

Oxygen-17 Hyperfine Interaction of the V_F Center in MgO^\dagger

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An ESR study of v_F centers in single crystals of MgO enriched in ^{17}O is reported. The ^{17}O hyperfine tensor components are found to be $|t_{\parallel}^{17}| = 104.5 \pm 0.5$ G and $|t_{\perp}^{17}| = 14.5 \pm 0.5$ G. From these results and those for g_{\parallel} and g_{\perp} , two parameters of the O^- ion in MgO are determined: The hyperfine interaction parameter α^{17} is found to be 22.8 G and the average of r^{-3} over the $2p$ orbital is $\langle r^{-3} \rangle_s = 2.75 \times 10^{25} \text{ cm}^{-3}$.

The formation of V centers by γ irradiation of alkaline-earth oxides has been studied extensively by Wertz and co-workers.¹⁻⁴ These centers give rise to characteristic ESR spectra with axially symmetric g tensors. Their unique axes are parallel to the three equivalent $[100]$ -type directions. The g_{\parallel} values are centered upon the g_e value of the free electron, and the g_{\perp} values are about 2.04. It was proposed that these centers consist of a positive hole trapped on oxygen, adjacent to a positive- (alkaline-earth) ion vacancy and associated with a charge compensator, such as a trivalent transition-metal impurity (V_a), F^- impurity (V_F) or an $(OH)^-$ group (V_{OH}). The V_F and V_{OH} centers were found to exhibit hyperfine splittings due to F and H, respectively. The identification of the V centers as O^- ions with the unpaired electron essentially localized on the oxygen was based mainly on the observed g tensors. This conclusion can be substantiated and more information on the electronic structure of the center can be obtained by measurements of the hyperfine interaction with oxygen nuclei. However, the only stable magnetic oxygen isotope (^{17}O , $I = \frac{5}{2}$) has a very low natural abundance (0.037%) and thus normally no hyperfine splittings are observed. To overcome this limitation we have used MgO enriched in ^{17}O and the results obtained and reported in this note represent a significant test of a model of one of the intrinsic defects in solids.

Single crystals of ^{17}O -labeled MgO were grown by the flux evaporation method⁵ from PbF_2 using ^{17}O -enriched powder.⁶ The MgO powder was prepared by dissolving Johnson-Matthey's "Specpure" magnesium crystals in ^{17}O -enriched water (10%) in the presence of NH_4Cl . The resulting $Mg(OH)_2$ was transformed to MgO by heating to $550^\circ C$ in

vacuo for two hours and subsequently heating in a platinum crucible to $1300^\circ C$ in an argon atmosphere. The use of argon was necessary in order to prevent losses of heavy oxygen by exchange with the air. The crystals were also grown in an argon atmosphere, but despite this precaution the ^{17}O content in the crystals was reduced to about 0.5% as determined from the intensity of the satellites in the ESR spectra. X-ray diffraction and ESR indicate a significant amount of twinning in some of the crystals grown.

Upon γ irradiation of our crystals one dominant type of V center was observed. We studied this center at liquid-nitrogen temperature at both X -band and Q -band frequencies using a Varian model E-12 ESR spectrometer. The g values were determined relative to diphenylpicrylhydrazyl as a standard for which a value $g = 2.0037$ was taken. The magnetic field sweep was calibrated using the isotropic hyperfine splitting of the Mn^{2+} impurity which was taken as 86.8 G.⁷ Under low gain the signal of the V center consists of a doublet with a maximum splitting of $t_{\parallel} \cong 0.8$ G when the magnetic field is parallel to the g_{\parallel} axis and a minimum splitting of $t_{\perp} < 0.3$ G for the perpendicular direction. The g values were found to be $g_{\parallel} = 2.0032 \pm 0.0001$ and $g_{\perp} = 2.0389 \pm 0.0001$, where the errors are estimated from the uncertainty in the mounting of the crystal and the determination of the line positions. These results are almost identical to those found previously² for the V_F center: $t_{\parallel}^F = 0.74$ G, $t_{\perp}^F = 0.25$ G, $g_{\parallel} = 2.0031$, and $g_{\perp} = 2.0388$. The predominance of such centers in our sample is not surprising in view of the fact that it was grown from PbF_2 flux.

