

energies of excitons to the various centers associated with the lines  $I_1$ ,  $I_2$  and  $I_3$  (after Thomas and Hopfield<sup>3</sup>). As can be seen from this table, the exciton binding energy is greater than the exciton-to-center binding energy for all the complexes; consequently, the complex should dissociate before the exciton dissociates. On the other hand, a different situation may be operative for the  $I_6$  line (take the 5068 component, e.g.). Assuming that this line arises from an exciton complex, one observes that the exciton-to-center binding energy (0.109 eV) is greater than the exciton binding energy (0.028 eV); hence, the exciton would dissociate before the complex could undergo a mole-

TABLE II. Binding energies of excitons to various centers.

Complex	Line ( $\text{\AA}$ )	Energy (eV)	Binding energy: exciton to center (eV)
Neutral acceptor	$I_1(4888)$	2.53595	0.018
Neutral donor	$I_2(4867)$	2.5471	0.007
Ionized donor	$I_3(4861)$	2.5499	0.001

Note: The ground-state exciton  $\Gamma_6$  (4857  $\text{\AA}$ ) has a binding energy (hole to electron) of 0.028 eV.

cular-like dissociation. Such a situation might account for the observed polarization and magnetic field behavior of  $I_6$ .

## Quadrupole Interactions of Vanadium and Manganese in Corundum\*

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Hyperfine fields and quadrupole interactions have been measured for divalent vanadium and quadrivalent manganese in corundum by electron-nuclear-double-resonance (ENDOR) spectroscopy. This work, together with previous work on trivalent chromium, provides a study of electronic properties of dilute impurities in an isoelectronic sequence. The results show that the internal magnetic field due to the paramagnetic electrons is the same for all ions and equal to about  $-200$  kG. The quadrupole interaction is  $-0.021$  Mc/sec for  $V^{2+}$  and  $0.138$  Mc/sec for  $Mn^{2+}$ . This is to be compared with a value for the host aluminum nuclei of  $0.180$  Mc/sec. A theory based on the point-charge model is unable to account for this result in any simple way. The possible influence of covalent bonds on the observed field gradients is discussed.

### INTRODUCTION

THE system of transition-ion impurities in corundum has been the subject of many experimental and theoretical investigations.<sup>1</sup> The interest in this system is understandable since ruby, the best known example, was the first solid material to be used both for the maser and for the laser. Considerable progress has been achieved in the understanding of the optical and microwave absorption of impurity ions in this material. For the case of ruby the basic analysis of the optical spectrum was done by Sugano and Tanabe.<sup>2</sup> Using crystal-field theory, enlarged parametrically to include covalency effects, they were able to explain the observed optical spectra, at least as regards the position of the spectral lines. The calculation of transition probabilities, together with some of the subtler points of the structure of the energy levels, was somewhat less satisfactory. For example, a straightforward calculation of the splitting of the ground state gave the wrong sign. Including certain

third-order terms in the perturbation expression gave the right sign, but it was obvious that the theory, when applied to such fine details of the spectra, was inadequate.

In recent years a number of experiments have been directed to the determination of the magnitude of the trigonal component of the crystalline field. The measurements of Weakliem and McClure<sup>3</sup> attempted a determination of the trigonal field through measurements of splittings in the optical spectra of a series of transition metal ions in corundum. Their results indicate that the trigonal field is different for different ions. Since the trigonal field should only depend on the environment of an ion and not on the ion itself, they postulated that impurity ions do not assume a true substitutional position in the  $Al_2O_3$  lattice, but rather are slightly displaced along the "c" axis. This displacement varies with ion, causing the observed variation of the trigonal field. Such a distortion does not lower the symmetry, since the symmetry at the substitutional position is only  $C_3$ , the same symmetry as any position on the "c" axis.

\* A preliminary account of this work was presented at the March 1963 meeting of the American Physical Society. See Bull. Am. Phys. Soc. 8, 212 (1963).

<sup>1</sup> For a general review of the subject see the article by D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 399.

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

<sup>3</sup> H. A. Weakliem and D. S. McClure, Suppl. J. Appl. Phys. 33, 347 (1962). See also the article by D. S. McClure, J. Chem. Phys. 36, 2757 (1962).

Geschwind and Remeika<sup>4</sup> have performed measurements on a series of impurity ions in corundum and have determined the trigonal field for these ions. In this case they carried out precise measurements of the  $g$  shift from the paramagnetic-resonance spectra. The anisotropy in the  $g$  value is due to the fact that different excited states are coupled to the ground state in the parallel case than in the perpendicular case. In fact, the excited states so coupled are split by the trigonal field, so that the anisotropy of the  $g$  shift is a measure of the trigonal field splitting of the excited state. Their results showed a rather constant value for the trigonal field over a series of ions, which implied that the ions do assume a true substitutional position. There were two notable exceptions to their findings, that of  $\text{Cu}^{3+}$  and  $\text{Ni}^{2+}$ . For these ions they obtained the wrong sign of the trigonal field. Recent work of Kamimura<sup>5</sup> has explained these anomalous results by invoking distortion in the covalent bonds of the impurity ion and has implied that the correct value of the trigonal field for these ions is the same as for the other ions.

ENDOR measurements on ruby performed at this laboratory provided additional information on the question of the position of the impurity ion.<sup>6</sup> In these experiments the hyperfine parameters of the aluminum ions neighboring a chromium ion impurity were obtained. The quadrupole interaction of the aluminum ion which is the nearest neighbor to the impurity was 50% higher than an ion in the host material. One can explain this result on the point-charge model of the lattice if one assumes that this aluminum ion and the chromium ion impurity are displaced away from each other by 0.2 Å. In other words, the chromium ion is 0.1 Å away from its true substitutional position. The numerical values quoted should not be taken seriously since the motion of all other ions is ignored, but this calculation shows that a small amount of distortion can explain the observed effects. The value of the displacement required, 0.1 Å, is of the same order as the amount postulated by Weakliem and McClure.<sup>3</sup>

The foregoing discussion provides at least a partial motivation for the work to be reported here. The present paper is concerned with the determination of the quadrupole interaction of the nuclei of several impurities in corundum. Since the quadrupole interaction is proportional to the field gradient, we hope to be able to correlate the results with determinations of the trigonal field by other means. The ions considered here are divalent vanadium and quadrivalent manganese. These ions, together with trivalent chromium which has previously been measured,<sup>7</sup> form an isoelectronic sequence.

