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Forbidden Hyperfine Transitions in the Electron Paramagnetic Resonance of V^{++} in MgO†

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The forbidden hyperfine spectrum of the electron paramagnetic resonance of V^{++} in MgO has been studied to test the assumptions of Van Wierengen and Rensen that the fine structure is explained by local-site symmetry that is lower than cubic. Since a cubic field cannot lift a four-fold spin degeneracy, only lower symmetry perturbations can be used to appropriately mix neighboring hyperfine states such that the transitions $|\Delta M|=1$, $\Delta m=\pm1$ can exist. The axial-field splitting parameter D is computed from the intensity of the forbidden spectrum and an attempt to determine preferred axes of symmetry for the local sites by studying the angular dependence of the forbidden line intensity is made. Evidence is presented that indicates the local-site distortion is proportional to the concentration of vanadium in the crystal.

INTRODUCTION

THE electron-paramagnetic-resonance (EPR) spectrum of divalent manganese in MgO has been investigated and is, in general, well known.[1-3] The cubic crystalline field splits the sevenfold orbital levels of the $3d^3$ ion into two triplets and a singlet with the singlet lying lowest. The ground state is an effective S state with spin $S'=\frac{3}{2}$. Because the nucleus also has a spin, $I=\frac{7}{2}$, the resulting hyperfine interaction yields a spectrum of eight groups of three fine-structure lines each with theoretical intensity ratios of 3:4:3. The spin quartet cannot split in a cubic field, so that the separation of the satellites from the center line in each triad is due primarily to second-order hyperfine interaction and should be isotropic.

Recently however, Van Wierengen and Rensen[3] studied the satellites of the fine structure in detail and found a significant angular dependence to the linewidth which could not be explained by cubic fields but which they ascribed to small axial or rhombic distortions at the V^{++} site. Since the satellites showed broadening rather than anisotropic splitting, it was necessary to assume there might be different magnitudes of distortion at the different V^{++} sites and that the primary direction for the small distortions were along the $\langle 111\rangle$ cubic directions. They assumed that the reason for the lower symmetry was the existence of substitutional Cr^{+++} and Fe^{++} impurities in the crystal.

The present work is an attempt to corroborate the suggestions that lower-than-cubic distortions are present in $MgO\!:\!V^{++}$ by studying the forbidden hyperfine spectrum, and to provide an independent measure of the distortion. In addition, an independent attempt to find directions for the symmetry is made. Our investigations show that the lower symmetries are not proportional to the presence of other transition ions, and evidence for the distortion mechanism is presented.

RESONANCE SPECTRUM

A convenient Hamiltonian to describe an orbital singlet ion site with $S'=\frac{3}{2}$ in a cubic crystalline field with lower symmetries present is

$$H=g\mathbf{H}\cdot\mathbf{S}+A\mathbf{I}\ \mathbf{I}+D(S_{z'}^2-5/4)+E(S_{x'}^2-S_{d'}^2),\quad(1)$$

where D and E are the axial and rhombic crystalline field parameters, respectively. The primed coordinates refer to the crystal axis, which is not in general along the magnetic field axis. If the z axis for the representation $|M,m\rangle$ is chosen to be the magnetic-field direction and if the hyperfine interaction is considered a perturbation on the Zeeman term in second order, there will be an isotropic fine-structure splitting so that the spectrum will appear as a triad, as mentioned above. The effect of the lower symmetry term in D will be to shift the outer lines in the fine-structure triad by an amount

$$\Delta H=D(M-\tfrac{1}{2})(3\cos^2\theta-1),\quad(2)$$

where θ is the angle between the distortion axis z' and the magnetic field direction z. If it is assumed that the z' axes lie along each of the four $\langle 111\rangle$ axes with equal probability, ΔH will vanish when the cubic crystalline axes coincide with the Cartesian axes. As the crystal is rotated in the x–z plane, two of the four superimposed lines will move in one direction, while the others move in the opposite direction. The average position of each observed line will be where predicted by the Zeeman and hyperfine terms in the Hamiltonian, but the linewidth will appear to increase. This will only be true if the value of D varies from site to site; otherwise the lines would be seen to split rather than broaden.

