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The Microwave Spectroscopy of Paramagnetic Salts; the Spectrum of Chromic Alum

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Some measurements on the resonance absorption of chrome alum are analyzed for the purpose of obtaining a quantitative estimate of the splitting of the lowest state of the chromic ion by the electric field in the crystal. It is found that a small cylindrical field in addition to the large cubic field present is sufficient to account for the structure of the absorption curves and that the magnitude of the splitting is 0.15±.01 cm^{-1}. It is pointed out that the methods used in the case of chrome alum can be applied to other similar salts such as iron alum and the hydrated gadolinium salts.

I. INTRODUCTION

A COMMON property of the salts used in the process of adiabatic demagnetization, namely, hydrated salts of the iron group and chemically dilute gadolinum salts, is that the spin of the paramagnetic ion is free to orient itself at low temperatures in a magnetic field. This permits the entropy of the salt to be decreased by the application of a magnetic field and the subsequent decrease in temperature when the field is removed adiabatically. The mechanism by which the orbital angular momentum is quenched and the spin left free is generally accepted to be the Stark splitting of the orbital states of the ions by the electric field of the surrounding water molecules. It is clear, however, that the spins cannot be completely free for then, overlooking the question of the relaxation time, the specific heat (in the absence of a magnetic field) would be zero and absolute zero would be attained on conclusion of the process. This hindering of the orientation of the spin, and the corresponding specific heat, arise from two sources which reveal themselves in somewhat different temperature regions, both lower than 0.1 degree abs. These are a fine splitting of the lowest energy state of the paramagnetic ion by non-cubic electric fields of the surrounding ions and a finer splitting because of the magnetic interaction of the spins. The nature of the latter is well known and, although its mathematical treatment is complex, it involves no unknown parameters. The fine splitting due to the electric fields, however, does involve unknown parameters, namely, the symmetry of the field and the magnitude of the splitting.

The lack of freedom of the spin in orienting itself also has the consequence that the Curie temperature computed from the susceptibility of the salt on the supposition that the spin is perfectly free is not the true temperature. Any theoretical procedure which attempts to determine the thermodynamic from the Curie temperature must necessarily involve the parameters of the electric field. Some estimates of these have been computed by Van Vleck[1] on the basis of assumed distributions of charges in the neighborhood of the paramagnetic ion but these at best are meant to obtain an order of magnitude. A different procedure is to deduce the magnitude of the splitting from measurements of specific heat made at very low temperatures. The results of these computations[2] which must of course separate the two contributions to the specific heat show the splitting by the electric field to be of the order of several tenths of a wave number. For example, the splitting in potassium chrome alum is taken to be due to a cylindrically symmetric electric field and found to be 0.12 cm^{-1}.

In the present paper we present some computations to evaluate this splitting in the case of ammonium chrome alum from measurements[3] made (at room temperatures) on the resonance absorption at 3.20 cm. These measurements have been made on both single crystals and powder and the results can be explained by a splitting

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[1] J. H. Van Vleck, J. Chem. Phys. 7, 61 and 72 (1939).

[2] M. H. Hebb and E. M. Purcell, J. Chem. Phys. 5, 338 (1937).

[3] P. R. Weiss, C. A. Whitmer, H. C. Torrey, and Jen-Sen Hsiang, Phys. Rev. 72, 975 (1947).

of 0.15 cm^{-1} induced by a cylindrically symmetric field.

The experimental method and the analysis of the measurements as presented here are applicable to other salts such as the other alums of the iron group, the hydrated gadolinium salts, and some of the Tutton salts. An important one of these is ferric alum. Preliminary measurements on *diluted* ferric ammonium alum indicate the splitting to be a great deal less than has been generally accepted. A detailed discussion of this salt in which the mechanism of the fine splitting is not so clear as in the case of chrome alum is being delayed until more complete experimental data have been obtained.

