Electron-Spin Resonance of Cr^{3+} in Gallium Alums. I

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The electron-spin resonance of Cr^{3+} impurities in $RbGa(SO_4)_2 \cdot 12H_2O$, $CsGa(SO_4)_2 \cdot 12H_2O$, and the deuterated forms of these alums was studied at 300 and 4.2 °K. Four magnetic complexes exhibiting trigonal symmetry were found in each crystal and the results were fitted to a suitable spin Hamiltonian giving the g and D parameters. The magnitude of the D parameter decreased by about 38% in the Rb alums and by only 8% in the Cs alums. Moreover, the D parameter had opposite signs in the Rb and Cs alums. The effect of deuteration did not produce any significant changes from the case of the hydrated alums. It seems probable that the size of the monovalent ion can affect the positions of the other ions in the unit cell of alum, which in turn can affect the chromium magnetic complexes.

I. INTRODUCTION

The electron-spin resonance (ESR) of Cr^{3+} has been studied previously in some alum crystals. This is true of the concentrated chromic alums and of Cr^{3+} impurities in diamagnetic hosts. The resonance can be done at room and low temperatures and the results can be compared in order to study some aspects of the behavior of the alums. It was found that some alums behave anomalously when cooled to low temperatures. The ESR of K, NH_4, Rb, Cs, and NH_3CH_3 chromic sulfate alums was studied at room temperature by Bagguley and Griffiths[1] and at low temperatures by Bleaney.[2] In these concentrated alums the chromium spectral lines are quite broad and the results are difficult to analyze. Nevertheless, it was found that at room temperature the chromium ions exist in four inequivalent, but otherwise similar, magnetic complexes subjected to a trigonal distortion. At low temperature it was observed that the magnitude of the trigonal distortion changed in all of the alums. Furthermore in NH_4 alum a crystallographic change took place, while in K alum an additional chromium spectrum appeared. The ESR of Cr^{3+} impurities in NH_3CH_3 aluminum alum was done by Baker[3] who showed that the trigonal distortion of a magnetic complex changed to rhombic symmetry at about 160 °K.

The present work involves the ESR of Cr^{3+} impurities in $RbGa(SO_4)_2 \cdot 12H_2O$ and $CsGa(SO_4)_2 \cdot 12H_2O$, including the deuterated forms of these alums. The study was done at 300 and 4.2 °K. The motivation behind the work was threefold: (i) It is useful to study the Cr^{3+} impurity substituting for a Ga^{3+} host ion since these ions have similar ionic radii of 0.64 and 0.62 Å, respectively. Consequently, the size discrepancy existing when Cr^{3+} is substituted for Al^{3+} (with ionic radius 0.50 Å) is avoided and any explanations regarding alum behavior as described by the ESR results cannot be attributed to size effect. This feature is especially important when analyzing alum behavior from precise electron-nuclear-double-resonance (ENDOR) data, as is done in Paper II.[4] (ii) It is desirable to obtain more information about the effects of deuteration in the alums. Also, the effect of deuteration is said to produce narrower chromium linewidths enabling more precise ESR measurements to be made. (iii) It is desirable to study the angular variation of the ESR lines in the crystals in order to determine the chromium spin-Hamiltonian parameters prior to performing ENDOR.

Another important group of hydrated crystals that has been studied extensively using ESR is quanidine aluminum sulfate hexahydrate (GAlSH), $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$, and its isomorphs. In these crystals, as in alums, Ga can replace Al, Se can replace S, and D_2O can replace H_2O. However, the alums are a more versatile group of crystals to study than is GAlSH and its isomorphs since the monovalent ion such as Rb, Cs, and

NH_3CH_3 can also be varied in the alums. This feature could be decisive in understanding the behavior of these crystals. In both the alums and GAlSH the trivalent ion is coordinated to six water molecules. ESR studies[5-8] of Cr^{3+} in GAlSH and its isomorphs show that the chromium magnetic complexes exhibit axial symmetry with the zero-field splitting ($2D$), increasing with decreasing temperature. A similar temperature effect was observed[1,2] in methylamine chromic alum, (NH_3CH_3) $Cr(SO_4)_2 \cdot 12H_2O$, but the opposite was observed[1,2] in Rb and Cs chromic alums down to 20 °K and in NH_4 and K chromic alums down to 193 °K. These latter two alums behave anomalously at lower temperatures as stated above.

