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Formation and stability of V^- and V_{Al} centers in MgO[†]

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V^- and V_{Al} centers in MgO have been shown to possess identical electronic g values at low temperatures and this paper reports on the distinction between the two centers. Although these two centers have almost identical EPR spectra, their electron-nuclear-double-resonance (ENDOR) spectra are clearly different. Optical-absorption measurements, supported by ENDOR and EPR, were used to study the formation and annihilation of these two centers. Trapped-hole centers have also been observed which are charge compensated by silicon and off-axis aluminum. The V^- center cannot be produced in all MgO single crystals, and we attribute this to impurity dependence. The high cross section for V^--center production by electron irradiation, $\sim 10^2$–10^3 b (as compared to only a few barns for its antimorph, the negative-ion vacancy) indicates that the predominant formation mechanism is that of ionization rather than a knock-on process. This assertion is confirmed by the relative ease with which V^- centers are formed by low-energy x rays. Irradiations with photons possessing energies of 1.25 MeV down to a few keV reveal a lack of energy dependence for V^- center production.

I. INTRODUCTION

The exposure of an as-grown MgO crystal to moderate doses of ionizing radiation such as x, γ, β, or uv rays produces a broad optical-absorption band at 2.3 eV[1] which decays at room temperature. This band has been correlated with an axially symmetric defect whose EPR g values have been given as $g_\parallel = 2.0032$ and $g_\perp = 2.0385$.[1-3] For many years, this center has been accepted as the V^- center, a Mg vacancy with a trapped hole.[4,5]

Five years ago, it was suspected that more than one type of defect exists with this set of g values and optical-absorption band because of both radiation-damage and thermal-stability data.[6] Specifically, in some crystals, certain types of irradiation produced a much longer-lived species of V^- center. In a recent letter,[7] we gave conclusive evidence that (i) in crystals subjected to ionizing radiation an aluminum electron-nuclear-double-resonance (ENDOR) signal was associated with this set of g values, and we named this the V_{Al} center; (ii) upon a detailed EPR and ENDOR survey covering a wide assortment of crystals (from various sources used by past investigators), it was established that the center researchers have previously accepted as the V^- center was primarily this same V_{Al} center; and (iii) another center, which we found to be present in crystals irradiated with energetic particles (neutrons or 2-MeV electrons), coexists at the same g values, but has no aluminum ENDOR signal. We believe this latter center, which is distinguished by being electronically stable at room temperature, to be the V^- center.

The present work is a report, on a broader scope, of our continuing investigations of the V-type centers, with emphasis on the V_{Al} and V^- centers. In the first part, we shall document the EPR and ENDOR results cited earlier,[7] and in particular, the remarkable coincidence of the g values of V_{Al} and V^- centers. Our studies show that some crystals can harbor either center exclusive of the other, or contain both centers simultaneously. We shall show that the ENDOR technique is capable not only of identifying the presence of the aluminum nucleus in the V_{Al} center but also of giving a semiquantitative ratio of the concentrations of V_{Al} to V^- centers in the same crystal. Second, we shall briefly discuss some of the other charge-compensating centers observed. Third, the experimental evidence relating to the production mechanisms and thermal stabilities of the V_{Al} and V^- centers will be presented. We shall show that the observed cross section for the production of the V^- center by means of high-energy-electron irradiation is inconsistent with the mechanism of knock-on production of Mg^{2+} vacancies, and that the center can be produced by ionizing radiation of quite low energy. Fourth, sample-dependent production rates have been correlated with impurities to the extent that one can postulate a connection between the presence of OH in the crystal and formation of V^- centers by means of ionization.

