

## VIII. SUMMARY

In this work, one has endeavored to express the EFG tensor in ferrous compounds in terms of the  $d_\epsilon$  splitting parameters,  $\Delta_1$  and  $\Delta_2$ , and also the covalency factor,  $\alpha^2$ , which roughly governs the values of  $\langle r^{-3} \rangle$  and the spin-orbit coupling constant,  $\lambda$ . In doing so, detailed study of the complete problem, ferrous ion plus ligands, has necessarily been avoided. At the same time one has gained some insight as to the actual behavior of the complete EFG tensor, as a function of axial and rhombic field strengths, and, of course, temperature.

This study has also permitted one to make an estimate of the electric quadrupole moment of  $\text{Fe}^{57m}$  which essentially agrees with that obtained from studies of ferric compounds. At the same time, the Mössbauer

data alone permits one to estimate crystalline field splittings which are generally consistent with those obtained from other methods. Therefore, the electric quadrupole splittings measured by the Mössbauer method should prove to be a valuable aid in understanding, not only ferrous compounds, but other paramagnetic substances, as well.

## ACKNOWLEDGMENTS

The author is grateful to S. DeBenedetti, S. A. Friedberg, C. E. Johnson, and R. Cohen for stimulating talks; to R. E. Watson and A. J. Freeman for a preprint of their paper; to K. Kumar for the use of his matrix-diagonalization computer program; and to P. Zory for preliminary low-temperature Mössbauer results.

Effect of a Static Electric Field on the  $R$  Lines of  $(3d)^3$  Ions in Corundum

M. D. STURGE

*Bell Telephone Laboratories, Murray Hill, New Jersey*

(Received 6 September 1963)

The pseudo-Stark splitting of the  $R$  lines of  $\text{V}^{2+}$  and  $\text{Mn}^{4+}$  in  $\text{Al}_2\text{O}_3$  has been measured in electric fields up to 170 kV/cm. For fields parallel to the  $c$  axis the splitting is  $1.5 \times 10^{-6} \text{ cm}^{-1}/(\text{V}/\text{cm})$  for  $\text{V}^{2+}$  and  $4.5 \times 10^{-6}$  for  $\text{Mn}^{4+}$  (compare  $5.3 \times 10^{-6}$  for  $\text{Cr}^{3+}$ ). There is no detectable splitting for an electric field perpendicular to the  $c$  axis. The effect for  $\text{Mn}^{4+}$  is much greater than one would expect from the oscillator strengths of the crystal-field transitions, which, like the pseudo-Stark splitting, depend primarily on the hemihedral part of the crystal field. The large effect in  $\text{Mn}^{4+}$  appears to be principally due to the movement of the ion in the field and the consequent change in overlap with its neighbors. The principal effect for the other two ions appears to be polarization of the ion itself.

## INTRODUCTION

CONSIDER an impurity ion in a substitutional position in an otherwise perfect lattice. If the ion is at a center of symmetry, its electronic wave functions have a definite parity. In this case an odd parity perturbation, such as that due to an applied electric field, has no diagonal matrix elements, and can produce no first-order effect on the energy levels. This is a well-known result in atomic spectroscopy, where a linear Stark effect is only observed in the case of hydrogen, in which levels of odd and even parity are "accidentally" degenerate. If the ion is not at a center of symmetry, on the other hand, parity is no longer a good quantum number, and a shift of the energy level linear in electric field can, in principle, occur. It is usually sufficiently accurate to treat the deviation from inversion symmetry as a small perturbation mixing levels of well defined parity.

The corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) lattice has  $D_{3d}$  symmetry, but an individual  $\text{Al}^{3+}$  ion is not at a center of symmetry and its site has only  $C_3$  symmetry (see Fig. 1) sites of type  $a$  and  $b$  being connected by inversion through the

point  $d$ . An electric field applied along the  $c$  axis acts in equal and opposite senses on ions at the two sites, shifting their energy levels in opposite directions. Thus, an apparent splitting of a level can be produced, called by Kaiser, Sugano, and Wood<sup>1</sup> (who first observed the effect optically) the pseudo-Stark splitting. This paper reports an extension of their measurements on ruby (chromium-doped corundum) to the isoelectronic ions  $\text{V}^{2+}$  and  $\text{Mn}^{4+}$  in the same lattice. The size of the splitting varies by a factor of 30 through the isoelectronic sequence, although the optical spectra are in other respects very similar. Comparison of the results with simple models shows that we have to take into account the change in covalency produced by the motion of the ion in the electric field in order to explain them.

## EXPERIMENTAL

Specimens of corundum containing  $\text{V}^{2+}$  (concentration of the order one part in  $10^5$ ) were prepared by

<sup>1</sup> W. Kaiser, S. Sugano, and D. L. Wood, Phys. Rev. Letters **6**, 605 (1961).

