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Crystal Vacancy Evidence from Electron Spin Resonance*

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Three distinct patterns have been observed in the electron spin resonance spectrum of chromium (+3) ions in single crystals of magnesium oxide. The chromium (present in naturally-occurring amounts or augmented) replaces magnesium (+2) ions substitutionally. The Cr(+3) spectrum depends upon whether compensation for the extra charge occurs in the immediate vicinity, and if so, upon the position of the compensating charge. The first pattern is a single line surrounded by a hyperfine quartet, representing that expected for a ^4F ion in a purely cubic electric field if most of its isotopes have zero nuclear spin I, and one isotope has $I=\frac{3}{2}$. This means that charge compensation cannot occur in a position as close as that of the next-nearest magnesium ion. The second pattern has nine lines (each with a hyperfine quartet), the angular dependence of which shows axial symmetry about the principal crystal axes. It is explained in terms of a vacancy in the magnesium position next-nearest the chromium ion. The third pattern arises from ions with axes of symmetry in face-diagonal ([110]-type) directions. This symmetry is ascribed to the effects of a magnesium ion vacancy in a position nearest the central ion.

THE electron spin resonance (ESR) spectrum of a paramagnetic ion depends upon the symmetry of the electrical field of the ions which surround it. The spectrum is normally simplest if the symmetry is cubic, becoming progressively more complex if there is axial or yet lower symmetry. All magnesium oxide crystals we have been able to secure (more than forty specimens) show the presence of Cr(+3) ions in Mg(+2) positions. The ESR spectrum of chromium (+3) in these crystals may be sorted into lines arising from ions in three different electric field symmetries. Figure 1 represents the extended spectrum (shown as the first derivative of the absorption *vs* field strength) while Fig. 2 shows an expanded portion in the region of a strong isotropic line with spectroscopic splitting factor g equal to 1.9797. Centered upon this line is a quartet of lines of about one-fortieth the intensity of the central line. We shall disregard two extra lines in Fig. 2 due, respectively, to manganese (+2) and vanadium (+2) ions.

A ^4F ion such as Cr(+3) in a purely cubic field should have the sevenfold orbital degeneracy removed by splitting into a single and two triplet levels, the singlet lying lowest. However, the fourfold spin degeneracy should not be removed by a purely cubic electric field. Application of a magnetic field should cause uniform splitting into four spin levels. Since they are equally separated in energy, only one transition should be observed, and the strong central line then becomes an ideal example of expected behavior. The line width in one crystal was measured as 0.75 gauss, one of the narrowest observed in ionic solids. When the concentration of paramagnetic ions is high, the width may exceed 5 gauss. The line occurs only 1.4 gauss higher in field than the fourth principal hyperfine line of manganese and is only partially resolved from it in this trace. [Better resolution is attained when the relative proportions of Cr(+3) and Mn(+2) are more nearly the same, and the derivative curve crosses the base line.] The quartet arises because of the 9.5% abundance of ^{53}Cr with nuclear spin $I=\frac{3}{2}$, while the remaining isotopes of mass 50, 52, and 54 have $I=0$. The separation of successive hyperfine components is 17.85 gauss. It may at first seem surprising that one should find the major fraction of the Cr(+3) ions in a purely cubic field, indicating that any vacancy or unipositive ion necessary for charge compensation in MgO must not be immediately adjacent to the oxygen ion octahedron which surrounds the chromium. The location of nearest and next-nearest positive-ion vacancy sites is shown in Fig. 3. However, since one positive-ion vacancy compensates for two trivalent ions, there must be *at least* one ion without an associated vacancy for each associated vacancy. The excess positive charge doubtless causes a uniform shrinkage of the oxide octahedron, and this rearrangement apparently stabilizes the system in the absence of nearby vacancies. The line shows little tendency toward saturation with moderate microwave power, unlike the Mn(+2) ion. Up to 20 milliwatts of microwave power, the line amplitude increases with power, though there is some broadening. Further, the line amplitude diminishes more rapidly than that of Mn(+2) with increasing temperature.