The ground state of a free Cr^{3+} ion is $^4F_{3/2}$, with an orbital degeneracy of 7 and a spin degeneracy of 4. The effect of the cubic crystalline electric field is to remove the sevenfold orbital degeneracy leaving an orbital singlet in the lowest energy state with the next highest state approximately 18 000 cm^{-1} higher. The ground state is then described by an effective spin quantum number $S = \frac{3}{2}$. The effect on the ground state of an additional small trigonal distortion, in conjunction with the spin-orbit coupling, is to remove some of the ground-state spin degeneracy leaving two Kramers's doublets with quantum numbers $M_s = \pm \frac{1}{2}$ and $\pm \frac{3}{2}$. The energy spacing of the doublets in the alums is of the order 0.15 cm^{-1} at room temperature. When an external magnetic field is applied the remaining degeneracy is lifted and three allowed ESR fine-structure transitions are observed at microwave frequencies for each inequivalent magnetic complex.

Chromium in its natural abundance consists chiefly of two isotopes: ^{52}Cr, which has an isotopic abundance of 84% with no nuclear spin and ^{53}Cr, which has an abundance of 9.5% with a nuclear spin $I = \frac{3}{2}$. The hyperfine interaction in the odd isotope causes a futher splitting of the energy levels, producing three groups of four ESR hyperfine transitions at microwave frequencies. However, the hyperfine lines within a group have small intensities and splittings and so are masked by the fine-structure lines. The ESR was performed with chromium in its natural abundance and hence only the positions of the fine-structure lines was studied.

II. CRYSTALLOGRAPHY

The alums belong to the cubic system and possess space group $T_h^6(Pa3)$. However, slight differences in atomic arrangement enable three types of alum structures to be determined, termed α, β, and γ. In each case there are four formula units per unit cell, with the general formula for the sulfate alums being $M^+ M^{+3}(SO_4)_2 \cdot 12H_2O$. In this formula M^+ and M^{+3} are monovalent and trivalent cations, respectively. Each trivalent ion has as its nearest neighbors six water molecules forming a nearly regular octahedron. Each monovalent ion is surrounded by a somewhat distorted octahedron of waters, with the distortion being along the threefold axis of the cell. The groups of waters around the monovalent and trivalent ions exhibit mutual bonding with each other.

The crystallography and classification of the aluminum alums was originally done by Lipson and Beevers[9] and Lipson.[10] It was shown that in the α type of alums the [111] axis of the octahedron of water molecules surrounding an aluminum atom coincides with the [111] axis of the crystal, but the cubic axes of the octahedron are displaced from the cubic axes of the crystal by a rotation of approximately 9.5° about the [111] direction. The β alums are described as having perfectly regular groups of water molecules with the cubic axes of the octahedron being directed along the cubic axes of the crystal. The γ alums are said to differ from the α and β alums in that the sulfate groups of the γ alums are oriented oppositely along the crystal body diagonals to those of the α and β alums. The cubic axes of the octahedron in the γ alums are rotated about the [111] crystal direction by about 40°. The only known γ alum is soda alum, $NaAl(SO_4)_2 \cdot 12H_2O$. Kromer et al.[11] have recently obtained refined x-ray data on soda alum and they show that the water molecules about the Al atom form a perfect octahedron.

