size is accompanied by a relatively small loss in spin memory. However, details depend on the relative strength of the cubic and noncubic modes. The usefulness of the model could be further

checked by measuring the spin memory in the optical-pumping cycle of the F band of the cesium halides, and by investigating the change of  $\epsilon$  with the photon energy.

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PHYSICAL REVIEW B

### VOLUME 6, NUMBER 3

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# Spectroscopy of $Cr^{3+}$ in $CsCr(SO_4)_2 \cdot 12H_2O/D_2O$ , a $\beta$ -Alum

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The trigonal-field splitting of  ${}^{2}E$  into  $\overline{E}$  and  $2\overline{A}$  states is found to be  $\overline{E} - 2\overline{A} = -120 \text{ cm}^{-1}$  by identifying  $2\overline{A}$ . The no-phonon lines of deuterated samples are isotope shifted 6 cm<sup>-1</sup> to the red. The following generalizations suffice to relate the spectra of the Cr-alums: (i) They are due to  ${}^{4}A_{2} \rightarrow \overline{E}$ ,  $2\overline{A}({}^{2}E)$  transitions. The splitting of  ${}^{2}E$  is large for the  $\beta$ -alums, small for the  $\alpha$ -alums. (ii) Sulfate-group disorder, found in all  $\alpha$ -alums, complicates their spectra by adding inequivalent Cr<sup>3+</sup> sites.

Sugano and Tanabe<sup>1</sup> have repeatedly called attention to the "difficulties in the problem of the Cralums." This is ironic because modern crystalfield theory, otherwise successful, originated in the work of Finkelstein and Van Vleck<sup>2</sup> which "laid down the method of calculation employed by all inquiry that followed."<sup>3</sup> We present new data on  $Cr^{3+}$ in pure  $CsCr(SO_4)_2 \cdot 12H_2O/D_2O$ , a  $\beta$ -alum. We conclude with the main point, a speculation on the relationship between structure and spectroscopy in all Cr-alums which proposes a resolution of the apparent "difficulties" using conventional crystalfield theory.

The formula of the alums is  $A^*B^{3*}(RO_4)_2 \cdot 12H_2O$ .  $A^*$  is a monovalent cation (K, Rb, ...);  $B^{3*}$  is a trivalent metal ion (Al, Fe, ...); and R is S, Se, or Te. The unit cell contains four formula units. The space group is cubic  $Pa3(T_h^6)$ . Lipson<sup>4</sup> showed that the alums exhibit three types of structure which he named  $\alpha$ ,  $\beta$ , and  $\gamma$ . The structure is shown in Fig. 1. The caption summarizes the difference between the  $\alpha$ ,  $\beta$ , and  $\gamma$  structures. These have been refined by Cromer *et al.*<sup>6</sup> who find, in addition, that all  $\alpha$ -alums show sulfate-group disorder consisting of some sulfate groups in reversed orientation along the threefold axis. Hausühl<sup>7</sup> classifies 65 alums: 40 ( $\alpha$ ), 24 ( $\beta$ ), 1 ( $\gamma$ ). The only known  $\gamma$  alum is NaAl(SO<sub>4</sub>)<sub>2</sub>· 12H<sub>2</sub>O.

There are four equivalent  $Cr^{3*}$  in the unit cell: one on each of the four body diagonals. The nearest neighbors of  $Cr^{3*}$ ,  $6H_2O's$ , are arranged about the  $Cr^{3*}$  in a perfect octahedron.<sup>4,6</sup> The crystal field due to them is therefore cubic. However, the "distant" atoms, i.e., those other than nearest neighbors are arranged about  $Cr^{3*}$  in trigonal symmetry  $(C_{3i})$ .<sup>8</sup> These are bonded to the oxygens of the  $Cr^{3*}$  waters by hydrogen bonds<sup>6</sup> as shown in Fig. 1.

In spite of the fact that the  $Cr^{3+}-6H_2O$  octahedron is undistorted, next-nearest neighbors may deform



