Electron Spin Resonance of *F* Centers in Magnesium Oxide; Confirmation of the Spin of Magnesium-25*

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An electron spin resonance (ESR) spectrum induced in magnesium oxide crystals by pile irradiation has been interpreted as arising from *F* centers. After an oxide ion is displaced from its normal position by neutrons, an electron donated by ever-present divalent impurities may become trapped at the vacancy. Those centers having only Mg^{24} and Mg^{26} neighbors give a single ESR line with $g=2.0023$, while those with one or more Mg^{25} neighbors give hyperfine patterns corresponding to the nuclear spin value of $\frac{5}{2}$. The magnitudes of the isotropic and anisotropic parts of the hyperfine interaction show strong localization of the electron in the vacancy.

ABUNDANT evidence has been adduced by electron spin resonance (ESR) measurements to substantiate the model of the *F* center in alkali halides as an electron trapped at a negative-ion vacancy.[1–4] In a remarkable application of the double-resonance technique, Feher resolved the hyperfine structure of the (inhomogeneously broadened) *F*-center ESR line to display components arising from successive shells of alkali and halide ions.[4] In MgO the spectrum should be simpler since the only abundant (10.11%) isotope of nonzero spin is Mg^{25}. Since 53% of all magnesium ion octahedra should have only Mg^{24} and Mg^{26} ($I=0$), one should see a single narrow line for an electron in a negative-ion vacancy with such an environment. There are also centers with one or two Mg^{25} ions around the negative-ion vacancy, and these should give a six- or an eleven-line hyperfine pattern centered upon the strong component. Such centers constitute, respectively, 36 and 10% of the total number.

One might hope to see the electron spin resonance absorption of such centers in crystals of magnesium oxide heated in magnesium vapor or subjected to ultraviolet or x-irradiation. Experiments begun in 1953 have failed to show lines attributable to *F* centers from such treatments.[5] Instead, one sees the effects of electron exchanges between the ever-present impurities of the iron group, which can exist in either the (+2) or the (+3) states.[6] The trivalent form may be accompanied by appreciable concentrations of *positive*-ion vacancies,[7] but we infer that the number of *negative*-ion vacancies is usually very small. The density of negative-ion vacancies should be enhanced by neutron bombardment. After pile irradiation, Weeks and Silsbee noted a strong peak surrounded by apparently eight satellites, symmetrically but not uniformly spaced about the central line.[8] The central line was observed independently at Oxford.[9]

In a subsequent study, two groups of crystals were subjected to an irradiation of 1×10^{19} and 3×10^{19} neutrons/cm^2, respectively. The central line for each of these is isotropic within the accuracy of our measurements and has a spectroscopic splitting factor g equal to 2.0023 ± 0.0001. With the magnetic field applied perpendicular to a [100] axis, rotation of the crystal about this axis gives one set of six lines which is stationary and two other sets of six lines which vary in position. The splitting d of each of the three sextets as a function of orientation is given by:

$$d=4.00+0.47(3\cos^2\theta-1) \text{ gauss.}$$

Here θ is the angle between the field and the cubic axis [100], [010], or [001] appropriate to the particular sextet. The maximum deviation of observed separations from the values given by this equation is 0.1 gauss. The extreme separations of outermost members of a sextet vary between 17.6 and 24.7 gauss. We assume these values to correspond to angles of 90 and 0 degrees, respectively, between the magnetic field and the symmetry axis for one Mg^{25} in an octahedron surrounding a negative-ion vacancy. Gourary and Adrian express the hyperfine interaction in *F* centers in terms of an isotropic and a dipolar contribution, the latter containing a $(3\cos^2\theta-1)$ factor.[10] Feher observed a similar dependence of the hyperfine lines from *F* centers in KCl.[4]

As expected, the three sextets coincide when the magnetic field lies along a unit cube body diagonal ([111] axis). The ESR spectrum for this orientation is shown in Fig. 1, together with a sketch of the expected spectra for *F* centers with 0, 1, and 2 Mg^{25} neighbors. The location and the uniformity of spacing and intensity of the members of the sextet are in satisfactory agreement with expectation.

