

ature more than  $0.2K^\circ$  distant from the critical-current curve. In this experimental run the point denoted by a cross was measured after pump-down, following the recording of the three circled points on the initial fluxoid curve. The solid curve shown was fitted to these three points using the method discussed above. Within the limits of experimental error the point shown with a cross, measured after pump-down, falls on the same curve. The current variation in this experiment is thus *reversible* within the limits of experimental error.

A quite different approach has been used by Mercereau and Crane<sup>20</sup> to observe variations in the persistent current in rings whose temperature oscillates rapidly. In their experiment the ring comprises one wall of a cylindrical second-sound resonant cavity and a loosely coupled sensing coil is used to detect variations in the persistent current corresponding to the small ( $10^{-3}K^\circ$ ) temperature oscillations produced by the second sound. Under these more rapid perturbations the maximum possible reversible variation in the trapped flux appears to be only one "quantum" of flux.

<sup>20</sup> J. E. Mercereau and L. T. Crane, Phys. Rev. Letters **12**, 191 (1964).

## V. CONCLUSIONS

Persistent currents have been observed in thin films for which the film thickness is two orders of magnitude less than the penetration depth. In these films the field penetration is essentially complete and it is thus clear that the presence of a good Meissner effect is by no means essential for the stability of persistent currents.

The prediction that the fluxoid through a superconducting ring is conserved has been verified by an investigation of the temperature dependence of the magnetic flux trapped by such rings in the pure superconducting state. The experimental results show clearly both the decrease in trapped flux with rising temperature and an increase in trapped flux with falling temperature which are direct consequences of fluxoid conservation. Previous experiments carried out to observe flux quantization have explored only the properties of the electromagnetic part of the fluxoid since the effects of the mechanical term in those cases were negligible. The present experiments are sensitive to both terms comprising fluxoid and thus fill a conspicuous gap in the experimental picture of trapped flux and persistent currents in superconducting rings.

## Magnetic- and Electric-Field Effects of the $B_1$ and $B_2$ Absorption Lines in Ruby\*

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A pseudo-Stark splitting of the  $B_1$  ( $20\,993\text{ cm}^{-1}$ ) and the  $B_2$  ( $21\,068\text{ cm}^{-1}$ ) absorption lines in ruby has been observed at  $2^\circ K$ . The splitting of each  $B$  line is  $2.8 \times 10^{-5}\text{ cm}^{-1}/V/\text{cm}$  for an electric field parallel to the  $c$  axis. This is a factor 3.7 larger than the corresponding splitting of the  $R$  lines. There is no observable effect for fields perpendicular to the  $c$  axis. Crystal-field theory satisfactorily predicts these properties, which are determined by the symmetry of the  $Cr^{3+}$  site. The point-charge model does not correctly predict the absolute value of the observed electric splitting, nor the matrix elements of the  $B$  lines.

### I. INTRODUCTION

THE  $B_1$  and  $B_2$  absorption lines of the  $Cr^{3+}$  ion in a lattice of  $Al_2O_3$  were observed and named by Gibson<sup>1</sup> in 1916. Since that time, studies of these lines have been far less numerous and extensive than the studies of the narrower  $R_1$  and  $R_2$  lines which appear strongly in fluorescence as well as in absorption. In 1958 Sugano and Tanabe<sup>2</sup> identified the green and blue absorption bands and  $R$  and  $B$  lines with transitions to levels predicted by the crystal-field theory, reproduced

in Fig. 1. Their predictions of the relative transition probabilities between the Zeeman components of each  $R$  and  $B$  line were partially confirmed by Sugano and Tsujikawa.<sup>3</sup> Since the latter's work was only semi-quantitative, Schawlow, Varsanyi, and Wood<sup>4</sup> made a careful investigation of the  $R_1$ -line Zeeman structure and completely confirmed the predictions.<sup>2</sup> Wieder<sup>5</sup> detected microwave absorption between the  $m = \pm \frac{3}{2}$  and  $m = \pm \frac{1}{2}$  ground-state levels by observing the change in  $R$ -line optical absorption upon application of microwave power, and Geschwind, Collins, and Schawlow<sup>6</sup> used selective reabsorption of the  $R_1$ -line fluores-

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<sup>1</sup> K. S. Gibson, Phys. Rev. **8**, 38 (1916).

<sup>2</sup> S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

<sup>3</sup> S. Sugano and I. Tsujikawa, J. Phys. Soc. Japan **13**, 899 (1958).

<sup>4</sup> A. L. Schawlow, F. Varsanyi, and D. L. Wood, Phys. Rev. Letters **3**, 544 (1959).

<sup>5</sup> I. Wieder, Phys. Rev. Letters **3**, 468 (1959).

<sup>6</sup> S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters **3**, 545 (1959).

cence to detect paramagnetic resonance in the  ${}^2E(t_{2g}^3)$  state.