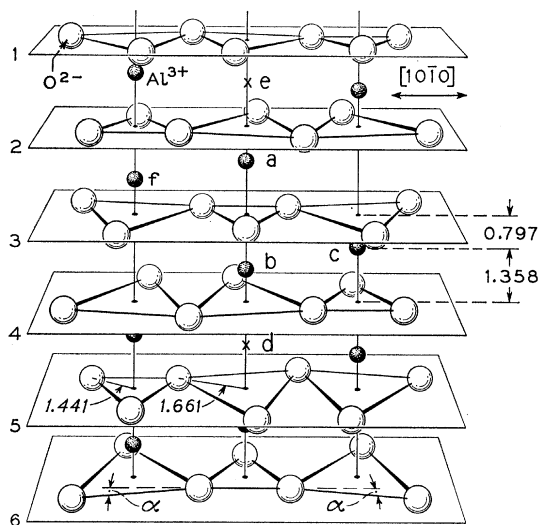


FIG. 1. The  $\text{Al}_2\text{O}_3$  lattice [from S. Geschwind and J. P. Remeika, Phys. Rev. **122**, 757 (1961)]. The  $\text{Al}^{3+}$  ions are in octahedral oxygen coordination, the octahedron being distorted, reducing the point symmetry at the  $\text{Al}^{3+}$  ion to  $C_3$  ( $C_{3v}$  if the angle  $\alpha$  were zero; it is actually about  $2^\circ$ ). Sites of type  $a$  and  $b$  are connected by inversion. Site  $d$  is a center of inversion and has  $C_{3i}$  symmetry, but is not normally occupied.

$\gamma$  irradiation of Linde vanadium corundum ( $\text{Al}_2\text{O}_3: \text{V}^{3+}$ ) as described previously.<sup>2,3</sup> Corundum containing  $\text{Mn}^{4+}$  was obtained from Linde via Dr. S. Geschwind; it is compensated in the starting material with  $\text{MgO}$ .<sup>4</sup> Slabs a few mm on the side and about 0.7-mm thick were mounted between electrodes as shown in Fig. 2. Undoped corundum surrounding the specimens ensured a reasonably uniform electric field. The electric field was limited by the onset of surface breakdown to about 160 kV/cm. Aquadag electrodes were painted on. The

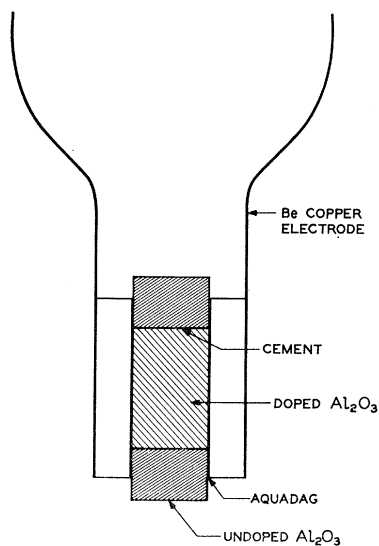


FIG. 2. Method of mounting specimens for electric-field-effect measurements (not to scale).

<sup>2</sup> J. Lambe and C. Kikuchi, Phys. Rev. **118**, 71 (1960).

<sup>3</sup> M. D. Sturge, Phys. Rev. **130**, 639 (1963).

<sup>4</sup> S. Geschwind, P. Kisliuk, M. P. Klein, J. P. Remeika, and D. L. Wood, Phys. Rev. **126**, 1684 (1962).

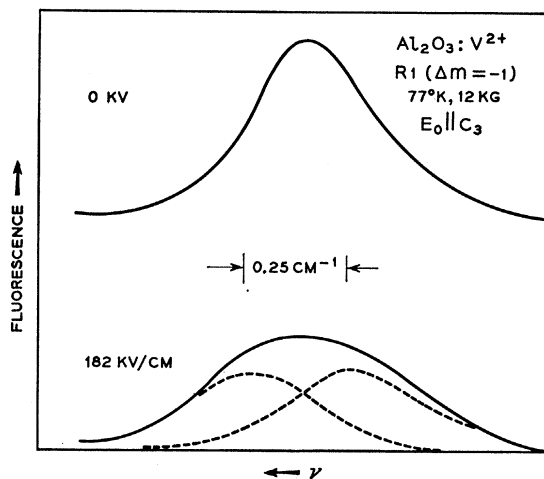


FIG. 3. Effect of an electric field parallel to the  $c$  axis on one Zeeman component of the  $R_1$  line of  $\text{Al}_2\text{O}_3: \text{V}^{2+}$ . A magnetic field of 12 kG brings the two  $\Delta m = 1$  components of the  $R_1$  doublet (split by  $0.32 \text{ cm}^{-1}$  in zero field) into approximate coincidence.

$R$  lines were observed in fluorescence with a Jarrell-Ash 1.8-m scanning spectrometer, using an RCA-7102 photomultiplier. Fluorescence was excited by tungsten filament projector lamps, filtered through copper sulphate solution. Both  $R$  lines were measured, the  $R_1$  and  $R_2$  lines being, respectively, at  $11\,679.2$  and  $11\,691.5 \text{ cm}^{-1}$  for  $\text{V}^{2+}$  and  $14\,782$  and  $14\,862 \text{ cm}^{-1}$  for  $\text{Mn}^{4+}$ .