FIG. 1.  $A^{+}B^{3+}(SO_4)_2 \cdot 12H_2O$  structure. One-eighth of unit cell is shown. Hydrogen bonds are shaded directed lines; open circles are oxygen of H<sub>2</sub>O's of  $[A^{+}(H_2O)_6]$  group (not shown); tetrahedron are SO<sub>4</sub> group; octahedron are  $[B^{3+}(H_2O)_6]$ group; shaded circles are A<sup>+</sup> ion. Structure of  $\alpha$ -alum equals the structure of the  $\beta$ -alum except for sixfold coordination of  $A^*$  in  $\alpha$  and 12-fold in  $\beta$ . Structure of  $\gamma$ -alum is the same as the  $\alpha$ alum except for reversal of orientation of SO<sub>4</sub> group along threefold axis. In addition, the  $\alpha$  alums are disordered, some of the sulfate groups being in a reversed orientation along threefold axis (Ref. 6). In all alums  $[B^{3+}(H_2O)_6]$  octahedron is regular. In  $\beta$ -alum principal axes of this octahedron coincide with axes of unit cell (Ref. 4). O-O distances for  $CsAl(SO_4)_2 \cdot 12H_2O$  shown.  $Al-6O_{W}=1.882$  Å,  $Cs-6O_{W}=3.367$  Å,  $Cs-6O_S=3.454$  Å (Ref. 6). Distances for  $CsCr(SO_4)_2 \cdot 12H_2O$  are not expected to differ markedly. For details see Refs. 4 and 6. Figure after Okaya et al. (Ref. 5).

the charge cloud of the nearest-neighbor-water oxygens to which they are linked by hydrogen bonds (Fig. 1). For example, contrast emerald  $[Be_3Al_2 (SiO_3)_6$ : Cr] with ruby  $[Al_2O_3: Cr]$ . In emerald<sup>9</sup> the  $Cr^{3+}-6O$  octahedron is almost regular. Despite this, the splittings due to the polarization of the six oxygens by the next-nearest neighbors, are 63  $\text{cm}^{-1}$  (<sup>2</sup>E splitting) and 1.8 cm<sup>-1</sup> (<sup>4</sup>A<sub>2</sub> splitting). By contrast, <sup>10</sup> in ruby, the Cr<sup>3+</sup>-O octahedron is trigonally distorted by 8%, but the corresponding splittings<sup>10</sup> are 29 cm<sup>-1</sup> ( ${}^{2}E$ ) and 0.38 cm<sup>-1</sup> ( ${}^{4}A_{2}$ ). However, for  $CsCr(SO_4)_2 \cdot 12H_2O$  Bleaney<sup>11</sup> finds a splitting of only 0.13 cm<sup>-1</sup> ( ${}^{4}A_{2}$ ) from which one might conclude a small trigonal field. Nevertheless, as emphasized by Macfarlane, <sup>12</sup> the splitting of the  ${}^{4}A_{2}$  and  ${}^{2}E$  states depends predominantly on different trigonal-field parameters v and v'. Disparate  ${}^{4}A_{2}$  and  ${}^{2}E$  splittings are therefore possible. We shall show that this is, indeed, the case for  $CsCr(SO_4)_2 \cdot 12H_2O/D_2O$ , where we find a splitting of  $120 \text{ cm}^{-1}$  for the <sup>2</sup>E state.

Uesaka *et al.*<sup>13</sup> find that the symmetry of the lowest excited state of  $Cr^{3*}$  in  $CsCr(SO_4)_2 \cdot 12H_2O$  is  $\overline{E}$  from its Zeeman splittings. These authors did not locate the  $2\overline{A}$  state, but estimate  $|\overline{E} - 2\overline{A}|$  $\gg 3.5 \text{ cm}^{-1}$ . Figure 2 shows absorption and emission spectra of  $CsCr(SO_4)_2 \cdot 12D_2O$ . The vibronics are mirror images except for a line at 120 cm<sup>-1</sup>, seen in absorption but not in emission. This suggests that it is electronic rather than vibronic and that it may be due to the  ${}^{4}A_{2} \rightarrow 2\overline{A}$  transition. To verify this, the Zeeman effect, in absorption, on this line was studied.

From the results, shown in Fig. 3(a), we find the following:

(i) The transition is magnetic dipole, as is the transition studied by Uesaka *et al.*<sup>13</sup> A vibronic transition is expected to be electric dipole.

(ii) The experimental Zeeman pattern is different from that of the transition studied by Uesaka *et al.*<sup>13</sup> Its agreement with the theoretical pattern, calculated by these authors for the  ${}^{4}A_{2} \rightarrow 2\overline{A}$  transition, is reasonable considering the approximations used by them. For the effective g values, parallel and perpendicular to the  $C_{3}$  axis, we find  $g_{11}=2.1$ and  $g_{1}=0$ .  $g_{1}(2\overline{A})$  vanishes by symmetry.<sup>14</sup> They find  $g_{11}(\overline{E})=2.7$  and  $g_{1}(\overline{E})=0$  with which our measurements agree. We conclude that the splitting of  ${}^{2}E$  into  $\overline{E}$  and  $2\overline{A}$  is  $\overline{E} - 2\overline{A} = -120$  cm<sup>-1</sup>.