An applied electric field may induce linear shifts in the position of energy levels of ions which occupy lattice sites lacking inversion symmetry.<sup>7</sup> The Cr<sup>3+</sup> ions in Al<sub>2</sub>O<sub>3</sub> occupy sites possessing C<sub>3</sub> symmetry, and thus the spectrum of these ions may exhibit a linear electric-field effect. Because the Cr<sup>3+</sup> sites occur in pairs related to each other by inversion symmetry, the energy levels of ions at one site will undergo a shift, equal but opposite to the shift in ions at the related site. The electric-field effect has thus been detected in ruby as a pseudo-Stark splitting of the lines.<sup>8</sup> Artman and Murphy<sup>9</sup> have calculated the effect using a point-charge crystal-field model and claim good agreement between theory and experiment.

Maiman's<sup>10</sup> development of an optical maser using the R-line fluorescence has insured continued interest in and study of these lines. Since the validity of the theory of Sugano and Tanabe regarding the B lines was still in question, and since Royce and Bloembergen<sup>11</sup> had cast doubts on the correctness of Artman and Murphy's calculations regarding the microwave-electric-field effect in ruby, an experiment to detect the Zeeman splitting and the pseudo-Stark splitting of the B lines was planned.

In Sec. II of this paper these experiments and their results are described and compared with other recent experimental work.<sup>12</sup> A theoretical discussion in terms of crystal-field theory is given in Sec. III.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The R and B lines were observed in absorption using the spectrophotometer shown in Fig. 2. Since the Jarrell-Ash spectrometer used a 300-line/mm Harrison grating blazed at 60°, the red and blue lines were observed in eighth and twelfth order, respectively. This necessitated the use of visible transmitting filters to reduce the wavelength spread of the incident light in order to prevent overlap of orders at the exit slit. In addition, the filters used in the R-line measurements prevented blue and green radiation from stimulating unwanted R-line fluorescence. The spectral slitwidths used were substantially less than the half-width at half-height of the lines observed, so the effect of the spectrometer on line shape and intensity was insignificant. In the Linde 0.50% Cr<sup>3+</sup> sample used in the electric-field experiments, the full width of the R<sub>1</sub> and R<sub>2</sub> lines was 0.35 cm<sup>-1</sup>, while the width of B<sub>1</sub> and B<sub>2</sub>

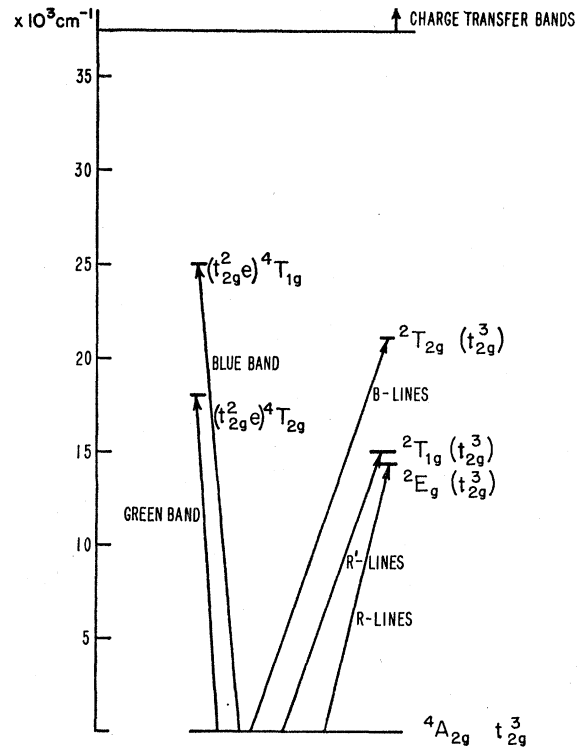


Fig. 1. Observed energy levels of Cr<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub>.

was 2 cm<sup>-1</sup> and 4 cm<sup>-1</sup>, respectively. These latter values were also found in the Meller 0.17% Cr<sup>3+</sup> sample used for the Zeeman studies of the B lines. All widths reported were measured at 2.1°K. The samples were directly immersed in a helium bath below the λ point to prevent bubbling in the optical path.

A Harvey-Wells magnet with tapered pole caps and a 2-in. gap provided magnetic fields up to 16 kG. For the electric-field experiment, transparent conducting electrodes of SnO<sub>2</sub> were applied to the ruby using the method of Goodall.<sup>13</sup> A ring of DuPont conductive silver paint No. 6216 was baked onto the sample in contact with the outer edge of each electrode, thus preventing light absorption in that portion of the sample where the electric field was nonuniform and also providing a surface on which to soft solder the lead wires. Samples were of the order of 1 mm thick and 1 by 1 cm in area. The electrodes were made as small as possible, consistent with the requirement of good signal intensity. By leaving an insulating area around the electrodes, the breakdown path around the edge of the sample from one electrode to the other was lengthened, thus raising the breakdown voltage. The sample was mounted so as to allow free circulation of the surrounding superfluid helium, an excellent insulator. Surface breakdown occurred at various field strengths between 100 and 400 kV/cm, depending on the total area of the sample

<sup>7</sup> N. Bloembergen, Science **133**, 1363 (1961).  
<sup>8</sup> W. Kaiser, S. Sugano, and D. L. Wood, Phys. Rev. Letters **6**, 605 (1961).  
<sup>9</sup> J. O. Artman and J. Murphy, Proceedings of the International Conference on Paramagnetic Resonance (Academic Press Inc., New York, 1963), Vol. II.  
<sup>10</sup> T. H. Maiman, Nature **187**, 493 (1960).  
<sup>11</sup> E. Royce and N. Bloembergen, Phys. Rev. **131**, 1912 (1963).  
<sup>12</sup> K. Aoyagi, A. Misu, and S. Sugano, J. Phys. Soc. Japan **13**, 1448 (1963).

