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Magnetic Resonance Absorption in the Chrome Alums

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Measurements of paramagnetic resonance absorption at room temperature in single crystals of potassium chrome alum and ammonium chrome alum made at a frequency of 9375 mc/sec. are described. The method makes use of a magic-*T* bridge with a low level crystal detector which essentially measures the magnetic susceptibility. Data are given for three orientations of the crystals for both the diluted and undiluted salts. The Stark splitting and the *g* factor of the ground state are evaluated from the positions of the absorption peaks. The theory which is used for the computation of the Stark splitting is extended to include the (110) orientation.

I. INTRODUCTION

THE magnetic resonance absorption of microwaves by paramagnetic salts first reported by Zavoisky[1] provides a direct and powerful method for investigating the lowest quantum states of the paramagnetic ion of the salt. The method as usually applied[2–4] consists in subjecting the salt to a fixed frequency microwave magnetic field and a d.c. magnetic field perpendicular to the r-f field. When the intensity of the d.c. field is adjusted to the resonant value an absorption of r-f power occurs, corresponding to induced transitions between the lowest energy states of the paramagnetic ion. The magnetic absorption as a function of the d.c. field shows one or more absorption peaks having line widths of the order of several hundred oersteds.

The condition for resonant absorption is given by the well-known relation,

$$h\nu = g\beta H, \tag{1}$$

where ν is the frequency of the r-f field, g is the gyromagnetic ratio, β is the Bohr magneton, and H is the intensity of the d.c. field. For a free electron spin ($g=2$) and a frequency of 9375 mc/sec. the resonant value of the d.c. field is 3340 oersteds.

In the hydrated salts of the iron group, measurements at low temperatures of the paramagnetic susceptibility and the specific heat indicate that the orbital angular momentum of the paramagnetic ion is quenched by the cubic electric fields of the neighboring atoms and molecules. There is, in addition, a fine splitting of the ground state of the order of 0.1 cm^{-1}. In magnetic resonance absorption experiments, the d.c. field produces a Zeeman splitting of these levels. Consequently, different pairs of levels are brought into the resonance condition by different values of the applied field. From these values of the d.c. field it is possible to deduce the magnitude of the zero-field splitting.

In the case of chrome alum the zero-field fine splitting can be explained by the presence of a small cylindrically symmetric electric field. In the unit cell there are four paramagnetic ions, and the axes of the cylindrical fields are arranged along the body diagonals of the cube. The level separations depend on the orientation of the axes of the cylindrical electric field with respect to the d.c. magnetic field. The energy level separations have been computed by one of us[5] as a function of d.c. field strength and zero-field splitting. There, computations were made for two orientations of the d.c. field, namely, perpendicular (a) to a (111) face, and (b) to a (100) face. The alums belong to the cubic system so that in orientation (a) the d.c. field is parallel to one of the body diagonals of the unit cell. In the present paper computations are included in Section V for the case in which the d.c. field is perpendicular to the (110) face. Similar computations have been made independently by Kittel and Luttinger[6] for chrome alum for the (100) orientation.

For a given value of δ, the zero-field splitting,

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[1] E. Zavoisky, J. Phys. U.S.S.R. **10**, 170, 197 (1946).

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

[3] D. M. S. Bagguley and J. H. E. Griffiths, Nature **160**, 532 (1947).

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

[5] P. R. Weiss, Phys. Rev. **73**, 470 (1948).

[6] C. Kittel and J. M. Luttinger, Phys. Rev. **73**, 162 (1948).

the theory predicts a set of values of the d.c. field at which resonance peaks may be expected. Conversely, if the peak fields are known, a value of δ can be chosen which gives best agreement between computed and experimentally determined positions of the peaks for each of the three crystal orientations.

We have previously reported in Letters to the Editor of this journal[4, 7] preliminary results of our measurements at room temperature of the resonance absorption in single crystals of ammonium chrome alum and potassium chrome alum, and in diluted crystals of these salts in which some of the chromium ions are replaced by aluminum ions. It is the purpose of this paper to give a more complete and detailed account of the experimental methods and results.