In the classification of the aluminum alums Lipson[10] postulated that the structure of a particular alum is dependent on the size of the monovalent ion. The α structure represents medium sized ions, β represents the larger ones, and γ represents the small Na atom. As the radius of the ion increases the SO_4 groups are translated along the triad axes. In the x-ray study of methylamine chromic alum Ledsham and Steeple[12,13] showed that the size of the trivalent cation can also affect the class of an alum. A similar effect was seen by Klug and Kieffer[14] when Cr^{3+} was replaced by Al^{3+} in the Rb alum.

The structure type and lattice parameters of several gallium alums are given by Klug and Kieffer.[14] They show that $RbGa(SO_4)_2 \cdot 12H_2O$ is of the α type with lattice parameter 12.245 Å and $CsGa(SO_4)_2 \cdot 12H_2O$ is β type with lattice parameter 12.377 Å. The crystals used in the present work were grown by slow evaporation at room temperature of a saturated solution consisting of the constituent sulfates plus a small amount of chromium sulfate dopant. They were colorless and had dimensions of about $5 \times 5 \times 2$ mm. The Cr^{3+} concentration is estimated to be less than 0.01 wt% in all the crystals. The Rb alums grew in tabular

form with prominent {111} planes. The Cs alums grew in two distinct habits, one which was the same as in the case of Rb alum, while the other exhibited additional prominent planes giving the crystals a more rounded appearance.

III. EQUIPMENT

Two X-band spectrometers operating in the 9.4-GHz microwave-frequency range were used in the course of the study. Measurements at room temperature were made using a commercial spectrometer manufactured by Hilger and Watts Co., England. It was a balanced-bridge design with the microwave frequency stabilized to an auxiliary cavity. The magnetic field was modulated at 100 kHz, with the modulation coils placed inside the cylindrical sample cavity. Measurements at 4.2 °K were obtained using a superhetrodyne spectrometer constructed in this laboratory utilizing commerically available components. Following Llewellyn et al.,[15] a single klystron was used as the power source for both the sample cavity and the local oscillator. However, the present spectrometer differs from theirs in that they obtained the local-oscillator power by frequency modulating the klystron and then separating one of the resulting sidebands. In our case a portion of the microwave power was removed via a directional coupler and then amplitude modulated at 30 MHz by a microwave switch to produce sidebands about the klystron frequency. One sideband was then selected by a tuned transmission cavity and fed to a balanced mixer to mix with the power reflected from the sample cavity. The klyston frequency

was stabilized against a high harmonic of a temperature-controlled crystal oscillator. The microwave frequency was read off a calibrated transmission cavity to an accuracy of 0.002 GHz. A block diagram of the spectrometer system is shown in Fig. 1. A rectangular TE_{014} sample cavity with a loaded Q of 4500 was used in conjunction with this spectrometer. The magnetic field was modulated at 200 Hz via the reference frequency of the phase-sensitive detector (PSD).

A glass double-Dewar system was used for the cryostat, with liquid helium in the inner Dewar and liquid nitrogen in the outer one. The cavity was fastened to a stainless-steel waveguide stem and the unit was immersed in the liquid helium. The helium filled the entire cavity and stem. The Dewar held two liters of helium, which lasted for about 6 h. An 8-in. Newport magnet was used with both spectrometers. The magnetic field value was measured using proton resonance.