<sup>13</sup> R. Goodall, Rev. Sci. Instr. **31**, 344 (1960).

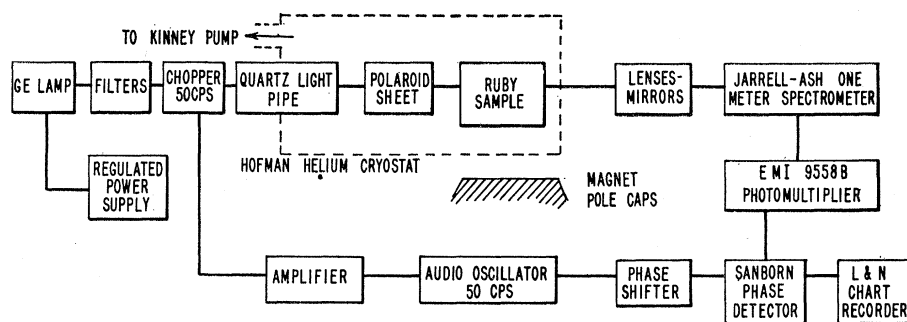


FIG. 2. Diagram of spectro-photometer.

used and the care taken in preserving the cleanliness of the insulating area during the electrode preparation.

The relative values of the squared dipole moment matrix elements predicted by Sugano and Tanabe for the Zeeman components of the  $B_1$  and  $B_2$  lines are presented in Table I. Because the widths of the  $B$  lines were too large to allow splitting of the lines in the magnetic fields available, the following method was used to interpret the absorption data. A trace of the  $B_1\pi$  line was first taken in zero magnetic field. The squared dipole matrix element of the line in arbitrary units was found by dividing the measured maximum intensity by the known population of the  $\pm\frac{3}{2}$  ground-state level. In a magnetic field, the  $-\frac{3}{2}$  and  $+\frac{3}{2}$  level share this matrix

TABLE I.  $B$ -Line squared dipole matrix elements.  $\sigma$  radiation  $\mathbf{E}\perp C$ ;  $\pi$  radiation  $\mathbf{E}\parallel C$ .

${}^4A_2$	$ p^z ^2$				
	$\frac{1}{2}$	$B_1$	$-\frac{1}{2}$	$B_2$	$\frac{1}{2}$
3	$\pi$				$\sigma^0$
$\frac{3}{2}$	$\frac{\pi}{2}$				$\frac{\sigma^0}{2}$
1	$\sigma$	$\sigma^0$		$\pi$	$\frac{\sigma}{3}$
$\frac{1}{2}$	$\frac{\sigma}{3}$	$\frac{\sigma^0}{6}$		$\frac{\pi}{6}$	$\frac{\sigma}{3}$
$-\frac{1}{2}$	$\frac{\sigma^0}{6}$	$\frac{\sigma}{3}$		$\frac{\sigma}{3}$	$\frac{\pi}{6}$
3		$\pi$		$\sigma^0$	
$\frac{3}{2}$		$\frac{\pi}{2}$		$\frac{\sigma^0}{2}$	

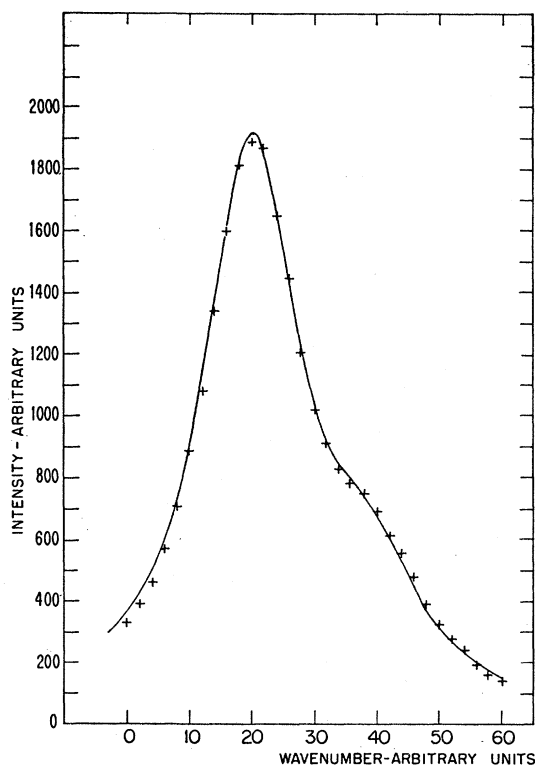


FIG. 3. The shape of the  $B_1\pi$  line in a magnetic field of 8850 Oe. The drawn curve is the theoretical sum of two Lorentzian curves. The crosses represent experimental points.