In the case of  $\text{V}^{2+}$ , the splitting produced by the electric field is less than the ground-state splitting of  $0.32 \text{ cm}^{-1}$ , and was barely resolved even at the highest fields. To avoid errors due to overlapping components of the line, a magnetic field of 11 kG was applied parallel to the  $c$  axis. Because of the difference between the  $g$  factors in the upper and lower states, the magnetic field brings two Zeeman components originating in different zero-field components into approximate coincidence, providing an initially unsplit line to be split by the electric field. As the apparent splitting is due to bodily shifts of the levels of two different ions, the Paschen-Back effect introduces no complication.

The effect of an electric field on the  $R_1$  line of  $\text{V}^{2+}$  is shown in Fig. 3. The splitting is barely resolved, but the curve can be analyzed into two components as shown, and the splitting determined to an accuracy of about  $0.05 \text{ cm}^{-1}$ . The splitting is shown as a function of electric field in Fig. 4.

The  $R$  lines of  $\text{Mn}^{4+}$  are much broader,  $2.5 \text{ cm}^{-1}$  in the best specimen at  $77^\circ\text{K}$ , and the ground-state splitting of  $0.39 \text{ cm}^{-1}$  is completely obscured. However, the splitting in an electric field parallel to the  $c$  axis is so large that it is easily resolved (Fig. 5). The splittings of the  $R_1$  and  $R_2$  lines are shown as a function of field in Fig. 6.

When the electric field is approximately parallel to a two fold  $[11\bar{2}0]$  axis there is no detectable effect on the  $R$  lines of vanadium. Those of manganese are

broadened by about  $0.2 \text{ cm}^{-1}$  in a field of  $150 \text{ kV/cm}$ , an amount consistent with the misorientation of the specimen (about  $4^\circ$ ).

### THEORY

#### a. "Electronic" Effect

As pointed out by Royce and Bloembergen,<sup>5</sup> in connection with the microwave-electric effect in ruby, there are two contributions to the effect of an electric field on the levels of an impurity ion. They call these the "electronic" and "ionic" effects, the first being the shift of the energy levels due to polarization of the individual ion, which is regarded as fixed, and the second, the effect of movement of the ion relative to its neighbors. Phenomenologically these are indistinguishable, and the second can be included in the first by an appropriate choice of local field; but microscopically they are quite distinct, and Royce and Bloembergen have demonstrated the dominance of the "ionic" term in the microwave-electric effect in ruby.

Let us first consider the "electronic" term, which has been treated previously by Artman and Murphy.<sup>6</sup> We will give a simplified version of their argument, making only the minimum assumptions necessary to achieve a result. The electronic term is closely related to the oscillator strength for electric-dipole transitions within the  $(3d)^3$  configuration. The general energy-level schemes for the three  $(3d)^3$  ions, as determined spectroscopically, are shown in Fig. 7. A greatly simplified energy-level scheme, applicable to all three ions and retaining the general features of Fig. 7, is shown in Fig. 8. The odd parity states, which could be states of the  $(3d)^24p$  configuration of the ion but are more probably "charge-

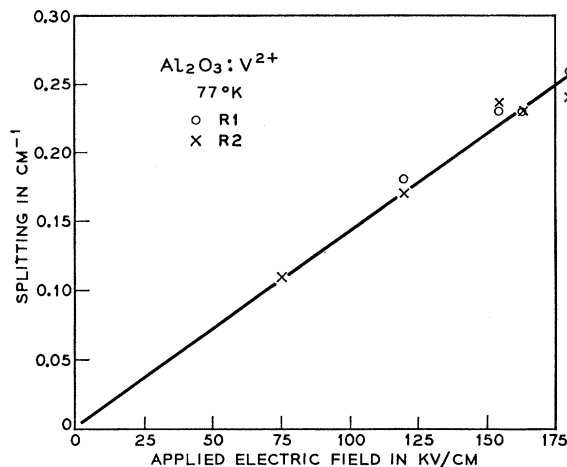


FIG. 4. Splitting of the  $R_1$  and  $R_2$  lines of  $\text{Al}_2\text{O}_3:\text{V}^{2+}$  as a function of applied electric field.

<sup>5</sup> E. B. Royce, U. S. Office of Naval Research, Tech. Report No. 379, Contract No. 372-012 (unpublished); E. B. Royce and N. Bloembergen, Phys. Rev. **131**, 1912 (1963).

<sup>6</sup> J. O. Artman and J. C. Murphy, Proceedings of the First Conference on Paramagnetic Resonance, Jerusalem, 1962 (to be published); J. Chem. Phys. **38**, 1544 (1963).

