Isotropic ESR Line of the V^- Center in MgO at Room Temperature*

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Neutron irradiation of MgO produces V^- centers (holes trapped at cation vacancies). X irradiation is reported to give V_{Al} centers: $O^- - [=] - O^{2-} - Al^{3+}$. Both give identical ESR spectra at 77 K. At 295 K the three lines of the anisotropic V_{Al} spectrum only broaden, whereas V^- lines coalesce to an isotropic line. Since quenched, x-irradiated crystals show this line, the presence of isolated vacancies and not the type of radiation governs formation of V^- centers.

The facile removal of an electron from an O^{2-} ion in an oxide by ionizing radiation leaves a positive hole which migrates rapidly if the oxide ion is in an unperturbed lattice site. The hole may be trapped at the site of a negative charge, e.g., at a cation vacancy,[1,2] or at a univalent cation substituting for a divalent cation.[3-5] Except for charge magnitudes, the hole trapped at an isolated cation vacancy corresponds to the Seitz model of the V_1 center—proposed for the alkali halides but not observed in them. This intrinsic center has been given various designations, but the presently accepted symbol in the alkaline earth oxides is V^-.[6] It is produced by fast-neutron or high-energy electron irradiation of MgO at room temperature. Isolated cation vacancies created by knock-on processes may trap holes generated by the concomitant γ irradiation.[7] The basis for the V^--center model is the ESR spectrum at 77 K. For an arbitrary orientation of the magnetic field, there are three ESR lines representative of defects of tetragonal symmetry equally distributed over the three principal axes of the MgO crystal. Initially, to justify the tetragonal crystal field, it was postulated that there should be a trivalent impurity ion as the next-nearest neighbor to the vacancy, i.e., $Mg^{2+} - O^- - [=] - O^{2-} - M^{3+}$.[1] We shall refer to this as a V_M center. Subsequently, the presence of the trivalent ion was deemed to be unnecessary to generate the tetragonal distortion of the octahedral symmetry; relaxation of the oxygen atom away from the vacancy would also provide a tetragonal distortion.[2]

Recent publications adduce electron-nuclear double resonance (ENDOR) evidence to show that in a variety of MgO crystals (presumably untreated thermally), the V centers produced by x-ray or uv irradiation are V_M centers, where $M = Al^{3+}$,[8,9] whereas those produced by fast-neutron irradiation are V^- centers.[8] The ESR spectra of both centers at 77 K are thus far indistinguishable; both have $g_{\parallel} = 2.0032$ and $g_{\perp} = 2.0385$. This would seem to imply that the effective magnitude of the tetragonal component of the crystal field is determined by the relaxation of the O^- ion away from the vacancy. Nevertheless, it seems remarkable that the presence of an associated trivalent ion does not give rise to detectable differences in the g components at 77 K. The preference for taking V-center ESR spectra at this temperature is twofold: Typically, most V centers generated by x, γ, or uv irradiation tend to decay at room temperature, and, more importantly, at room temperature the lines are much broadened [Fig. 1(b)]. It has been reported that at room temperature the broadened V-center lines do not coalesce.[10] However, there has been no detailed study of the V-center spectra at room temperature and above. Recently, magnetic-circular-dichroism data have been interpreted as being inconsistent with the localized-hole model of the V^- center.[10] However, the localized-hole model *for the ground state* appears to be strongly supported by a study of the intensities of ^{25}Mg hyperfine spectra.[11]