Since it is desirable to vary as few parameters as possible in a comparison among impurities, this is an especially attractive system. The electronic structure of these ions is very similar; they differ only in nuclear charge. From the electron-paramagnetic-resonance (EPR) spectra of  $\text{V}^{2+}$  and  $\text{Mn}^{4+}$ , which has been reported previously,<sup>8,9</sup> one can obtain the magnetic hyperfine parameters. The quadrupole interaction parameter, however, is too small to be seen directly in EPR. To obtain this parameter it is necessary to employ the more sensitive ENDOR technique. ENDOR will also provide more accurate determination of the magnetic hyperfine parameters, but these values are only of academic interest at the present time, since the precision available experimentally far exceeds that available theoretically.

Having obtained values of the quadrupole interaction from ENDOR measurements, it is necessary to combine these with values of the nuclear quadrupole moments to obtain values for the field gradient. For the case of  $\text{V}^{51}$  and  $\text{Mn}^{55}$  (both of which are 100% naturally occurring isotopes) the quadrupole moments have been measured.<sup>10,11</sup> For  $\text{Cr}^{53}$  (the only stable chromium isotope with nuclear spin), which is only 10% abundant, the quadrupole moment is unknown. In the original ENDOR work on chromium in corundum, Terhune *et al.*<sup>7</sup> used the ENDOR data to infer a value for the quadrupole moment. They assumed that the chromium ion experienced the same field gradient as the host aluminum ions, made appropriate corrections for differences in antishielding of the two ions, and used the quadrupole interaction value to infer a value for the nuclear quadrupole moment. However, the constancy of the field gradient with respect to the type of ion, which they assumed, is the specific question we wish to examine. So, lacking an independent value of the quadrupole moment for chromium, we will confine our attention to the other two ions. These results will then be compared with the optical parameters obtained for these ions.<sup>9,12</sup>

#### EXPERIMENTAL PROCEDURE

The samples used in this investigation were grown by the Linde Company. In the case of the vanadium sample, a corundum crystal was grown containing about  $10^{-4}$  mole fraction vanadium. The vanadium ion enters the lattice as  $\text{V}^{3+}$ . To prepare  $\text{V}^{2+}$  the crystal was exposed to 50-kV x rays for approximately 1 h. The resulting  $\text{V}^{2+}$  persisted in the lattice at room temperature for several weeks. In the case of manganese a crystal was grown by Linde containing both manganese and magnesium in amount of about  $10^{-4}$  mole fraction. The divalent magnesium tends to stabilize the quadrivalent

<sup>4</sup> S. Geschwind and J. P. Remeika, *Suppl. J. Appl. Phys.* **33**, 371 (1962).

<sup>5</sup> H. Kamimura, *Phys. Rev.* **128**, 1077 (1962).

<sup>6</sup> N. Laurance, E. C. McIrvine, and J. Lambe, *J. Phys. Chem. Solids* **23**, 515 (1962).

<sup>7</sup> R. W. Terhune, J. Lambe, C. Kikuchi, and J. Baker, *Phys. Rev.* **123**, 1265 (1961).

<sup>8</sup> J. Lambe and C. Kikuchi, *Phys. Rev.* **118**, 71 (1960).

<sup>9</sup> S. Geschwind, P. Kisliuk, M. P. Klein, J. P. Remeika, and D. L. Wood, *Phys. Rev.* **126**, 1684 (1962).

<sup>10</sup> K. Murakawa and T. Kamei, *Phys. Rev.* **92**, 325 (1953).

<sup>11</sup> H. Walther, *Z. Physik* **170**, 507 (1962).

<sup>12</sup> M. D. Sturge, *Phys. Rev.* **130**, 639 (1963).

state of manganese. Although there was some  $Mn^{4+}$  present in the "as-received" crystals, here also the crystals were exposed to 50-kV x rays which enhanced the  $Mn^{4+}$  concentration. The spectra of the two ions are very similar; for vanadium  $I = \frac{7}{2}$  and the spectra contains 8 resolved components, while for manganese  $I = \frac{5}{2}$  and the spectra consists of 6 lines. Details of the EPR spectra have been reported previously.<sup>8,9</sup>

Because the zero-field splitting of the ground state of the vanadium ion is nearly equal to X-band frequency, it was found necessary to perform the experiments at a higher microwave frequency. A spectrometer designed to operate at 17 000 Mc/sec was constructed similar in design to the X-band spectrometer previously described.<sup>6</sup> The cavity was fabricated of micarta, and used a "crossed guide" coupling technique.<sup>13</sup> Crystal alignment was done by viewing the sample through crossed polaroid filters. This gave approximate orientation of the crystal axes. Final critical alignment was done by examining the microwave spectrum as will be described below. All the data to be reported was taken with the magnetic field either parallel to the "c" axis (0-deg case) or at right angles to the "c" axis (90-deg case).

