Structure of the Fluorine-Containing Trapped-Hole Center in Magnesium Oxide*

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(Received 18 November 1968)

A trapped-hole center (V_F center) induced in MgO by ionizing radiation has previously been assigned the structure O^+—[=]—F^+ (only deviations from normal site charge shown). ENDOR data confirm the identification of the interacting nucleus as fluorine. The contact and dipolar splitting constants are, respectively: $a = 0.234 \pm 0.010$ MHz and $b = 0.923 \pm 0.010$ MHz. The value of b implies a hole-fluorine distance of 0.432 nm, compared with the normal O-O lattice distance of 0.420 nm. Calculations of the isotropic hyperfine splitting due to overlap of the hole with the fluorine $2s$ orbital suggest that the hole is primarily localized on one oxygen atom. This conclusion is supported by a comparison of g factors for trapped-hole centers.

INTRODUCTION

HYDROGEN and fluorine are often detected as impurities in MgO crystals. Both can be found in lattice sites adjoining a positive-ion vacancy. In the case of hydrogen, when a hole is trapped on an oxygen adjoining the same positive-ion vacancy, the linear V_{OH} center is formed. Electron nuclear double resonance (ENDOR) experiments[1] unambiguously identified the proton and suggested the structure $OH^+[=]O^+$ (only deviations from normal site charge are shown). This was the first description of the geometry of a hydrogen-containing point defect in MgO.

More recently, the ESR spectrum of a magnesium oxide hole center similar to the V_{OH} was reported.[2] The doublet structure characteristic of a nucleus with $I = \frac{1}{2}$ suggests the presence either of hydrogen or of fluorine interacting with the trapped hole. The axial symmetry of the center, determined from the angular behavior of the ESR lines, together with the similarity of g components to those of the V_{OH}, suggests that the new center has a similar structure. ESR spectra of MgO powders heated after treatment with HF reveal a partially resolved doublet corresponding to the $g_\perp$ doublet of the new center in a single crystal. This strongly suggests that a fluorine nucleus is responsible for the hyperfine interaction. The structure proposed for this center is $F^+[=]O^+$.[2]

We undertook ENDOR measurements on the V_F center to confirm the presence of fluorine in the defect and to measure more precisely the hyperfine parameters.

EXPERIMENTAL

The ENDOR spectrometer is an X-band microwave bridge employing superheterodyne detection. The signal klystron is frequency-locked either to the sample cavity or to a reference cavity for observation of absorption or dispersion ESR signals. Single crystals of MgO are placed on the bottom of an evacuated TE_{111} cavity. ESR signals are obtained with field modulation at 1000 Hz and phase detection of the i.f. output at this frequency. ENDOR signals are obtained by monitoring the first derivative of the ESR dispersion signal while the nuclear frequency is swept slowly.

V centers are produced in an MgO crystal of low-transition metal-ion content by 70-kV x irradiation at 77°K, and ENDOR experiments are carried out at 4.2°K.

RESULTS

Figure 1 shows the ESR spectrum of V_{OH} and V_F centers when the external field is perpendicular to the symmetry axis. The ENDOR spectrum for the same orientation is displayed in Fig. 2. A remarkable feature of this spectrum is the appearance of V_{OH} ENDOR lines (as well as the pair due to fluorine) while saturating a V_F ESR line. Unfortunately, a V_F line overlaps one V_{OH} line at $\theta = 45°$, but at $\theta = 90°$ the V_F-V_{OH} pair are resolved [Fig. 2(a)]. The overlap at 45° is compensated by the fact that the V_{OH} lines constitute a built-in proton probe for measuring the external field.

Table I shows the ENDOR frequencies obtained at $\theta = 0°$, 45°, and 90°, as well as the mean frequencies ($\bar{\nu}_F$ and $\bar{\nu}_H$) for V_F and V_{OH} at 0° and 90°. Since the hyperfine interaction is small, the latter correspond to
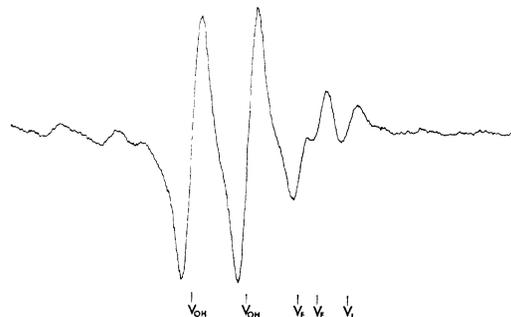
FIG. 1. ESR spectrum of trapped-hole centers for the external field perpendicular to the symmetry axis. The V_F doublet is just barely resolved.