Independent experiments similar to ours on undiluted chrome alum have been reported by Bagguley and Griffiths[3] and by Halliday and Wheatley.[8] A comparison of results is given in Section VI of this paper.

Accurate determinations of the zero-field splitting are necessary to establish a theoretical relationship between the absolute temperature scale and the Curie scale used at very low temperatures. Measurements of the resonance absorption of microwaves therefore afford a very convenient tool for the accurate determination of this quantity. Recent experiments by Bleaney and Penrose,[9] who determined the zero-field splitting in ammonium chrome alum as a function of temperature down to 20°K, show that the splitting decreases down to about 80°K, at which temperature an abrupt increase occurs. It is necessary therefore to make these measurements at very low temperatures for the purpose mentioned.

II. EXPERIMENTAL METHOD

The resonance absorption was obtained by observing the decrease in the Q of a resonant cavity containing the salt, through the measurement of the reflected power in a magic-T bridge.

The equivalent admittance of a resonant cavity is given by

$$Y = G + j\omega C + 1/j\omega L. \tag{2}$$

The magnetic absorption from a paramagnetic salt in the cavity may be regarded as a change in the complex permeability, $1+4\pi(\chi' - j\chi'')$, of the salt, where $\chi' - j\chi''$ is the complex susceptibility of the salt. The total inductance, L, of the cavity and salt is given by

$$L = L_c + L_s(1 + 4\pi\chi' - 4\pi j\chi''), \tag{3}$$

where L_c is the contribution of the inductance of the cavity alone and $L_s(1+4\pi\chi' - 4\pi j\chi'')$ is the contribution of the salt.

With zero magnetic absorption

$$L = L_0 = L_c + L_s. \tag{4}$$

This condition is realized experimentally by tuning the cavity to resonance for a value of the d.c. magnetic field large compared to that for which resonance absorption occurs.

The reflection coefficient, γ, for a cavity terminating a transmission line of characteristic conductance G_0 is given by

$$\gamma = |(Y - G_0)/(Y + G_0)|. \tag{5}$$

Equations (2), (3), and (5) combine to give

$$\gamma = \left| \frac{G - G_0 + j\omega C + \{j\omega[L_c + L_s(1 + 4\pi\chi' - 4\pi j\chi'')]\}^{-1}}{G + G_0 + j\omega C + \{j\omega[L_c + L_s(1 + 4\pi\chi' - 4\pi j\chi'')]\}^{-1}} \right|. \tag{6}$$

Since the cavity is matched to the transmission line and tuned to resonance for zero magnetic absorption,

$$G = G_0 \quad \text{and} \quad j\omega C + 1/j\omega L = 0.$$

Since χ' and χ'' are small compared to unity, Eq. (6) reduces to

$$\gamma = \left| \frac{-(4\pi/j\omega L_0)(L_s/L_0)(\chi' - j\chi'')}{2G_0 - (4\pi/j\omega L_0)(L_s/L_0)(\chi' - j\chi'')} \right|. \tag{7}$$

The small term in the denominator can be neglected and

$$\gamma^2 = 4\pi^2 Q_0^2 (L_s/L_0)^2 (\chi'^2 + \chi''^2), \tag{8}$$

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[7] C. A. Whitmer, R. T. Weidner, and P. R. Weiss, Phys. Rev. **73**, 1468 (1948).

[8] D. Halliday and J. Wheatley, Bull. Am. Phys. Soc. **23**, No. 3, 13 (1948).

[9] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. **60** 395 (1948).

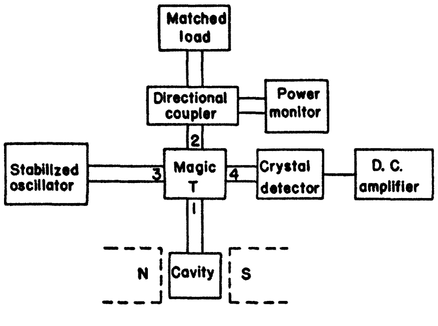

FIG. 1. Block diagram of the apparatus.

where

$$Q_0 = 1/\omega L_0 G_0.$$

Thus Eq. (8) shows that the measured power is proportional to $\chi'^2+\chi''^2$, the absolute value squared of the complex susceptibility of the salt. If a single resonance alone is involved and if the absorption follows a dispersion law (which is highly unlikely in these measurements), it follows that $\chi'^2+\chi''^2$ is proportional to the imaginary part of the susceptibility. That is,

$$\chi'^2+\chi''^2 = \nu_0\chi_0\chi''/\Delta\nu,$$

where ν_0 is the resonance frequency, $\Delta\nu$ the width of the absorption peak, and χ_0 the d.c. susceptibility.