IV. RESULTS

In each of the four alums studied it was found that the chromium impurities existed in four inequivalent, but otherwise similar, magnetic complexes of trigonal symmetry. This was true at 300 and at 4.2 °K. Each complex consisted of three fine-structure lines characteristic of $^{52}Cr^{3+}$ exhibiting transitions within the $S = \frac{3}{2}$ manifold with selection rules $\Delta M_s = \pm 1$. Some extra lines of low intensity were also observed at low field and these are attributed to forbidden transitions, presumably of the type $\Delta M_s = \pm 2$. When operating at 4.2 °K,
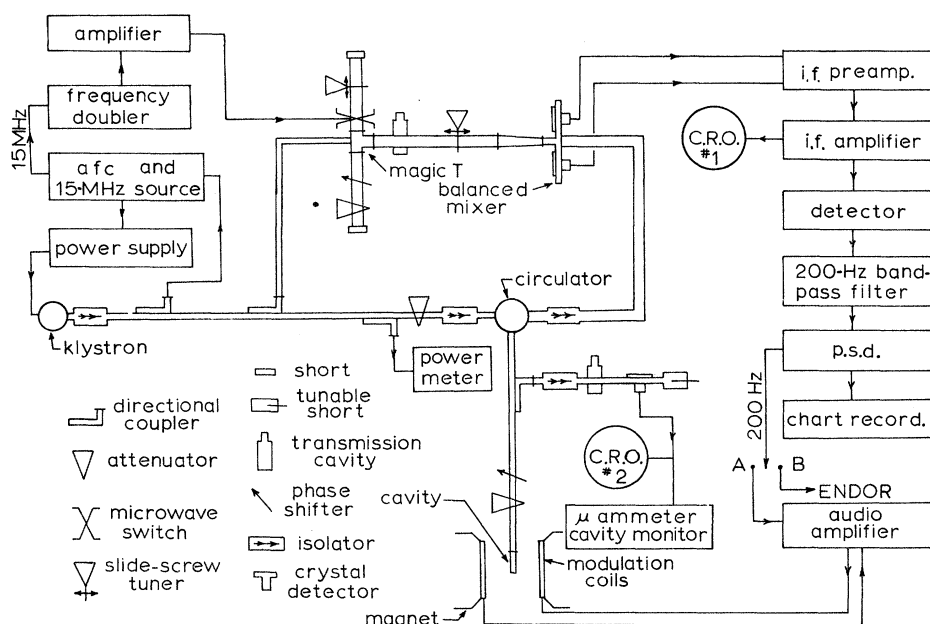

FIG. 1. Block diagram of superheterodyne spectrometer. Cathode-ray oscilloscope (C.R.O.) No. 1 is used to monitor the 30 MHz i.f. level, while C.R.O. No. 2 is used to observe the cavity-absorption dip on a klystron power mode. p.s.d. is the phase-sensitive detector and afc stands for automatic frequency control.
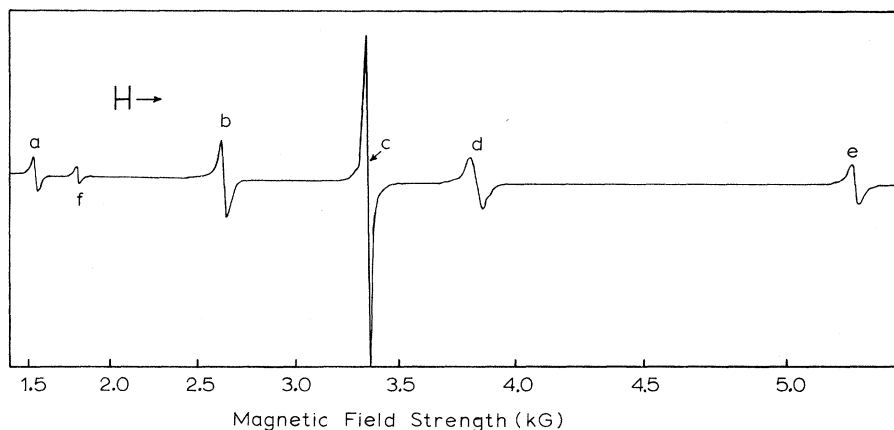
FIG. 2. Z-axis room-temperature spectrum of Cr^{3+} in $RbGa(SO_4)_2 \cdot 12H_2O$. Lines marked a and e are single, b and d are triple, and c consists of four lines. The lines belonging to the z axis in question are a, e, and and one of c. The letter f represents a forbidden transition.

and when the magnetic field direction was close to a z axis, additional low-intensity lines with a separation of over 70 G appeared on either side of the allowed lines. These lines are likely due to chromium-pair interaction.[3,16] Since the ESR linewidths are narrower at low temperature it is also possible to see the outer two ^{53}Cr hyperfine lines as small bumps on the wings of the ^{52}Cr lines.