To measure the ENDOR frequency, the magnetic field was adjusted to one of the hyperfine components of the EPR spectra. The derivative spectra were observed, and the field was adjusted to the maximum of the absorption derivative. The microwave power was increased until the line was partially saturated. The frequency of an rf oscillator, coupled to the sample by a single turn coil, was varied until resonance was observed by a change in the level of the EPR signal. The frequency of the oscillator (Hewlett Packard Model 608) was measured with a frequency counter (Hewlett Packard Model 524C). In general one sees four ENDOR frequencies for each EPR component observed. For the extreme hyperfine lines of the set one sees only two ENDOR frequencies. This may be understood as follows. Each EPR line corresponds to a transition in which the  $z$  component of the electronic angular momentum changes from  $M_1$  to  $M_2$  while the nuclear  $z$  component of angular momentum is  $m$ . For these ions  $S = \frac{3}{2}$  and  $M_1$  and  $M_2$  can take any values from  $-\frac{3}{2}$  to  $+\frac{3}{2}$ .  $m$  can take values from  $-I$  to  $+I$ , so that for vanadium there are 8 hyperfine lines and for manganese there are 6. When ENDOR transitions are excited, this corresponds to holding the electron quantum number  $M$  constant and changing the nuclear quantum number  $m$  by 1. For each line we have the 4 possibilities:  $M_1, m \rightarrow m-1$ ;  $M_1, m \rightarrow m+1$ ;  $M_2, m \rightarrow m-1$ ;  $M_2, m \rightarrow m+1$ . In the case of the extreme lines of the EPR spectra  $m$  is either  $I$  or  $-I$  and two of the transitions indicated above do not exist. The ENDOR lines then naturally group themselves into sets of 14 for the case of vanadium (7 for  $M, m \rightarrow m-1$ , 7 for  $M, m \rightarrow m+1$ ),

and 10 in the case of manganese. We will consider the ENDOR lines grouped in these sets, since the linear variation of the ENDOR frequency across such a set is related simply to the quadrupole interaction. The magnetic field was measured with a proton resonance spectrometer. This value and the value of the ENDOR resonance frequency were the two numerical measurements necessary for the analysis of the data.

The ENDOR linewidth was approximately 15 kc/sec, and it is estimated that the center of the line could be located to within 1 kc/sec. The error in measurement of the oscillator frequency is negligible. The error in measurement of the magnetic field occurs principally because the proton resonance sample is not at the same position as the sample. A separate determination of the error involved was made, and all the magnetic field measurements were corrected for this error. It is estimated that the error in the difference of the magnetic field in successive measurements is less than 0.25 G. The error introduced in the resonance values of vanadium or manganese through such an error is less than 0.5 kc/sec.

#### THEORY AND TREATMENT OF DATA

The results of the ENDOR measurement were analyzed with respect to the following spin Hamiltonian.

$$\mathcal{H} = g\beta H_0 S_z + D[S_z^2 - \frac{1}{3}S(S+1)] + AS_z I_z - \gamma H_0 I_z + Q'[I_z^2 - \frac{1}{3}I(I+1)] + \frac{1}{2}B[S_+ I_- + S_- I_+]. \quad (1)$$

All the coefficients in this Hamiltonian except  $Q'$ , the lumped quadrupole interaction constant, are known approximately from EPR measurements. Nevertheless, in the course of these measurements, we had occasion to remeasure all the parameters, and the results will be included. The constant  $Q'$  which we have used is given by

$$Q' = \frac{3eqQ}{4I(2I-1)}(1-\gamma_\infty), \quad (2)$$

where  $Q$  is the quadrupole moment of the nucleus,  $q$  is the field gradient external to the ion,  $I$  is the nuclear spin, and  $(1-\gamma_\infty)$  is the so-called Sternheimer anti-shielding factor which reflects the influence of the electrons on the external field gradient as seen by the nucleus. The Hamiltonian (1) as written applies only to the case in which the external field  $H_0$  is parallel to the "c" axis of the crystal. If this is not the case off-diagonal elements proportional to  $\sin\theta$ ,  $\cos\theta$ , and to  $\sin^2\theta$  arise from the zero-field splitting term  $D$ , and from the quadrupole term. Therefore, for accurate analysis, it was necessary to insure that the magnetic field was parallel to the crystal field. This was accomplished in the following way. For the Hamiltonian (1) the allowed transitions under a microwave field are those for which  $\Delta M = \pm 1$ ,  $\Delta m = 0$ , where  $M$  and  $m$  are the  $z$  components of the spin and nuclear angular momentum, respectively. If there is a

<sup>13</sup> R. Ager, T. Cole, and J. Lambe, Rev. Sci. Instr. **34**, 308 (1963).

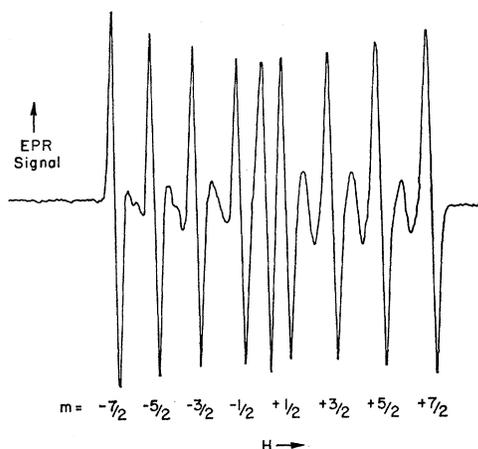


FIG. 1. EPR spectrum of  $V^{2+}$  in corundum showing the electron transition  $M = -\frac{1}{2}$  to  $M = \frac{1}{2}$ . The spectrum was taken with a klystron operating at 16 900 Mc/sec in a magnetic field of approximately 6000 G. The eight hyperfine components are labeled according to the value of nuclear spin. ( $I = \frac{7}{2}$  for  $V^{51}$ .) The extra line in the exact center of the pattern is due to a trace amount of  $Cr^{3+}$ . The magnetic field is directed about  $2^\circ$  away from the crystalline "c" axis. The small lines appearing between the main lines are forbidden transitions partially allowed by the misalignment.