II. EXPERIMENTAL PROCEDURES

Crystals used in this work were obtained from three sources: General Electric, Spicer, and Oak Ridge National Laboratory.[8] The starting powder for the crystals grown at Oak Ridge was from the Kanto Chemical Company. Irradiation sources were a *CuKα* x-ray source, a ^{60}Co γ source (1.8×10^6 R/h, average energy $\bar{E} = 1.25$ MeV), a ^{137}Cs γ source (1.2×10^6 R/h, $\bar{E} = 0.66$ MeV), and a 2.0-MeV Van de Graaff electron accelerator. For low-temperature irradiation and optical measurements, a Sulfrian cryostat with rotatable aluminum and quartz windows was used.

The EPR measurements were made at 3-cm wavelengths using either a homodyne spectrometer employing a Varian V-4531 rectangular cavity and 100-kHz field modulation or a superheterodyne spectrometer for measurements at liquid-helium temperatures. For ENDOR measurements, a coil was wound on the outside of the latter spectrometer's TE_{102} rectangular cavity. A 0.050-in. slot in the cavity wall permitted entry of the radio-frequency magnetic field. Direct signal averaging of the video spectrometer output was employed[9] using frequency-sweep rates appropriate for the relaxation times encountered for the ENDOR transitions under consideration.

III. RESULTS AND DISCUSSION

A. EPR and ENDOR

Previously the existence of the V_{Al} center in MgO has been established by ENDOR.[7,10] The spectrum was described by the following spin Hamiltonian:

$$\mathcal{H} = g_\parallel \mu_B H_Z S_Z + g_\perp \mu_B (H_x S_x + H_y S_y) + A_\parallel I_z S_z + A_\perp I_x S_x + P[I_z^2 - \tfrac{1}{3}I(I+1)] - g_N \mu_N \vec{H}\cdot\vec{I}, \qquad (1)$$

with the parameters $g_\parallel = 2.0033 \pm 0.0002$, $g_\perp = 2.0386 \pm 0.0002$, $A_\parallel = \pm 0.176 \pm 0.005$ MHz, $A_\perp = \mp 0.073 \pm 0.005$ MHz, $P = \mp 0.552 \pm 0.005$ MHz, and $g_N = +1.456$. These magnetic hyperfine parameters give contact and dipolar interaction constants of $a = \pm 0.011 \pm 0.005$ MHz and $b = \pm 0.082 \pm 0.005$ MHz. The dipolar interaction constant can be used to calculate the mean distance of the $^{27}\mathrm{Al}$ nucleus from the hole wave function. Ignoring corrections for the finite extent of the trapped-hole wave function, one obtains $\langle R \rangle = 6.30 \pm 0.13$ Å. This distance is in excellent agreement with the lattice distance to the (0, 0, 3) Mg^{++} in the perfect lattice (6.320 Å), and demonstrates that the V_{Al} is charge-compensated by an Al^{3+} in the configuration $\mathrm{O}^-[++]\mathrm{O}^-\mathrm{Al}^{3+}$ where $[++]$ represents a cation vacancy. The trapped hole is highly localized on an oxygen adjacent to the Mg vacancy, as will be shown later.

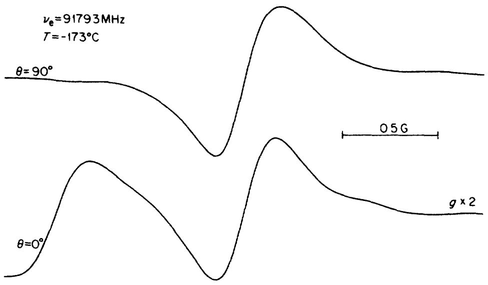

FIG. 1. EPR spectrum observed in two MgO crystals which were glued together. One sample was electron irradiated two years previously and contained only the stable V^- center, while the other contained primarily V_{Al} centers produced by γ irradiation. For $\theta = 0°$, the low-field line is due to Fe^{3+}.