In the experimental arrangement[3] the absorption is measured as a function of the magnitude of a magnetic field applied perpendicular to the r-f magnetic field. The latter had a constant frequency of 9375 mc/sec. Two different orientations of single crystals relative to the d.c. field were used: (I) the field perpendicular to a (100) plane and (II) the field perpendicular to a (111) plane. In the second case, and also when the powder was used, several absorption maxima were observed which arise as follows: Because of the splitting the energy levels of the spin ($S=\frac{3}{2}$) in the d.c. field are displaced from those of a perfectly free spin. Consequently, different pairs of levels are brought into the resonance separation by different values of the applied field. When this occurs and the corresponding transition is allowed a maximum in the absorption is measured. The spin-spin interaction serves to broaden the absorption peaks. The positions of the peaks lead to a value of 1.97 for the effective g-value and 0.15 cm^{-1} for the splitting.

II. THE CRYSTALLINE STARK SPLITTING

The spin energy levels of chrome alum in a magnetic field have already been stated by Broer[4] in connection with a different problem. In view of the high precision possible in the measurements of absorption it is worth computing the effective g-value of the spins and the magnitude of the terms quadratic in the applied field H. The x-ray analysis[5] shows that each chrome ion (Cr^{+++}) is surrounded by an octahedron of water molecules. These produce a large cubic electric field which quenches the orbital angular momentum of the normal $4F$ state of the chromic ion. However the analysis shows the symmetry about the ion is actually trigonal rather than cubic with the axis of the trigonal field along a body diagonal of the unit cube. There are four such ions per unit cell, the trigonal axes of the different ions being along the different body diagonals of the unit cell. The trigonal field about a single ion is taken to be[6]

$$Q\{(10)^{\frac{1}{2}}(Y_4^{+3}-Y_4^{-3})-(7)^{\frac{1}{2}}Y_4^0\}+aY_2^0, \tag{1}$$

where the Y's are the surface harmonics whose axes are taken along the trigonal axis of symmetry. The terms in Q represent the cubic field, that in a a field of cylindrical symmetry. In addition to this potential there are to be considered the spin orbit coupling $\lambda(L\cdot S)$ and the magnetic energy $\beta(L_z+2S_z)H_z$ (β is the Bohr magneton, the z axis is along the magnetic field which is parallel to the trigonal axis of symmetry). The cubic representation of wave functions which diagonalizes the terms in Q can be obtained in a straightforward fashion. The terms in a, the spin-orbit coupling, and the magnetic energy are then treated as perturbations. A second order perturbation computation yields the following results: (I) the separation between the levels is

$$\delta=60\bar{a}\lambda^2/(15\bar{Q})^2, \tag{2}$$

where $\bar{a}$ and $\bar{Q}$ are certain averages of a and Q over radial parts of the wave functions; (II) the effective g-value is

$$g=2\{1-4\lambda/(15\bar{Q}+5\bar{a})\}; \tag{3}$$

(III) the terms quadratic in H_z are

$$-4\beta^2H_z^2/15\bar{Q}\{1-O(5\lambda/15\bar{Q})\}, \tag{4}$$

where O indicates "of the order of." $15\bar{Q}$ is the splitting in the orbital state, between the lowest and next highest state, induced by the cubic field alone. The spin-orbit coupling parameter λ is known from spectroscopic data to be 87 cm^{-1}. Consequently, measurements of δ and g determine, though with little precision, $\bar{a}$ and $\bar{Q}$.

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[4] L. J. F. Broer, Physica 9, 547 (1942).

[5] H. Lipson and C. A. Beevers, Proc. Roy. Soc. 148A, 664 (1935).

[6] J. Becquerel and W. Opechowski, Physica 6, 1039 (1939).

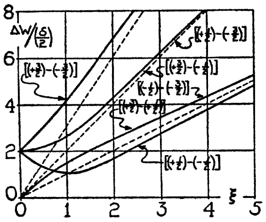

FIG. 1. Level separations (in units of $\delta/2$) as function of $\xi=2g\beta H/\delta$ in orientation I in which H is perpendicular to a (100) plane. The labeling is appropriate to very high field values.