[1] P. W. Kirklin, P. Auzins, and J. E. Wertz, J. Phys. Chem. Solids 26, 1067 (1965).
[2] J. E. Wertz and P. Auzins, Phys. Rev. 139, A1645 (1965).
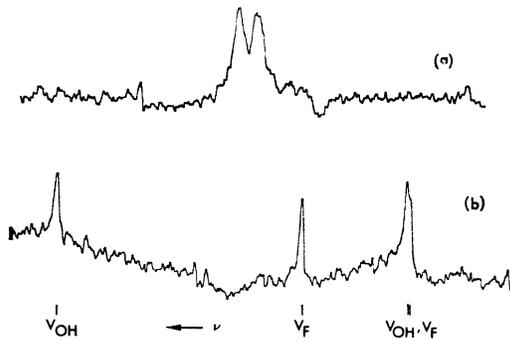
FIG. 2. ENDOR spectrum of V_F and V_{OH} centers for $\theta = 90°$. The upper trace (a) is a slow sweep through the 12.9-MHz line showing the 30-kHz separation of the V_F-V_{OH} pair.

the nuclear Zeeman interaction of the corresponding nuclei.

DISCUSSION

ENDOR transition frequencies are given by

$$\nu(M; m, m+1) = M[a+b(3\cos^2\theta - 1)] - g_N\beta_N H/h, \quad (1)$$

where M is the electronic spin quantum number and m is the nuclear spin quantum number. The average frequency is

$$\bar\nu = \tfrac{1}{2}[\nu(+\tfrac{1}{2}; -\tfrac{1}{2}, \tfrac{1}{2}) + \nu(-\tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2})] = g_N\beta_N H/h. \quad (2)$$

This is exact at $\theta = 0°$ and $\theta = 90°$, but at other angles a correction must be made.[3] Thus, one can see that the nucleus interacting with the hole is indeed fluorine by comparing the mean V_F ENDOR frequency with that of V_{OH} at $0°$ and $90°$. The ratio $\bar\nu_F/\bar\nu_H$ at the two angles corresponds to μ_F/μ_H within experimental error.

The hyperfine splitting follows an $a+b(3\cos^2\theta - 1)$ dependence, where θ is the angle between the external field and an [001] axis. Values of a and b computed from the frequencies in Table I are 0.234 ± 0.010 and 0.923 ± 0.010 MHz, respectively. Expressed in Gauss they are 0.084 and 0.330, in excellent agreement with the values 0.08 and 0.33 reported by Wertz and Auzins.[2]

TABLE I. ENDOR frequencies in MHz for V_F and V_{OH}. The average V_F frequency divided by average V_{OH} frequency is shown for $\theta = 90°$ and $\theta = 0°$.

	V_F	V_{OH}	$\bar\nu_F/\bar\nu_H$	μ_F/μ_H[a]
$\theta = 90°$	12.9137	12.9360	0.94089	0.94078
	13.6031	15.2465		
$\bar\nu$	13.2584	14.0914		
$\theta = 45°$	13.0446			
	13.7403			
$\theta = 0°$	12.4411	11.9270	0.94082	
	14.5483	16.7601		
$\bar\nu$	13.4947	14.3435		

[a] *Varian Associates NMR Table* (Varian Associates, Palo Alto, Calif., 1964), 4th ed.

[3] J. J. Davies, Phys. Letters **28A**, 9 (1969).

Values of the hyperfine parameters for the V_{OH} center agree with those obtained by Kirklin *et al.*[1] to within experimental error.

The location of the fluorine ion with respect to the trapped hole may be inferred from the dipolar interaction parameter b assuming that the hole is localized. Using the relation $b = \mu_e\mu_N R^{-3}$, we compute a value of $R = 0.432$ nm for the average hole-nucleus separation. A similar result is obtained for the W center (the linear hole-vacancy-hole system $O^+[=]O^+$). The value of the zero-field splitting parameter D obtained for this $S = 1$ configuration is $D/hc = 212.5\times10^{-4}$ cm^{-1}.[4,5] The assumption that D is wholly attributable to spin-spin interaction gives a hole-hole separation of 0.453 nm. Both of these values are significantly larger than the O-O lattice distance of 0.420 nm, and suggest a considerable relaxation away from the positive-ion vacancy.

It is of interest to estimate the isotropic part of the hyperfine interaction on the assumption that the hole is localized on one oxygen ion 0.432 nm from the fluorine nucleus. There are several possible mechanisms by which the interaction may arise; here we shall restrict ourselves to the contribution caused by direct overlap between the hole function (ψ) and the fluorine orbitals. The major part of the contribution arises from overlap with the fluorine $2s$ orbitals, and may be written

$$a = A_{2s}|\langle\psi|2s(F^-)\rangle|^2,$$

where

$$A_{2s} = \tfrac{1}{3}8\pi g g_N\beta\beta_N|\psi_{2s}(0)|^2.$$

We assume that the hole is in an oxygen $2p$ orbital directed towards the vacancy. Using an O^- $2p$ orbital due to Watson[6] and an analytical fit[7] to Froese's[8] fluorine $2s$ function, we compute $|\langle2p(O^-)|2s(F^-)\rangle|$ $= 0.00629$. For the fluorine $2s$ function, Sugano and Tanabe[9] quote