The three resonance lines of a typical complex showed an extremum as a function of the magnetic field strength when the field direction was along a [111] axis. This means that the z axes of the magnetic complexes are along the ⟨111⟩ directions. A typical chromium z-axis spectrum is shown in Fig. 2. In this figure the lines marked a and e are single, b and d are triple, and c consists of

four lines. The lines belonging to the z axis in question are a, e, and one of c. The letter f represents a forbidden line. When the magnetic field was varied in a plane perpendicular to a z axis there was no angular variation of the corresponding three lines. Figure 3 shows the angular variation of the allowed lines for all four complexes when the magnetic field is varied in a perpendicular plane. The three solid horizontal lines are due to the complex in question while the lines of the other three complexes exhibit a 60° repetitive pattern. Figure 4 shows the angular variation of the lines when the magnet is varied in the (1$\bar{1}$0) plane. The spacing between the lines at the points rr and ss are equal, and also some of the lines are double, as required for trigonal symmetry.
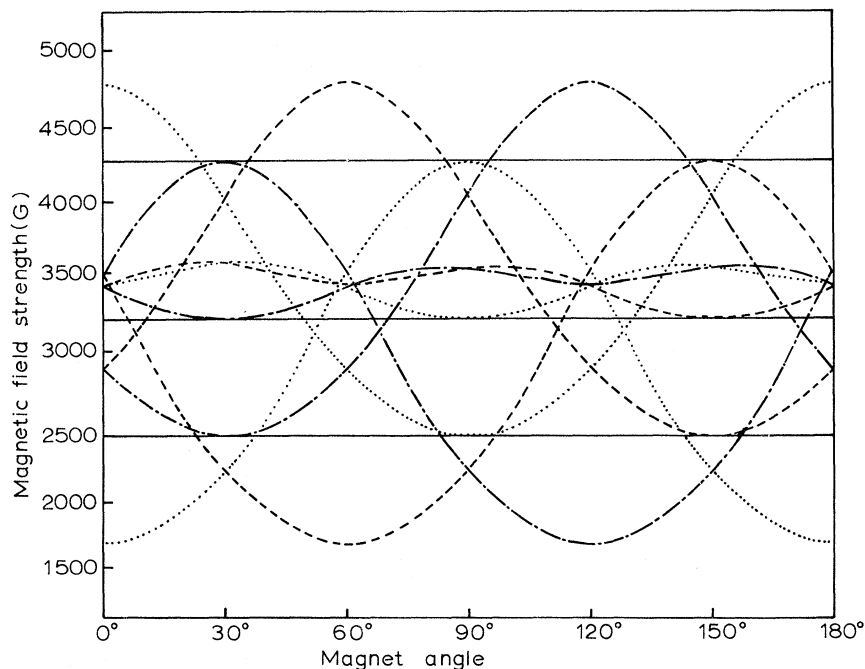

FIG. 3. Angular variation of Cr^{3+} ESR lines in a perpendicular direction for $RbGa(SO_4)_2 \cdot 12H_2O$ at 300 °K. The horizontal solid lines belong to the complex in question while the other lines exhibit at 60° repetitive pattern.