slight degree of misalignment, the quantum states become mixed by the off-diagonal elements described above, and the transitions  $\Delta M = \pm 1$ ,  $\Delta m = \pm 1$  become slightly allowed. These appear as small lines between the allowed lines of the EPR spectra. Such a situation is shown in Fig. 1 for the  $M = -\frac{1}{2}$  to  $M = +\frac{1}{2}$  transition of vanadium corundum. The misalignment in this case is about  $2^\circ$ . The extra line in the center of the pattern is due to a trace of chromium present in this crystal. The intensity of the forbidden lines is proportional to the misalignment angle, and so to align the crystal it is only necessary to rotate the crystal (or the magnet) until the lines disappear. Notice also that the intensity of the allowed lines is not constant, but is greater for the lines at the ends of the pattern than for the lines in the center. Figure 2 shows the same spectra after correction of the misalignment. The maximum error introduced into the energy levels from misalignment can be directly calculated from the ratio of intensity of the forbidden lines to the allowed lines. Assuming from Fig. 2 that this ratio is of order of 0.01, the error in the energy levels from this source is less than 0.1 kc/sec. The structure of these forbidden lines has been analyzed and applied to a determination of the quadrupole interaction of  $V^{2+}$  in  $MgSiF_6$  and to  $Mn^{2+}$  in corundum.<sup>15</sup> The spacings between the forbidden lines depends both on the quadrupole parameter  $Q'$  and on third-order terms in the zero-field splitting. In the cases quoted the quadrupole interaction was much larger than the third-order term; in the present case the reverse is true. Unfortunately, there was an error in the treatment of the third-order

<sup>14</sup> B. Bleaney and R. S. Rubens, Proc. Phys. Soc. (London) **77**, 103 (1961). Note: errata to this paper in Proc. Phys. Soc. (London) **78**, 778 (1961).

<sup>15</sup> V. J. Folen, Phys. Rev. **125**, 1581 (1962).

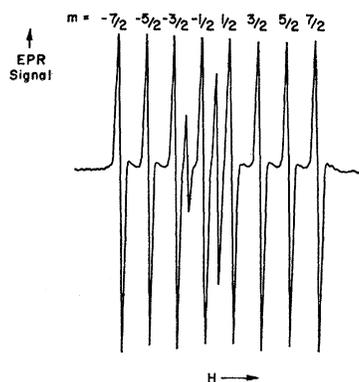


FIG. 2. Same spectra and details as Fig. 1 except that the magnetic field is parallel to the "c" axis. The forbidden lines have disappeared and the allowed lines are of uniform height. The extra line between the  $-\frac{3}{2}$  and  $-\frac{1}{2}$  line is due to some trace impurity, probably Fe.

term in both these papers. The correct expression for the spacings (in field) between two adjacent forbidden lines is

$$\Delta H_a = 7B^2/2H + 2(\gamma\beta n/g\beta)H - (Q' - 3B^2D/2H^2)(3\cos^2\theta - 1)(2m+1). \quad (3)$$

In the case of the present experiment the quadrupole interaction is much smaller than the term in  $B^2D$  with which it competes, and it is impossible to obtain the quadrupole interaction from this measurement. However, we can use these lines to obtain the relative sign of  $A$  and  $D$ . Expression (3) shows that the spacing between forbidden lines varies across the set of lines. The part independent of  $m$  is positive definite for both vanadium and manganese. Therefore, the greatest separation between forbidden lines comes when the second term is positive definite. Since we can ignore the effect of  $Q'$ , this condition is  $Dm > 0$ . To lowest order the resonant field is given by

$$H = (1/g\beta)[f - Am], \quad (4)$$

where  $f$  is the (fixed) frequency of the klystron. The low-field end of the spectrum are those lines for which  $Am > 0$ . Since the greatest spacing between forbidden lines occurs at low field, we conclude that  $A$  and  $D$  have the same sign. The sign of  $D$  for vanadium was determined in an independent measurement by observing the relative intensities of several EPR lines as the temperature was varied from 4.2 to  $2^\circ K$ . The results of this measurement indicate that  $D$  is negative for  $V^{2+}$  in corundum and, hence, that  $A$  also is negative. The same forbidden lines were observed in the case of manganese corundum, and since  $D$  is known to be negative in this case,<sup>9</sup> we conclude that  $A$  is negative also.

The ENDOR measurements were obtained as has been described, and the results were analyzed by a digital computer. The procedure was as follows: An approximate set of values for the parameters in the Hamiltonian were obtained from the EPR spectra and

from direct inspection of the ENDOR results. The computer was programmed to diagonalize the Hamiltonian with the assumed set of parameters and the measured value of the magnetic field. An ENDOR value was computed by taking the difference between the two appropriate energy levels and the result was compared with the observed value. The process was repeated for each of the ENDOR observations and the results used to improve the estimates of the parameters in the Hamiltonian. This iterative procedure was continued until the resulting errors appeared random. The final agreement between calculation and experiment was better than 10 kc/sec in most cases.

The program used for diagonalization of the matrix was developed at New York University and is based on a method of solution due to Givens.<sup>16</sup> It has proved both reliable and efficient in use on matrices up to  $32 \times 32$  needed for the present work.

Since the use of the computer tends to obscure the physical relations involved in the solution, we will give an expression for the ENDOR frequency from second-order perturbation theory. However, it must be emphasized that this relation was not used for any computation. It only provided the initial estimates of the parameters, and the criteria for judging errors. We express the ENDOR frequency as a function of the nuclear quantum number since this will show explicitly the variation in frequency from one hyperfine component to another. The natural variable to use in this case is one which has an average value 0 taken over the set of observations, and so we define  $m^* = m \pm \frac{1}{2}$  according as we are dealing with a transition  $\Delta m = \pm 1$ . With this as the independent variable, we write

$$\nu = AM - \gamma H - \frac{1}{4}B^2(R_+ + R_-) + m^*[2Q' + \frac{1}{2}B^2(R_+ - R_-)], \quad (5)$$

where

$$R_{\pm} = \frac{[S(S+1) - M(M \pm 1)]}{f - A(M \pm 1)} \quad (6)$$

and  $f$  is the frequency of the klystron.