$$|\psi_{2s}(0)|^2 = 10.7 \text{ a.u.}$$

This gives $a = 1.78$ MHz, which is seven times greater than the experimental value. However, agreement with experiment is not expected to be close, because the overlap at such a distance involves mainly the tails of the wave functions. The region far from the nucleus of an atom makes little contribution to the total energy of the system and it is not well characterized by a self-consistent field wave function. The essential point is that it is not necessary to postulate delocalization of the hole in order to obtain an isotropic hyperfine component of the observed magnitude. (See note added in proof.)

Further evidence in favor of a localized-hole model is provided by the close similarity of the g factors of the

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[6] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[7] S. Sugano, and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

[8] C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

[9] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **20**, 1155 (1965).

various V centers.

$$V_1; g_{11} = 2.00327, \quad g_\perp = 2.03859,$$
$$W; g_{11} = 2.0032, \quad g_\perp = 2.0408,[4]$$
$$V_{OH}; g_{11} = 2.0032, \quad g_\perp = 2.0396,[1]$$
$$V_F; g_{11} = 2.0031, \quad g_\perp = 2.0388.[2]$$

The quantity $g_\perp - 2.0023$ is a measure of the orbital contribution to the g factor. If the hole were greatly delocalized into the equatorial oxygen orbitals, the substitution of OH^-, F^-, or O^- for $O^=$ at the nnn site would be expected to perturb the hole orbital (and therefore $g_\perp$) significantly. However, the g factors of all the modified trapped holes are remarkably close to those of the V_1 center. This again suggests that the hole is largely localized on a single oxygen atom.

Note added in proof. Recently an improved O^-2p wave function due to Nagai[10] was brought to our attention. This function was developed for the calculation of hyperfine parameters in MnO, and in presenting it, Nagai mentions that Watson's orbital has been found to be too large in the tail for these calculations. The overlap calculated from this new function is $|\langle 2p(O^=)|2s(F^-)\rangle| = 0.00168$, which gives a value of $a = 0.128$ MHz for the isotropic hyperfine coupling. This is much closer to the observed value of a than that obtained using Watson's orbital, and strengthens our argument regarding the tightly-bound hole model.

ACKNOWLEDGMENT

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Magneto-Optical Structure of the MgO F Band*

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(Received 17 October 1968)

The paramagnetic Faraday-rotation pattern of the MgO F center has been investigated, using the ESR-optical double-resonance method, at 12 kG and 1.8°K. The rotation is centered precisely upon the familiar 4.95-eV absorption band, in agreement with the extrapolated position predicted from a previous observation on the extreme low-energy tail of the band. The p-state spin-orbit parameter λ is given as $-(12\pm3)$ cm^{-1}. The pattern is highly symmetrical, consistent with a very nearly Gaussian absorption band. The width of the pattern is about 30% less than the width which would correspond to a Gaussian absorption band with rigid magneto-optic shift, if the F band is assumed to be Gaussian with the accepted half-width of 0.48 eV. This implies that noncubic electron-lattice interaction is present: The third moment of the circular dichroism (computed from the observed rotation) in fact has a value such as to indicate that noncubic modes are strongly dominant. The same rotation spectrum is observed in samples of both neutron-irradiated and additively colored MgO. However, in the latter there are curious discrepancies between the apparent F-center densities as gauged by the absorption band intensity, the ESR signal strength, and the Faraday rotation amplitude. This is discussed in terms of a postulated near coincidence of the F and F' bands, and the occurrence of F'-F conversion during the measuring operation; the connection with other observations on the F-F' relationship in MgO is indicated.

I. BACKGROUND

THE utility of magneto-optic observations in isolating the F bands in the IIA oxides[1] was recognized over two years ago.[2] Well-defined Faraday rotation (FR) patterns believed characteristic of the F center were discovered in CaO [2-4] and in SrO and BaO.[4] These patterns were obtained from conventional measurements[4] of the spectroscopic Faraday rotation $\theta(E,H,T)$, and in the case of CaO by the magneto-optical double-resonance method.[2,3] The bands in these cases lie near 2 eV (BaO), 3.0 eV (SrO), and 3.7 eV (CaO), i.e., in the visible and near uv range.

The MgO F band is understood to be the familiar 4.9-eV band, at about 2500 Å. Rotation measurements on this band are difficult, first, because of the usual instrumental difficulties in the uv (weak light sources, etc.) and, second, because of the relatively weak paramagnetic rotation, i.e., the small rotation per unit sample absorbance (small spin-orbit coupling λ). Up to the present work, only a study of the rotation on the

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