When the total chromium concentration in the MgO crystal is not high, one can nearly eliminate the five lines by x-irradiation, suggesting that the chromic ion has been reduced by an electron to Cr(+2). The source of the electron is probably Fe(+2), since one observes an enhanced Fe(+3) ESR spectrum at the same time. However, when the chromium concentration is of the order of 0.01%, the reduction of line amplitude on x-irradiation may be only twofold. The quintet grows slowly after irradiation, and much faster if the crystal is heated. In one case heating in vacuum at 1450° C increased the line amplitudes tenfold. The five lines are isotropic so they are readily observed for a powdered

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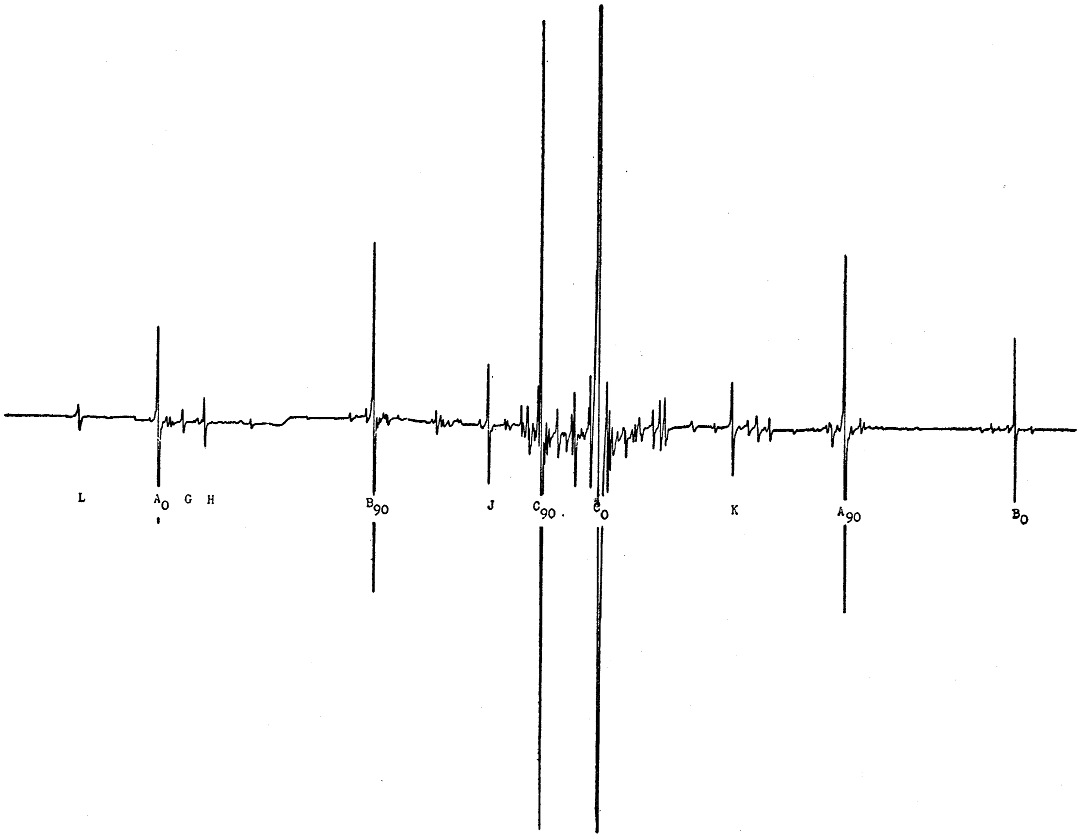

FIG. 1. The electron spin resonance (ESR) spectrum of chromium (+3). The most intense line is due to ions in a purely cubic field symmetry. The lines A_0, B_0, and C_0 arise from ions with an electric field symmetry axis along the applied magnetic field H_0, while B_{90}, C_{90}, and A_{90} are each twofold coincident lines from ions with symmetry axes perpendicular to H_0. L corresponds to a $\Delta M=2$ transition for such ions. G, H, J, and K arise from ions with a symmetry axis in a [110]-type direction.

crystal. In fact, the central line was observed in "reagent-grade" MgO powder.