Examination of Eq. (5) shows that part independent of  $m^*$  is principally determined by  $A$ , the magnetic hyperfine interaction. The part of the expression linear in  $m^*$  has a contribution from the second-order hyperfine term and from the quadrupole interaction. These facts were used in correcting the estimates of the Hamiltonian parameters in the exact solution of the matrix. For example, if the calculations showed a constant error when compared to the experimental observation, the estimate of  $A$  was in error. Likewise, if there was an error which was linear over the set of lines, the error in the estimate was either in  $B$  or in  $Q'$ . This expression also shows that it is possible to err in the estimate of  $Q'$  and satisfy the data by a compensating error in the estimate of  $B$ ; that is, our analysis is really only

<sup>16</sup> W. Givens, Oak Ridge National Laboratory Report, ORNL 1574, 1954 (unpublished).

sensitive to the coefficient of  $m^*$ , and the division of this coefficient into the quadrupole part and the second-order part is somewhat arbitrary. In order to circumvent this difficulty a series of measurements were made with the magnetic field at right angles to the "c" axis. We will not go into great detail for this case, but will only present the appropriate Hamiltonian. To arrive at this Hamiltonian it is necessary to perform a rotation of the operators to a new coordinate system as has been described by Strandberg.<sup>17</sup> In the following expression the  $z$  direction is the axis of quantization of the spin and the direction of the magnetic field, and the "c" axis of the crystal lies in the  $x$  direction. The Hamiltonian is

$$\begin{aligned} \mathcal{H} = & g\beta H_0 S_z - \frac{1}{2}D[S_z^2 - \frac{1}{3}S(S+1)] + BS_z I_z \\ & - \gamma H_0 I_z - \frac{1}{2}Q'[I_z^2 - \frac{1}{3}I(I+1)] \\ & + \frac{1}{4}(A+B)(S_+ I_- + S_- I_+) \\ & + \frac{1}{4}D(S_+^2 + S_-^2) + \frac{1}{4}Q'(I_+^2 + I_-^2) \\ & + \frac{1}{4}(A-B)(S_+ I_+ + S_- I_-). \quad (7) \end{aligned}$$

Although this Hamiltonian is formally more complicated than the zero-degree case (1), the principal change is that the diagonal hyperfine term has become  $BS_z I_z$ . This means that the constant term in an expression analogous to Eq. (5) will involve  $B$  instead of  $A$ . Therefore, we can expect that the solution of the Hamiltonian in the ninety-degree case will be quite sensitive to  $B$ . In actual practice, the ninety-degree data were used to obtain an accurate value of  $B$ . This was then inserted as a known parameter in the analysis of the zero-degree data which was used to obtain values of  $A$  and  $Q'$ . These in turn were reinserted in the analysis of the ninety-degree data to improve the estimate of  $B$ . In the final results  $B$  was obtained to better than 100 kc/sec. The error in the value of  $A$  was less than 25 kc/sec, and the error in the estimate of  $Q'$  was about 2 kc/sec. Of the error in  $Q'$ , about 1 kc/sec error is a direct consequence of the error in  $B$ ; the other 1 kc/sec is the cumulative effect of all other errors.

## EXPERIMENTAL RESULTS

The electron parameters and magnetic hyperfine parameters found in this work are listed in Table I. For purposes of comparison the results for  $\text{Cr}^{3+}$  from the ENDOR work of Terhune *et al.*<sup>7</sup> and from the resonance

TABLE I. Spin Hamiltonian parameters for the isoelectronic ions  $\text{V}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Mn}^{4+}$  in corundum.

Ion	$\text{V}^{2+}$	$\text{Cr}^{3+a}$	$\text{Mn}^{4+}$
$g$	1.991	1.984	1.993
$D$ (Mc/sec)	$-4803.6 \pm 1.0$	$-5723.5$	$-5868.0 \pm 1.0$
$A$ (Mc/sec)	$-220.615 \pm 0.025$	$+48.5$	$-208.825 \pm 0.025$
$B$ (Mc/sec)	$-222.890 \pm 0.100$	$= A$	$-211.440 \pm 0.100$
$A/\gamma$ (G)	$-197\ 200$	$-201\ 600$	$-197\ 900$

<sup>a</sup> After Terhune *et al.*, Ref. 7.

<sup>17</sup> M. W. P. Strandberg, J. Phys. Chem. Solids **16**, 39 (1960).

TABLE II. Quadrupole interaction data for the  $3d^3$  paramagnetic ions in corundum and for the host aluminum ions.

Nucleus	V <sup>51</sup>	Cr <sup>53</sup>	Mn <sup>55</sup>	Al <sup>27</sup>
$Q'$ (Mc/sec)	-0.021	-0.210 <sup>a</sup>	0.138	0.180 <sup>b</sup>
$Q$ (b)	0.3 <sup>c</sup>	-0.03 <sup>f</sup>	0.35 <sup>d</sup>	0.149 <sup>e</sup>
$(1-\gamma_\infty)eq$ (Mc/b)	-1.87	27.4	5.26	16.1

<sup>a</sup> After Terhune *et al.*, Ref. 7.

<sup>b</sup> After Pound, Ref. 30.

<sup>c</sup> After Murakawa and Kamei, Ref. 10.

<sup>d</sup> After Walther, Ref. 11.

<sup>e</sup> After H. Lew and G. Wessel, Phys. Rev. **90**, 1 (1953).