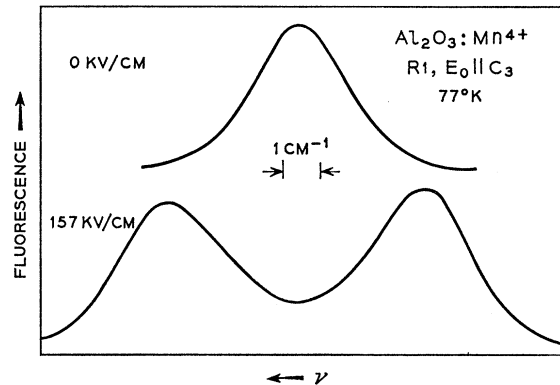


FIG. 5. Effect of an electric field parallel to the  $c$  axis on the  $R_1$  line of  $\text{Al}_2\text{O}_3:\text{Mn}^{4+}$ . Note the change in scale. The ground-state splitting of  $0.39 \text{ cm}^{-1}$  is considerably less than the width of the line.

transfer" states in which an electron is transferred from a predominantly ligand bonding orbital to an antibonding orbital of predominantly  $d$  character, are lumped together into a single quartet state at energy  $W_3$ , from the ground state. Doublet states are ignored, and the precise nature of the odd parity states is irrelevant to the present argument. The electric-dipole matrix element  $P_{03}$  for transitions from the  ${}^4A_{2g}$  ground state to the odd parity state  ${}^4\Gamma_u$  is given by

$$P_{03} = \langle {}^4A_{2g} | e\mathbf{r} | {}^4\Gamma_u \rangle. \quad (1)$$

Some of the  ${}^4\Gamma_u$  is mixed into the even parity states by the odd component of the crystal field  $V_u$  (sometimes called the hemihedral field). This mixture occurs for all the states but it could be expected to be most important for the excited states, and mixing into the ground state will be neglected for simplicity. The electric-dipole matrix element for transitions from the ground state to the  ${}^4T_{2g}$  excited state at  $W_2$  (i.e., the

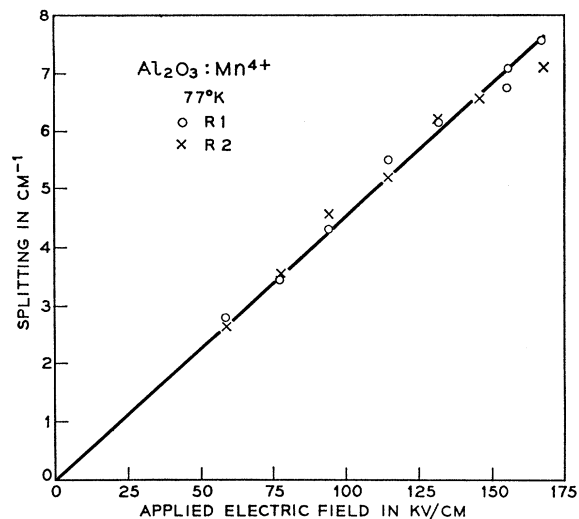


FIG. 6. Splitting of the  $R_1$  and  $R_2$  lines of  $\text{Al}_2\text{O}_3:\text{Mn}^{4+}$  as a function of applied electric field.

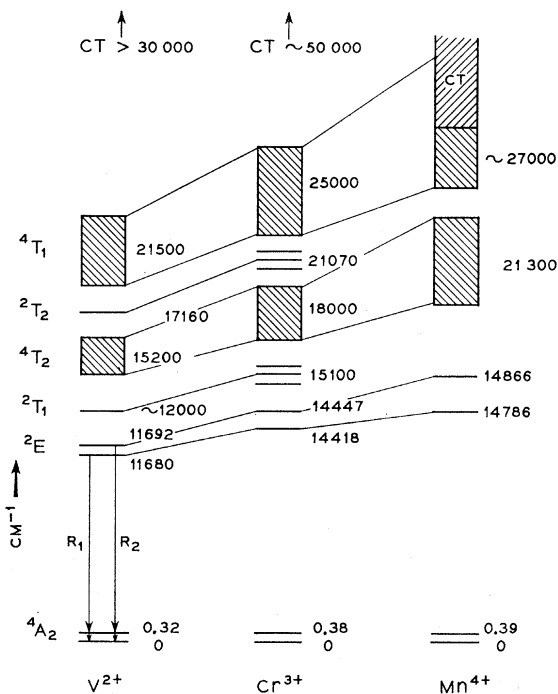


FIG. 7. Energy levels of the three  $(3d)^3$  ions in  $\text{Al}_2\text{O}_3$ , as determined from their optical spectra. "CT" refers to the strong absorption band normally attributed to parity allowed charge-transfer transitions.

first absorption band) is given by

$$P_{02} = \langle {}^4A_{2g} | \epsilon r | {}^4T_{2g} \rangle = UP_{03} / (W_3 - W_2), \quad (2)$$

where  $U = \langle {}^4T_{2g} | V_u | {}^4\Gamma_u \rangle$ . It is likely that  $V_u$  is predominantly of  $T_{1u}$  symmetry,<sup>7</sup> in which case  $P_{02}$  is predominantly  $\sigma$  polarized, as observed.<sup>8</sup>