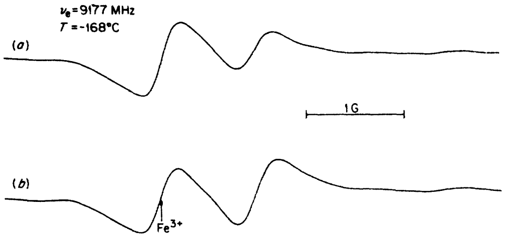

FIG. 2. EPR spectra of V^- and V_{Al} centers in a previously electron-irradiated MgO crystal at $\theta = 0°$ (a) before and (b) after a subsequent γ irradiation.

V_{Al} centers were produced by a short γ irradiation at room temperature and the corresponding EPR spectrum was compared to that from another MgO sample containing exclusively V^- centers. The latter crystal had been exposed to a high dose of electrons (> 10^{18} e/cm^2) and stored in the dark for two years. These two crystals were cleaved to a size such that they gave equal EPR signals individually, and then both were glued together. Figure 1 illustrates the EPR spectrum of this composite sample. Clearly, no splitting is observed at either $\theta = 0°$ or $\theta = 90°$. This remarkable coincidence of the electronic g values (less than one part in 10^4) demonstrates why EPR measurements have not previously succeeded in differentiating between the V_{Al} and the V^- centers.

As further verification of the g value coincidence of these two centers, we demonstrate the coexistence of both centers in the same crystal. Figures 2 and 3 show the EPR spectra in a room-temperature electron-irradiated sample before and after a subsequent room-temperature γ irradiation.

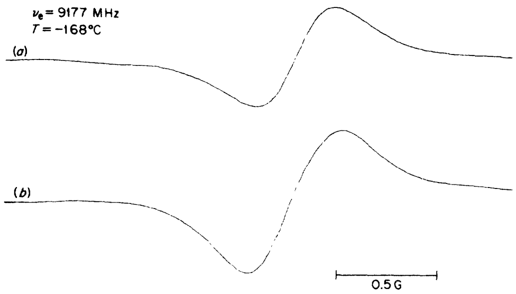

FIG. 3. EPR spectra of V^- and V_{Al} centers in a previously electron-irradiated MgO crystal at $\theta = 90°$ (a) before and (b) after a subsequent γ irradiation.

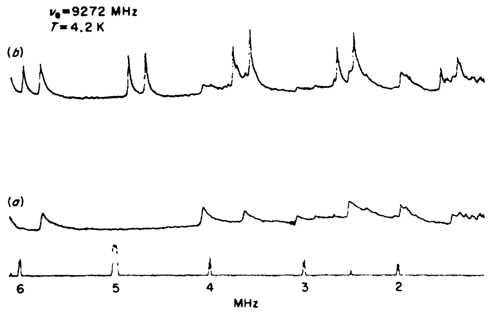

FIG. 4. ENDOR spectra observed in a previously electron-irradiated MgO crystal at $\theta = 0°$ (a) before and (b) after a subsequent γ irradiation. The five doublet lines in (b) are due to ^{27}Al nuclei. Also present are ^{25}Mg lines due to V^- and F^+ centers in both traces, and the V_{Al} center in trace (b).

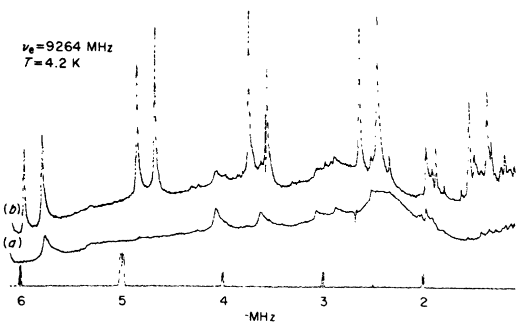

FIG. 6. ENDOR spectra observed in a previously neutron-irradiated MgO crystal at $\theta = 0°$ (a) before and (b) after a subsequent γ irradiation. Five doublet lines in (b) are due to ^{27}Al nuclei. Also present are ^{25}Mg lines due to V^- and F^+ centers in both traces, and the V_{Al} center in trace (b).

