split off by the Jahn-Teller distortion. The matrix elements $\langle j|V|0\rangle$ will be proportional to r^2, where r is the mean radius of the orbit.[17] Then

$$G\sim\lambda^2 r^2/\delta^2.$$

The Jahn-Teller splitting δ is proportional to r^4. Then

$$\frac{G_C}{G_F}\sim\left(\frac{\lambda_C}{\lambda_F}\right)^2\frac{r_F{}^6}{r_C{}^6}.$$

If the d-electron wave functions lie mostly outside the closed inner shells, we may imagine the d electrons move in a Coulomb field of some effective charge $Z_{\rm eff}$. Then $r^2\sim 1/Z_{\rm eff}{}^2\sim 1/I$, where I is the ionization potential. We then estimate

$$\frac{G_C}{G_F}\approx\left(\frac{\lambda_C}{\lambda_F}\right)^2\left(\frac{I_C}{I_F}\right)^3.$$

We employ the free-ion values for the ionization potential and the spin-orbit coupling parameter. From spectroscopic data[18] we find $\lambda_C/\lambda_F\sim 1.5$ and $I_C/I_F\sim 2.3$.[19]

This yields $G_C/G_F\approx 18$ or

$$G_C\approx 4\times 10^{-12}\text{ ergs}.$$

This estimate indicates that Cr^{4+} should couple to the lattice strongly enough for the lifetime of the normal modes to be determined by scattering from fluctuations in S_z.

ACKNOWLEDGMENTS

I am indebted to Professor C. Kittel for his many helpful comments.

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[17] Reference 16.

[18] C. Moore, Natl. Bur. Std. (U.S.), Circ. No. 467 (1952), Vol. II, pp. 18–19, 60–61.

[19] If our assumption that the d electron moves in a field of an effective charge $Z_{\rm eff}$ is meaningful, then we should find $\lambda\sim Z_{\rm eff}$, or $(\lambda_c/\lambda_F)\approx(I_c/I_F)^{1/2}$. This relation is well satisfied.

PHYSICAL REVIEW VOLUME 139, NUMBER 5A 30 AUGUST 1965

Trapped Hole Center Containing Fluorine in Magnesium Oxide*

JOHN E. WERTZ AND PETERIS V. AUZINS
Department of Chemistry, University of Minnesota, Minneapolis, Minnesota

(Received 12 April 1965)

An intrinsic defect center readily induced in MgO by ionizing radiation is the positive hole localized on an oxygen atom adjacent to a positive ion vacancy (V_1 center). This has a tetragonal symmetry axis along [001] or equivalent directions. A similar ESR spectrum but with each line a hyperfine doublet was identified earlier as arising from the center $\mathrm{O}^+-[=]-\mathrm{H}^+\mathrm{O}$ ($V_{\rm OH}$ center). This paper describes a similar ESR spectrum of a trapped hole center ($V_{\rm F}$) with smaller (anisotropic) hyperfine splitting than $V_{\rm OH}$. It is best observed in single crystals, but it may be induced in powdered MgO by fluorine doping and heating. It thus appears that fluorine is the nucleus responsible for hyperfine splitting. The contact and dipolar splitting constants are, respectively: $a=0.08$ G, $b=0.33$ G. The proposed model for the $V_{\rm F}$ center is $\mathrm{O}^+-[=]-\mathrm{F}^+$ (only deviations from normal site symmetry are shown).