In the ESR spectra of labeled crystals at high gain, satellites due to ^{17}O nuclei are readily observed. In Fig. 1 is shown a typical spectrum for

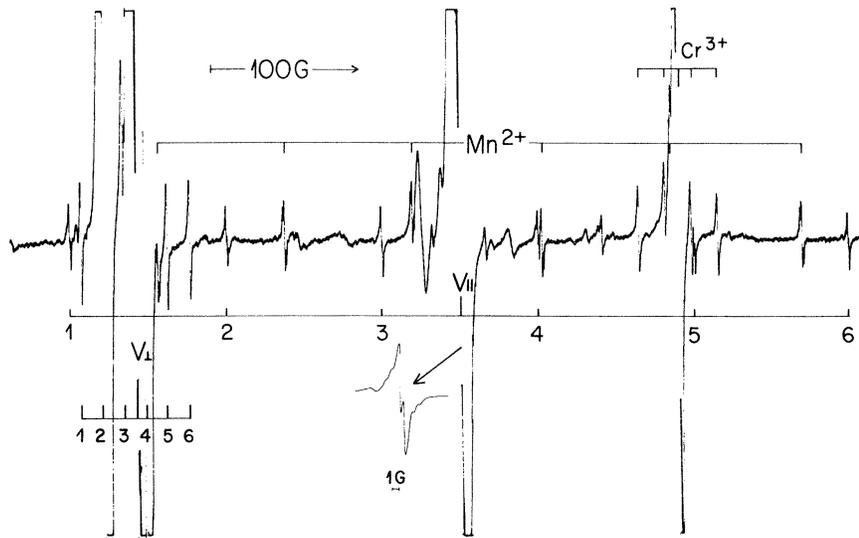


FIG. 1. Q-band ESR spectrum of a γ -irradiated single crystal of MgO enriched to ~ 0.5 at.% ^{17}O recorded at liquid nitrogen temperature. The magnetic field is along the [100] direction. The line positions of the v_F centers in the parallel ($v_{||}$) and perpendicular (v_{\perp}) directions, as well as their ^{17}O satellites (Nos. 1 to 6), are indicated. The main line of $v_{||}$ recorded at a much larger field expansion and higher attenuation is inserted to show the hyperfine splitting due to the fluorine nucleus. Some of the other peaks corresponding to known paramagnetic impurities are also labeled.

H_{dc} along the [100] direction. The six satellites due to the centers having axes parallel to the external field can all be seen, while those of the centers in the perpendicular direction which are of double intensity are partly hidden under peaks due to other species. The spectra can be fitted by the spin Hamiltonian

$$\mathcal{H} = \beta_e g_{||} H_z S_z + \beta_e g_{\perp} (H_x S_x + H_y S_y) + t_{||} {}^{17}\text{S}_z I_z + t_{\perp} {}^{17}(S_x I_x + S_y I_y),$$

with $t_{||} {}^{17} = 104.5 \pm 0.5$ G and $t_{\perp} {}^{17} = 14.5 \pm 0.5$ G.

These results are consistent with the identification of the V center in MgO as O^- . We shall discuss them along the same lines as Brailsford and co-workers,^{8,9} who studied the O^- radical in single crystals of alkali halides. They used the formalism due to Zeller, Shuey, and Känzig¹⁰⁻¹² to derive expressions for the g and t^{17} tensors. The g shifts result from mixing low-lying p_x and p_y orbitals, via the spin-orbit coupling, into the p_z orbital, carrying the unpaired electron. The corrected p_z orbital is given by

$$|\varphi^{\alpha}\rangle = C|p_z^{\alpha}\rangle - A(|p_x^{\beta}\rangle + i|p_y^{\beta}\rangle),$$

where

$$C = [1 + 2\delta/(2 + \delta)^2]^{-1/2}, \quad A = C\delta/(2 + \delta), \quad \delta = \lambda/E,$$

and E is the tetragonal crystal field splitting.