If overlapping absorption lines occur, an interference between the lines is present in the method used here. This affects the shape of the curve in a manner different from that which occurs in a method which measures χ'' alone for multiple resonances. Consequently, the locations of the absorption peaks are somewhat different in the two cases. In the present method the reflected waves tend to cancel in the region between the peaks and therefore tend to increase the observed peak separation. In a method which measures χ'' alone, the addition of the absorption from adjacent peaks tends to decrease the observed peak separation. The correction for these effects requires a knowledge of the shape of an absorption line. In the absence of these corrections it seems probable that the true peak separations lie between those determined by the two methods. It should be pointed out that the present method is advantageous in resolving lines which are close together, but it suffers from the fact that the quantity measured is not strictly the power absorbed.

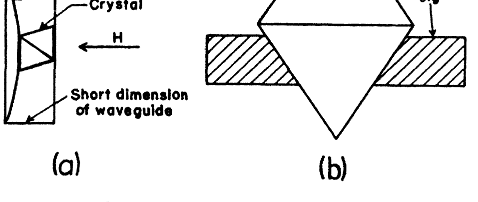

FIG. 2. (a) Crystal mount, (b) crystal grinding jig.

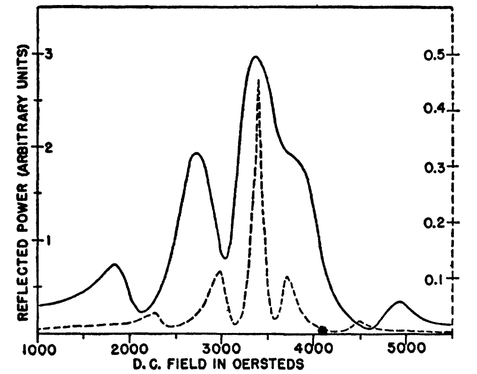

FIG. 3. Reflected power as a function of d.c. field for ammonium chrome alum with the d.c. field perpendicular to a (111) face. The full line curve refers to the undiluted, the dashed curve to the diluted salt. The scales for the undilute (left) and the dilute (right) salts refer to the same input power.

The power reflected from the cavity is measured by the apparatus shown in the block diagram of Fig. 1. Microwave power from the frequency-stabilized oscillator divides at the magic-T into arms 1 and 2, which are terminated, respectively, by the cavity and a matched load. The power is monitored by a crystal detector which is connected through a directional coupler to arm 2. The power incident upon the cavity was about one milliwatt. The cavity which contains the paramagnetic crystal is a shorted waveguide section which is tuned to resonance and matched by the use of a sliding micrometer tuning screw. The loaded Q of the empty cavity was 1700. A dielectric absorption Q of 500 was found for both undilute and dilute crystals. A paramagnetic absorption Q of 1400 was found for the undilute crystals; the corresponding value of χ'' is of the order of 0.3×10^{-25} cm^3/ion.

When the cavity is tuned to the matched condition no power reaches the low level square-law crystal detector terminating arm 4. When the magnetic field is adjusted for resonance absorption the detector current is accurately proportional to the power reflected from the cavity and hence proportional to γ^2.

The d.c. magnetic field was calibrated by means of a ballistic galvanometer and search coil with an accuracy of 0.2 percent. The calibration was checked against the proton magnetic resonance absorption using the accepted value of the proton moment.

III. PREPARATION OF THE SPECIMENS

The single crystals used in this investigation were grown from the saturated solution by evaporation at room temperature. Since the alums have a face-centered cubic lattice, the interatomic distance is least in the (111) plane and the crystals grow along the (111) face in the form of octahedra. The samples were grown to a thickness of about 1 cm between opposite (111) faces, corresponding to a mass of about 2 grams.