element equally. If the strength of the field  $H_0$  is known, then the splitting between the ground-state spin levels and hence the populations of these levels can be found. An intensity curve can be synthesized from the  $+\frac{3}{2}$  and  $-\frac{3}{2}$  curves, whose shapes are assumed Lorentzian. Figure 3 compares such a predicted curve with the actual observed absorption intensity for the  $B_1\pi$  line in a field of 8850 G along  $C$ . For the  $B_2$  line, shape analysis was precluded by the large width, but the synthesizing technique predicted the maximum intensity as a function of magnetic field and this could be compared with experiment. The results may be summarized as follows. Light polarized parallel to the  $C$  axis, is absorbed equally by the  $+\frac{3}{2}$  and  $-\frac{3}{2}$  levels at  $B_1$  only. For  $B_2$  this polarization is absorbed equally by only the  $+\frac{1}{2}$  and  $-\frac{1}{2}$  levels. Light polarized with  $\mathbf{E}\parallel C$  is absorbed into one line only, corresponding to the  $\sigma^0$  matrix element, from each of levels  $\frac{1}{2}$  and  $-\frac{1}{2}$  of  $B_1$ . If there is absorption into other lines from these levels, it is not more than five percent of the  $\sigma^0$  absorption. In  $B_2$ , this polarization is absorbed equally by the  $+\frac{3}{2}$  and  $-\frac{3}{2}$  levels only, and if there is absorption from  $\frac{1}{2}$  and  $-\frac{1}{2}$ , it is less than five percent of the  $\pm\frac{3}{2}$  absorption.

These experimentally observed values of  $\sigma^0=0.83\pi$ ,  $\sigma\cong 0$  for  $B_1$  and  $\sigma^0=1.02\pi$ ,  $\sigma\cong 0$  for  $B_2$  are in agreement with the recent results of Sugano, Aoyagi, and Mitsu<sup>12</sup> and supersede the earlier findings of Sugano and

FIG. 4. The splitting of the B<sub>1</sub> and B<sub>2</sub> absorption lines as a function of the applied electric-field strength.

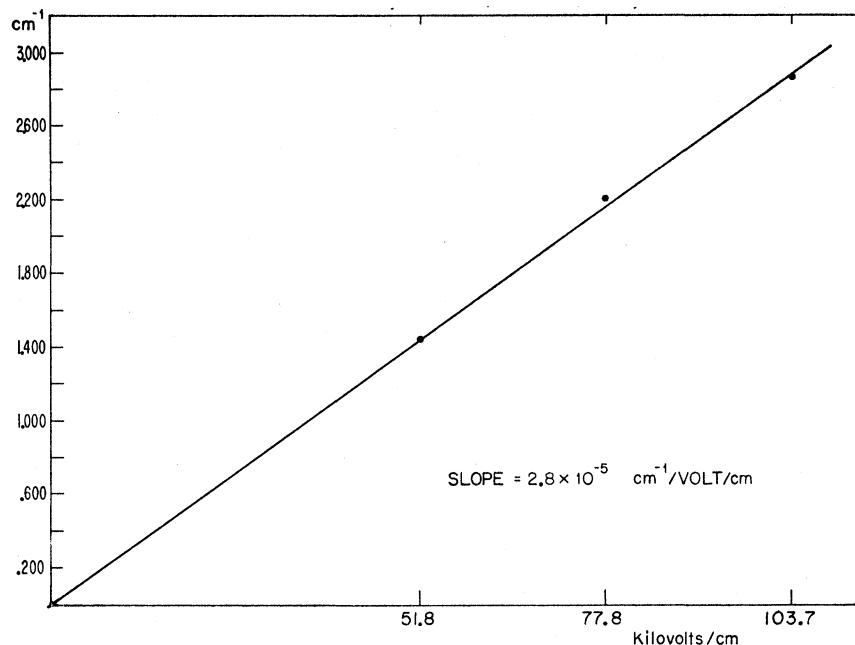


TABLE II. Absolute values of squared dipole matrix elements for B<sub>1</sub> and B<sub>2</sub>. All values are ×10<sup>-41</sup> (esu)<sup>2</sup>.

Experiment		Theory
B <sub>1</sub>	B <sub>2</sub>	B <sub>1</sub> and B <sub>2</sub>
π = 1.87	π = 1.27	π = 2.90
σ ≅ 0	σ ≅ 0	σ = 2.14
σ <sup>0</sup> = 1.55	σ <sup>0</sup> = 1.29	σ <sup>0</sup> = 4.97

Tsujikawa<sup>3</sup> who found σ<sup>0</sup> = 0.67π, σ = 0.33π for B<sub>1</sub> and B<sub>2</sub>. From the nominal Cr<sup>3+</sup> concentration and the measured line shape, the absolute values of the squared dipole matrix elements for B<sub>1</sub> and B<sub>2</sub> listed in Table II were derived. These absolute values, which must be viewed with caution since an accurate value of the Cr<sup>3+</sup> concentration was lacking, are compared with Sugano and Tanabe's predicted absolute values.