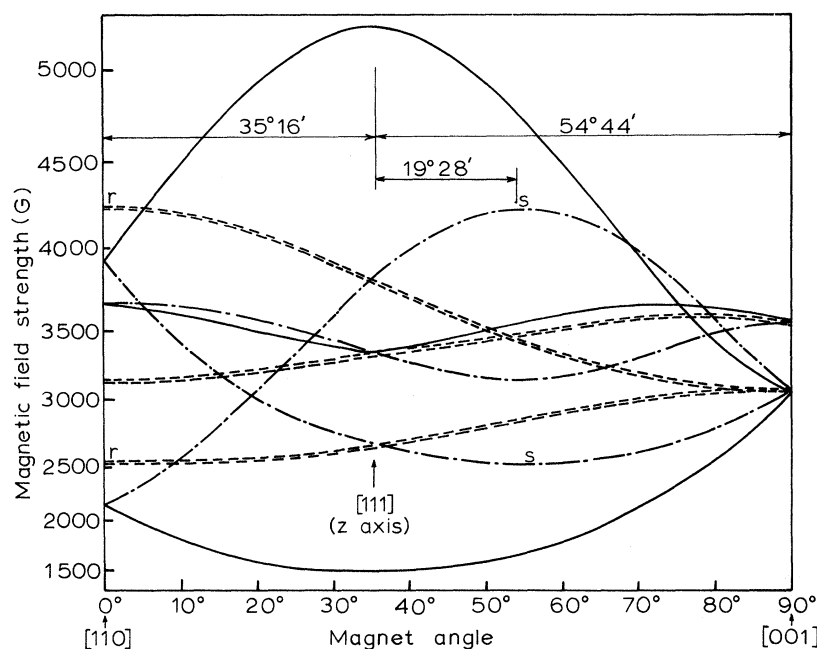FIG. 4. Angular variation of Cr^{3+} ESR lines in the ($1\bar{1}0$) plane for RbGa(SO$_4$)$_2$ · 12H$_2$O at 300 °K. The distance rr is equal to ss, and some of the lines are double as indicated.

The magnetic field positions of the ESR lines in the z and perpendicular directions of a typical complex were fitted to a spin Hamiltonian of the form

$$H_s = g_{||}\mu_B S_z H_z + g_\perp \mu_B (S_x H_x + S_y H_y) + D[S_z^2 - \tfrac{1}{3}S(S+1)] ,$$

where the terms have their usual meanings. The analysis was done for all four crystals and the results obtained for the g and D parameters are given in Table I.

The sign of D was obtained by comparing the relative intensities of the low- and high-field lines of a given complex at 300 and 4.2 °K when the magnetic field was along a z axis. It was determined that the ratio of the high-field line to the low-field line increased at 4.2 °K in the RbGa alums and decreased in the CsGa alums. This fixes the sign of D to be positive for RbGa alums and negative for CsGa alums. Using the calculated values of the

Hamiltonian parameters, and with the aid of an IBM 360 computer, it was possible to plot the ground-state energy levels as a function of the magnetic field strength. The results for RbGa(SO$_4$)$_2$·12H$_2$O at 300 °K including the allowed transitions are shown in Fig. 5.

V. DISCUSSION AND CONCLUSIONS

The chromium magnetic complexes exhibit trigonal symmetry in each of the gallium alums studied. In the temperature range 300–4.2 °K the magnitude of the D parameter decreased by about 38% in the Rb alums and by only 8% in the Cs alums; the parameter has opposite signs in these alums. The effect of deuteration did not reduce the ESR linewidths, contrary to expectations,[17] and the values of g and D did not change significantly either.

A central problem which exists in alums con-

TABLE I. Spin–Hamiltonian parameters of Cr^{3+} in gallium alums.