One notes in Fig. 1 a number of extra lines half-way

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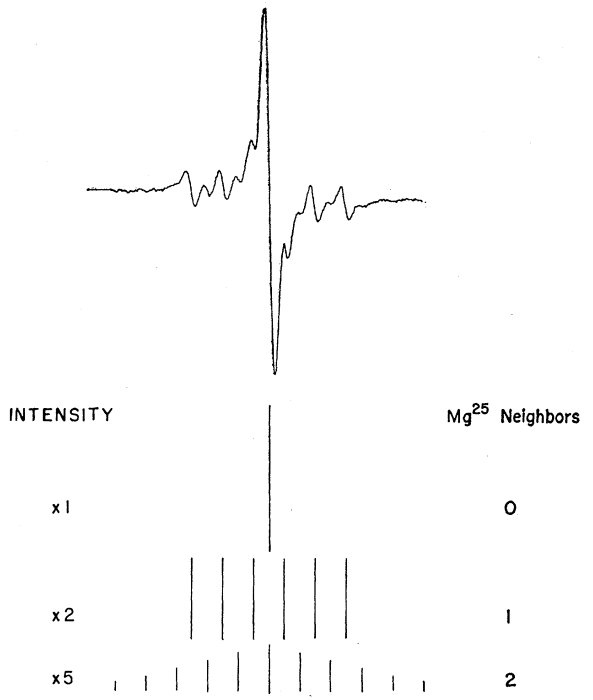

FIG. 1. The derivative of the electron spin resonance absorption spectrum of an electron trapped at a negative-ion vacancy (F center) in MgO. The trace shows a central component due to a trapped electron surrounded only by Mg^{24} and Mg^{26} ions. With the magnetic field along a [111] axis there is a uniform sextet from centers with one Mg^{25} neighbor. Some of the set of eleven lines from centers with two Mg^{25} neighbors are also seen. The expected spectra are shown below.

between some of the sextet components. Figure 2, taken (at the same orientation) at higher gain, shows these as well as a resolved set of two lines at either end of the sextet spectrum. Assuming a central line to coincide with the strong unsplit component, one has a set of eleven lines with a span just twice that of the coincident sextets. For other orientations, one would expect a large number of lines from centers having two Mg^{25} neighbors, the spectrum depending both upon the location of these two ions relative to one another and upon the field direction. We are not optimistic about the possibility of experimentally resolving these lines for arbitrary orientations.

When the magnetic field is along a [111] axis, the relative intensities of the components of the total F-center spectrum are in reasonable agreement with the predicted values. For unit intensity of the central line, one should have an intensity of 0.11 for the sextet lines and $0.0052n$ for the group of eleven lines, where $n=1, 2, 3, 4, 5, 6, 5, \cdots 1$. This increase in intensity from the outer to the central components is very fortunate, for the weakest lines occur outside the sextets, while the strongest observable ones are on the tails of the intense central component.

The number of F centers produced in the crystal whose F-center ESR spectra are shown was about $1.4\times10^{19}/cm^3$. This value was obtained by comparison of the area under the (integral) absorption curve shown in Fig. 3(a) with that for 267 micrograms of the free radical diphenylpicrylhydrazyl shown in Fig. 3(b). This concentration corresponds to one F center produced for every 5.7 incident neutrons. The maximum concentration of negative-ion vacancies producible in MgO by irradiation and their fractional occupation by electrons are to be the topic of further study. This system represents an unusually favorable one for observing in comparable environments the interaction of an unpaired electron with one or two nuclei. The observed hyperfine patterns definitely confirm the nuclear spin of $\frac{5}{2}$ for Mg^{25}, in agreement with the prediction of the shell model. Ramsey had considered that this value was not fully established from an experimental standpoint.[11] The value $\frac{5}{2}$ had been inferred from application of the interval rule to optical hyperfine spectra.[12]