(iii) In addition, we find that deuteration shifts the spectrum 6 cm<sup>-1</sup> to the red [Fig. 3(b)]. The separation  $\overline{E} - 2\overline{A}$  and the Zeeman patterns for the  $2\overline{A}$  state are unchanged. Böhm<sup>15</sup> reports an isotope shift in KCr(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O/D<sub>2</sub>O and KCr(SeO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O/D<sub>2</sub>O. In the region of the sharp lines (~ 14 900 cm<sup>-1</sup>), his isotope shifts are opposite to ours.

Connection with other work is provided by that of



FIG. 2. Absorption and emission spectra of  $CsCr(SO_4)_2 \cdot 12D_2O$  at 4 K. The  ${}^{4}A_2 \rightarrow \overline{E}$  transition (14473.3 cm<sup>-1</sup>) is used as reference. The line at 120 cm<sup>-1</sup>, seen in absorption but not in emission, is assigned to  ${}^{4}A_1 \rightarrow 2\overline{A}$  transition.  $D_1$ ,  $D_2$ , and  $D_3$  are no-phonon lines assumed to be due to sulfate-group disorder. Spectra are slit width limited. Widths of nophonon lines ~ 0.5 cm<sup>-1</sup> (4 K), 10 cm<sup>-1</sup> (77 K). Intensity of emission of protonated sample factor of 50 weaker than that of deuterated.

Kraus and Nutting<sup>16</sup> who measured the absorptionline spectra of 13 Cr-alums which they divide into three classes according to the number of "sharp, prominent lines" in the region 14 500-15 000 cm<sup>-1</sup>. Those of class I have a strong doublet accompanied by a "variable number of weaker lines" near 14 900 cm<sup>-1</sup>. In class II the spectrum is shifted in its entirety about 400 cm<sup>-1</sup> toward the red and in place of the doublet there is a single sharp line near 14 500 cm<sup>-1</sup>. Alums of class III show about six strong lines near 14 900 cm<sup>-1</sup>. These authors suggest a correspondence between structure type and class of spectrum. Table I summarizes this corre-

spondence which is consistent if Hausühl's<sup>7</sup> structure identification is adopted, but is inconsistent with that of Klug.<sup>17, 18</sup>

The following generalizations suffice to relate the spectra of the Cr-alums and reconciles them with those of  $\operatorname{Cr}^{3*}$  in other solids: (i) They are due to  ${}^{4}A_{2} \rightarrow \overline{E}$ ,  $2\overline{A}$  ( ${}^{2}E$ ) transitions. (ii) The splitting of  ${}^{2}E$  is large for the  $\beta$ -alums (class II), small for the  $\alpha$ -alums (class I). (iii) Sulfate-group disorder, found in all  $\alpha$ -alums,  ${}^{6}$  complicates their spectra by adding inequivalent sites (classes I and III). In support, we cite the Zeeman studies of TlCr(SO<sub>4</sub>)<sub>2</sub>  $\cdot$  12H<sub>2</sub>O, an  $\alpha$ -alum of class I, by Koshizuka *et* 

		Structure type	
Traus-Nutting classification <sup>a</sup>		Klug <sup>b</sup>	Hausühle
	$RbCr(SO_4)_2 \cdot 12H_2O$	β	α
	$RbCr(SeO_4)_2 \cdot 12H_2O$		α
	$TlCr(SO_4)_2 \cdot 12H_2O$	β	α
	$TlCr(SeO_4)_2 \cdot 12H_2O$		
I (2 lines)	$CsCr(SeO_4)_2 \cdot 12H_2O$		α
	$\mathrm{KCr}(\mathrm{SeO}_4)_2 \cdot 12\mathrm{H}_2\mathrm{O}$		
	$NH_3OHCr(SO_4)_2 \cdot 12H_2O$		α
	$\mathrm{NH}_4\mathrm{Cr}(\mathrm{SO}_4)_2 \cdot 12\mathrm{H}_2\mathrm{O}^{\mathrm{d}}$	α	$\alpha$
	$\mathrm{NH}_4\mathrm{Cr}(\mathrm{SeO}_4)_2\cdot 12\mathrm{H}_2\mathrm{O}^{d}$		α
II (1 line)	CH <sub>3</sub> NH <sub>3</sub> Cr(SO <sub>4</sub> ) <sub>2</sub> · 12H <sub>2</sub> O	β	β
	$CH_3NH_3Cr(SeO_4)_2 \cdot 12H_2O$		
	$CsCr(SO_4)_2 \cdot 12H_2O$	β	β
	$\mathrm{KCr}(\mathrm{SO}_4)_2 \cdot 12\mathrm{H}_2\mathrm{O}$	α	α
III (~6 lines)	$NH_4Cr(SO_4)_2 \cdot 12H_2O^{e}$		
	$NH_4Cr(SeO_4)_2 \cdot 12H_2O^e$		

TABLE I. Correspondence between class of spectrum and structure type of 13 Cr-alums. Class to which a Cr-alum belongs is defined (see Ref. 16) by the number of "sharp prominent lines," found in absorption in the region 14500 to 15000 cm<sup>-1</sup> as described in text.