Using $\delta=0.15\text{ cm}^{-1}$ and $g=1.97$, the values are $\bar{a}=180\text{ cm}^{-1}$ and $15\bar{Q}=23{,}000\text{ cm}^{-1}$. Finally, the terms quadratic in H_z are small and such terms in $1/\bar{Q}$ cancel in the separation between neighboring levels. To a high degree of precision the quadratic terms can be neglected. In view of this, the lowest state, a spin quadruplet, can be treated separately, the g-value being determined by (3). The Hamiltonian of this state can readily be shown to be[7]

$$\begin{matrix} A_1 & B & C & 0 \\ B^* & A_2 & 0 & C \\ C^* & 0 & A_3 & -B \\ 0 & C^* & -B^* & A_4, \end{matrix} \tag{5}$$

with

$$A_{\substack{1\\4}}=\pm\frac{3}{2}g\beta H+\frac{\delta}{4}(1-3\cos^2\theta),$$

$$A_{\substack{2\\3}}=\pm\frac{1}{2}g\beta H-\frac{\delta}{4}(1-3\cos^2\theta),$$

$$B=-\frac{\delta}{2}\sqrt{3}\sin\theta\cos\theta\exp -i\varphi,$$

$$C=-\frac{\delta}{4}\sqrt{3}\sin^2\theta\exp -2i\varphi,$$

θ and φ are the polar and azimuthal angles made by H with respect to the trigonal axis of symmetry.

III. SINGLE CRYSTALS

In orientation I of the single crystal, the magnetic field is perpendicular to a (100) plane, along one of the crystalline axes. In this orientation all four ions of the unit cell are equivalent in that the trigonal axes of symmetry all make the same polar angle ($\theta=\cos^{-1}1/\sqrt{3}=54°43'$) with the magnetic field. This is one of the three values of θ for which the secular equation of the Hamiltonian (5) can be solved exactly. The energy levels are,[4] in units of $(\delta/2)$,

$$W=\pm\{(\tfrac{5}{4}\xi^2+1)\pm(\xi^4+3\xi^2)^{\frac{1}{2}}\}^{\frac{1}{2}}. \tag{6}$$

Here ξ is the magnetic energy in units of $\delta/2$, $\xi=2g\beta H/\delta$. The level separations are plotted in Fig. 1 as a function of ξ, the labeling of the curves being taken according to the nature of the spin levels at high values of the magnetic field, namely where the Paschen-Back effect is complete. Not all the transitions shown are allowed, however, over the complete range of ξ. The strengths of the different transitions are proportional to the absolute value square of the corresponding matrix elements of the perpendicular (to H) component of the spin. These have been obtained by a numerical computation at several values of ξ of the transformation matrix which diagonalizes the Hamiltonian and then applying this matrix to obtain the appropriate spin matrix. These strengths are shown in Fig. 2. For values of $\xi=2$ and greater the allowed transitions and their strengths are essentially the same as for a perfectly free spin. An additional fact to be pointed out is that because of the symmetry of the arrangement of the four axes of symmetry, no changes occur on rotating the crystal about the field direction.

On using the value $\delta=0.15\text{ cm}^{-1}$ for the separation and an r-f frequency of 9375 mc/sec., the

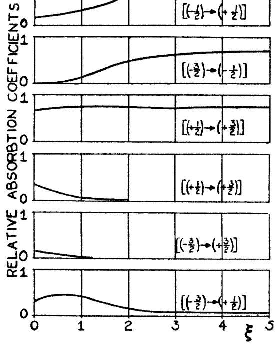

FIG. 2. Quantities proportional to strengths of absorptions as functions of ξ in orientation I. The labeling is appropriate to very high field values.