It is in the lifetimes that one observes striking

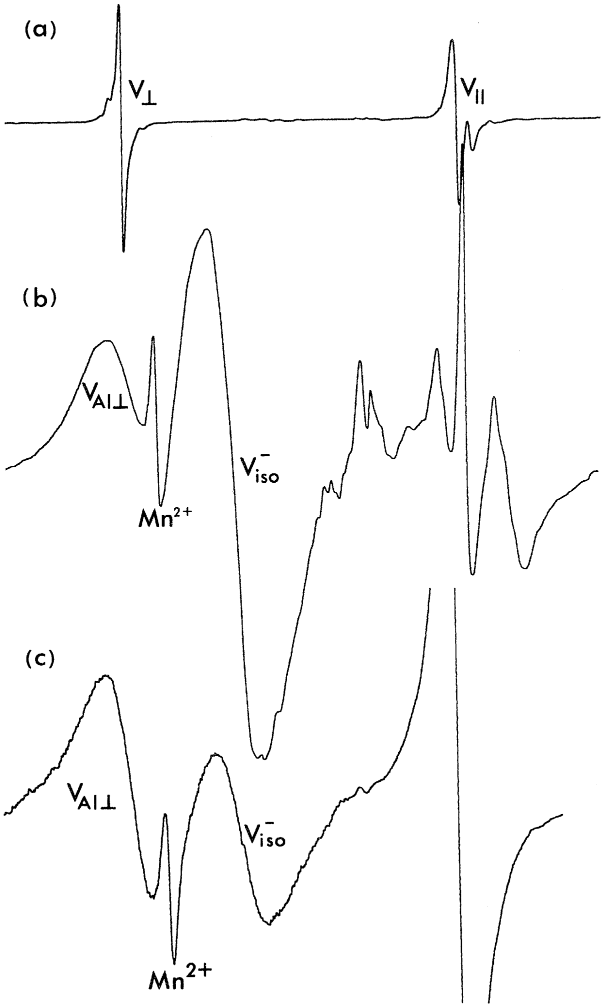

FIG. 1. (a) ESR spectrum ($\nu = 9.09$ GHz) at 140 K of an MgO crystal which has been irradiated with fast neutrons and then x irradiated. The lines marked $2V_\perp$ are coincident lines from those V^- and from V_{Al} centers having their tetragonal axes perpendicular to the magnetic field; the line marked $V_\parallel$ corresponds to those centers of both types having axes parallel to the field. (b) Spectrum at 295 K of the sample giving the above spectrum at 140 K. The line $V_{\mathrm{Al}\perp}$ is unchanged in position, and it arises only from V_{Al} centers. The line V_{iso}^- is the coincidence of the $V_\perp^-$ line shifted to higher field, and the $V_\parallel^-$ line shifted to lower field. The gain is higher by a factor of 7.3 than in (a), and the modulation is larger by a factor of 4. In the region of $V_\parallel$ there is considerable overlapping, in part because of trapped-electron-center lines. (c) ESR spectrum of MgO quenched from 1000°C to room temperature, x irradiated, and heated at 50°C for 45 min. $T = 295$ K; $\nu = 9.10$ GHz. The appearance of the V_{iso}^- line on x irradiation shows that the intrinsic V^- center is formed if *isolated* cation vacancies are present. Its persistence during an order of magnitude decay of the V_{Al} line is consistent with the assignment to the V^- center.

differences between V^- and V_{Al} centers. In some samples irradiated with neutrons two years ago and stored at room temperature, we have noted little change in intensity of the V^--center ESR spectrum at 77 K. For V_{Al} centers made by x, γ, or uv irradiation of thermally untreated crystals, we have observed half-lives of 2 to 15 h. The lifetimes are at least in part determined by the concentrations of certain transition-metal ions.

The MgO crystals used were obtained from the Oak Ridge National Laboratories and from W. & C. Spicer, Ltd. Most showed a low concentration of V_{OH} centers (having an OH^- ion opposite the O^- ion about the vacancy) after irradiation with x or γ rays or neutrons. Some MgO crystals were heated for 30 min in a furnace at 1000°C, then quenched as quickly as possible in mechanical-pump oil. X irradiation was done with a Thermax tungsten-target tube operated at 80 kV. γ irradiation was done in the Oklahoma State University $^{60}\mathrm{Co}$ source. Fast neutron irradiation was done in the University of Missouri reactor, with the sample in the reflector region and cooled by circulating helium gas. Fast-neutron doses ranged from $2.5\times10^{17}nvt$ to $5.0\times10^{17}nvt$.