From these equations one obtains

$$g_{||} = g_e C^2, \quad g_{\perp} = g_{||} + 4lAC,$$

where l is the orbital reduction factor. Comparison with our experimental results shows that C^2 is very nearly unity. The positive shift of $g_{||}$ indicates that a small contribution to $|\varphi\rangle$ from high-lying atomic orbitals also exists. Neglecting this small effect and taking $l=1$ we find $A=0.0096$. For the t^{17} tensor components the relevant equations, neglecting second-order terms in A , are

$$t_{||} {}^{17} = \alpha^{17} + 2\beta^{17}(1 - 3A),$$

$$t_{\perp} {}^{17} = \alpha^{17} + 4h\gamma_{17}A\langle r^{-3}\rangle_i - \beta^{17}(1 - 3A),$$

where $\beta^{17} = \frac{2}{5}h\gamma_{17}\langle r^{-3}\rangle_s$ and $\alpha^{17} = \frac{8}{3}\pi h\gamma_{17}|\psi_0|^2$. Taking $\langle r^{-3}\rangle_s/\langle r^{-3}\rangle_i = 1.13$,^{8,13} two sets of results for α^{17} and β^{17} are obtained depending on the relative signs of $t_{||} {}^{17}$ and $t_{\perp} {}^{17}$.¹⁴ These results together with those for O^- in KI are summarized in Table I.

In previous work⁸ on O^- the sign of $t_{\perp} {}^{17}$ was chosen so that a negative α would result, as was found in ${}^3\text{P}$ atomic oxygen.¹³ This choice also gave $\langle r^{-3}\rangle_s$ values close to those calculated for the $2p$ orbital in a free oxygen atom.^{13,15,16} In the present case of the V_F center in MgO, neither of the two possible choices results in a negative α^{17} and for both cases $\langle r^{-3}\rangle_s$ assumes values considerably lower than those for the free atom. On the

TABLE I. g values and ^{17}O hyperfine splitting constants for O^- .

	g_{\parallel}	g_{\perp}	t_{\parallel}^{17} (G)	t_{\perp}^{17} (G)	α^{17} (G)	$2\beta^{17}$ (G)	$\langle r^{-3} \rangle_s$ (10^{25} cm^{-3})	Ref.
V_F in MgO	2.0032	2.0389	104.5	+14.5	42.7	63.7	2.08	This work
			104.5	-14.5	22.8	84.2	2.75	This work
O^- in KI	1.9733	2.3023	81.4	+17.5	20.4	79.1	2.585	8
			81.4	-17.5	-13.9	121	3.97	8
Hartree-Fock oxygen $2p$ orbital						103	3.37	15
Hartree-Fock oxygen $2p$ orbital						120	3.92	16
Oxygen 3P					-6.4	106	3.46	13

other hand if the t_{\perp}^{17} is chosen to be negative for O^- in KI and positive for the V_F center, the respective values of α^{17} and $\langle r^{-3} \rangle_s$ are very nearly the same: about 21.6 G for α^{17} and $2.67 \times 10^{25} \text{ cm}^{-3}$ for $\langle r^{-3} \rangle_s$. A positive sign for α^{17} is not an unlikely possibility; after all, an O^- radical in a crystal is not the same as a free atom. The O^- radical might show a greater resemblance to an oxygen atom in a π radical where the spin polarization at the oxygen nucleus was shown to be positive.¹⁷⁻²⁰ Also since the V_F center lacks reflection symmetry in the xy plane, a small amount of sp hybridization will result in a positive contribution to α^{17} .

The low value of $\langle r^{-3} \rangle_s$ for O^- compared to that calculated for the free atom might result from higher screening by the inner-shell electrons in O^- . This effect is expected to vary continuously from O^- to the free atom. It would therefore be interesting to determine the $\langle r^{-3} \rangle_s$ values in the series of radicals O^- , O_2^- , O_3^- and other oxy- π -radicals in which the effective charge on the oxygen is gradually decreasing.

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