The splitting of the  $R$  lines by an electric field results from shifts of both the initial and final states of the transition. Artman and Murphy<sup>6</sup> showed by reducing to one-electron matrix elements that the shift of the  ${}^2E$  level is  $-\frac{1}{3}$  of that of the  ${}^4A_2$ , if the  $\Gamma_u$  are made up of  $t_{1u}$  ( $p$ -like) orbitals; neglecting it will anyway

<sup>7</sup> S. Sugano and Y. Tanabe, J. Phys. Soc. Japan, **13**, 880 (1958).

<sup>8</sup> It turns out to be experimentally more convenient to consider the oscillator strength of the  $R$  lines, which are due to transitions between the  ${}^4A_{2g}$  ground state and the  ${}^2E_g$  state at  $W_1$ . This transition borrows its intensity from the transition to  ${}^4T_{2g}$  via the spin-orbit coupling  $V_{so}$ , and its matrix element is given by (Ref. 7)

$$P_{01} = \langle {}^4A_{2g} | \epsilon r | {}^2E_g \rangle = \frac{2}{\sqrt{3}} \zeta' UP_{03} / (W_3 - W_2)(W_2 - W_1),$$

where  $\zeta' (= \frac{1}{3}\sqrt{3} \langle {}^2E_g | V_{so} | {}^4T_{2g} \rangle)$  is the one-electron spin-orbit coupling parameter. What we actually measure is the integrated absorption of a band or line, conventionally represented by the oscillator strength  $f_{ij}$ , and we must include absorption due to vibrationally assisted transitions as well as that in the no-phonon line

$$f_{ij} = 4.3 \times 10^{-7} \frac{n}{\rho^2} \int \epsilon_{ij} d\nu = \frac{2\pi m}{3\hbar^2 c} W_{ij} |P_{ij}|^2.$$

Here  $\epsilon_{ij}$  is the molar extinction coefficient for the transition  $i \rightarrow j$ ,  $n$  the refractive index, and  $\rho$  the local field correction  $[(n^2+2)/3]$  for the Lorentz case, 1 for an extended center].

make no essential difference to the argument. They show that the shift  $\Delta$  of the  ${}^4A_2$  level produced by an electric field  $F$  parallel to the  $c$  axis is<sup>9</sup>

$$\Delta = 2\rho_0 F U' P_{03}^{||} / W_3, \quad \text{where } U' = \langle {}^4A_{2g} | V_u | \Gamma_u \rangle. \quad (3)$$

Here  $\rho_0$  is the local field correction for a static field, and  $P_{03}^{||}$  is the component of  $P_{03}$  parallel to the  $c$  axis. The charge-transfer band contains a number of states of all possible symmetries not differing greatly in energy. We can thus take the same  $W_3$  in Eqs. (2) and (3), and take  $U'/U$  as a constant near unity.

The  ${}^4T_2$  bands and the  $R$  lines are predominantly  $\sigma$  polarized, so it is the perpendicular moment  $P_{03}^\perp$  which enters the formulas for  $f_{01}$  and  $f_{02}$ . On the other hand, it is  $P_{03}^{||}$  which is important in the electric effect; this is dominant in the  ${}^4T_1$  band. For  $\text{Cr}^{3+}$ ,  $P_{03}^{||}$  and  $P_{03}^\perp$  are roughly equal; the situation is rather obscure in the cases of  $\text{V}^{2+}$  and  $\text{Mn}^{4+}$  because of experimental difficulties, but the same appears to be true. We therefore assume that the ratio  $P_{03}^{||}/P_{03}^\perp$  does not vary greatly through the isoelectronic sequence (McClure<sup>10</sup> and Artman and Murphy<sup>6</sup> treat  $P_{03}$  as isotropic). If we now take  $W_3$  to be the energy of the charge-transfer bands in Fig. 7, and assume the local field correction  $\rho$  to be independent of the impurity ion, we can calculate relative values of  $U|P_{03}^{||}|/W_3$  for the isoelectronic sequence. The results are given in arbitrary units in Table I. If  $\rho_0$  is also constant we would expect  $\Delta/F$  to be proportional to  $UP_{03}^{||}/W_3$ . Table I shows that this is true for  $\text{V}^{2+}$  and  $\text{Cr}^{3+}$ , but out by a factor of 8 for  $\text{Mn}^{4+}$ . This seems too large a discrepancy to be accounted for by errors in the assumptions (in particular the assumption that  $\rho_0$  is constant).