X irradiation of our unquenched MgO crystals gave a spectrum at 77 K similar to that in Fig. 1(a) (actually taken at 140 K). The lines broaden progressively on heating to room temperature, but for a given field orientation they appear to remain in their original positions. This is seen for the line labeled $V_{\mathrm{Al}\perp}$ in Fig. 1(b) at 295 K. The line which at 140 K is labeled $V_\parallel$ cannot be seen because of overlap of extraneous lines at this orientation.[12] For such crystals the line at the position of V_{iso} in Fig. 1(b) may be very weak.

For neutron-irradiated crystals or for those which have been quenched and x irradiated, the behavior is very different. For neutron-irradiated samples, the only broad line ordinarily observed at room temperature will be the isotropic line marked V_{iso}^- in Fig. 1(b).[13] At 295 K this line has a width which is 1.3 times that of the $V_{\mathrm{Al}\perp}$ line. In a quenched, x-irradiated crystal, the amplitude of the V_{iso}^- line may be $\frac{1}{10}$ or less that of the $V_{\mathrm{Al}\perp}$ line initially. Upon heating gently, e.g., up to a temperature of 50°C, one finds the V_{iso}^- line to grow somewhat and the $V_{\mathrm{Al}\perp}$ line to decay to the extent shown in Fig. 1(c). If one x irradiates a neutron-irradiated crystal, one gets the spectrum shown in Fig. 1(b), with both broad lines prominent. The position of V_{iso}^- is $\frac{1}{3}$ the separation in field between $V_\perp$ and

$V_\parallel$, with $g_{\mathrm{iso}} = 2.027$. On heating a neutron-irradiated crystal from 77 to 200 K, there is some broadening; between 215 and 230 K the broadening is more marked, and the low-field line shifts to higher fields. At the same time it is joined by a weaker line moving downfield from the $V_\parallel$ position. When the temperature has reached 245 K, the coalescence is complete.

The broadening without shift of ESR lines from unquenched x-irradiated crystals is to be expected for V_{Al} centers. Since the Al^{3+} ion and the vacancy are immobile at room temperature, one does not expect a reorientation of V_{Al} axes. We attribute the line broadening to a decrease of T_1 with increasing temperature; a similar dependence of T_1 with temperature may be expected for the V^- centers. However, for the latter above 200 K there is an extra linewidth contribution resulting from the rapid hopping of the hole among the six oxygen ions surrounding the vacancy. When the frequency of reorientation is sufficiently great relative to the separation (in frequency units) of the anisotropic lines, one observes the isotropic line. Indeed, its existence implies the absence of other defects which would distort the surroundings. The g factor of the isotropic line should be $g_{\mathrm{iso}} = \frac{1}{3}(2g_\perp + g_\parallel) = 2.0267$, in satisfactory agreement with the measured value 2.027. All V^- centers present contribute to the V_{iso}^- line intensity; however, the line marked V_{Al} represents only $\frac{2}{3}$ of the V_{Al} centers present.

If the room-temperature isotropic line is correctly assigned to V^- centers, (1) it should be produced by ionizing radiation if isolated cation vacancies are already present in significant numbers; if they are not, they can be produced by quenching, by fast neutrons, or by energetic electrons. (2) It should have the maximum intensity for samples in which the concentration of isolated vacancies is expected to be greatest. With regard to (1), sufficiently rapid quenching from high temperatures makes it possible for isolated vacancies to survive to room temperatures without entrapment. Irradiation of these samples with x or γ rays does indeed give a V_{iso}^- line. The occurrence primarily of V_M centers after ionizing irradiation of unquenched samples reflects the strong tendency of vacancies to associate with trivalent impurity ions during the cooling through the crucial range of 1000°C to perhaps 300°C, below which vacancies are presumably not mobile. In neutron-irradiated samples subsequently x irradiated, one provides holes for many of the existent vacancies associated with impurities; however, these centers decay by hole escape far more rapidly than the V^- centers. In the quenched samples, it is satisfying to see the persistence of the V_{iso}^- line at room temperature, while the $V_{\mathrm{Al}\perp}$ line decreases in intensity by an order of magnitude, as it has in Fig. 1(c). With reference to (2) above, the maximum intensity of the V_{iso}^- line is observed for neutron-irradiated samples, where one expects collisions to produce primarily isolated vacancies (in relatively pure crystals).