All of these lines are easily saturated at room temperature in crystals having a low impurity content. This behavior would be expected for a center with $g=2.0023$ and a weak coupling with the lattice. At 9200 Mc/sec, with a microwave power of 0.3 mw, we have observed line widths (between points of maximum slope) to be the same for all measurable components. These widths have ranged from as low as 0.7 gauss in some crystals to 0.9 gauss in others. Further studies of the relaxation behavior of this system are being undertaken.

We take these data to confirm the correctness of the assignment of the ESR lines as due to F centers. A parallel study of electron spin resonance and optical absorption of F centers is under way and is expected to provide more detailed information.

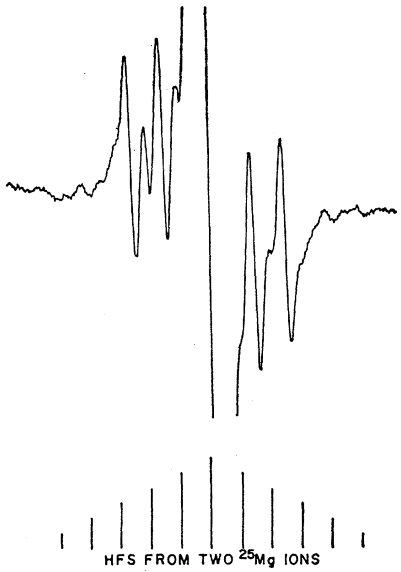

FIG. 2. At high gain the system of Fig. 1 shows ten of a set of eleven lines arising from an F center with two Mg^{25} neighbors. Some extraneous lines of other origin appear at the left, causing several lines to appear unduly intense.

[11] N. F. Ramsey, *Nuclear Moments* (John Wiley and Sons, Inc., New York, 1953), p. 79.
[12] Crawford, Kelly, Schawlow, and Gray, Phys. Rev. **76**, 1527 (1949).

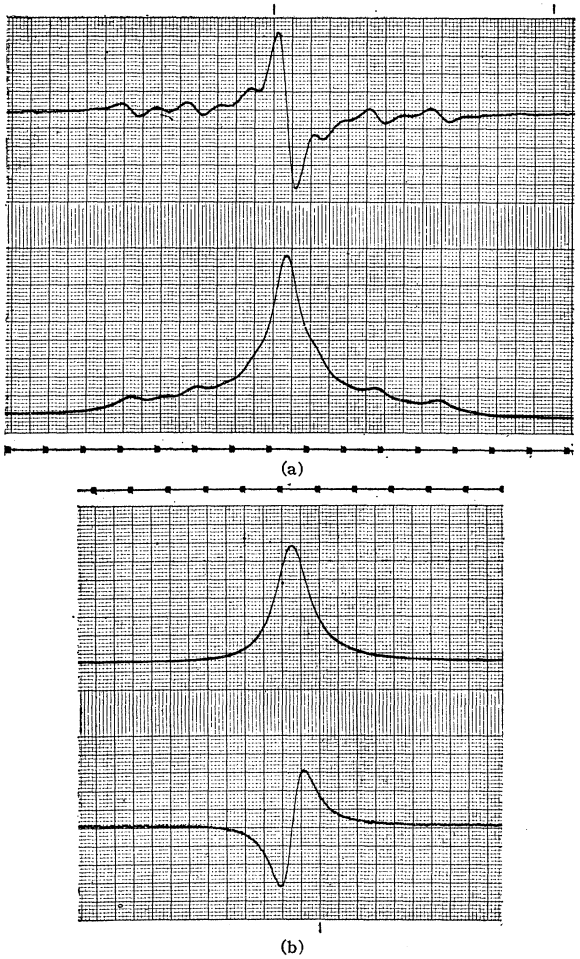

FIG. 3. (a) Derivative (above) and integral ESR absorption curve (below) for the F center in MgO. The field is oriented along a [111] axis. (b) Integral (above) and derivative (below) ESR absorption curves for 267 μg of the free radical diphenylpicrylhydrazyl taken under the same experimental conditions as (a).