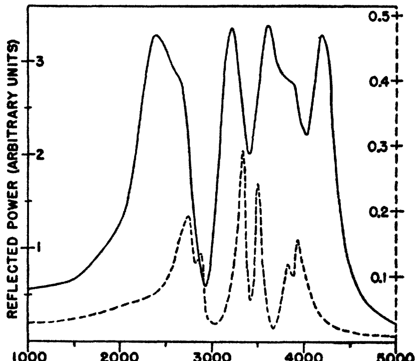

FIG. 4. Reflected power as a function of d.c. field for ammonium chrome alum with the d.c. field perpendicular to a (110) face. The remarks in the title of Fig. 3 apply here.

The diluted crystals were grown from a solution made up of 5 parts by weight of aluminum alum to one part chrome alum. A quantitative analysis showed the ratio of aluminum to chrome atoms to be 8.5 to 1.

The samples were mounted on curved strips of polystyrene which fitted into the wave-guide as shown in Fig. 2a. A crystal is mounted so that its center is about one-half wave-guide wavelength from the shorted end.

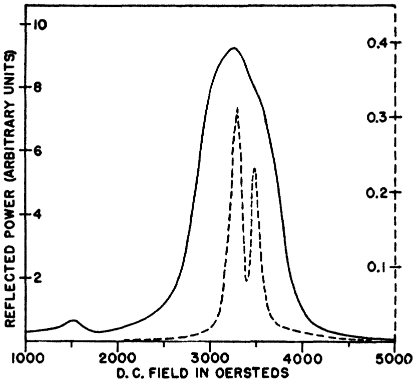

FIG. 5. Reflected power as a function of d.c. field for ammonium chrome alum with the d.c. field perpendicular to a (100) face. The remarks in the title of Fig. 3 apply here.

Three orientations of the crystal with respect to the d.c. field were used, namely, with the d.c. field perpendicular (a) to the (111) face, (b) to the (110) face, and (c) to the (100) face. For orientations (b) and (c) surfaces were ground along the appropriate crystal faces by mounting the crystal in a jig and grinding the surfaces with dry emery paper. The jig consists of a V-shaped slot in a metal plate which holds the crystal as shown in Fig. 2b. The part of the crystal projecting through the slot is ground off flush with the surface of the plate. The angle between the faces of the slot is 70° 32′ for the (100) orientation and 109° 28′ for the (110) orientation.

The curved strip of polystyrene (Fig. 2a) presses the appropriate face of the crystal against the broad face of the wave-guide, perpendicular to the d.c. magnetic field, thereby fulfilling the condition of perpendicularity of the

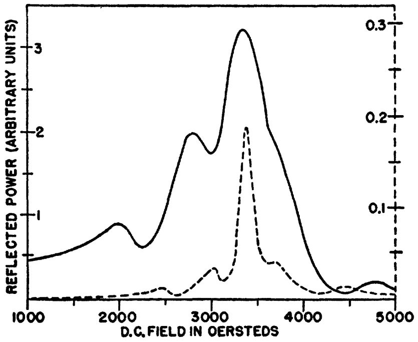

FIG. 6. Reflected power as a function of d.c. field for potassium chrome alum with the d.c. field perpendicular to a (111) face. The remarks in the title of Fig. 3 apply here.

Table I. Observed and calculated magnetic field values of the absorption maxima for $\nu=9375$ mc/sec The values of δ and g used for the calculated values are those listed in the table. Spaces marked with an asterisk indicate unresolved peaks.