Contrasted with the isotropic behavior of the lines from Cr(+3) in a cubic electrical field, there is a set of nine lines whose angular variation shows axial symmetry about the principal identical crystal axes *a*, *b*, or *c*.[1] The spectrum shown in Fig. 1 was taken with an MgO crystal oriented such that *a* is parallel to H_0 and *b* is parallel to H_1, where H_0 and H_1 are the static and microwave magnetic fields, respectively. For convenience, this will be referred to as the 0° orientation. At 9225 Mc/sec, the ESR lines with this type of axial symmetry range from 1555 to 5105 gauss at this orientation. Lines A_0 and B_0 are centered upon C_0, corresponding to $g_{\parallel}=g_{\perp}=1.9782$. They arise from Cr(+3) ions with an axis of electric field symmetry along *a* (and H_0). The central line C_0 shown in Fig. 2 is only partially resolved from the far more intense central cubic chromium (+3) line Cr_0, lying about 2.5 gauss higher in field than the latter. There will also be similar ions with electric field symmetry axes along *b* or *c*, each of which will give rise to a set of three lines. For the 0° orientation, they will be coincident in pairs. These doubly intense lines labeled A_{90}, B_{90}, and C_{90} appear at approximately 4195, 2480, and 3135 gauss, respectively. For a 90-degree rotation of the crystal about H_1, the lines A_0, B_0, and C_0 will respectively interchange places with one each of the components of A_{90}, B_{90}, and C_{90}. The angular variation is shown in Fig. 4. When the field H_0 lies along a unit-cube body diagonal, there should be a sixfold coincidence near 3020 gauss and a threefold coincidence near 3540 gauss. The field H_0 then makes equal angles with *a*, *b*, and *c*. With very careful alignment of the crystal, the coincidences may be observed at the expected positions. We take these coincidences to mean that if $g_{\parallel}$ and $g_{\perp}$ are not exactly equal, the difference is very small. Each of the nine lines shows a hyperfine quartet arising from ^{53}Cr, with just the

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[1] The spectrum of Cr(+3) with cubic or [100]-type axial symmetry was also found independently at Oxford University and the University of Chicago. The Oxford results (with the axial symmetry ascribed to unipositive ions in magnesium ion positions) were kindly communicated by Professor B. Bleaney. W. Low cited his work at the conclusion of this (post-deadline) paper when it was presented November 23, 1956 at the American Physical Society Chicago meeting. *Note added in proof.*—Recently Low published his results for chromium in a cubic field (Phys. Rev. **105**, 801 (1957)).

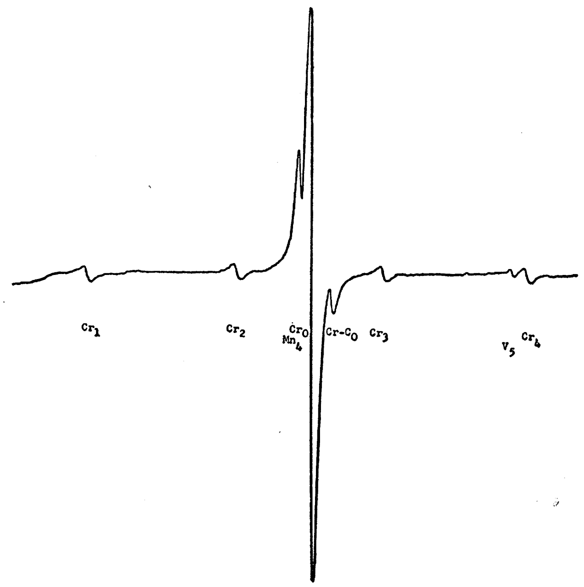

FIG. 2. The ESR spectrum of chromium (+3) in an electric field of cubic symmetry. Line Cr_0 is the transition due to the isotopes 50, 52, and 54, while the quartet Cr_1, Cr_2, Cr_3, and Cr_4 is due to the 53 isotope of 9.5% abundance. Line $Cr-C_0$ is the central transition for Cr(+3) in a field of [100]-type axial symmetry. Lines Mn_4 and V_5 are, respectively, due to Mn(+2) and V(+2).

17.85-gauss separation of components which was found for Cr(+3) in a cubic field. The line multiplicity for arbitrary or special orientations is just that expected for [100]-type symmetry.