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[7] H. A. Kramers, Proc. Acad. Sci. Amsterdam **33**, 953 (1930); **34**, 965, (1931).

resonance separation is found to be $\Delta W = 4.17$. According to Figs. 1 and 2 the only strong transitions allowed are the $(-\frac{1}{2})\rightarrow(+\frac{1}{2})$ transitions at $\xi = 4.37$ and the $(-\frac{3}{2})\rightarrow(-\frac{1}{2})$ and $(+\frac{1}{2})\rightarrow(+\frac{3}{2})$ transitions at $\xi = 3.85$. Taking into account the fact that there are two coincident transitions at $\xi = 3.85$, the ratio of the strength at $\xi = 3.85$ to that at 4.37 is 5/3. The separation between the two is 420 gauss. The width of a single line is due practically entirely to spin-spin interaction and has a half-width at half maximum of[8]

$$\begin{aligned}\Delta H &= N(2.40)^{\frac{1}{2}} g\beta S(S+1),\\ &= 230 \text{ gauss.}\end{aligned} \tag{7}$$

Here N is the number of ions per cc and S is the spin per ion ($S = \frac{3}{2}$). The separation is sufficiently large compared to the widths of the lines to make the two absorption lines apparent. Actually an interference* in the absorption of the two lines is possible in the experimental arrangement used. When this is taken into account the absorption curve should have the appearance shown in Fig. 3. The interference effects emphasize the separation of the two lines. The results of measurements in this orientation are shown in Fig. 4, where only one peak is apparent. The reason for this is that insufficient care was taken in aligning the crystal in this orientation. When $\theta = \cos^{-1} 1/\sqrt{3}$ the diagonal elements of the Hamiltonian are those of a perfectly free spin. Consequently the distortion of the energy levels which give rise to the separate lines arises entirely from the off-diagonal elements. A misalignment of the crystal introduces diagonal elements causing three absorption peaks for each ion. Since the misalignment could easily be different for all four ions per unit cell, there could be twelve absorption peaks all close together. The net result in such an event would be a single peak, as shown in Fig. 4, rather than two separate lines.

In orientation II the magnetic field is along one of the body diagonals of the unit cube. There are then two different types of atoms: one for which $\theta = 0°$ and three for which $\theta = 70°33'$.

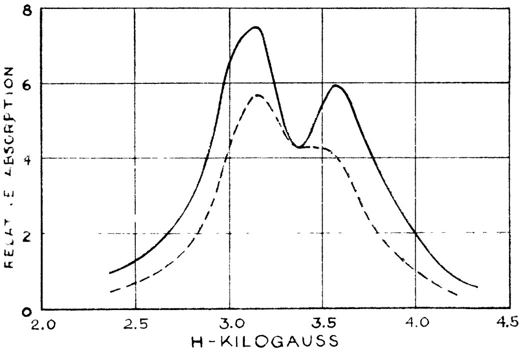

FIG. 3. Theoretical appearance of two absorption peaks when incident frequency is 9375 mc/sec. and orientation is I. The full-line curve includes the interference effects, the dashed curve does not take these into account.

The energy levels for the atom for which $\theta = 0$ are

$$\begin{aligned}&\pm\tfrac{3}{2}\xi - 1,\\ &\pm\tfrac{1}{2}\xi + 1.\end{aligned} \tag{8}$$

The separations are shown in Fig. 5 by the curves labeled I. The energy values for the case $\theta = 70°33'$ cannot be obtained exactly; for $\xi \geq 2$ they were obtained by a second-order perturbation procedure while the values for $\xi < 2$ were obtained from the secular equation by numerical computation. The corresponding separations are shown in Fig. 5 by the curves labelled II. The only transitions allowed in the case $\theta = 0$ are those involving neighboring levels and the strengths of these are proportional to

$$\begin{aligned}&[+\tfrac{1}{2}\rightarrow+\tfrac{3}{2}]:3,\\ &[-\tfrac{1}{2}\rightarrow+\tfrac{1}{2}]:4,\\ &[-\tfrac{3}{2}\rightarrow-\tfrac{1}{2}]:3.\end{aligned} \tag{9}$$