When the lower-than-cubic symmetry direction is not along the magnetic-field direction and when a hyperfine interaction is present, all the ingredients are available for mixing neighboring hyperfine states, thus allow-

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† Work supported by the National Science Foundation.

[1] W. Low, Phys. Rev. **101**, 1827 (1956).

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[3] J. S. Van Wieringen and J. G. Rensen, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. 1, p. 105.

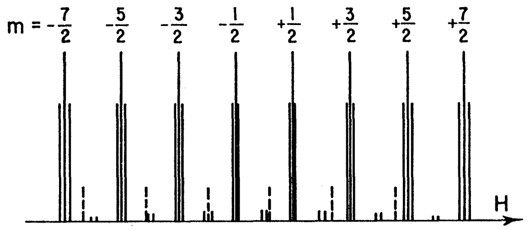

FIG. 1. Schematic spectrum of MgO:V^{++} showing the small forbidden doublets between each allowed triad. The dashed lines show the positions of allowed Mn^{++} lines at X band.

ing the so-called forbidden transitions to appear.[4] In particular, when the primed axes of Eq. (1) are transformed to coincide with the magnetic field, spin-raising (and lowering) operators are formed which can be combined with the spin-lowering (and -raising) and nuclear-spin-raising (and -lowering) operators in higher-than-first-order perturbation theory to mix neighboring hyperfine levels. Apparent forbidden lines can occur, then, in the spectrum corresponding to $|\Delta M|=1$, $\Delta m=\pm 1$ and occur as small doublets between the main hyperfine lines. These are shown in the schematic of Fig. 1.

The intensity of these forbidden doublets $|\frac{1}{2}, m\rangle \leftrightarrow |-\frac{1}{2}, m+1\rangle$ and $|\frac{1}{2}, m+1\rangle \leftrightarrow |-\frac{1}{2}, m\rangle$ relative to the allowed spectrum $|\frac{1}{2}, m\rangle \leftrightarrow |-\frac{1}{2}, m\rangle$ was first given by Bleaney and Rubins[5] and for the transitions of V^{++} can be written as

$$16(3D\sin 2\theta/4g\beta H)^2[I(I+1)-m(m+1)]. \qquad (3)$$

The intensity of the forbidden lines therefore affords an independent measure of the effective average of the axial-field splitting of the spin quartet. Forbidden transitions owing to other fine-structure levels are possible but are not observed because of their low intensity and angular dependence.

Samples with varying amounts of vanadium impurities were investigated but only in the heaviest doped (0.5% mole) were forbidden lines observed. The intensities of the seven doublets relative to each other were found to be 7:12:15:16:15:12:7, as predicted. The intensity of the center pair relative to the allowed spectrum was about 1:300, from which an average D of about 20 G can be computed by using Eq. (3). This figure is in reasonable agreement with the value deduced from an extrapolation of the rate of broadening of the allowed lines. Equation (3) can be modified to include a rhombic distortion by replacing D with $D-E$. Since E can be as large as $\frac{1}{3}D$, we must assume that amount of uncertainty in our value of D. Our inability to observe the forbidden spectrum in a crystal with 0.1% V^{++} suggests a value of D less than 5 G in that crystal, which is again compatible with the rate of broadening of the allowed lines.

TABLE I. Calculated and measured separation of forbidden doublets (in Gauss).

m	$-\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
Theory	7.79	8.27	8.74	9.22	9.69	10.18	10.66 (±0.01)
Obs.	8.2	9.0[a]	8.9[a]	8.0[a]	9.8	10.3	10.1 (±0.5)

[a] Doublet computed using only one line and its approximate position from center of two nearest hyperfine lines.