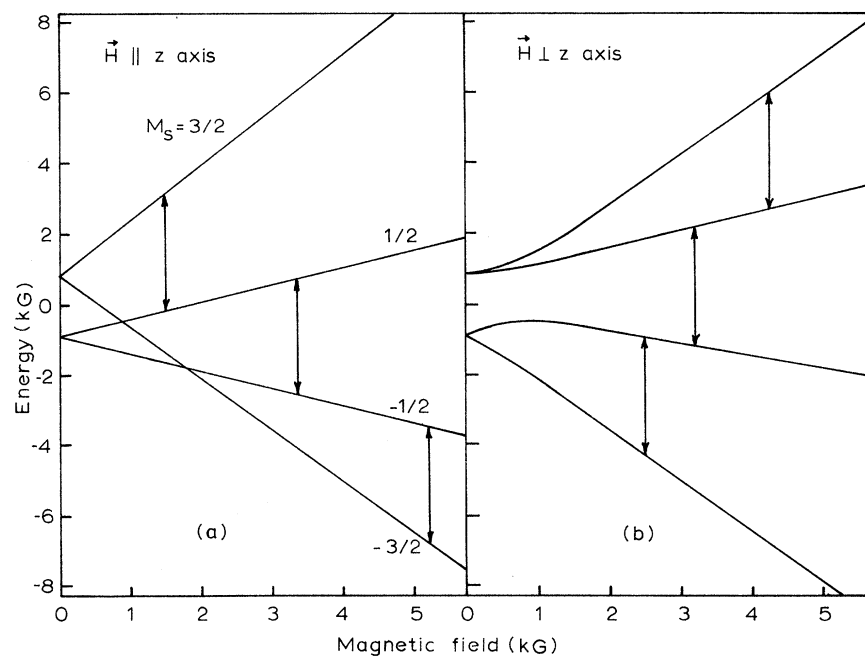| Parameter	RbGa alum				CsGa alum			
	300 °K		4.2 °K		300 °K		4.2 °K	
	H$_2$O	D$_2$O	H$_2$O	D$_2$O	H$_2$O	D$_2$O	H$_2$O	D$_2$O
$g_{||}$ ($\pm$0.0050)	1.9754	1.9754	1.9751	1.9799	1.9715	1.9746	1.9718	1.9747
$g_\perp$ ($\pm$0.0050)	1.9675	1.9653	1.9734	1.9688	1.9694	1.9663	1.9722	1.9696
D (10^{-4} cm^{-1}) ($\pm$2.0)	864.7	869.1	534.2	526.7	-731.7	-753.3	-670.1	-698.4

FIG. 5. Energy level diagrams of Cr^{3+} in $RbGa(SO_4)_2 \cdot 12H_2O$ at 300 °K. (a) $\vec{H}$ is parallel to the z axis and (b) $\vec{H}$ is perpendicular to the z axis.

taining paramagnetic ions is to explain the origin of the trigonal distortion of the magnetic complexes. Such a distortion is found in all chromic or chromium-doped alums, at least at room temperature, with magnitudes of D parameters between 0.05 and 0.08 cm^{-1}. This is true even in soda alum where Kromer et al.[11] showed by means of x-ray crystallography that the six water molecules coordinated to an aluminum atom in the undoped crystal formed a perfect octahedron. The ESR of chromium-doped soda alum was studied by Manoogian and Danilov,[18] who found trigonal magnetic complexes with a D parameter of -0.57 cm^{-1}.

In the theory of the D parameter for Cr^{3+} subjected to a trigonal distortion McGarvey[19] shows that a negative D value can be produced by compression of the coordinated octahedron of waters along the trigonal axis. The effect is to polarize the chromium d electrons along the trigonal axis. Presumably a positive D value would correspond to an extension of the octahedron. Van Vleck[20] postulated three mechanisms which might be responsible for the trigonal distortion in alums. (i) The direct effect from distant atoms: The distant atoms, i.e., atoms other than the six waters coordinated to the paramagnetic ion, are distributed with trigonal symmetry and they could directly cause the distortion observed. (ii) The indirect effect of the distant atoms: The octahedron of coordinated waters may be distorted from cubic symmetry by the action of distant atoms. (iii) The Jahn–Teller effect: The six water molecules arrange themselves around the paramagnetic ion in such a way that the latter is in a nondegenerate

state. This effect ensures that the g factor of the ground state and discrete excited states will be approximately two. However, the Jahn–Teller effect is not expected to be important for Cr^{3+} since the cubic-field splitting leaves an orbital-singlet ground state.