INTRODUCTION

IN MgO crystals, a predominant intrinsic defect which may be induced by ionizing radiation is the hole trapped adjacent to a positive ion vacancy[1] (i.e., the V_1 center proposed by Seitz but not observed in the alkali halides). Uniform delocalization of the trapped hole over the six oxygen atoms surrounding the vacancy would give an isotropic ESR spectrum, whereas the spectrum observed has pure tetragonal symmetry. We have tended to regard the hole as strongly localized. However, Dr. T. E. Feuchtwang points out that there may be delocalization such that the hole density on the four oxygens girdling the vacancy and the axis is different from that of atoms on the axis.[2] In some MgO crystals there are "satellite" lines about but not centered upon the principal lines of the V_1 spectrum; it can easily be shown that these are not a part of the same line system. One group of three hyperfine doublets was recently shown by an electron-nuclear-double-resonance (ENDOR) study[3] to arise from a V_1-type center ($V_{\rm OH}$) with the array: $-\mathrm{O}^+-[=]-\mathrm{H}^+\mathrm{O}$ along [001], [010], or [100]. (Only deviations from normal site charge are shown.) The infrared spectrum shows that the O-H stretching frequency is shifted from 3296 to 3323 cm^{-1} when a positive hole is trapped on the oxygen atom on the opposite side of the positive ion vacancy. The hyperfine splitting for $V_{\rm OH}$ is given by the expression $a+b(3\cos^2\theta-1)$, where $a=0.016$ G and $b=0.848$ G.

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* This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under grant No. AF-AFOSR 200-63.

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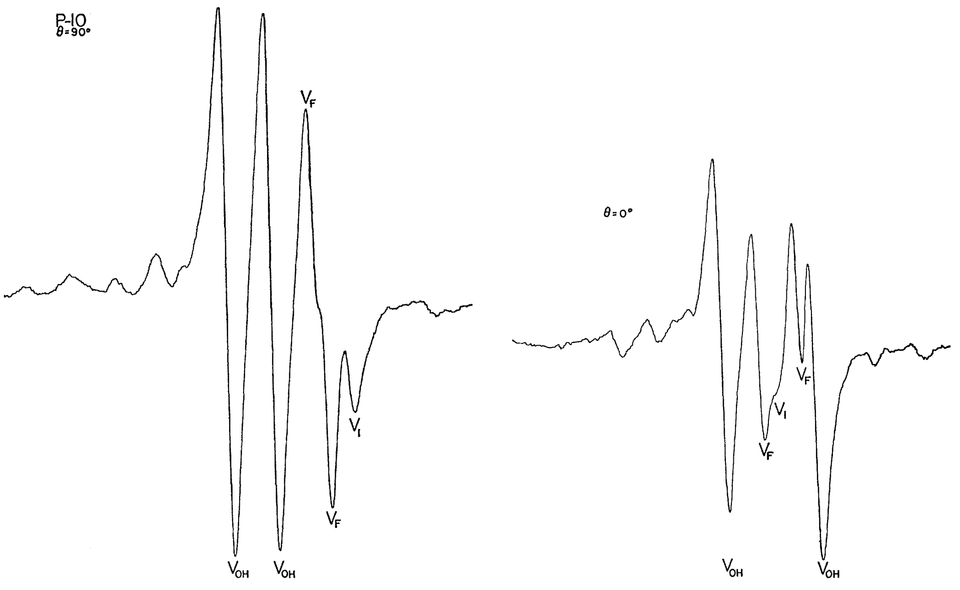
[2] Dr. T. E. Feuchtwang (private communication).

[3] P. W. Kirklin, P. Auzins, and J. E. Wertz, J. Phys. Chem. Solids 26, 1067 (1965).



(a) (b)

FIG. 1. ESR spectrum of V_F trapped hole center ($O^+ -[=]- F^+$) in MgO showing line groups consisting of V_1, V_{OH} and V_F lines at 77°K, for $\nu = 9.422$ Gc/sec $H_0 \| [001]$. (a) Low-field lines. The V_F hyperfine doublet arises from centers with axes $\| [100]$ and $[010]$. (b) High-field lines. The resolved V_F doublet arises from centers with axes $\| [001]$.