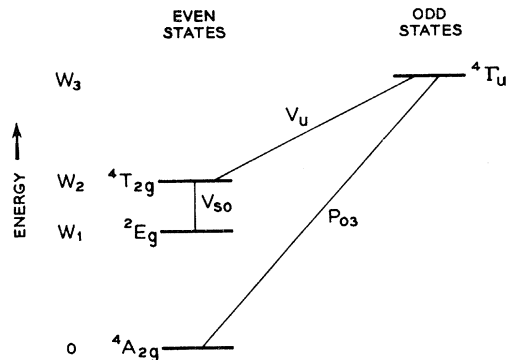


FIG. 8. Simplified energy-level scheme for a  $d^3$  ion. The transition from the quartet ground state 0 to the doublet state 1 borrows its intensity from the spin-allowed transition  $0 \rightarrow 2$  via the spin-orbit coupling  $V_{so}$ . The parity-forbidden transition  $0 \rightarrow 2$  in turn borrows its intensity from the allowed transition  $0 \rightarrow 3$  via the odd component of the crystal field  $V_u$ .  $P_{03}$  is the electric dipole matrix element for the allowed transition.

<sup>9</sup> Terms containing matrix elements of the form  $\langle {}^2E | V_u | {}^2\Gamma_u \rangle$  are neglected, as they appear to make little or no contribution to the oscillator strength of the  $R$  lines. According to C. S. Naiman [Symposium on Optical Masers, New York, April, 1963 (unpublished)] they could be important for the very high-energy doublet states.

<sup>10</sup> D. S. McClure, J. Chem. Phys. **36**, 2757 (1962).

The absolute magnitude of the "electronic" term cannot be calculated accurately because we do not know  $\rho_0$ ,  $U'/U$ , or  $P_{03}^{11}/P_{03}^1$ . Taking the Lorentz value for  $\rho_0$  (probably an overestimate) and putting  $P_{03}^{11} = P_{03}^1$ , we find  $2\Delta/F = 24 U'/U \text{ cm}^{-1}/(\text{MV}/\text{cm})$  for  $\text{Cr}^{3+}$ . The experimental value is 5.3, so  $U'/U \sim 0.2$ , which is the right order of magnitude, as the  ${}^4T_{2g}$  state can interact through  $V_u$  with two or three times as many states as can the  ${}^4A_{2g}$ .

We can conclude that the electronic effect can account satisfactorily for the effect of an electric field on the  $R$  lines of  $\text{V}^{2+}$  and  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$ , but completely fails to account for the very large effect in the case of  $\text{Mn}^{4+}$ .

### b. "Ionic" Effect

Under the influence of an external electric field, the positively charged impurity ion will, in general, move relative to its negatively charged neighbors, altering the overlap of its electronic wave functions with those of the ligands. A rough estimate of the distance moved by the  $\text{Al}^{3+}$  sublattice relative to the  $\text{O}^{2-}$  sublattice can be got from the static dielectric constant of  $\text{Al}_2\text{O}_3$  (11.5 for  $E||c$ ); we find  $2 \times 10^{-12} \text{ cm}$  for 100 kV/cm. This is a reasonable estimate for  $\text{Cr}^{3+}$ ; however, the distance moved by the differently charged ions  $\text{V}^{2+}$  and  $\text{Mn}^{4+}$  could be rather different.

It was possible to treat the "electronic" effect quantitatively, making reasonable assumptions. This is not possible for the "ionic" effect, and we have to content ourselves with some qualitative observations.

The energy of the  ${}^2E \rightarrow {}^4A_2$  transition is primarily determined by the exchange interaction within the metal ion (approximately  $9B+3C$  in terms of the Racah parameters).<sup>11</sup> For reasons which are still not clearly understood the exchange interaction is always reduced in the solid relative to the free ion, as is the spin-orbit coupling. Qualitatively this can be described as a reduction of the  $d$ -electron density on the metal ion, due either to covalency (sharing of the  $d$  electrons with neighboring ions) or to radial expansion of the  $d$ -wave function due to shielding by the ligand electrons.<sup>12</sup> It is not clear which of these is the dominant effect, but calculations of the first effect give little or no reduction.<sup>13</sup> In either case, the sensitivity of the exchange interaction to motion of the ion will go up rapidly, probably exponentially, with overlap, as measured by the reduction of  $B$  and  $C$ . Estimates of the reduction in  $B$  can be made from the spectroscopic data if the ratio  $B/C$  is assumed constant; we find

<sup>11</sup> Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 766 (1954).

<sup>12</sup> W. Marshall and R. Stuart, Phys. Rev. **123**, 2048 (1961).

<sup>13</sup> Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **11**, 864 (1956). S. Sugano and R. G. Shulman [Phys. Rev. **130**, 517 (1963)] have successfully calculated the reduction in  $B$  for  $\text{Ni}^{2+}$  in  $\text{KNiF}_3$ , without invoking radial expansion of the wave function, but the reduction in  $B$  is much less than in the (3d)<sup>3</sup> ions discussed here.

TABLE I. Hemihedral fields and electric-field effects in  $\text{Al}_2\text{O}_3$ .