	$NH_4Cr(SO_4)_2\cdot 12H_2O$				$KCr(SO_4)_2\cdot 12H_2O$			
	Undiluted		Diluted		Undiluted		Diluted	
δ	0.143 cm^{-1}		0.100		0.130		0.91	
g	1.99		1.97		1.99		1.98	
H (oersteds)	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
(111)	1830	1830	2310	2270	1990	1990	2390	2450
	2780	2720	2970	2980	2840	2800	3020	3020
	3370	3370	3400	3400	3370	3340	3390	3380
	3770	*	3720	3710	3750	*	3670	3670
	4910	4920	4490	4480	4760	4760	4380	4450
(110)	2390	2380	2740	2740	2500	2530	2790	2850
	2630	*	2860	2880	2730	*	2890	
	3240	3220	3330	3330	3280	3240	3330	3340
	3580	3600	3500	3500	3550	3600	3480	3460
	3910	*	3830	3820	3850	*	3790	3850
	4130	4190	3910	3920	4070	4130	3880	
(100)	3120	3250	3280	3300	3170	3260	3280	3300
	3540		3480	3480	3520		3450	*

r-f and d.c. magnetic fields. The error in the orientation of the crystals is estimated to be no more than one degree.

IV. RESULTS

Figures 3–5 show the absorption at a frequency of 9375 mc/sec. of undiluted and dilute single crystals of ammonium chrome alum ($NH_4Cr(SO_4)_2\cdot 12H_2O$) for the three orientations, and Figs. 6, 7, and 8 are corresponding absorption curves for undiluted and diluted single crystals of potassium chrome alum ($KCr(SO_4)_2\cdot 12H_2O$). All experimental points fell accurately on the curves shown, and all curves were checked by measurements on at least two crystals. The positions of the sharp peaks could be determined to within ±10 oersteds. The scale of the reflected power has been adjusted for the same input power in all the curves.

It is seen that the dilution improves the resolution of the peaks by decreasing the widths of the lines; also it is to be noted that the resolution is more pronounced for both the undilute and dilute crystals of the ammonium salt than for those of the potassium salt. Furthermore the dilution decreases the crystalline field splitting for both salts, as shown in Table I.

Table I shows the magnetic field strengths for the peaks, taken from the absorption curves, and as calculated from the theory using the g-values and zero-field splittings, δ, shown there. The g-values are calculated from the principle absorption peak in the (111) orientation, as described by one of us in an earlier paper.[5] It is clear that there is some uncertainty in the g-value because of the effect on the position of this peak of the interference from adjacent peaks.

All the principal lines predicted by theory for the three crystal orientations are resolved for the dilute ammonium salt. The agreement between the observed and calculated peak positions is better for the diluted salts than for the undiluted salts; the discrepancies for the undiluted salts are probably due to interference in amplitude and phase between the several overlapping resonances.

The crystalline field splitting is smaller in the potassium than in the ammonium salt for both the undiluted and diluted salts.

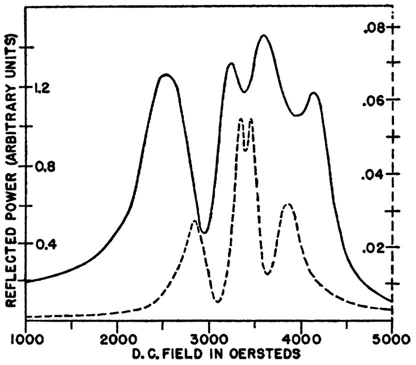

Fig. 7. Reflected power as a function of d.c. field for potassium chrome alum with the d.c. field perpendicular to a (110) face. The remarks in the title of Fig. 3 apply here.

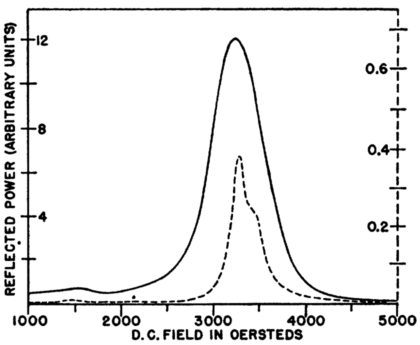

Fig. 8. Reflected power as a function of d.c. field for potassium chrome alum with the d.c. field perpendicular to a (100) face. The remarks in the title of Fig. 3 apply here.

Since the absorbed power was found to be proportional to the incident power, no saturation effects occur at the power level used. The dielectric losses were found to be closely the same for all diluted and undiluted crystals used, whose volumes differed by no more than a factor of 1.5. Nevertheless, the measurements show a marked diminution in the peak absorption with dilution.