Prior to γ irradiation, the crystal contained primarily stable V^- centers, while afterwards relatively unstable V_{Al} centers were also present. Hence, the signal intensity was larger. However, subsequent to γ irradiation, neither the linewidth nor the shape of the signals had changed significantly, although if one makes a detailed examination of the lines individually in separate crystals a difference in linewidth can be observed. Assuming the V^--center linewidth is the intrinsic linewidth, and including the additional broadening due to the small ^{27}Al hyperfine interactions, one can obtain a good fit to the slightly broader line shape observed for the V_{Al} alone.

The corresponding ENDOR spectra are shown in Figs. 4 and 5. The aluminum signals, which are present only after the γ irradiation, are readily identified as a set of five doublet lines centered to first order on the nuclear-resonance frequency of the 100%-abundant ^{27}Al nucleus. The separation within the doublet is due to the small hyperfine splitting and the separation between the doublets is due to the quadrupole interaction. The additional signals at lower frequency are due to ^{25}Mg nuclei and will be discussed in a later publication.[11] (There are some additional ENDOR signals evident in the $\theta = 0°$ spectra arising from ^{25}Mg nuclei neighbors of the F^+ center which is also produced upon heavy electron irradiation. These F^+-center ENDOR lines are not present in the $\theta = 90°$ orientation due to the difference in the electronic g values.) ENDOR spectra were also taken on neutron-irradiated MgO samples before and after a subsequent γ irradiation, and are shown in Figs. 6 and 7. There were no differences between these spectra from the neutron-irradiated sample and those obtained from the electron-irradiated sample.

The relative signs of the spin Hamiltonian parameters were determined from experimental observation of the angular variation of the ENDOR

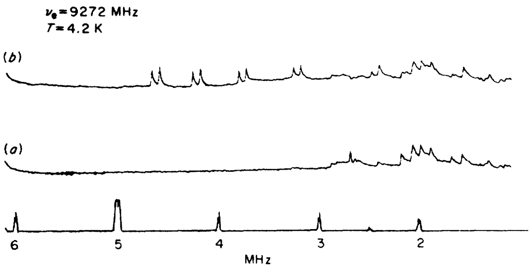

FIG. 5. ENDOR spectra observed in a previously electron-irradiated MgO crystal at $\theta = 90°$ (a) before and (b) after a subsequent γ irradiation. Five doublet lines in (b) are due to ^{27}Al nuclei. Also present are ^{25}Mg lines due to the V^- in both traces, and V_{Al} only in trace (b). The F^+-center ENDOR lines are not present in the $\theta = 90°$ orientation due to the difference in the electronic g values.

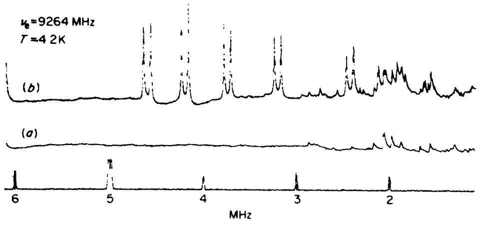

FIG. 7. ENDOR spectra of a previously neutron-irradiated MgO at $\theta = 90°$ (a) before and (b) after a subsequent γ irradiation. Five doublet lines in (b) are due to ^{27}Al nuclei. Also present are ^{25}Mg lines due to the V^- center in both traces, and the V_{Al} center in trace (b).