The observed symmetry may arise in several ways. Charge compensation with an extra electron on an oxygen ion O(−3) may be dismissed as representing a very unstable configuration. This leaves one with two reasonable possibilities outside the oxygen octahedron for producing distortions which give rise to axial symmetry of this type. First, one could have one of the six next-nearest Mg(+2) ions (lying along one of the principal axes from a central Cr(+3) ion and shown as V_1 in Fig. 3) replaced by a unipositive ion.[1] The alternative is to have a Mg(+2) vacancy at a similar position. The presence of Li(+1) ions was postulated by Prener[2] who found that the fluorescence spectrum of MgO which had been heated with $MnSO_4$ in an oxygen atmosphere depended upon whether Li_2CO_3 was also present or not. He concluded that manganese ion could be present in an oxidation state greater than +2 if charge compensation occurred through replacement of Mg(+2) by Li(+1) ions. However, no analyses were given to demonstrate that an appreciable amount of Li(+1) was present. In MgO crystals one must take cognizance of the inevitable impurities of several transition group elements having at least two stable valence states (usually +2 and +3). By taking up or losing oxygen at high temperatures, the oxidation states of these impurities may be altered without requiring unipositive ions.[3] Taking the radius of Mg(+2) as 0.65 A, one should expect that Li(+1) should fit readily into the crystal (with Na(+1) less likely) while any other unipositive ion is probably too large to fit without undue distortion. However, a spectrographic analysis failed to detect the presence of Li, Na, or K in a crystal which had 0.05% of Cr and showed the [100]-type axial spectrum strongly. By elimination, one is left with the Mg(+2) vacancy as the cause of axial electric field symmetry. Such vacancies, while overcompensating for the single extra positive charge of the nearly Cr(+3) ion with axial symmetry, serve to help compensate for

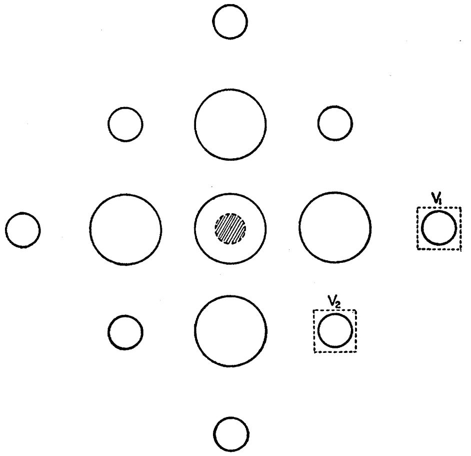

FIG. 3. A portion of the MgO crystal showing a Cr(+3) ion at a Mg(+2) site (cross-hatched). If the Mg(+2) site at V_1 is vacant, the electric field about the Cr(+3) ion will have tetragonal symmetry. A similar vacancy at site V_2 will give rise to a symmetry axis in a [110]-type direction.

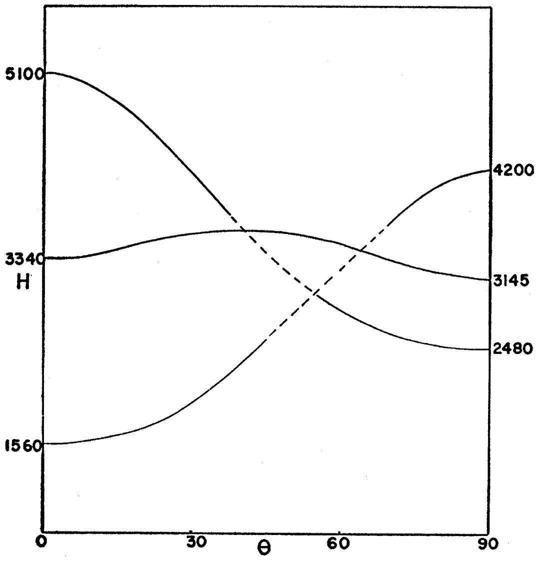

FIG. 4. Angular dependence of ESR lines of Cr(+3) in a [100]-type axial field.

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[2] J. S. Prener, J. Chem. Phys. 21, 160 (1953).
[3] Wertz, Vivo Acrivos, and Auzins (to be published).

the many extra Cr(+3) ions in a purely cubic electric field. The number of vacancies is intimately related to the presence of other impurities and to their changes of oxidation state.[3]

The Hamiltonian appropriate for the Cr(+3) ion in a field of axial symmetry (neglecting hyperfine interactions) is[4]:

$$\mathcal{H}_z=\mu_B(g_zH_zS_z+g_xH_xS_x+g_yH_yS_y)+D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2).$$