Here θ is the angle between H_0 and a defect axis. The very small isotropic component could only be measured by the ENDOR technique. Another neutral trapped hole center presumed to involve a trivalent ion has been reported.[4]

EXPERIMENTAL PROCEDURES AND RESULTS

The ESR spectra of undoped MgO single crystals from commercial sources were run at 77°K on an x-band spectrometer near 9.2 Gc/sec. We selected samples usually low in iron, chromium and manganese, as monitored by ESR spectra. Powder samples were prepared by washing reagent-grade MgO (Baker and Adamson) with a 0.1 M HF solution, heating to dryness and firing near 1200°C in an oxygen-gas flame for several hours. The samples were x irradiated at 70 kV, 15 mA for periods of 15 minutes or more.

A spectrum of a slightly milky MgO crystal (P-10) is given in Fig. 1 for $H_0 \| [001]$. It is remarkable in two respects: 1. The V_1 lines are usually weak relative to the "satellite" lines; one of the V_1 components appears only in vestigial form. 2. It shows complete resolution of the high-field V_{OH} doublet which is normally obscured by an interfering Fe^{3+} ESR line at this orientation. Additionally, one sees two new doublets, one partially resolved. Using the V_1 lines for reference, we determined the following Δg values: $\Delta g_{\|} = -5 \times 10^{-4}$, $\Delta g_{\perp} = +3.1 \times 10^{-4}$. Taking $g_{\|} = 2.0032$, $g_{\perp} = 2.0385$ for V_1, one gets for the new center: $g_{\|} = 2.0031$, $g_{\perp} = 2.0388$. On rotation of the static field H_0 in the (010) plane, one observes the separations of the hyperfine doublet components to be given by the expression: $a + b(3\cos^2\theta - 1)$, where $a = 0.08$ and $b = 0.33$ G. The line width is 0.2 G in this crystal. Again, as closely as we are able to ascertain, one has a center of pure tetragonal symmetry.

Several of the HF-treated and x-irradiated powders were also examined for their ESR behavior. For reference, the spectrum of the original powder is given in Fig. 2(a), while that of the doped powder is given in Fig. 2(b). The parallel and perpendicular components of the V_1 spectrum are readily discerned even though the sample is a powder. The line shapes agree qualitatively with those predicted for polycrystalline solids.[5] The two line components arise from centers with axes (very nearly) perpendicular and parallel to the field H_0.

In Fig. 2(b) one sees, partially resolved from the perpendicular component of V_1, another line at lower field. The figure insert, which has a much lower sweep rate, shows better the separation of the lower lobes of the perpendicular components of V_F and V_1 centers. Further, one sees an incipient hyperfine splitting of this V_F line at the position marked by the arrow. The high-field line, which for V_1 alone present is very sharp, is symmetrically broadened. The hyperfine splitting is not resolved; a hyperfine doublet drawn as positions expected from the single crystal spectrum are consistent with the observed spectrum. Likewise the g values corresponding to the peaks of the asymmetric lines of Fig. 2 are 2.003 and 2.038.

DISCUSSION

Fluorine is commonly found in MgO crystals at an atom fraction of 10^{-5} or more, as determined either by chemical analysis or by the solids-analysis mass spectrometer. Having an atomic radius of 1.36 Å as

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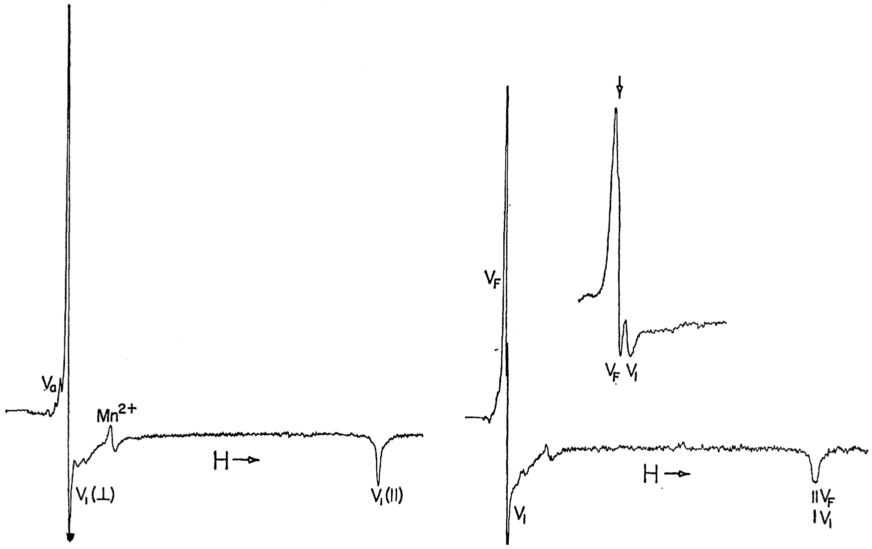