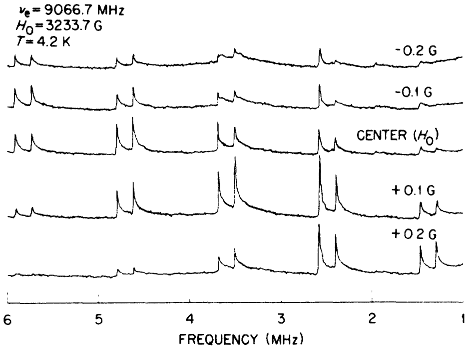

FIG. 8. ENDOR spectra taken at different positions on the V_{Al} EPR lines at $\theta = 0°$. The data were taken at nominal increments of 0.1 G relative to the central resonance field (H_0). rf heating changes the cavity resonance thereby shifting the field position of the EPR line during measurement.

spectrum and the intensity of the ENDOR signals obtained while saturating various portions of the narrow EPR line (Fig. 8). Direct diagonalization of the axial Hamiltonian, using the various possible combinations of signs of the hyperfine parameters, gives predictions of the EPR transition locations within the unresolved line and the ENDOR frequencies to be expected for transitions between the various energy levels. For a positive nuclear g value, the results predict that the high-frequency ENDOR transitions are associated with the low-field EPR transitions (as in Fig. 8) for the combination of relative signs listed below Eq. (1). If one accepts the positive sign of the nuclear g value[12] as determining the sign of the dipolar interaction as well, then the upper signs are the correct ones. The electronic g values agree to within ± 0.0001 with the values quoted in the literature.[13]

The evidence in Figs. 1–3 shows that at low temperatures the V^- and V_{Al} centers can coexist in the same crystal, and that their g values coincide, $g_{\parallel} = 2.0033 \pm 0.0002$, $g_{\perp} = 2.0386 \pm 0.0002$. Some of the conclusions and implications we shall draw thus rest upon means of distinguishing between the two centers in a given sample and of measuring their relative concentration. There are two resonance methods available. The first involves the property that the anisotropic g values of the V^- center average toward an isotropic g value at elevated temperatures, whereas those of the V_{Al} do not.[14] This difference in behavior follows naturally from the structural differences between the two centers. The trapped hole can be thermally excited to jump between the six equivalent oxygens of the centrosymmetric framework of the V^- center, while the axial compensation of the Al^{3+} to a large extent inhibits g-value averaging in the case of the V_{Al} center. Similar distinctions between centrosymmetric and axial structures have previously been shown to lead to g-value averaging in the case of $[Li]^0$ and $[Na]^0$ centers[15,16] and undoubtedly inhibit it in the case of V_{OH} and V_F centers.[17] In principle, one can examine the room-temperature EPR spectrum of a crystal containing both centers and separate the spectrum into that contribution due to the V_{Al} at the g values listed above, and that due to the V^-, at the mean g value of 2.0268. Such a spectrum is shown in Fig. 1 of Ref. 13. In practice, several difficulties are encountered in the application of this method. The temperature required to separate clearly the two centers (~ 300 K) is such that the V_{Al} centers thermally decay to some extent. A more serious problem arises from the line shapes involved in this comparison. Because the motional averaging leaves the resonance second moment invariant,[18] one must compare two spectra with quite different line shapes. In the case of the V^-, this involves a line whose second moment is ~ 2500 G^2 but whose peak-to-peak derivative separation is only ~ 15 G. The observed peak-to-peak derivative is a strong function of the degree of narrowing and hence of the actual temperature used in the measurement. A reasonable measurement of the resonance intensity of this line then requires accurate temperature and an accurate baseline over a field range of at least 150 G in a region where Mn^{2+} and Fe^{3+} impurity lines generally have comparable intensities, and which includes the lifetime broadened (but not drastically averaged) V_{Al} lines with which one hopes to make an intensity comparison. Therefore, direct comparisons of the peak-to-peak derivative amplitudes at room temperature of the V_{Al} lines and the V^- line do not directly establish the relative concentration of these two centers in a particular crystal.