When an electric field is applied along the C axis, pseudo-Stark splittings are observed for both the R lines and the B lines. In each case the splitting is linear in the field strength, as shown in Fig. 4. The R-line splitting is readily resolved. Both R<sub>1</sub> and R<sub>2</sub> have the same splitting, 0.76 × 10<sup>-5</sup> cm<sup>-1</sup>/V/cm. This value is 25% higher than the previously reported value of Kaiser *et al.*<sup>8</sup> In our experiment great care was taken to insure a homogeneous electric field in the light path.

The resolved B<sub>1</sub> splitting is shown in Fig. 5. The splitting of the broader B<sub>2</sub> line was determined by the method of shape analysis. Both B lines have a splitting of 2.8 × 10<sup>-5</sup> cm<sup>-1</sup>/V/cm. When the electric field is applied perpendicular to the C axis, no observable effect is found for the R lines up to 400 kV/cm, nor for the B

lines up to 150 kV/cm. The perpendicular effect is less than 5% of the parallel effect.

III. COMPARISON WITH THEORY

The semiempirical crystal-field theory has been successful in interpreting most of the features of the optical spectrum of ruby.<sup>14</sup> This approach will be adopted here bearing in mind the inherent limitations of this theory arising from the nature of the approximations made.

The effect of an applied electric field on an optical absorption line is found by calculating the shifts in the positions of the energy levels responsible for the transition. As shown in Fig. 1, the R and B lines result from

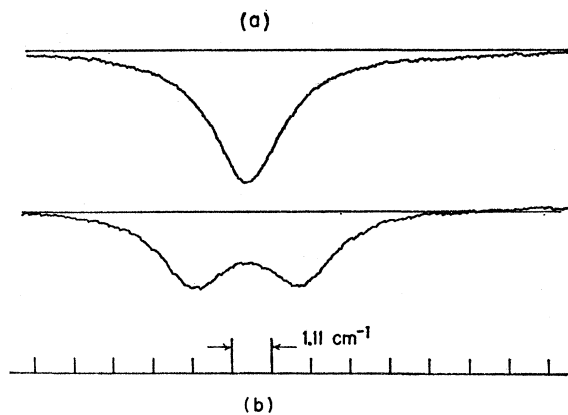


FIG. 5. Experimental recordings of the B<sub>1</sub> absorption line in ruby; (a) without electric field, E<sub>a</sub> = 0; (b) splitting in applied field, E<sub>a</sub> = 1.04 × 10<sup>5</sup> V/cm.

<sup>14</sup> S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961).

transitions from  ${}^4A_{2g}(t_{2g}^3)$  ground state to the  ${}^2E_g(t_{2g}^3)$  and  ${}^2T_{2g}(t_{2g}^3)$  excited states, respectively. Before beginning a calculation of the shift induced for each level, the symmetry of the  $\text{Cr}^{3+}$  site and the effect of this symmetry on the energy levels and wave functions of the ion must be discussed. The  $\text{Cr}^{3+}$  ion occupies a site surrounded by six oxygen atoms forming a distorted octahedron. The crystalline electrostatic potential  $V_{cr}$  due to these ligands is predominantly cubic, i.e., of  $O_h$  symmetry. It is this potential, together with the nonspherically symmetric part of the electrostatic Coulomb interaction between the ( $3d$ ) electrons, which determines the wave function assignments and the approximate positions of the energy levels of the ion. Expanding in terms of spherical harmonics in the usual manner, the cubic field potential is given by<sup>15</sup>

$$V_{cr}^c = \Delta[Y_4^0 + (10/7)^{1/2}(Y_4^3 - Y_4^{-3})], \quad (1)$$

where the  $\hat{z}$  axis, the axis of quantization, is chosen along a threefold axis of the cube. The constant  $\Delta$  is usually determined empirically. It is the energy difference between the  $t_{2g}$  and  $e_g$  orbitals in a cubic field. The distortion of the oxygen octahedron in the  $\text{Al}_2\text{O}_3$  lattice occurs along a threefold axis and the  $\text{Cr}^{3+}$  site symmetry is reduced to  $C_3$ . Additional terms must therefore be added to the crystal-field potential, and it is convenient if the  $\hat{z}$  axis is taken along the  $C_3$  axis. One additional term is the so-called trigonal-field potential proportional to  $Y_3^0$ . Together with the spin-orbital coupling it is responsible for the splitting of the  ${}^2E_g$  and  ${}^2T_{2g}$  terms.<sup>2</sup> Odd potentials, invariant under the symmetry operations of  $C_3$  can occur because the  $\text{Cr}^{3+}$  site lacks inversion symmetry. They are

$$\begin{aligned} V_{(T_{1u})_0}^{(1)} &= k_{T_1}^{(1)} r Y_1^0, \\ V_{(T_{1u})_0}^{(3)} &= k_{T_1}^{(3)} (r^3/3) [2Y_3^0 - (\frac{5}{2})^{1/2}(Y_3^{-3} - Y_3^3)], \\ V_{(T_{2u})_0} &= k_{T_2} r^3 (-i) 2^{-1/2} [Y_3^{-3} + Y_3^3], \\ V_{(A_{2u})_i} &= k_{A_2} r^3 [5^{1/2} Y_3^0 + 2^{1/2} (Y_3^{-3} - Y_3^3)]. \end{aligned}$$

The subscripts indicate that these combinations of spherical harmonics transform like  $A_{2u}$  and  $T_{1u}$  and  $T_{2u}$  in  $O_h$  symmetry. The  $k$ 's are constants to be determined later.