(a) (b)

FIG. 2. (a) ESR spectrum of the V_1 center in x-irradiated MgO powder at 77°K with $\nu=9.313$ Gc/sec, showing parallel and perpendicular components for reference. The line shapes are in accord with prediction (Ref. 5). The small line labelled V_a is believed to arise from a V_1-type center associated with a trivalent ion (Ref. 4). (b) ESR spectrum of a similar powder doped with HF, heated and x irradiated. The distortion of the parallel component is consistent with a hyperfine doublet of spacing taken from Fig. 1(b). The perpendicular component of V_F lies at lower field than that for V_1. Since the expected hyperfine splitting is much less than for the parallel component, one sees only an indication at the position of the arrow in the expanded insert.

compared with 1.40 for O^{2-}, F^- can readily substitute for oxygen in MgO. Charge compensation for F^- is a trivial matter; one cation vacancy can compensate for two fluoride ions. Introducing a readily acceptable impurity by way of the surface may be another matter. While one can easily detect hydrogen in MgO by its absorption in the 3300-cm^{-1} region, it is a very difficult matter to incorporate it into existent powders or crystals.[3] We have been unsuccessful in incorporating deuterium either by heating MgO crystals in the gas at 1 atm and 1200°C for three days or by heating in a pressure of 0.5 atm of D_2O at 1050°C for 30 days. No O-D stretching bands were observed. Neither have we yet been successful in introducing deuterium into MgO powder samples by boiling in D_2O, drying and firing. In contrast, brief washing of powders with HF, followed by heating, gave the split V_1-like ESR spectrum after x irradiation. This rapid diffusion is remarkable in view of the difficulty of creating negative ion vacancies in MgO. Ordinarily, one must either neutron-irradiate MgO or subject it to grinding to get enough such vacancies that F centers may be detected by ESR absorption.[6]

The correspondence (within limitations of powder spectra) in Figs. 1 and 2 gives strong support to the identity of the centers responsible for ESR spectra in the two cases. The similar anisotropy in the present spectrum and the very slight differences in g values from the V_1 center strongly suggest that the positive hole-associated vacancy is the essential aspect of the defect. A perturbing nucleus with $I=\frac{1}{2}$ is collinear with the hole-vacancy pair, for otherwise a rhombic electric field component would have been introduced. The implication of the experiments on HF-treated samples is that fluoride ion substitutes for the oxide ion. It therefore cannot be any closer than the *nnn* anion position, i.e., adjacent to the cation vacancy opposite to the positive hole:

$$O^+-[=]-F^+.$$

Here again only deviations from normal site charge are shown. This center, which we designate V_F, is neutral, as is the V_{OH} center. Notwithstanding the greater separation of F than of H from the positive hole in the two cases, there is a contact contribution directly detectable even from ESR (rather than from ENDOR) spectra. The dipolar interaction, however, is much smaller than for the V_{OH} center. Justification of these contributions is being sought by detailed calculations being carried out by Dr. T. E. Feuchtwang and his group. The V_F center, perhaps better than any of the known V_1-type centers in MgO, affords an opportunity to establish the extent of delocalization of the trapped hole.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. T. E. Feuchtwang for helpful discussions. We express gratitude to Don Johnson of Picker Northcentral Corporation and W. A. Wolstenholme of Associated Electrical Industries, Ltd. for fluorine analysis of two samples by the MS-7 solids-analysis mass spectrometer.

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