The separation of these doublets in a small axial field, neglecting quadrupolar terms, and for $S=\frac{3}{2}$, is given by[6,7]

$$\delta H=17A^2/2H+(2g_n\beta_n/g\beta)H$$
$$+(4A^2D/H^2)(3\cos^2\theta-1)(2m+1). \qquad (4)$$

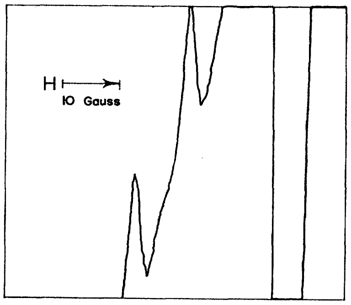

FIG. 2. Sample datum showing the first derivative of the absorption lines of the doublet between $m=\frac{1}{2}$ and $m=\frac{3}{2}$ shown on the shoulder of a Mn^{++} line. Ratio of doublet intensity to allowed V^{++} intensity is about 1:300.

Note that the leading terms of this expression are from the hyperfine and the nuclear Zeeman terms and therefore are isotropic. The position of the doublets is also nearly isotropic, which means that the doublets occur in nearly the same place in the spectrum for all directions and magnitudes of the lower symmetry.

Table I shows the calculated doublet separation and the experimentally observed separation for the most heavily doped sample.[8] The crystals used invariably showed a strong manganese spectrum which tends to obscure the V^{++} forbidden lines, but for all values of m at least one line of the doublet was visible. The positions of the ubiquitous manganese lines relative to the doublets at X band are also shown in Fig. 1. Figure 2 shows the forbidden doublet between the

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[4] For an explanation of the axial case as an example, see John E. Drumheller and R. S. Rubins, Phys. Rev. **133**, A1099 (1964). The most recent detailed axial work can be found in Refs. 6 and 7 below. References to other work on forbidden transitions can be found in these papers.

[5] B. Bleaney and R. S. Rubins, Proc. Phys. Soc. (London) **77**, 103 (1961).

[6] V. J. Folen, Phys. Rev. **139**, A1961 (1965).

[7] D. H. Lyons and R. W. Kedzie, Phys. Rev. **145**, 148 (1966).

[8] The crystals used were obtained from the Norton Company, Niagara Falls, Ontario, and Semi Elements, Inc., Saxonburg, Pennsylvania. The color of the 0.1% sample is pale green, while the 0.5% is nearly black, possibly very dark green.

$m=\frac{1}{2}$ and $m=\frac{3}{2}$ allowed triads, recorded as the first derivative of the absorption.[9] The forbidden linewidths are isotropic and are all identical with the width of the $M=\frac{1}{2}\leftrightarrow M=-\frac{1}{2}$ allowed lines, which are about 1.8 G between inflection points.

An attempt was made to determine the principal directions of the distortions by studying the angular dependence of the intensities of the forbidden doublets. This analysis is similar to that of Tanimoto and Kemp,[10] who were able to detect small axial departures from cubic symmetry of about 20×10^{-4} cm^{-1} in the $\langle100\rangle$ directions for Mn^{++} in SrO. If the distortion for our case of V^{++} in MgO were along the $\langle111\rangle$ directions of the octahedron, the forbidden intensity would be proportional to $2-\sin^2 2\theta$ when rotating about a $\langle100\rangle$ axis. While a tendency toward this behavior is observed, the maximum-to-minimum ratio is less than 2:1, indicating that other directions are also distortion axes for these sites. No special directions in $MgO{:}V^{++}$ can be claimed using this technique for the most heavily doped sample.