It has been suggested that one requires the ENDOR technique to discriminate between the V_{Al} and the V^- centers.[8] However, we have shown here that it is experimentally far simpler to observe the room-temperature ESR spectrum, from which one can also get a direct measure of the relative numbers by line intensities. More precisely, one can observe the V_{iso}^- line at any temperature above 245 K, up to and beyond room temperature. It is desirable to take the spectra promptly to minimize the decay of V_{Al} centers. No quantitative comparisons are possible with the ENDOR approach, which detects only the V_{Al} centers.[14] It has been inferred that V centers generated by ionizing radiation are always V_M (primarily V_{Al}) centers, while those made from energetic particles are V^- centers. This is not wholly correct, as we have shown.

In summary, we have shown the occurrence of the intrinsic V^- center under those conditions in which isolated cation vacancies are present. Rapid hopping of the hole among equivalent oxygen ions about the vacancy leads to an isotropic ESR line which serves to distinguish this center from those centers associated with impurities.

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[12] The nonappearance of Mn^{2+} lines in Fig. 1(a) and their appearance in 1(b) for the same crystal is partially due to their greater saturation at the lower temperature, at which their relaxation time T_1 is greatly increased; the spectrometer gain is also higher in Fig. 1(b) than in 1(a).

[13] In the time required for the decay of induced radioactivity of MgO crystals to a level where they may be handled conveniently, the V_{A1} centers which have been populated by accompanying γ radiation will have decayed at room temperatures. They are easily regenerated by any ionizing radiation.

[14] If one were able to distinguish ^{25}Mg ENDOR lines from the V_{A1} and V^- centers, discrimination could be made, but a far greater effort is involved.

Charge Densities and Binding Energies in Hydrogen Chemisorption

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The chemisorption of hydrogen on metals is treated by a self-consistent calculation. Three-dimensional charge densities, interaction energies, and dipole moments are given as a function of position of the hydrogen adatoms. The results are compared with experiment. The experimental picture of a dissociated adsorbate of small dipole moment is substantiated, and the calculations are consistent with the observation that hydrogen field desorbs together with the surface atoms of the substrate.

Hydrogen chemisorption on metal surfaces is well studied experimentally.[1-5] Any theoretical description must be in accord with experimental heats of adsorption, changes in work function, adsorbate structure, and desorption-kinetics data. We have completed a three-dimensional self-consistent calculation of hydrogen chemisorption from which many properties can be obtained and compared with experiment. In addition, the calculated charge densities and potentials allow visualization of the chemisorption process for the first time.

Earlier theoretical work has been thoroughly reviewed by Schrieffer.[6] The theoretical advance here stems from our requirement that Poisson's equation be satisfied point by point. That is, there is complete self-consistency between the electrostatic potential used and the charge density obtained. Such self-consistency is now established as essential in metal-surface calculations.[7,8] It has also been shown to be important in the screening of impurities in metal surfaces.[9]

The calculation proceeds from the linear response formulation for a metal surface.[9] The unperturbed metallic surface is treated in the jellium model, the ion-core distribution of the solid being represented by the charge density $\rho_0^{\mathrm{ex}}(\vec{r}) = \rho_+\theta_-(x)$, where x is the coordinate perpendicular to the surface and $\theta(x)$ is the Heaviside (step) function. The x coordinate of the nuclei for the surface plane is $-\frac{1}{2}d$, where d is the distance between planes parallel to the surface.

The unscreened (or zeroth order) configuration of the chemisorbed hydrogen is taken as a proton situated in the surface region plus an extra electron in the conduction band of the metal. The actual elec-