<sup>f</sup> This value was obtained by Terhune *et al.* under the assumption that the ionic field gradient was identical to that for Al<sup>27</sup> and that the antishielding factor increased by 1.7.

work of Manenkov and Prokhorov,<sup>18,19</sup> and Geusic<sup>20</sup> have been included. In the case of V<sup>2+</sup> the parameters were only approximately known,<sup>8</sup> and this represents the first precise determination of them; in the case of Mn<sup>4+</sup> these parameters had been determined by Geschwind *et al.*,<sup>9</sup> and our results are in substantial agreement with theirs. The  $g$  value has been reported to be nearly isotropic in these ions<sup>18,19</sup>; we did not investigate the isotropy but only measured the  $g$  value for the parallel case. Also,  $B$  was not independently determined in the case of Cr<sup>3+</sup> as we have done for the case of V<sup>2+</sup> and Mn<sup>4+</sup>; Terhune *et al.* assumed it to be equal to  $A$ . Comparison with the results for the other ions suggest that this is probably not true.

The hyperfine interaction can be interpreted as a magnetic field created by the electron distribution acting on the magnetic moment of the nucleus. It is instructive to calculate the value of this magnetic field, since this value is independent of the nuclear parameters. To do this we divide  $A$  by the gyromagnetic ratio, or equivalently, by the magnetic moment of the nucleus times the nuclear spin. The values of the effective field are given in the last line of Table I. The constancy of this quantity for the three ions is striking. On the one hand, we would expect a similarity of hyperfine fields for these ions because they are isoelectronic; but, on the other hand, one might expect that the difference in valency, which results in a disparity of ion size, would cause a systematic variation of core polarization in these ions. Furthermore, an ion with a  $3d^3$  configuration is not spherically symmetric and therefore the orbital angular momentum is not completely quenched (the  $g$  value bears witness to this fact). The hyperfine field then contains a contribution from the orbital moment as well as from the  $s$ -state polarization, and the experimental results state that this composite quantity is constant over these three ions to within 2%. A similar effect has been observed by Geschwind<sup>21</sup> in the case of the isoelectronic ions Cu<sup>3+</sup> and Co<sup>3+</sup> in corundum. We must conclude that the internal field (which is negative in agree-

ment with the ideas of core polarization<sup>22-24</sup>) is insensitive to quantities such as valency, ion size, and (as we shall see) field gradient. Hopefully, such results will ultimately produce a better theory of hyperfine field; present theories are inadequate to explain it. The entire question of hyperfine fields in corundum is treated more fully by Geschwind.<sup>25</sup>

The quadrupole interaction parameter for V<sup>51</sup>, as determined by our ENDOR measurements, is  $-0.021 \pm 0.002$  Mc/sec. For the case of Mn<sup>55</sup> the quadrupole interaction is  $0.138 \pm 0.002$  Mc/sec. Table II contains the appropriate quadrupole data for our isoelectronic sequence of ions, as well as the corresponding values for Al<sup>27</sup>, the host nucleus. The relation between the various quantities is given by Eq. (2). The last line of the table is the field gradient times the Sternheimer antishielding factor, as computed from the measurement of the quadrupole moment and the quadrupole interaction. In the case of Cr<sup>53</sup> the quadrupole moment has not been measured, and Terhune *et al.* assumed that the field gradient at the chromium site is the same as that at the aluminum site. Then, using theoretical estimates of the antishielding factor, they arrived at the value of the quadrupole moment shown in the table.

If the ions were at the true substitutional position in the lattice, the quantity  $q$ , the crystalline field gradient, would be the same for all ions. In this case the variations in the last line of Table II would be due solely to the variations in the quantity  $(1-\gamma_\infty)$ . Such fluctuations as given by Table II are completely unreasonable. Sternheimer<sup>26</sup> has recently estimated the antishielding factors for these ions to be  $(1-\gamma_\infty) = 12.7$  for V<sup>2+</sup>, 10.8 for Cr<sup>3+</sup>, and 9.5 for Mn<sup>4+</sup>, assuming a  $3d^3$  configuration in each case. In terms of the present discussion we may treat the antishielding factor as a constant for all three ions, since we are dealing with effects in which the apparent field gradient varies by an order of magnitude and in sign. Recently Blumberg, Eisinger, and Geschwind<sup>27</sup> have made ENDOR measurements on Cu<sup>3+</sup> in corundum, and here also they find a nuclear quadrupole interaction that is an order of magnitude smaller than one would predict assuming the same field gradient and antishielding factor as for aluminum. So we are confronted with the situation where the hyperfine fields are almost identical for each ion, but the quadrupole fields show no regularity at all. In view of the present results one must conclude that the value of the quadrupole moment ascribed to Cr<sup>53</sup> by Terhune *et al.*<sup>7</sup> is very unreliable and may even be of the wrong sign.

## DISCUSSION

The last line of Table II gives the value for the effective field gradient at the nucleus, i.e., the field gradient

<sup>22</sup> R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

<sup>23</sup> V. Heine, Phys. Rev. **107**, 1002 (1957).

<sup>24</sup> D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

<sup>25</sup> S. Geschwind (to be published).

<sup>26</sup> R. M. Sternheimer (private communication).

<sup>27</sup> W. E. Blumberg, J. Eisinger, and S. Geschwind (to be published).

<sup>18</sup> A. A. Manankev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **28**, 762 (1955) [translation: Soviet Phys.—JETP **1**, 611 (1955)].

<sup>19</sup> A. A. Manankev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **31**, 346 (1956) [translation: Soviet Phys.—JETP **4**, 288 (1957)].

<sup>20</sup> J. E. Geusic, J. Appl. Phys. **102**, 1952 (1956).