In the case $\theta = 70°33'$ at high fields only these transitions are allowed and their strengths are the same. At lower fields, the strengths of these

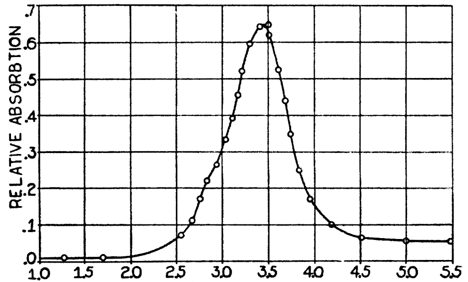

FIG. 4. Measured relative absorption as function of H in orientation I.

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[8] J. H. Van Vleck, J. Chem. Phys. 5, 320 (1937).

* I am indebted to Dr. H. C. Torrey for pointing out to me this possibility. It will be considered in detail in a forthcoming paper from this laboratory concerned with the experimental method.

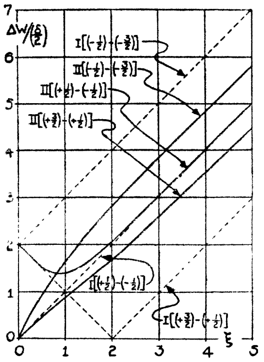

Fig. 5. Level separations (in units of $\delta/2$) as function of ξ in orientation II in which field is perpendicular to a (111) plane. The curves labeled I belong to atoms the axes of whose cylindrical electric fields make a polar angle $\theta = 0$ with the magnetic field; the curves labeled II belong to atoms for which $\theta = 70°33'$.

decrease and those of transitions between other than neighboring levels increases. As in the orientation (I) however, these changes are small until the field is decreased to the region $\xi = 3$. A second-order perturbation theory in $1/\xi$ gives the results shown in Table I for the variation of the strengths in high fields.

The transitions allowed when δ is taken as 0.15 cm^{-1} and the r-f frequency is 9375 mc/sec. are shown in Table II. Columns 1 and 2 give the nature of the transition along with the appropriate value of θ; column 3, the value of ξ, column 4, the value of H at which the absorption peak occurs; column 5 gives the relative strength of the peak and takes into account the 3 to 1 weighting that must be assigned to the two different types of atoms.

For both values of θ the separation $(-\frac{1}{2}) \rightarrow (+\frac{1}{2})$ is at these field strengths unaffected by the cylindrical field and in view of the fact that the corresponding absorption peak occurs at $H = 3400$, we conclude that the effective g-value is 1.97. The values of the field strengths in column 4 were computed with this value of g. These values are shown in Fig. 6 by short vertical lines. The value of $\delta = 0.15$ cm^{-1} was found by trial to give the best fit to the experimental curve. This is by trial estimated to be accurate to 0.01 cm^{-1}. The relative intensities listed in column 5 do not correspond to the strengths of the corresponding absorption peaks shown in Fig. 6. Because of the instability of the oscillator the magnitudes of peaks as measured are not reliable and this type of comparison must await the results of improved measurements. It should be noted that slight misalignments in this orientation do not smear out the absorption peaks as was the case in orientation I. In addition, this orientation is preferable because the natural growth of the crystals is along (111) planes and makes an accurate alignment of the magnetic field perpendicular to this plane extremely easy to perform.

IV. POWDER

The powder pattern obtained experimentally, Fig. 7, is notable[9] for having two small peaks in addition to the large central peak. A fair representation of these facts can be had by taking into consideration only the first-order effects, namely, only the diagonal elements of the Hamiltonian. Here it is necessary to include the interference effects. It can be shown that in the method used, the crystal current is proportional to the absolute value squared of the reflection coefficient. This in turn is proportional to the complex susceptibility which, on assuming the simple resonance formula to be valid, is proportional to

$$\gamma \propto \frac{1}{(\nu - \nu_0) - i(\Delta\nu/2)}. \tag{10}$$

Here γ is the reflection coefficient, ν the (fixed)