A second approach involves the use of ENDOR to make this distinction. The ^{25}Mg superhyperfine transitions of both centers are easily visible in the EPR spectra, but are identical and therefore indistinguishable. The ENDOR transitions between these superhyperfine levels, however, are significantly different for the two centers due to the axial charge-compensation in the case of the V_{Al}, which produces a different electric field gradient at the nearest-neighbor ^{25}Mg nuclei from that found for the case of the V^-. The two centers can easily be distinguished by their ENDOR spectra. ENDOR spectra taken over a small frequency range on the low-field ^{25}Mg single neighbor EPR satellite line at $\theta = 90°$ are shown in Fig. 9 for two separate crystals, one of which has only V^- centers and the other exclusively V_{Al} centers. Two of the ENDOR lines arising from the nonequivalent single ^{25}Mg neighbor for each center along the ⟨100⟩ direction are shown. The spectra are clearly dif-

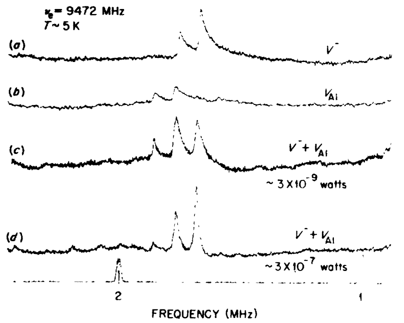

FIG. 9. ENDOR spectra at $\theta = 90°$ taken on the low-field ^{25}Mg satellite line of (a) a crystal containing only V^- center; (b) a crystal containing exclusively V_{Al} center; (c) both crystals glued together with microwave power at $\sim 3 \times 10^{-9}$ W; and (d) same as (c) but with power $\sim 3 \times 10^{-7}$ W.

ferent. However, even at 4.2 K and below, these two centers have somewhat different spin-lattice relaxation rates (apparently the hole can still hop between its equivalent positions in the case of the V^-), leading to different saturation conditions in an ENDOR measurement of both centers. Figure 9 also shows a similar ENDOR spectra of the two crystals glued together taken at two different microwave power levels showing that the V_{Al} is more easily saturated. In practice, this saturation behavior can lead to errors of ~ 50% in an ENDOR measurement of the relative concentration of the two centers. More detailed ENDOR results will be presented in a forthcoming publication.[11]

Hence, while both methods permit measurements which indicate the presence of one or both centers, only semiquantitative measurements are possible in either case. Our experience has been that the 4.2-K ENDOR provides a better measurement of the relative concentrations and is easier to correlate with the combined optical absorption of the two centers when they coexist in the same crystal. Fortunately, as discussed below, complete separation of the effects due to these two centers can be accomplished because of their different thermal decay rates at room temperature.

It should be emphasized that only the ENDOR can identify the nucleus in question.[7,10] An EPR measurement cannot unequivocally identify the aluminum charge compensator. Thermal averaging of one of the centers in the EPR[14] shows that there are two centers (already noted in Ref. 7), and that one of these must be centrosymmetric in the absence of the trapped hole.

Our EPR and ENDOR measurements[11] confirm the localized nature[19] of the hole at a single oxygen site for the ground state of the V^- center in MgO and show that it is true for the V_{Al} as well. It is expected that this localization is also valid for such related centers as the V_{OH}, V_F, $[\text{Li}]^0$, $[\text{Na}]^0$, and $[\text{K}]^0$ centers.[4,5,15,16,20,21] Localization does not imply the absence of hopping between oxygen sites. On the contrary, the faster spin-lattice relaxation of the V^- is consistent with the idea that the hole is still hopping even at 4.2 K. Any hopping in the V_{Al}, V_{OH}, and V_F centers is expected to be inhibited since these centers are not centrosymmetric defects.[17]