<sup>21</sup> S. Geschwind (private communication).

due to all external charges. If we suppose that the principal contribution to the quadrupole interaction is due to the ionic lattice, suitably modified to account for the electrons of the central ion, we write the field gradient as  $q(1-\gamma_\infty)$  where  $q$  is the field gradient due to a lattice of point charges and  $(1-\gamma_\infty)$  is the antishielding factor arising from the electron distribution. We have given a theoretical estimate of  $(1-\gamma_\infty)$  for the three paramagnetic ions due to Sternheimer in the previous section. The most important fact for our present discussion is that  $(1-\gamma_\infty)$  is nearly a constant for these three ions. The antishielding factor  $(1-\gamma_\infty)$  has been calculated for  $\text{Al}^{3+}$  to be 3.6 by Das and Bersohn.<sup>28</sup> Bersohn's calculation of the ionic field gradient<sup>29</sup> is consistent with the measured quadrupole interaction<sup>30,31</sup> if one assumes  $(1-\gamma_\infty)$  to be about five. This is viewed as satisfactory agreement because of the approximate nature of both calculations. For the remainder of our discussion it will be sufficient to assume that the antishielding factor is the same for the three paramagnetic ions, and about twice the value for  $\text{Al}^{3+}$ .

The results of the previous section indicate, at the very least, that the simple view of one ion substituting for another in a rigid ionic lattice cannot be valid. The effective field gradients seen by these ions are not only widely disparate in magnitude, they also vary in sign. Furthermore, the simple model we proposed, that of the impurity ion being displaced along the "c" axis from the substitutional position, is also found to be inadequate. This is shown by Fig. 3 where we plot the field gradient due to a rigid lattice of point charges evaluated at various positions along the "c" axis. The field gradient was computed by evaluating the lattice sum

$$\sum_j' \sum_i \frac{(3 \cos^2 \theta_{ij} - 1)}{|\mathbf{r}_{ij} - \mathbf{R}|^3} e_i, \quad (8)$$

where  $e_i$  is the charge on the  $i$ th ion in the unit cell, the sum over  $i$  runs over all the ions in the unit cell, and the sum over  $j$  runs over all the unit cells in the infinite lattice. The prime on the sum indicates that the point  $\mathbf{r}_{ij} = 0$  is not included in the sum. In performing the sum we used the crystallographic data of Newnham<sup>32</sup> to specify the position of the ions in the unit cell. Since this sum presents convergence difficulties, care must be exercised in the order of summation. In the present case the sum was carried out using the mathematical methods of Nijboer and deWette.<sup>33</sup> This sum was first calculated by Bersohn<sup>29</sup> for the substitutional position and later by McClure<sup>3</sup> for three points on the axis. A similar circulation has been performed by Artman and

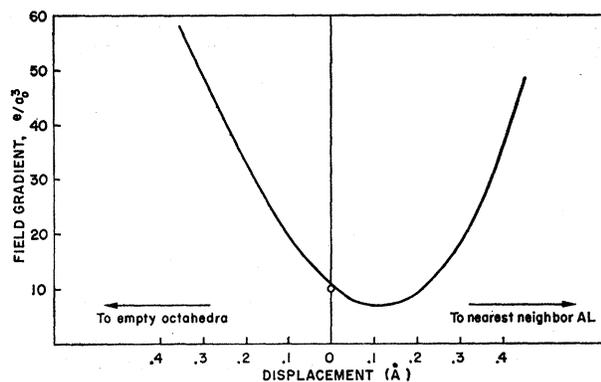


FIG. 3. Field gradient computed on the point-charge model of the lattice as a function of position of the ion on the "c" axis. The ordinate is in units of  $e/a_0^3$  where  $e$  is the (absolute) value of the electronic charge and  $a_0$  is the rhombohedral cell parameter,  $a_0 = 5.128 \text{ \AA}$ . O value computed by R. Bersohn, Ref. 29.

Murphy,<sup>34</sup> and the results shown here are in essential agreement with theirs. The main points for attention here are that the field gradient never becomes smaller than half its value at the substitutional position, and that it never becomes negative. Contrasting this with the variation in sign of the field gradient given in Table II we see that the displacement model is also insufficient to explain the results.

Artman and Murphy<sup>34</sup> have investigated a model in which all the oxygen ions in the neighboring octahedron are displaced away from the impurity, and the impurity is displaced along the "c" axis. They report that with a sufficient displacement of the oxygen ions the field gradient will change sign. This shows that for an accurate prediction of the field gradient the motion of the neighbors around an impurity is important. Since their model, like any local distortion model, involves many degrees of freedom, it is impossible to "prove" with a single experimental fact. Hence, we can only conclude here that the impurity ion displacement model is insufficient to explain the results.

Our discussion thus far has been limited to field gradients produced by a point-charge lattice. In actual fact, however, corundum certainly has some degree of covalent bonding. This means that we must consider the contribution to the field gradient from the electrons bonding the impurity to the neighboring oxygen ions. (We neglect the effect of the field gradient produced by bonds between other ions.) The oxygen ions form a distorted octahedron around the impurity; were the octahedron regular, the effect of the bonds would cancel and produce no field gradient at the nucleus. The fact that it is distorted prevents exact cancellation and gives a finite contribution to the field gradient. In addition, the oxygen ion above the impurity are not arranged at the same distance and angle as those ions below the impurity. This results in an imbalance in the amount of  $p$  character in the two types of bonds, and it is the  $p$

<sup>28</sup> T. P. Das and R. Bersohn, *Phys. Rev.* **102**, 360 (1956).  
<sup>29</sup> R. Bersohn, *J. Chem. Phys.* **29**, 326 (1958).  
<sup>30</sup> R. V. Pound, *Phys. Rev.* **79**, 689 (1950).  
<sup>31</sup> A. H. Silver, T. Kushida, and J. Lambe, *Phys. Rev.* **125**, 1147 (1962).  
<sup>32</sup> R. E. Newnham and Y. M. deHaam, *Z. Krist.* **117**, 235 (1962).  
<sup>33</sup> B. R. A. Nijboer and F. W. deWette, *Physica* **23**, 309 (1957).