	$\text{V}^{2+}$	$\text{Cr}^{3+}$	$\text{Mn}^{4+}$
$f_{01}^a$	$3 \times 10^{-8}$	$6 \times 10^{-7}$	$1.2 \times 10^{-6}$
$f_{02}$	...	$4 \times 10^{-4}$	$2 \times 10^{-3}$
$U P_{03} /W_3^b$	1.5	3.5	5.0
$U P_{03} /W_3^c$	...	5.5	6.0
$2\Delta/F \text{ (cm}^{-1}/(\text{MV}/\text{cm}))$	$1.5 \pm 0.3$	$5.3^d$	$45 \pm 2$

<sup>a</sup>  $f_{01}$  includes the vibrational satellites of the  $R$  lines; for  $\text{V}^{2+}$  it is calculated from the fluorescent lifetime, no absorption data being available, and is therefore an upper limit.

<sup>b</sup> Calculated from  $f_{01}$  and normalized to agree with  $2\Delta/F$  for  $\text{V}^{2+}$ . The following values are taken for  $f'$ :  $120 \text{ cm}^{-1}$  for  $\text{V}^{2+}$  (Ref. 3),  $170 \text{ cm}^{-1}$  for  $\text{Cr}^{3+}$  [S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961)],  $200 \text{ cm}^{-1}$  for  $\text{Mn}^{4+}$  (Ref. 4).  $W_3$  is taken as  $50\,000 \text{ cm}^{-1}$  for  $\text{V}^{2+}$  (the answer is insensitive to the exact value of  $W_3$  so long as it is large),  $50\,000 \text{ cm}^{-1}$  for  $\text{Cr}^{3+}$  and  $30\,000 \text{ cm}^{-1}$  for  $\text{Mn}^{4+}$ .

<sup>c</sup> Calculated from  $f_{02}$ .

<sup>d</sup> See Ref. 1.

$B/B_0 = 0.78$  for  $\text{V}^{2+}$ ,<sup>14</sup>  $0.76$  for  $\text{Cr}^{3+}$ , and  $0.66$  for  $\text{Mn}^{4+}$  ( $B_0$  is the free-ion value). The difference in  $B/B_0$  between  $\text{V}^{2+}$  and  $\text{Cr}^{3+}$  is not significant, so we would expect them to have much the same change in  $B$  for a given ionic displacement, while  $\text{Mn}^{4+}$  would have a much bigger effect. We would not expect  $\text{Cr}^{3+}$  to be displaced three times as far as  $\text{V}^{2+}$  by the same electric field, so it does look as if the "electronic" effect, rather than the "ionic" effect, gives the best explanation of the results for  $\text{V}^{2+}$  and  $\text{Cr}^{3+}$ . This does not mean that displacement of the ion does not occur; only that the change in  $B$  produced by the displacement is not the major contribution to the splitting. Thus, our conclusion is not inconsistent with that of Royce and Bloembergen,<sup>5</sup> who find that the "ionic" term is dominant in the microwave electric effect in ruby. The difference is probably due to the different orders of magnitude of the "electronic" effect in the two cases; in the optical case second-order perturbation theory is sufficient to produce an effect, while in the microwave case fourth-order theory is required.

We would expect displacement towards the nearest oxygen triangle to increase the screening and covalency, and reduce  $B$ ; on the other hand, this displacement increases the microwave splitting  $|2D|$ . The relative signs of the optical and microwave effects are thus the same as calculated for the "electronic" effect by Artman and Murphy.<sup>6</sup> The relative signs of the effects could in principle be measured in a microwave-optical experiment.

### CHARGE COMPENSATION

No mention has so far been made of charge compensation, which must occur in the cases of  $\text{V}^{2+}$  and  $\text{Mn}^{4+}$ . As far as  $\text{V}^{2+}$  is concerned, the method of preparation of the specimens probably precludes local charge compensation. The crystal as grown contains only  $\text{V}^{3+}$  which presumably has no charge defect associated with it. Irradiation with  $\gamma$  rays produces electron-hole pairs

<sup>14</sup> This is larger than the value of 0.73 quoted in Ref. 3, which was based on the positions of the no-phonon lines in the spectrum; all the estimates here are based on the band maxima.

throughout the crystal, and so long as the electron diffusion length is more than a few atomic spacings, any charge-compensating center will be produced too far from the  $V^{2+}$  to affect it appreciably. This conclusion is confirmed by the experimental fact that no deviation from trigonal symmetry, such as would be produced by a neighboring defect off the  $c$  axis, is seen in the microwave<sup>2</sup> or optical spectrum.<sup>3</sup>

The case of  $Mn^{4+}$  is more complicated, as the charge-compensating center ( $Mg^{2+}$ ) is introduced during growth and is necessary to produce the required charge state of manganese. While the microwave and optical spectra show the principal  $Mn^{4+}$  site to have trigonal symmetry,<sup>4</sup> the most likely place for the compensating  $Mg^{2+}$  ion is the nearest  $Al^{3+}$  site, which is on the  $c$  axis and therefore leaves the symmetry unaltered. There seems to be no evidence on this point though the view is sometimes expressed that the many weak lines observed in the optical spectrum to the blue of the  $R$  lines are due to locally charge-compensated sites.<sup>15</sup> The

