering the interpretation of the results difficult when only physical adsorption occurs. However, if a phase change occurs in the adsorbed film on one of the electrodes it may be accompanied by a change in surface potential, the measurement of which will lead to a greater understanding of the nature of the phase change. Likewise, if a chemical reaction occurs slowly at one of the surfaces there may be a drift in the value of the potential which can be correlated with the reaction, and such a