<sup>34</sup> J. O. Artman and J. Murphy, Bell System communication (unpublished).

character of the bond which is primarily responsible for the field gradient. This situation was analyzed in a previous paper,<sup>6</sup> where it was shown that the measured field gradient in corundum can equally well be explained by postulating a 100% ionic lattice, or a 100% covalent lattice, or any intermediate combination of the two. Here the simple displacement model of the impurity position offers some promise. As the position of the ion on the "c" axis is changed, so are the angles between the bonds to the oxygen neighbors. The change in angle will produce two effects in the covalent field gradient. First, the partial cancellation between the various bond contributions depends quite sensitively on the angles involved. Second, since the bonds are required to be orthogonal, the amount of *p* character itself will change with angle. Calculations of the field gradient on such a model have not been made, although some of the other details of the electronic structure have been analyzed in terms of a molecular orbital model of the wave functions.<sup>35</sup>

On the crystal field model the field gradient should be related to some of the optical parameters, most notably the trigonal field splitting. Unfortunately, in the case of *d*<sup>3</sup> complexes, the two electronic states of the most interest, namely the ground state and the excited state which gives rise to the *R*-line fluorescence, do not split under the action of the trigonal field. The splitting of the excited state, <sup>2</sup>*E*, comes about through the combined action of the trigonal field and the spin-orbit interaction. It is this splitting which gives the two *R* lines characteristic of the fluorescence spectrum of ruby. The ground state is an orbital singlet, fourfold degenerate, whose splitting into two Kramers doublets is still incompletely understood.<sup>5,35,36</sup> Nevertheless, this splitting too involves the spin-orbit interaction. The fact that we must contend with variations in spin-orbit interaction constants as well as variations in crystal field parameters in a comparison of results for these three ions, makes the situation far from ideal. However, some legitimate conclusions can be drawn. The splitting of the *R* lines shows a marked dependence on ion, varying from 12.4 cm<sup>-1</sup> for V<sup>2+</sup>, to 29 cm<sup>-1</sup> for Cr<sup>3+</sup>, to 85 cm<sup>-1</sup> for Mn<sup>4+</sup>. On the basis of an empirical fit to the observed optical data, Sturge<sup>12</sup> reports values for the trigonal field parameter  $-K$  ( $=\frac{1}{3}v$ ) to be 160 cm<sup>-1</sup> for V<sup>2+</sup>, 330 cm<sup>-1</sup> for Cr<sup>3+</sup>, and 700 cm<sup>-1</sup> for Mn<sup>4+</sup>. The crystal field expression for the trigonal field parameter has been given by McClure.<sup>3</sup> It involves a term proportional to the field gradient and another term which has the symmetry of a *g* electron. (The field gradient has the symmetry of a *d* electron.) On the point ion model these two terms tend to oppose, and McClure notes that a small displacement along the "c" axis will change the sign of the trigonal field. The reported trigonal field values are all of the same sign, but since the field gradient changes sign for vanadium,

crystal field theory leads us back again to the distortion around the impurity.

The zero-field splitting term *D*, is somewhat a subject of controversy. As has been noted, the simple crystal field theory would predict the wrong sign for the interaction. Kamimura<sup>5</sup> has invoked an anisotropy in the spin-orbit interaction due to a distortion in the covalent bonds with the result that he is able to predict the ground-state splitting for ruby, Cr<sup>3+</sup> in Al<sub>2</sub>O<sub>3</sub>. His theory has not been tested on the other ions because of a lack of experimental values of the anisotropy in the *g* value. Artman and Murphy<sup>26</sup> have advanced an alternative approach, again based on crystal field theory, in which they consider the effect of the terms in the crystal potential of odd parity. These are usually neglected on the basis that the states with which they mix are too far removed in energy to be effective. Artman and Murphy, however, show that the amount of odd parity mixing necessary to explain the observed oscillator strength of the optical transitions is sufficient to explain the zero-field splitting. Sturge<sup>12</sup> has criticized their theory, on the basis that it does not satisfactorily account for the relation between the zero-field splitting and the oscillator strength in the isoelectronic sequence V<sup>2+</sup>, Cr<sup>3+</sup>, and Mn<sup>4+</sup>. The zero-field splittings are fairly constant (cf., Table I), while the oscillator strength, as evidenced by the fluorescence lifetime, varies from 3×10<sup>8</sup> for V<sup>2+</sup> to 3×10<sup>7</sup> for Cr<sup>3+</sup> and Mn<sup>4+</sup>.

In his recent study of the effects of an electric field on the paramagnetic resonance spectra of ruby, Royce<sup>37</sup> criticized crystal field theory because of the large number of adjustable parameters necessary to bring experimental findings into agreement with the basic structure of the theory. Indeed, it would appear that the current experimental work demands a more general theoretical approach, one which incorporates such obvious facts as finite ion size, partial covalent character, and nonspherical symmetry of the ions into the basic structure of the theory, and does not append them as parameters to be fitted empirically. Royce makes use of a qualitative form of molecular orbital theory to explain his results, and we have just indicated how a form of covalent bond interaction may explain the present results. Ultimately, we may expect that detailed studies of isoelectronic sequences of ions will provide the exacting tests necessary to produce a new, quantitative theory of paramagnetic ions in crystals.

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<sup>35</sup> L. L. Lohr and W. Lipscombe, *J. Chem. Phys.* **38**, 1607 (1963).

<sup>36</sup> J. O. Artman and John C. Murphy, *Bull. Am. Phys. Soc.* **7**, 196 (1962); *J. Chem. Phys.* **38**, 1544 (1963).

<sup>37</sup> E. B. Royce, ONR Technical Report No. 379, Contract Nonr 1866 (16), 1963 (unpublished).