If a strong magnetic field is oriented along the z axis, one obtains the following secular determinant:

$$\begin{vmatrix} \tfrac{3}{2}g_z\mu_BH+D-W & 0 & \sqrt{3}E & 0 \\ 0 & +\tfrac{1}{2}g_z\mu_BH-D-W & 0 & \sqrt{3}E \\ \sqrt{3}E & 0 & -\tfrac{1}{2}g_z\mu_BH-D-W & 0 \\ 0 & \sqrt{3}E & 0 & -\tfrac{3}{2}g_z\mu_BH+D-W \end{vmatrix}=0.$$

This fourth-order equation has roots

$$W_{1,2}=a\pm[(D+2a)^2+3E^2]^{\frac{1}{2}},$$
$$W_{3,4}=-a\pm[(D-2a)^2+3E^2]^{\frac{1}{2}},$$

where $a=\frac{1}{2}g_z\mu_BH$. For a purely axial electric field, $E=0$, and at zero magnetic field the energy levels are separated by $2D$. Our best value of D is 887.0 gauss or 0.08194 cm^{-1}. The energy levels and transitions are shown in Fig. 5.

When one applies a magnetic field perpendicular to an axis of symmetry, D should be replaced by $\frac{1}{2}(D-3E)$ and E by $-\frac{1}{2}(E+D)$. Designating the magnetic field for the C_0 line as H_{00} and that for the twofold A_{90} lines as H', one gets:

$$h\nu=g_z\mu_BH'+[D^2+Dg_z\mu_BH'+(g_z\mu_BH')^2]^{\frac{1}{2}}-[D^2-Dg_z\mu_BH'+(g_z\mu_BH')^2]^{\frac{1}{2}}.$$

Since one also observes a transition when $h\nu=g_z\mu_BH_{00}$, one may obtain the relation:

$$\frac{H'}{H_{00}}=1-\left(d^2+\frac{dH'}{H_{00}}+\frac{H'^2}{H_{00}{}^2}\right)^{\frac{1}{2}}+\left(d^2-\frac{dH'}{H_{00}}+\frac{H'^2}{H_{00}{}^2}\right)^{\frac{1}{2}}.$$

Substituting observed values for H' and H_{00}, the two sides should be identical. The discrepancy for the doublet A_{90} is less than 0.1%. Similar relations for B_{90} and C_{90} show consistency with observed values to within 0.1 and 0.2%, respectively. This agreement we take as indicating that our g and D values are reasonably accurate and that E is essentially zero.

A prominent line group shown as L in Fig. 1, appearing at fields of 900 gauss or below also shows axial symmetry in [100]-type directions, appearing as a single line at 0° orientation. The line L arises from an axis at right angles to H_0 and H_1. When no axis makes a small angle with H_0 or H_1, one observes the expected three lines. These disappear whenever one magnetic field makes an angle of less than five degrees with an axis of symmetry. This group shows the hyperfine quartet with the same spacing as for cubic chromium (+3). However, the quartet is slightly displaced to low field with respect to the central line. If one calculates the position expected for the $\Delta M=2$ transition from $-\frac{1}{2}$ to $+\frac{3}{2}$ levels for 0° orientation, it agrees with the observed value (extrapolated from angles at which it is visible) of 780 gauss to about 0.1%. However, the calculated position for a 90-degree rotation about a principal axis is rather higher than that observed. The companion line arising from the $M=-\frac{3}{2}$ to $M=+\frac{1}{2}$ transition should appear near 2600 gauss. A line group showing appropriate axial symmetry but at somewhat lower field is a possible candidate for this transition.

When a crystal of MgO is very carefully oriented at 0°, there are four line groups labeled G, H, J, and K in Fig. 1. For random orientations, the first two are fourfold, while the last two are twofold. The approximate positions at 0° orientation for 9200 Mc/sec are 1640, 1700, 2940, and 3790 gauss, respectively. These groups have an angular dependence which indicates that they have a [110]-type symmetry axis. We fail to see lines from axes which are parallel to the magnetic field, while the lines are strongest for axes at 90° to