ESR measurements alone do not give sufficient data on which to postulate the reason for the trigonal distortion of the chromium complexes in alums. However, an important observation can be made when comparing the chromium ESR results in alums with those in GAlSH. In this respect it is noted that in all the alums reported, with the exception of methylamine alum, the magnitude of the D parameter decreases with lowering temperature. The magnitude of D increases in methylamine alum and in GAlSH. This characteristic behavior can be attributed to the monovalent ions in these crystals. The methylamine ion, NH_3CH_3, is quite similar in formula to the quanidine ion, $C(NH_2)_3$, with the latter having two extra N atoms. The size of the monovalent ion determines the distortion of the six water molecules coordinated to it and also the distribution of the sulfate groups. These waters and sulfate groups can then influence the chromium magnetic complexes.

For purposes of comparison we have measured the D parameters of Cr^{3+} in $RbAl(SO_4)_2 \cdot 12H_2O$ and $CsAl(SO_4)_2 \cdot 12H_2O$ at 300 °K and found that they have the values 683×10^{-4} and -773×10^{-4} cm^{-1}, respectively. The corresponding results in the gallium alums are 864.7×10^{-4} and -731.7×10^{-4} cm^{-1}, respectively. Hence one can conclude that the size difference between Cr^{3+} and Al^{3+} is not the

cause of the trigonal distortion in the aluminum alums. However, one would not expect the Cr^{3+} to bond to its surroundings in the same manner as Al^{3+} or Ga^{3+} since the latter two ions have closed electron shells. The best one can say at this stage is that many of the atoms in the unit cell can contribute to the trigonal distortion of the chromium complexes, and it is not certain which of Van Vleck's first two postulates is operative. Additional data on the physical behavior of the chromium magnetic complexes are obtained from ENDOR studies, which is the subject of Paper II.[4]

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Electron-Nuclear Double Resonance of ⁵³Cr³⁺ in Gallium Alums. II

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Electron-nuclear-double-resonance (ENDOR) studies are reported for the isotope ⁵³Cr³⁺ enriched to 96% in the gallium alums $RbGa(SO_4)_2 \cdot 12H_2O$ and $CsGa(SO_4)_2 \cdot 12H_2O$, including their deuterated forms. All measurements were made at 4.2 °K and at X-band microwave frequencies (~ 9.4 GHz). The study allowed accurate values of the various hyperfine parameters to be determined and ENDOR patterns to be classified. The hyperfine parameters A and B had the relationships $A > B$ in RbGa alum and $A < B$ in CsGa alum. A model for the behavior of the alums as a function of temperature is postulated, with the result that the quadrupole moment of ⁵³Cr is determined to be $eQ = -0.035 \pm 0.005$ b. The magnetic moment of ⁵³Cr³⁺ was found to be approximately $-0.464\mu_N$ which is slightly lower than the accepted value. The effect of deuteration did not show significant differences from the hydrated alums. ENDOR transitions are observed relating three adjacent hyperfine levels of ⁵³Cr instead of the usual two. Possible mechanisms for this effect are qualitatively discussed.

I. INTRODUCTION

Electron-nuclear-double-resonance (ENDOR) experiments were carried out on chromium-doped alums in order to obtain more information about their physical behavior. The study was done on the gallium alums $RbGa(SO_4)_2 \cdot 12H_2O$ and $CsGa(SO_4)_2 \cdot 12H_2O$, including their deuterated forms. The chromium dopant was 96%-enriched ⁵³Cr³⁺ and its concentration in the samples was estimated to be less than 0.01 wt %. The crystals were grown from saturated solutions of the constituent sulfates by slow evaporation at room temperature. They were colorless and had dimensions of about $4 \times 3 \times 2$ mm. All measurements were done at a temperature of 4.2 °K and at X-band microwave frequencies (9.4 GHz).

No ENDOR work on the alums has been previously reported, but the rather varied paramagnetic behavior of alums provides motivation for further study by this technique. This is especially true at low temperatures where many of the alums