A simple computation based on the supposition that the width of the line is due to spin-spin interaction shows that the peak intensity is independent of the density of the absorbing spins. Actually this involves the tacit assumption* that the change in density is brought about by a change in lattice size but no change in the regularity of the positions of the spins. When, however, the change in density is achieved by the substitution of non-absorbing atoms in the lattice, the absorbing spins may occupy random positions in the lattice. In case the positions are completely random, the width of the line is affected by space fluctuations in the positions of the absorbing spins. In this case the width of the line is proportional to the square root of the density of the absorbing spins rather than to the density. In this event the peak absorption is proportional to the square root of the density. Further experiments are in progress to study the effect of dilution on peak absorption.

V. SOME ADDITIONAL THEORY

Detailed computations of the magnitudes of the d.c. field at which resonance absorption occurs in chrome alums have been recorded for the (111) and (100) orientations of the d.c. field. In this section the corresponding results are presented when the d.c. field is perpendicular to a (110) plane. In this orientation, the axes of the cylindrical electric fields at two of the four chrome ions of the unit cell are perpendicular to the magnetic field; the axes of the electric fields at the other two chrome ions make an angle of 35° 16′ ($\sin^{-1}1/\sqrt{3}$) with the magnetic field. The Hamiltonian of the ion in the case of perpendicularity can be solved in closed form. The levels are:

$$E=\pm\tfrac{1}{2}\xi+(\xi^2\mp\xi+1)^{\frac{1}{2}}$$

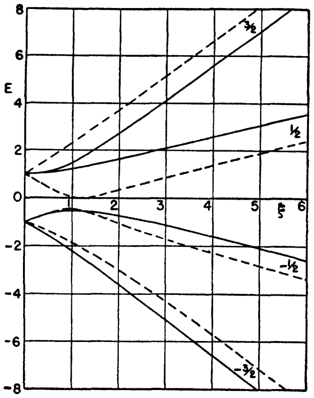

FIG. 9. Energy levels (in units of $\delta/2$) as a function of $\xi=2g\beta H/\delta$ for chrome alum crystals oriented with the d.c. field perpendicular to a (110) plane. The full line curves belong to atoms for which the axis of the cylindrical electric field makes a polar angle of $\theta=90°$ with the magnetic field; the dashed curves belong to atoms for which $\theta=35°\ 16'$.

and

$$E=\pm\tfrac{1}{2}\xi-(\xi^2\mp\xi+1)^{\frac{1}{2}}.$$

The notation is the same as in reference 5, namely, δ is the energy separation of the levels in the absence of a d.c. field; g, the effective g-value of the spin; β, the Bohr magneton; H, the magnitude of the d.c. field; $\xi=2g\beta H/\delta$ and $E=2W/\delta$. A plot of these energy levels in units of $\delta/2$ as a function of the magnetic energy in the same units is shown by the full line curves in Fig. 9. In the case where the angle between the d.c. field and the axis of the electric field is $\theta=35°\ 16'$, the secular equation expressing the energy levels is the quartic

$$E^4-E^2(2+(5/2)\xi^2)-2\xi^2E+(1-\tfrac{3}{4}\xi^2)^2=0.$$

For each value of ξ this can be solved by successive approximation. The results, the energy levels as functions of ξ, are shown by the dashed curves in Fig. 9.

When the frequency of the r-f field is large compared to δ/h ($h=$Planck's constant), the resonance absorption occurs only at large values of the d.c. field; that is, large values of ξ. For this region, the only allowed transitions are those of a "free" spin in a magnetic field. The energy levels can be designated by the usual m-values and the selection rule is $\Delta m=\pm1$. Consequently, six absorption peaks appear in this region as shown in Fig. 10, where the energy differences

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* This was pointed out to us in a private communication from Dr. E. M. Purcell.