The experimentally observed hyperfine interaction gives a severe test of theoretical F-center wave functions and can also serve to give useful qualitative information about the F center. The isotropic part of the hyperfine interaction implies a value of the square of the wave function at the Mg nucleus of $|\psi(\mathrm{Mg})|^2=0.276\times10^{24}$ cm^{-3} to be compared with the value $|\psi(\mathrm{K})|^2=0.70\times10^{24}$ cm^{-3} for the F center in KCl.[2] These values are to be contrasted with the free ion and atom values of $|\psi(\mathrm{Mg_{II}})|^2=17.1\times10^{24}$ cm^{-3},[12] and $|\psi(\mathrm{K_I})|^2=7.5\times10^{24}$ cm^{-3}.[2] These results clearly indicate the increased localization of the electron in the vacancy for the case of the oxide, due presumably to the larger Madelung energy in the divalent crystal.

The anisotropic part of the hyperfine interaction may be interpreted, with more justification than is at first apparent, as the sum of a contribution from the dipolar interaction of the nucleus with a spherical dipole distribution centered on the vacancy, and a contribution from the p character of the F-center wave function very near the nucleus. The observed anisotropy corresponds to the interaction of the nuclear moment with a moment of magnitude $f\beta$ at the center of the vacancy with $f=2.5$, and β the Bohr magneton. The dipolar interaction with the spherical charge distribution gives a computed f which is the fraction of the F-center charge included within a sphere of radius equal to nearest neighbor distance. This f must be less than one and this term cannot account for all of the observed anisotropy. Assuming the p character of the wave function near the Mg nucleus to be described approximately by an atomic $3p$ function[13] with coefficient b, the second contribution to the anisotropy may be expressed as an effective f,

$$f_{3p}=\tfrac{2}{5}d^3\langle 1/r^3\rangle_{3p}b^2=29.6b^2.$$

An LCAO (linear combination of atomic orbitals) wave function of the form $\psi_F=\sum_{i=1}^{6}(a\psi_{3s}+b\psi_{3p})$ was considered, with the coefficients a and b chosen to give the correct normalization and isotropic hyperfine interaction. These conditions were satisfied with the choices $a=0.121$ and $b=0.146$. The anisotropic hyperfine interaction calculated with this wave function was one-half of the observed value.

This disagreement is not surprising. First, the LCAO function is not orthogonal to the Mg core functions[10] and hence cannot represent the true F-center function. Orthogonalization of this function to the cores, however, is expected to make the agreement worse rather than better. The principal reason for the disagreement is suggested by the large values of the overlap integrals. The LCAO approximation might be reasonable if the F-center electron spends most of its time near the Mg ions. However, in the normalization integral only 20% of the integral is from one center integrals and the remaining 80% is from overlap integrals. Hence the electron spends most of its time in the vacancy where the LCAO wave function cannot be expected to be appropriate.

Note added in proof.—Recently we have found an F center spectrum in MgO crystals heated in magnesium vapor and subjected to prolonged irradiation with 50-kv x-rays. Rapid quenching of thin (0.2 mm) plates of MgO in water after heating to 1500°C has been found to provide enough negative ion vacancies so that subsequent x-irradiation gives F centers. Alternatively, one may use 2537 A radiation instead of x-rays after quenching. As a stringent test of identification of the central F-center line, the quenched crystal was ground to a powder. Addition of a good crystal showing F centers gave a combined ESR line of the expected amplitude with no apparent broadening.

ACKNOWLEDGMENTS

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