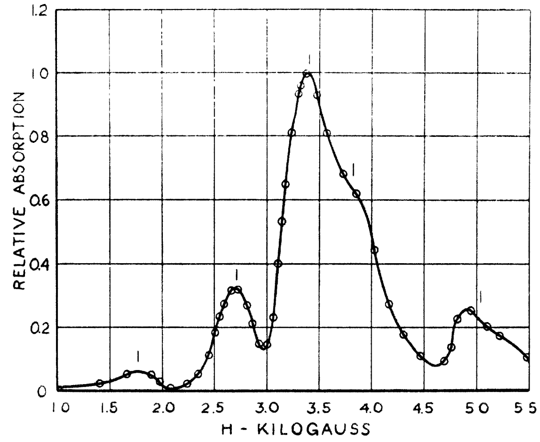

Fig. 6. Measured relative absorption as function of H in orientation II. The short vertical lines give the computed positions of the absorption peaks.

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[9] See for example, E. Zavoisky, J. Phys. U.S.S.R. 10, 170 and 197 (1946).

incident r-f frequency, ν_0 the resonant frequency, and $(\Delta\nu/2)$ the half-width at half-power. Each ν_0 is a function of angle and field. It is necessary now to add (preserving phase) the contributions of the three groups of resonances: the low field one for which

$$\nu-\nu_{0-1}=3\cos^2\theta-(\xi+1-\nu), \qquad (11)$$

the principle absorption

$$\nu-\nu_{00}=\nu-\xi, \qquad (12)$$

and the high field one for which

$$\nu-\nu_{0+1}=(\nu-\xi+1)-3\cos^2\theta. \qquad (13)$$

In 11, 12, and 13, and in what follows ν and $\Delta\nu/2$ are expressed in units of $(\delta/2)$. Thus:

$$\gamma\propto\int_0^\pi \sin\theta d\theta \sum_{k=-1}^{+1}\frac{g_k}{(\nu-\nu_{0k})-i(\Delta\nu/2)}. \qquad (14)$$

The g_k are the weights to be assigned to the groups $\sqrt{3}$, $\sqrt{2}$, $\sqrt{3}$, in the order mentioned. The integration removes the angular dependence leaving γ a function of H and of ν. The reflected power is then proportional to $|\gamma|^2$. The integrations can be performed in the complex plane for $\xi+1-\nu$ and $\xi-\nu+1$, both near zero where the resulting expressions have maximum values. In taking the absolute value square cross product terms arise between the main maximum and the other two, which in the vicinity of $\xi=\nu-1$ and $\xi=\nu+1$ are rather large. The dependence of $|\gamma|^2$ on H is shown in Fig. 8 where one can see the principal maximum but only two flat regions rather than two subsidiary peaks. To obtain Fig. 8, $(\Delta\nu/2)$ was taken to be the equivalent of 230 gauss and ν to correspond to 9375 mc/sec. The reason why the secondary peak portions are small arises essentially from the fact that these transitions are spread by the angular dependence of the level separation over a large range of field strengths (rather than over the range $(\Delta\nu/2)$). It is likely that, on taking into account higher order terms in the level separation or by adjusting $(\Delta\nu/2)$, one could make the theoretical results show the slight secondary peaks that the measurements reveal. This is hardly worth while, however, since it is difficult, by this method, to obtain as accurate an estimate of δ as from the patterns obtained from single crystals. An arbitrary criterion used in drawing the vertical lines in Fig. 7 asserts the peaks occur at

$$\xi=\nu-1+\frac{1}{\sqrt{3}}(\Delta\nu/2)$$

and (15)

$$\xi=\nu+1-\frac{1}{\sqrt{3}}(\Delta\nu/2).$$

It should be pointed out that the separation of the secondary peaks is $2-(2/\sqrt{3})(\Delta\nu/2)$, and this is roughly independent of the r-f frequency.