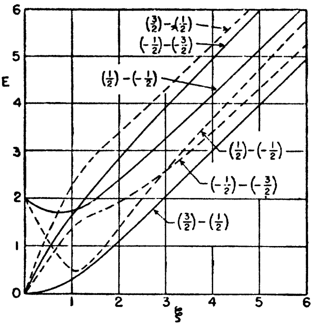

FIG. 10. Level separations (in units of $\delta/2$) as a function of $\xi=2g\beta H/\delta$ for chrome alum crystals oriented with the d.c. field perpendicular to a (110) plane. The full line curves belong to atoms for which the axis of the cylindrical electric field makes a polar angle $\theta=90°$ with the magnetic field; the dashed curves belong to atoms for which $\theta=35°\ 16'$.

between levels involved in the absorption are plotted as a function of ξ. The width in field strength of the entire pattern is less in the (110) orientation than in the (111) orientation. For very large frequencies of the r-f field this width is roughly δ as measured in oersteds for the (110) orientation compared to 2δ for the (111) orientation. The resolution of the lines in the (111) orientation is better than in the (110) orientation. The lines occur in closely neighboring pairs. The width of the lines causes overlapping of these lines and therefore obscures the fundamental pattern more so in this than in the (111) orientation. When the frequency of the r-f field is not large compared to δ/h, the selection rules stated above do not apply and the intensities of other transitions become significant. The pattern then can contain more than six absorption lines. For purposes of computation in the region of large field strengths it is convenient to use series expressions for the positions in field strength of the six lines. These are, to terms in ξ^{-3},

$$\theta=\sin^{-1}1/\sqrt{3}=35°\ 16'$$

$$\begin{array}{rllll}
(\frac{3}{2}\leftrightarrow\frac{1}{2}): & \xi-1 & & +\frac{3}{8}\xi^{-2} \\
(\frac{1}{2}\leftrightarrow\frac{1}{2}): & \xi & +\frac{3}{4}\xi^{-1} & \\
(-\frac{1}{2}\leftrightarrow\frac{3}{2}): & \xi+1 & & -\frac{3}{8}\xi^{-2}
\end{array}$$

$$\theta=90°$$

$$\begin{array}{rllll}
(\frac{3}{2}\leftrightarrow\frac{1}{2}): & \xi+1 & +(4/3)\xi^{-1} & -(11/8)\xi^{-2} \\
(\frac{1}{2}\leftrightarrow-\frac{1}{2}): & \xi & -(5/8)\xi^{-1} & \\
(-\frac{1}{2}\leftrightarrow-\frac{3}{2}): & \xi-1 & +(4/3)\xi^{-1} & +(11/8)\xi^{-2}.
\end{array}$$

VI. CONCLUSION

Our values of the zero-field splitting for undiluted single crystals of ammonium chrome alum and potassium chrome alum are compared with the published results of others in Table II. All of the values listed in this table were computed from data taken at room temperature. The first, second, and third columns in the table list, respectively, the values obtained by the authors, by Bagguley and Griffiths,[3,**] and by Halliday and Wheatley.[8] It can be seen that the results obtained by the authors are larger than the other reported values; this discrepancy is considerably larger than can be accounted for by the experimental error in fitting the computed peaks to the experimental values. The interference effects discussed earlier in this paper may account for the discrepancy in the values of the splitting computed from the absorption peaks. A comparison of our curves with those of Bagguley and Griffiths shows that our method yields a better resolution of the lines.

TABLE II. Published values of the zero-field splitting, δ, of the undiluted chrome alums.

Salt╲Reference	7	3	8
$NH_4Cr(SO_4)_2\cdot 12H_2O$	0.143 cm^{-1}	0.135 cm^{-1}	0.13 cm^{-1}
$KCr(SO_4)_2\cdot 12H_2O$	0.130	0.12	0.12

The results of experiments described here show excellent agreement with the theory and substantiate the following conclusions:

1. The Stark splitting of the ground state of the chrome ion can be explained by the presence of a cylindrical electric field.
2. The splitting is larger for ammonium than for potassium chrome alum.
3. The effect of dilution is to narrow the line widths and decrease the zero-field splitting for both ammonium and potassium chrome alum. The peak intensities are markedly diminished by dilution.

In conclusion we should like to acknowledge the support of the Rutgers University Research Fund, the Research Corporation, and the Office Naval Research. We are indebted to Dr. H. C. Torrey, who suggested the use of a magic-T bridge for this work.

[**] The value of 0.135 cm^{-1} for ammonium chrome alum is quoted by Bleaney and Penrose (reference 9) from unpublished results of Bagguley and Griffiths.