<sup>15</sup> Four of these lines were studied at 4°K with an ac lock-in technique which permits the measurement of unresolved splittings.

presence of local charge compensation not affecting the symmetry of the center would not affect the argument regarding the relative size of the "electronic" effect, as the contribution to  $V_u$  from the charge defect would affect the oscillator strength as well as the electric field splitting; it might affect the static local field correction, but surely not by a factor of 8. On the other hand, an exceptionally large "ionic" effect for  $Mn^{4+}$  could perhaps be due to a change in the nearest-neighbor geometry produced by a local defect. Thus, the present results are certainly consistent with, though they do not require, local charge compensation.

#### ACKNOWLEDGMENTS

I am grateful to Professor N. Bloembergen, Dr. P. S. Pershan, Dr. S. Geschwind, and Dr. D. L. Wood for helpful discussions; and to J. W. Ammons and K. A. Ingersoll for technical assistance.

The lines at 14 908 and 14 914  $cm^{-1}$  are split  $18 \pm 5 cm^{-1}/(MV/cm)$ ; the line at 14 976  $cm^{-1}$  is split  $13 \pm 2 cm^{-1}/(MV/cm)$ . The line at 15 087  $cm^{-1}$ , which is much sharper than the others (it is 1  $cm^{-1}$  wide at 4°K) is apparently not split, the limit of detection being 2  $cm^{-1}/(MV/cm)$ .

## Infrared Absorption of Magnesium Stannide

HERBERT G. LIPSON AND ALFRED KAHAN

*Air Force Cambridge Research Laboratories, Office of Aerospace Research, Bedford, Massachusetts*

(Received 27 August 1963)

Infrared transmission and reflection measurements have been made on  $n$ - and  $p$ -type semiconducting  $Mg_2Sn$  single crystals of different impurity concentrations between 2 and 30  $\mu$ , at temperatures ranging from 15 to 296°K. At incident energies less than 0.22 eV, strong free-carrier absorption is present; with  $\alpha$  as the absorption coefficient and  $\lambda$ , the wavelength, this may be expressed as  $\alpha = c\lambda^{3/2}$  at all temperatures where acoustical mode lattice scattering predominates. The absorption spectra due to other mechanisms has been analyzed after subtraction of the  $\lambda^{3/2}$  free-carrier dependence. At energies of 0.22 eV and above, the rapid increase in absorption is attributed to the intrinsic edge. From the energy dependence of the absorption coefficient in the edge region, the mechanism of indirect transitions between the valence and conduction band can be established, with a phonon energy of 0.008 eV. A band in the 0.08 to 0.22 eV energy range present at all temperatures in  $n$ -type and above 196°K in  $p$ -type samples is interpreted in terms of transitions between two conduction band minima separated by 0.165 eV at 15°K. Below 0.06 eV an additional sharp rise in absorption occurs. A peak in this absorption at 26  $\mu$  may correspond to a second harmonic of the fundamental lattice vibration which is centered around 53  $\mu$ . An energy band picture for  $Mg_2Sn$  is suggested, and conductivity ( $m_n^* = 0.15m$ ,  $m_h^* = 0.10m$ ), and density of states ( $m_n^* = 1.2m$ ,  $m_p^* = 1.3m$ ) effective masses are calculated.

#### INTRODUCTION

MAGNESIUM stannide is a compound semiconductor of the II-IV series which crystallizes in  $CaF_2$  structure, with Mg occupying the  $F^-$  sites and Sn occupying the  $Ca^{++}$  sites. This lattice is face-centered cubic with respect to Sn and contains a cube of eight atoms of Mg symmetrically located within the tin lattice. The electrical properties of  $Mg_2Sn$  have been the subject of a number of investigations,<sup>1-3</sup> but relatively

little information is available on the optical properties<sup>3,4</sup> and their relation to the band structure.<sup>5</sup> With the acquisition of single crystals whose electrical measurements indicate high purity, an investigation of their

<sup>1</sup> U. Winkler, *Helv. Phys. Acta.* 28, 633 (1955).

<sup>2</sup> H. P. R. Frederikse, W. R. Hosler, and D. E. Roberts, *Phys. Rev.* 103, 67 (1956).

<sup>3</sup> W. D. Lawson, S. Neilsen, E. H. Putley, and V. Roberts, *J. Electron.* 1, 203 (1955).

<sup>4</sup> R. F. Blunt, H. P. R. Frederikse, and W. R. Hosler, *Phys. Rev.* 100, 663 (1955).

<sup>5</sup> J. Della Riccia, in *Proceedings of the International Conference on Semiconductor Physics, 1960* (Czechoslovak Academy of Science, Prague, 1961), p. 51.