There exist unobserved odd states in the energy level spectrum of the  $\text{Cr}^{3+}$  ion. These states arise from the promotion of one  $3d$  electron to a  $4p$  state or in "strong-field" terms, from configurations  $t_{2g}^2 t_{1u}$  instead of  $t_{2g}^3$ . The exact energy positions of the odd states are unknown since the strong absorption of the charge-transfer band in the ultraviolet obscures any narrow absorption lines or bands which might exist. An average value of  $70\,000\text{ cm}^{-1}$  above the even  $t_{2g}^3$  or  $t_{2g}^2 e_g$  states is usually taken for the odd-state energy. The significance of the odd crystal-field potentials is their ability to mix into the predominantly even wave functions of the ob-

served energy level some of the odd character of the wave functions of the unobserved odd states.

The shift with applied electric field for an energy level with eigenfunction  $|\psi\rangle$  is given by first-order perturbation theory,

$$\Delta W = \langle \psi | V_{\text{eff}} = -e \mathbf{E}_{\text{eff}} \cdot \mathbf{r} | \psi \rangle. \quad (3)$$

The appropriate internal effective field lies somewhere between the value of the macroscopic field, appropriate for the case of a delocalized electron, and the Lorentz-corrected value, appropriate for ionic solids. In order for the matrix element in Eq. (3) to exist, the direct-product representation,  $\Gamma_\psi \times \Gamma_{V_{\text{eff}}} \times \Gamma_\psi$ , must contain the totally symmetric representation (identity representation). Since  $\mathbf{r}$  transforms like an odd representation,  $\psi$  must therefore contain some odd character in addition to its predominantly even character, or the first-order electric-field effect vanishes. From first-order perturbation theory,

$$\psi = |g\rangle - \frac{\langle u | V_{cr}^u | g \rangle | u \rangle}{W_u - W_g}, \quad (4)$$

where  $|g\rangle$  represents the even wave function of the level of interest and  $|u\rangle$  the odd wave function admixed with  $|g\rangle$  by the odd crystalline-field potentials  $V_{cr}^u$  as explained above. The shift of the energy level with applied field becomes

$$\Delta W = \frac{-2 \langle g | V_{\text{eff}} | u \rangle \langle u | V_{cr}^u | g \rangle}{W_u - W_g}. \quad (5)$$

When there exists more than one odd upper state which couples to the lower even state via  $V_{cr}^u$ ,  $\Delta W$  is written as a sum over the allowed odd states. The condition imposed above on the direct-product representation determines not only the even and odd character of the wave functions involved but also the correct representation of the odd upper state for each even lower state of interest.  $V_{\text{eff}}$  transforms like an odd representation, in particular like  $T_{1u}$  in  $O_h$ . The transformation properties of the terms in  $V_{cr}^u$  are as given in Eq. (2). Using the tables of coupling coefficients in Griffith,<sup>16</sup> the energy shifts of the pertinent levels are

$$\Delta({}^4A_{2g}) = \frac{-2 \langle {}^4A_{2g} | V_{\text{eff}} | {}^4T_{2u} \rangle \langle {}^4T_{2u} | V_{cr}^u | {}^4A_{2g} \rangle}{W({}^4T_{2u}) - W({}^4A_{2g})}, \quad (6)$$

$$\Delta({}^2E_g) = \frac{-2 \sum \langle {}^2E_g | V_{\text{eff}} | \Gamma_i \rangle \langle \Gamma_i | V_{cr}^u | {}^2E_g \rangle}{W(\Gamma_i) - W({}^2E_g)}, \quad (7)$$

where the summation is over intermediate states  $\Gamma_i = {}^2T_{2u}, {}^2T_{1u}$ .

$$\Delta({}^2T_{2g}) = \frac{-2 \sum \langle {}^2T_{2g} | V_{\text{eff}} | \Gamma_i' \rangle \langle \Gamma_i' | V_{cr}^u | {}^2T_{2g} \rangle}{W(\Gamma_i') - W({}^2T_{2g})}, \quad (8)$$

where the summation is over intermediate states  $\Gamma_i' = {}^2A_{2u}, {}^2E_u, {}^2T_{1u}, {}^2T_{2u}$ .

<sup>15</sup> C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Company, Inc., New York, 1962).

<sup>16</sup> J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, England, 1961).