<sup>a</sup>See Ref. 16.

<sup>b</sup>See Ref. 17.

<sup>c</sup>See Ref. 7.

<sup>d</sup>High-temperature form (see Ref. 16).

<sup>e</sup>Low-temperature form (see Ref. 16).



FIG. 3. (a): A,  $D_2O$  crystal  $H_0$ =0; C,  $H_0$  = 39 kG,  $\vec{H} \parallel \vec{H}_0$  ( $\pi$  spectrum); D,  $H_0 = 39 \text{ kG}$ ,  $\vec{H} \perp \vec{H}_0$  ( $\sigma$ spectrum). Some weak lines in A, C, and D are drawn out below. The 14592.9-cm<sup>-1</sup> line has one component in  $\alpha$  spectrum (not shown) at 63 kG with a shift of 2.56  $\mu_B H_0$ . The shifts in the  $\sigma$ and  $\pi$  spectra are 2.6  $\mu_B H_0$  and 3.3  $\mu_B H_0$ , respectively, thus  ${}^4A_2$  $\rightarrow 2\overline{A}$  is magnetic dipole.  $\mu_B$  is the Bohr magneton. (b): A,  $D_2O$ ; B, H<sub>2</sub>O crystal at  $H_0 = 0$ . The  ${}^4A_2$  $\rightarrow \overline{E}$  transition shows a single line for protonated sample, for deuterated 4-5 lines spaced 1.2 cm<sup>-1</sup> and decreasing in intensity toward the blue. Coincidence in emission with these absorptions lines shows they are electronic. The first two are easily seen. This result is likely due to proton contamination in which D's of 6D<sub>2</sub>O's surrounding  $CR^{3+}$  are replaced by 1, 2,...12 H's.

al.<sup>19</sup> who identify the prominent doublet at 14 944 cm<sup>-1</sup>, split by 2 cm<sup>-1</sup>, as  ${}^{4}A_{2} \rightarrow \overline{E}$ ,  $2\overline{A}$  (<sup>2</sup>E) transitions. However, a weaker line 28 cm<sup>-1</sup> to the red is tentatively identified by them as an electronic transition also of  ${}^{2}E$  character. In our view, the latter is a manifestation of sulfate-group disorder as are the "variable number of weaker lines" <sup>16</sup> accompanying the prominent doublet of the  $\alpha$ -alums of class I. The prominence of the disorder spectrum depends on the disorder parameter k which is equal to the fraction of reversed sulfate groups. k = 0.3 for KAl(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O and 0. 1–0. 15 for the corresponding alums of Rb and  $NH_4$ .<sup>6</sup> k is expected to decrease as the size of  $A^+$  increases.<sup>6</sup> Thus the complicated spectrum<sup>20</sup> of KCr(SO<sub>4</sub>)<sub>2</sub>  $\cdot$  12H<sub>2</sub>O, an  $\alpha$ -alum of class III, is likely due to a large disorder parameter. Even in the  $\beta$ -alum CsCr(SO<sub>4</sub>)<sub>2</sub>  $\cdot$  12H<sub>2</sub>O the lines  $D_1$ ,  $D_2$ , and  $D_3$  at 7, 15, and 23

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 $cm^{-1}$  (Fig. 2) are possibly due to sulfate-group disorder for which k is probably too small to be detected by x-ray diffraction.

The different order of magnitude of the trigonal field in the  $\alpha$ - and  $\beta$ -alums, respectively, is probably caused by the difference in coordination of the  $A^*$  ion, 12 in the  $\beta$ -alum, six in the  $\alpha$ -alum.<sup>4,6</sup> which must be reflected in a change of distribution of strength of the hydrogen bonding. The sulfategroup disorder is conjectured to be static because of the strength of the hydrogen bonds linking it to other groups. It may be important in other physical properties of the Cr alums reviewed by Eisenstein<sup>21</sup> and, because of the closely spaced inequivalent sites presented by the disorder, in energy transfer also.