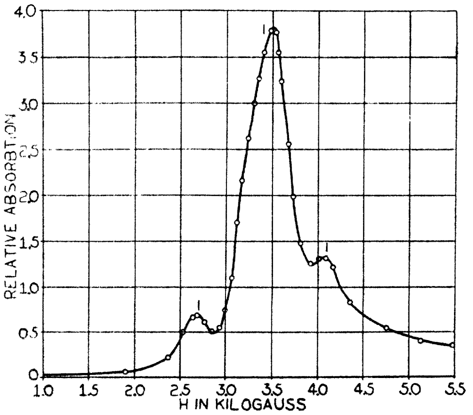

FIG. 7. Measured relative absorption as function of H in powder. The vertical lines show the computed positions of the absorption peaks as explained in the text.

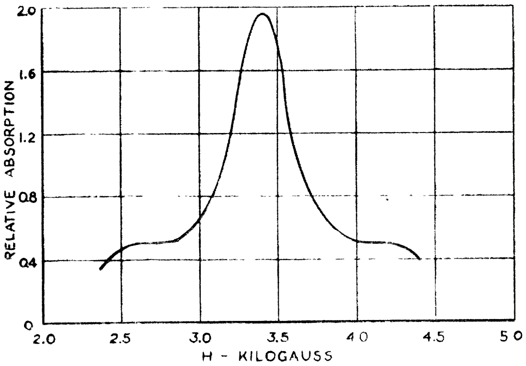

FIG. 8. Computed relative absorption of powder as function of H taking interference into account.

V. CONCLUSIONS

The analysis carried out here shows that the measurement of resonance absorption in hydrated salts like chrome alum forms a direct and very convenient method of measuring the fine

TABLE I. Variation of strengths of transitions in high fields.

$[+\frac{1}{2}\rightarrow+\frac{3}{2}]:3(1-0.592\xi^{-2})$	$[-\frac{1}{2}\rightarrow+\frac{3}{2}]:1.18\xi^{-2}$
$[-\frac{1}{2}\rightarrow+\frac{1}{2}]:4(1-0.888\xi^{-2})$	$[-\frac{3}{2}\rightarrow+\frac{1}{2}]:1.18\xi^{-2}$
$[-\frac{3}{2}\rightarrow-\frac{1}{2}]:3(1-0.592\xi^{-2})$	$[-\frac{3}{2}\rightarrow+\frac{3}{2}]:.198\xi^{-4}$

TABLE II. Positions and relative intensities of absorption lines in orientation II.

$[+\frac{1}{2}\rightarrow+\frac{3}{2}]$,	$\theta=70°33'$	$\xi=3.35$	$H=2730$ gauss	9
$[-\frac{1}{2}\rightarrow+\frac{1}{2}]$,	70°33′	4.17	3400	12
$[-\frac{3}{2}\rightarrow-\frac{1}{2}]$,	70°33′	4.70	3830	9
$[-\frac{3}{2}\rightarrow-\frac{1}{2}]$,	0	2.18	1780	3
$[-\frac{1}{2}\rightarrow+\frac{1}{2}]$,	0	4.17	3400	4
$[+\frac{1}{2}\rightarrow+\frac{3}{2}]$,	0	6.17	5030	3

splitting of the lowest energy levels of the paramagnetic ions by the crystalline field. The difficulties encountered because of the large widths of the lines can be overcome by using single crystals properly oriented in the magnetic field and also by dilution with similar non-paramagnetic salts such as aluminum ammonium sulfate. In particular, the analysis shows the g-value of chromic ammonium sulfate to be 1.97 and that the splitting can be explained by a cylindrical electrical field, the magnitude of the splitting being $\delta=0.15\pm.01$ cm^{-1}. The constants of the electric fields are found to be $\bar{Q}=1500$ cm^{-1} and $\bar{a}=180$ cm^{-1}. The corresponding quantities computed by Van Vleck are 1000 cm^{-1} and 60 cm^{-1}, respectively. However, the accuracy with which these are determined experimentally is very small and it is questionable that there is any disagreement in these results.

VI. ACKNOWLEDGMENTS

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