The evaluation of the matrix elements in the above expressions is best accomplished by the method of irreducible tensors, as set forth by Griffith in his recent book.<sup>17</sup> In particular, the use of the  $V$  and  $W$  coefficients and the expression for the simplification of the many-electron reduced matrix elements greatly expedites the calculations, including the factorization of the matrix elements into  $V$  coefficients and three-electron reduced matrix elements and the simplification of the three-electron reduced matrix elements to one-electron reduced matrix elements. The evaluation of the one-electron reduced matrix elements using hydrogenic  $3d$ -orbital wave functions and crystal-field parameters calculated from a point-charge model<sup>18</sup> completes the calculation.

If  $a$ ,  $b$ , and  $c$  are representations and  $\alpha$ ,  $\beta$ , and  $\gamma$  the respective components of these representations, then

$$\langle a\alpha | c\gamma | b\beta \rangle = V \begin{pmatrix} abc \\ \alpha\beta\gamma \end{pmatrix} \langle a || c || b \rangle, \quad (9)$$

where  $\langle a || c || b \rangle$  is the reduced matrix element corresponding to the intrinsic factor and  $V \begin{pmatrix} abc \\ \alpha\beta\gamma \end{pmatrix}$  is the group-theoretic factor. The  $V$  coefficient is related to the more usual coupling coefficient by

$$V \begin{pmatrix} abc \\ \alpha\beta\gamma \end{pmatrix} = \lambda(c)^{-1/2} \langle ab\alpha\beta | abc\gamma \rangle,$$

where  $\lambda(c)$  is the dimension of the representation  $C$ . All of the nonzero  $V$  coefficients are tabulated by Griffith in the complex trigonal coordinate system. As given in Eq. (2), the terms in the crystalline-field potential transform like  $(T_{1u})_0$ ,  $(T_{2u})_0$ , and  $(A_{2u})_i$  where the subscripts 0, 0, and  $i$  refer to the components. When the matrix elements of terms of  $V_{cr^u}$  are factored as in (9), and the nonzero  $V$  coefficients found, the even states of interest are seen always to mix with components of odd excited states which can only be reached by  $V_{eff}$ , if  $V_{eff}$  transforms like  $(T_{1u})_0$ . If  $e\mathbf{E}_{eff} \cdot \mathbf{r}$  does not transform like  $(T_{1u})_0$ , i.e., like  $eE_{eff}z$ , then the  $V$  coefficient of  $\langle g | V_{eff} | u \rangle$  vanishes and hence any energy level shift with applied electric field vanishes. Since  $z$  was chosen along  $C_3$ , the crystal-field theory predicts no first-order electric-field effect, with the applied field perpendicular to  $C$ . This is in agreement with the absence of a detectable perpendicular effect on either the  $R$  line or  $B$  lines.

If the perturbation theory is carried to second order in  $V_{eff}$ , then nonvanishing matrix elements and thus nonvanishing shifts would appear. However, the magnitude of the available electric fields and the width of the lines involved precludes observation of the very small quadratic effect. In the microwave electric-field effect, Royce and Bloembergen<sup>11</sup> could destroy the

trigonal symmetry of the problem with a magnetic field at an angle to  $C$ , thereby mixing the spin states of the ground state to an extent sufficient to allow observation of an electric-field effect with the applied electric field at an angle to  $C$ . Unfortunately, similar mixing between the optical states would require unattainable magnetic-field strengths.

The application of Griffith's method revealed some discrepancies in the calculations of Artman and Murphy,<sup>9</sup> who reduced the three-electron wave functions by a brute force method. Artman and Murphy improperly antisymmetrize the three-electron wave functions of the odd states, and neglect the nature of the operator  $V_{cr^u}$  as the sum of three single-electron operators. Also the existence of another fractional parent for  ${}^2E_g$  besides  ${}^3T_{1g}$  is overlooked. When these errors and a numerical mistake in the simplification of a matrix element involving  ${}^2E_g$  are rectified the results of the two procedures can be made to agree.

The crystal-field theory is particularly successful in problems determined entirely by symmetry properties. Besides the absence of the perpendicular electric effect, the ratio of  $R$  and  $B$  line splitting can also be explained satisfactorily. Assume that the dominant odd term in the potential is  ${}^1Y_1$ , which transforms like  $T_{1u}$ . Put all energy denominators between even and odd states equal to  $70\,000\text{ cm}^{-1}$ . When the ratio of the shifts is formed, one-electron reduced matrix elements of  $V_{eff}$  and  ${}^1Y_1$  cancel. The coefficients of these reduced elements are determined by group theory. One finds, for the ratio of the shifts,

$$\frac{\Delta({}^2T_{2g}) - \Delta({}^4A_{2g})}{\Delta({}^2E_g) - \Delta({}^4A_{2g})} = 6.5.$$

The agreement with the experimental value of 3.7 is considered satisfactory in view of the rather drastic approximations.