DISCUSSION

The existence of lower-than-cubic symmetry at V^{++} substitutional sites in the MgO lattice is suggested by anisotropic linewidths in the allowed spectrum, and has been confirmed by the observation of the forbidden spectrum. The distortion axis takes a variety of nonequivalent directions, as determined from the angular dependence of the forbidden line intensities. The magnitude of the distortion can be computed from observations on either the allowed or the forbidden spectrum, and is found to vary from crystal to crystal. Our crystals contained differing amounts of other transition group ions such as Cr^{+++} and Mn^{++}. However, the crystal which showed the largest axial splitting and in which forbidden transitions were seen had no significant Cr^{+++} and the lowest concentration of Mn^{++}, while others with high Cr^{+++} and Mn^{++} concentrations showed small D values. On the other hand, the distortion magnitude seems to be proportional to the vanadium concentration. This is illustrated in Fig. 3, where the average D is plotted as a function of vanadium concentration. The computation of D is uncertain because of an unknown amount of rhombic distortion and because D must be averaged over all angles. These uncertainties, combined with deviations found after various heat treatments, are reflected in the vertical error limits of Fig. 3. Figure 3 also shows results of previous investigators for whose crystals the heat-treatment history is unknown.

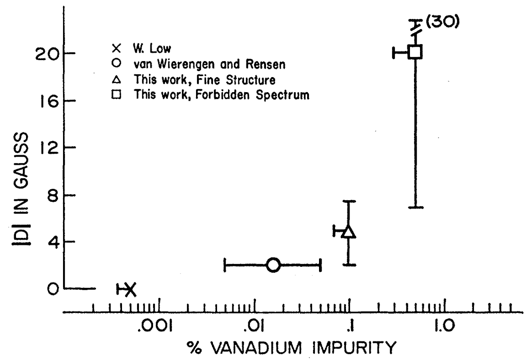

FIG. 3. Magnitude of local-site distortion as a function of vanadium concentration. The error bars are only approximate and are intended to include uncertainty in the average amount of rhombic distortion as well as lack of knowledge of heat-treatment history of each sample.

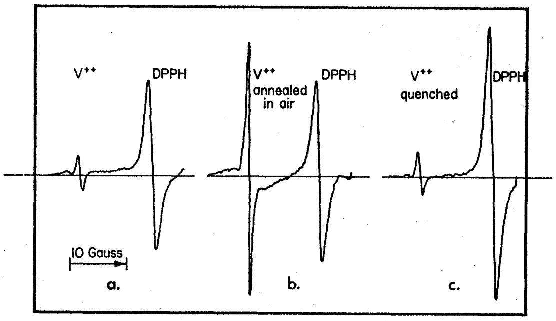

FIG. 4. A comparison of the $m=-\frac{1}{2}$ hyperfine allowed line of V^{++} in MgO: (a) as delivered, (b) after annealing, and (c) after quenching. Each case is compared against a standard DPPH sample. The change in amplitude of the DPPH signal only indicates a different gain in the spectrometer.

The most heavily doped crystal was annealed in air at 1250°C for several hours and then cooled at 1°C per h, after which the distortion magnitude was reduced to about one third of its former value, and the forbidden lines became so weak as to be unobservable. Reheating the crystal in air to 1250°C and quenching to room temperature restored the crystal to its former state. This behavior suggests that a valence state of vanadium other than V^{++} may be responsible for the distortion. For example, Sturge has seen from optical data that V^{+++} occurs in vanadium-doped MgO, and that it can be converted to V^{++} by annealing in a hydrogen atmosphere.[11] Specifically, he showed that the diminishing optical absorption of V^{+++} was associated with an increase in magnitude of the electron resonance spectrum of V^{++}. To check our own crystals, an attempt to correlate the EPR, and optical absorption for annealing in air was made. Figure 4 shows a schematic of the EPR results of this heat treatment on the allowed vanadium line nearest $g=2$ with a standard diphenyl-picryl-hydrazyl (DPPH) sample in the cavity. An increase of V^{++} signal on annealing

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[9] A superheterodyne X-band spectrometer was used, with sensitivity of about $5\times10^{12}\ \Delta H$ spins modulated and phase detected at 400 Hz and recorded on a strip-chart recorder. Measurements were taken at 300 and 78°K but all data presented here are at room temperature.

[10] D. H. Tanimoto and J. C. Kemp, J. Phys. Chem. Solids **27**, 887 (1965).