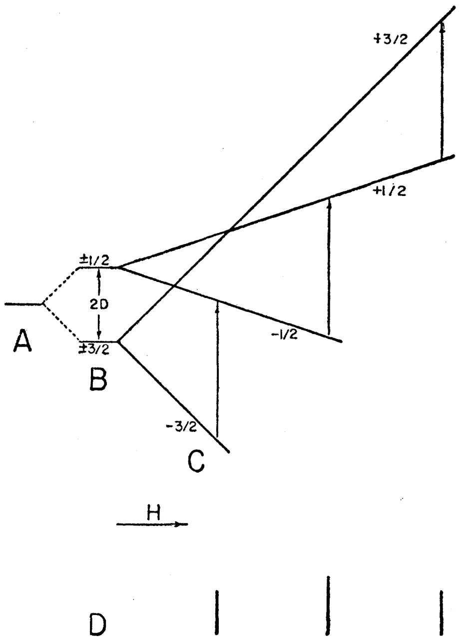

FIG. 5. Energy levels of a ^4F ion. A: free ion; B: axial electric field; C: superposed magnetic field; D: ESR spectrum.

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[4] K. D. Bowers and J. Owen, Repts. Progr. Phys. **18**, 304 (1955).

the field. As seen from Fig. 1, the intensity of the low-field line groups is smaller than that of the high-field groups. For a rotation of 90° about a [100]-type axis, a twofold component from the 1640-gauss group interchanges with a similar one from the 3790-gauss group, while a (twofold) line from the 1700-gauss group exchanges with another from the 2940-gauss group. Simultaneously, from each of the low-field line groups, a single line goes to low field and another to very high field for the same rotation. When the magnetic field lies along a unit cube body diagonal, there are four threefold coincidences at fields of about 1445, 1505, 4185, and 5955 gauss, respectively. For the two high-field groups at 0° one observes the same hyperfine quartet as for the other Cr(+3) lines and with the same spacing. All of the lines increase in intensity on heating to 1000°C and decrease upon x-irradiation. The same behavior is shown by Cr(+3) ions with other types of symmetry, though the relative effect is different in magnitude.

In seeking an explanation for orthorhombic symmetry, we reject the possibility of interstitial O(−1) ions, since there is hardly room in the lattice to accommodate them.[3] Rather, it appears reasonable to assume that these lines arise from Cr(+3) ions which have an associated vacancy at one of the twelve nearest-neighbor positions, i.e., in a [110]-type direction. If this interpretation is correct, it would be entirely analogous to that for Mn(+2) in NaCl.[5] For this case, Watkins has observed both types of symmetry and estimated energies of association in the two positions (which in MgO lie just 2.97 A apart). At sufficiently high temperatures he found that the lines broadened, and this was interpreted as meaning that the vacancies were rapidly shifting about over the twelve nearest-neighbor positions.[6]

While the interpretation of the [100]-type spectrum appears to be in good accord with theory for the most part, the [110]-type spectrum is not yet fully explored even from the experimental standpoint. Because of the intensity of the Mn(+2) spectrum which is always present, it is very difficult to follow lines through the region near $g=2$. Line broadening at some orientations also makes angular-dependence studies difficult. There are weak satellites below line group J and above K as well as numerous satellites about the [100]-type Cr(+3) axial lines.

We should like to suggest that "trapped holes" may produce axial symmetry. If an electron is lost from one of the six oxygen ions in the octahedron surrounding a magnesium ion vacancy near a trivalent ion, one would have local charge compensation also with this type of center. One should expect to see ESR absorption from such a center, but none has yet been established.[7]

If the interpretations in terms of vacancies are correct, it will be a matter of great interest to establish quantitatively their association with and dissociation from trivalent impurity ions under a variety of conditions. There is probably no other method which permits observations on vacancies with such directness. For example, one can conclude from the spectrum of Cr(+3) ion in a purely cubic field that there exist regions at least 13 A in diameter over which there is no vacancy or other type of compensation for an extra positive charge. Numerous other observations can be nicely correlated with the electronic properties of MgO.[3] We are hopeful that the interpretation of the Cr(+2) ESR spectrum will help to give a rather complete description of the behavior as an impurity ion of chromium in either valence state.

Thanks are due to G. D. Watkins and W. N. Lipscomb for helpful discussions. Dr. G. R. Finlay of the Norton Company, Chippawa, Ontario kindly supplied some of the crystals used in this work.

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[5] G. D. Watkins and R. M. Walker, Bull. Am. Phys. Soc. Ser. II, **1**, 324 (1956).

[6] G. D. Watkins (private communication).

[7] The line observed by J. E. Wertz and J. L. Vivo [Phys. Rev. **100**, 1792(A) (1955)] and attributed to an intrinsic defect center was the central component of the Fe(+3) quintet.