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#### PHYSICAL REVIEW B

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## Metallic-Field Effect and Its Consequences in Field Emission, Field Ionization, and the Capacitance of a Capacitor

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The metallic-field effect at a metal surface is calculated in a semi-self-consistent manner using an approximate version of Bardeen's method for the evaluation of the surface potential barrier. The consequences of the metallic-field effect in relation to field emission, field ionization, and the capacitance of a parallel-plate capacitor are considered. In field emission this produces, at high fields, a small deviation from the Fowler-Nordheim formula towards lower currents. In field ionization it leads to increased ion current and a narrower energy distribution. It has no significant effect on the capacitance of a capacitor.

#### I. INTRODUCTION

The penetration of an externally applied field into a metal at a metal-vacuum interface is of interest in problems of field ionization and field desorption,<sup>1,2</sup> in field emission,<sup>2,3</sup> and in relation to the capacitance of a thin-plate capacitor.<sup>2,4</sup> The similar problem of metal field "penetration" at a metal-insulator interface is of interest in relation to the capacitance and tunneling characteristics of a thin film (less than 30 Å or so) sandwiched between two metal electrodes.<sup>5,6</sup>

Tsong and Muller<sup>2</sup> attempted an evaluation of the field penetration factor at a metal-vacuum interface using the Thomas-Fermi model in a manner analogous to the one used for treating field penetration in semiconductors.<sup>7</sup> The Thomas-Fermi model is supplemented by the boundary condition that the electrostatic potential is such that dV/dx= F at the metal-vacuum interface taken at x = 0(F denotes the applied electric field). However, the Thomas-Fermi model is expected to give good results when the induced potential varies slowly over an electron wavelength. This is in fact the case in semiconductors, because of the small freeelectron density and the consequent large penetration of the electric field. It is hardly the case with a metal, where as a result of the comparatively high free-electron density at the metal-vacuum interface, one gets a small penetration of the electric field. Moreover, the boundary condition dV/

dx = F at a mathematical metal-vacuum interface is a restrictive one because it assumes an abrupt termination of the electronic charge density at the interface and in a proper calculation it must be replaced by

$$\lim_{x \to \infty} \frac{dV^{e1}}{dx} = F$$

In practice it will be sufficient to assume that the limiting value is acquired a few angstroms away from a mathematical metal-vacuum interface. which we shall define more precisely in Sec. II. As we shall see this may lead in the case of a metal to qualitatively different conclusions. Other authors<sup>3,8,9</sup> studied field penetration using a linear response formalism within the random-phase approximation (RPA) and assuming an infinite potential barrier at the surface. Again the imposition of the boundary condition  $dV^{el}/dx = F$  at a sharply defined metal-vacuum interface is a serious disadvantage of these calculations. The use of the RPA may also be very difficult to justify in the present problem. In particular, the assumption of a linear dielectric response to the externally applied field could be a disadvantage. Our results have shown that nonlinear effects are significant in this region.

In this paper we present an approximate semiself-consistent calculation which avoids the abrupt boundary condition at x = 0. Section II contains the basic assumptions and the method of numerical calculation.



FIG. 3. (a): A, D<sub>2</sub>O crystal  $H_0$ = 0; C,  $H_0$  = 39 kG,  $\hat{H} \parallel \hat{H}_0$  ( $\pi$  spectrum); D,  $H_0$  = 39 kG,  $\hat{H} \perp \hat{H}_0$  ( $\sigma$ spectrum). Some weak lines in A, C, and D are drawn out below. The 14592.9-cm<sup>-1</sup> line has one component in  $\alpha$  spectrum (not shown) at 63 kG with a shift of 2.56  $\mu_B H_0$ . The shifts in the  $\sigma$ and  $\pi$  spectra are 2.6  $\mu_B H_0$  and 3.3  $\mu_B H_0$ , respectively, thus  ${}^4\!A_2$  $\rightarrow 2\overline{A}$  is magnetic dipole.  $\mu_B$  is the Bohr magneton. (b): A,  $D_2O$ ; B, H<sub>2</sub>O crystal at  $H_0 = 0$ . The  ${}^4A_2$  $\rightarrow \overline{E}$  transition shows a single line for protonated sample, for deuterated 4-5 lines spaced 1.2 cm<sup>-1</sup> and decreasing in intensity toward the blue. Coincidence in emission with these absorptions lines shows they are electronic. The first two are easily seen. This result is likely due to proton contamination in which D's of 6D<sub>2</sub>O's surrounding  $CR^{3+}$  are replaced by 1, 2,...12 H's.