The absolute energy-level shifts can each be calculated when the additional terms in the odd crystal-field potentials are included and the one-electron reduced matrix elements are computed from hydrogenic  $3d$  orbitals, the Ballhausen-Ancmon tables<sup>19</sup> and point-charge crystal-field parameters<sup>18</sup>

$$\Delta({}^4A_{2g}) = -0.193 \times 10^{-5} \eta E_A \text{ cm}^{-1}, \quad (10)$$

$$\Delta({}^2E_g) = -0.164 \times 10^{-5} \eta E_A \text{ cm}^{-1}, \quad (11)$$

$$\Delta({}^2T_{2g}) = -0.027 \times 10^{-5} \eta E_A \text{ cm}^{-1}, \quad (12)$$

where  $\eta$  is the effective-field correction factor and the applied field  $E_A$  is expressed in V/cm. The  $R$  and  $B$  line shifts predicted fall short of the observed values by an order of magnitude when  $\eta$  is near one. The predicted ratio, 5.7, is substantially the same as before, since the point-charge theory indeed assigns a larger value to  ${}^1Y_1$  than to the other odd terms.

<sup>17</sup> J. S. Griffith, *The Irreducible Tensorial Method for Molecular Symmetry Groups* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962).

<sup>18</sup> D. S. McClure, *J. Chem. Phys.* **36**, 2757 (1962).

<sup>19</sup> C. J. Ballhausen and E. M. Ancmon, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.* **31**, No. 9 (1958).

The errors made by Artman and Murphy lead them to an incorrect expression for the shift  $\Delta(^2E_g)$ . Their expression attributes the entire  $R$ -line effect to the shift  $\Delta(^4A_{2g})$ . Equations (10) and (11) show that  $\Delta(^2E_g)$  is of the same order of magnitude as  $\Delta(^4A_{2g})$ . Errors in the calculation of the matrix elements relevant to formulas on the microwave electric-field effect also exist in Artman and Murphy's work. The point-charge model does not account quantitatively for the observed shifts.

Though the agreement between Sugano and Tanabe's theoretically predicted matrix elements and the experimentally observed values in Table II appears poor, their theory is not grossly in error. The discrepancies are probably due mainly to the limited nature of their calculation.

$$\langle ^4A_{2g} | \mathcal{O} | ^2T_{2g} \rangle = \frac{\langle ^4A_{2g} | \mathcal{O} | ^4\Gamma_u' \rangle \langle ^4\Gamma_u' | V_{so} | ^2\Gamma_u'' \rangle \langle ^2\Gamma_u'' | V_{cr^u} | t_{2g}^2 e(^2T_{2g}) \rangle \langle t_{2g}^2 e(^2T_{2g}) | V_{el} | t_{2g}^3(^2T_{2g}) \rangle}{(\Delta E_1)(\Delta E_2)(\Delta E_3)}$$

must be added to Sugano and Tanabe's Eq. (5.25). Other additions consist of elements of the form

$$\langle ^4A_{2g} | \mathcal{O} | ^2T_{2g} \rangle = \frac{\langle ^4A_{2g} | \mathcal{O} | ^4\Gamma_u' \rangle \langle ^4\Gamma_u' | V_{so} | ^2\Gamma_u'' \rangle \langle ^2\Gamma_u'' | V_{cr^u} | ^2T_{2g} \rangle}{(\Delta E_1)(\Delta E_2)}$$

as suggested by Artman and Murphy.

The crystal-field theory makes successful predictions of symmetry properties. When details of the point-charge model are brought into the calculation, the absolute magnitudes of the predicted shifts are smaller than the experimentally observed shifts by an order of magnitude. The predictions of the relative transition

Electric-dipole radiation between the ( $^4A_{2g}$ ) ground level and the ( $^2T_{2g}$ ) excited state appears both parity-forbidden and spin-forbidden at first glance. Sugano and Tanabe assume that the odd crystal-field potentials admix with  $^4A_{2g}$  and with  $^4T_{2g}$  and  $^4T_{1g}$  some of the odd character of the excited odd states. This permits electric-dipole radiation to the green and blue absorption bands which "lend" some of their intensity to  $^2T_{2g}$  via the spin-orbit coupling. However, configuration mixing was entirely neglected. Coulomb interaction significantly mixes states  $t_{2g}^3(^2s+1\Gamma)$  with states  $t_{2g}^2 e \times (^2s+1\Gamma)$ , because the calculated relative positions of the energy levels in  $^2T_{2g}$  for  $B_1$ ,  $B_2$ , and  $B_3$  are inverted from their positions as calculated without mixing. These inverted positions correctly match the experimentally observed positions.<sup>20</sup> Hence, matrix elements of the form

probabilities between the Zeeman components of the  $B$  lines are also in error. The point-charge model, based on assumptions of complete noninteraction between the chromium  $3d$  electrons and the ligand oxygen electrons, is a crude approximation. A molecular-orbital theory, based on a more realistic bonding scheme between ion and ligands is still an approximation, but a finer one. The successes Royce and Bloembergen<sup>11</sup> and Lohr and Lipscomb<sup>21</sup> had with the molecular-orbital approach in the calculation of the ground-state spin splitting ( $2D$ ) and the microwave-electric field effect indicate that the application of this approach to the calculation of the aforementioned optical properties would be worthwhile.

<sup>20</sup> W. Low, J. Chem. Phys. **33**, 1162 (1960).

<sup>21</sup> L. Lohr and W. Lipscomb, J. Chem. Phys. **38**, 1607 (1963).