[11] M. D. Sturge, Phys. Rev. **130**, 639 (1963).

and a loss on quenching are clearly indicated. The optical-absorption data in the range from 200–900 mμ was taken on a Beckmann DK-2 Spectrophotometer, and indicated the presence of V^{+++} in each sample. However, no conclusive evidence can be seen that the V^{+++} concentration diminished when annealed in air. In fact, in some cases the optical absorption due apparently to V^{+++} increased at the same time the resonance signal of V^{++} increased. This would indicate that yet a different valence state of vanadium is present in the crystal. The significant increase in V^{++} EPR signal on annealing would seem to rule out local strains as the strongest local distortion mechanism.

If the presence of these other valence states is responsible for the distortion, the mechanism is likely to be the presence of interstitial oxygen needed for charge compensation. The ionic radii of triply or quadruply ionized vanadium ions suggest that they may be more favorable in MgO than doubly ionized and may even be so after inclusion of the necessary interstitial oxygen.[12] The black color of the 0.5% sample suggests the formation of V_2O_3 or VO_2 complexes in the lattice, but no further evidence of this is available at present.

ACKNOWLEDGMENTS

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[12] See, for example, Linus Pauling, *The Nature of the Chemical Bond*, (Cornell University Press, Ithaca, New York, 1960), p. 518.

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Paramagnetic-Resonance Spectra of S_2^- in Alkali Halides*

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The impurity ion S_2^- has been introduced into six alkali-halide crystals: NaI, KCl, KBr, KI, RbBr, and RbI. The center is characterized by extreme g anisotropy; in KBr, for example, the principal g factors were 3.5037, 0.8434, and 0.8388. The first of these corresponds to the S-S bond direction which, in all crystals studied, was parallel to the ⟨110⟩ directions of the crystal. The direction of minimum g factor was associated with the direction of the molecular π orbital occupied by the unpaired electron. This direction was ⟨110⟩ for S_2^- in KCl, RbRr, and RbI, but ⟨100⟩ for S_2^- in NaI, KBr, and KI. Sulfur enriched in the isotope S^{33} was used to investigate the S^{33} hyperfine interaction. The largest S^{33} hyperfine interaction occurred when H_0 was parallel to the S-S bond direction, and not, as might have been expected, when H_0 was parallel to the direction of the π function. This was due to the dominant contribution from the $\mathbf{L}\cdot\mathbf{I}$ term in the hyperfine Hamiltonian. Hyperfine structure due to lattice nuclei could not be resolved but gave rise to the highly anisotropic linewidths of the resonances.

INTRODUCTION

IT was established some years ago[1] that the characteristic fluorescent emission exhibited by alkali-halide crystals containing hydroxide ion impurity was due to the presence of O_2^-. This identification was based on the band structure of the emission spectrum, the band interval of 1000 cm^{-1} being associated with transitions into various vibrational levels of the ground state of the diatomic molecule. Moreover, crystals exhibiting this fluorescence showed electron-paramagnetic-resonance (EPR) spectra[2] which were also consistent with the presence of O_2^-.

More recently an analogous fluorescence has been detected in crystals of KCl and KBr grown from the melt in an atmosphere of sulfur vapor.[3] The vibrational interval of 580 cm^{-1} suggested that in this case S_2^- ions might be present in the crystals. This was later confirmed by the detection of the EPR spectrum of S_2^- in the KBr crystals.[4]

The purpose of the present experiments was to introduce S_2^- into as many alkali halides as possible, with a view to using the paramagnetic resonance technique to detect and characterize the impurity, comparing the results with those obtained for O_2^-.

EXPERIMENTAL

Commercially available (Harshaw, Semi-Elements) ultrapure alkali-halide crystals were used. In order to introduce the S_2^- impurity into the samples, small crystals (typically $5\times2\times10$ mm^3) were placed, with a small amount of sulfur, in quartz ampoules, which were sealed off after evacuation. The ampoules were then heated in a furnace for 100–200 hours at a temperature close to the melting point of the crystal. In the case of KCl, KBr, and RbBr the temperature was 20° below

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* NRC No. 9726.

† National Research Council of Canada Postdoctoral Fellow 1966–68.

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