B. Other charge-compensating centers

In some crystals, in addition to the $\langle 100 \rangle$ V_{Al} center, trapped hole centers which involve aluminum charge-compensation along $\langle 110 \rangle$ directions with different g values were also observed. The EPR and ENDOR signals were about one-tenth the strength of those of the axial $\langle 100 \rangle$ V_{Al} center, reflecting the small probability of stabilizing the Mg^{++} vacancy from an off-axis position. There were two such centers observed for two possible $\langle 110 \rangle$ positions. Both have $g_{\parallel}$ values very near that of the $\langle 100 \rangle$ V_{Al}, but one $g_{\perp}$ value is less than, and the other greater than, $g_{\perp}$ for the $\langle 100 \rangle$ V_{Al}. Figure 10 shows these two resonances for $\theta = 90°$. It is not presently known which case corresponds to the Al^{3+} compensation closest to the trapped hole localized on an oxygen ion. It is remarkable, and another indication of the localized nature of the trapped hole that both these weak spectra have g-tensor principal axes oriented in a $\langle 100 \rangle$ direction, even though the electric-field-gradient principal axes are oriented in a nominal $\langle 110 \rangle$ direction.

Charge-compensating centers involving other nuclei have also been tentatively identified. Extremely weak ^{29}Si ENDOR responses were observed while saturating the region around the V_{Al}, but the low isotropic abundance of ^{29}Si deterred us from obtaining meaningful parameters. In these centers it was virtually impossible to follow the angular variation of the spectra due to interference from the large responses of the V_{Al} and its ^{25}Mg neigh-

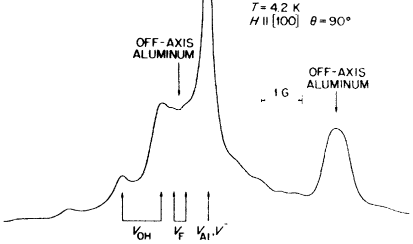

FIG. 10. EPR absorption spectrum of V-type centers in MgO for $\theta = 90°$, showing additional resonances due to off-axis aluminum-charge compensation.

bors. Nevertheless, the distant ENDOR response[22] at the free nuclear resonant frequency of ^{29}Si was easily observed, indicating an appreciable silicon impurity concentration.

Other charge-compensating impurities, as yet unobserved, are almost certainly present. A case in point is the Muscle-Shoals crystal mentioned in Ref. 7. Here the linewidth in question was broader by a factor of 2 than either the V_{Al} or V^- center, implying the presence of a charge-compensating impurity other than the axial aluminum. This conclusion was supported by the absence of thermal averaging and the ENDOR observation that relatively few V_{Al} centers were present.

C. Radiation effects and thermal stability

In this section we are concerned with the irradiation growth rate and thermal stability of the trapped-hole centers, primarily the V_{Al}, V_{OH}, and V^-. Optical absorption measurements, supported by EPR and ENDOR, were used. The broad absorption band centering at about 2.3 eV has been attributed to these centers.[1,3] Recently, Izen *et al.*[23] definitely confirmed the association of the band with the EPR composite of V_{Al} and V^- centers using an EPR–magnetic-circular-dichroism double-resonance technique and concluded that the optical band is not due to an $A(p_z) \rightarrow E(p_x, p_y)$ transition. The 2.3-eV band therefore appears to be a transition from a localized ground state to a very diffused excited state, whose wave function was shown by Searle and Bowler[24] to have an approximate Bohr radius of 4 nm.

1. *Electron irradiation*

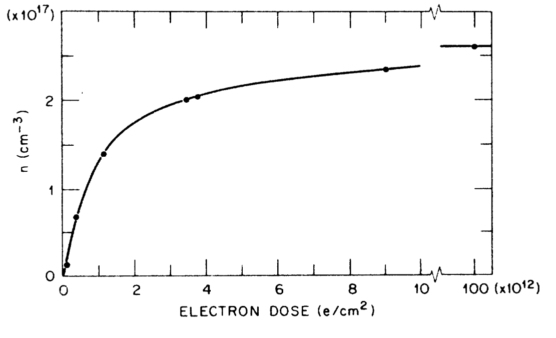

FIG. 11. Growth curve of V_{Al} and V_{OH} centers upon electron irradiation. From the absorption coefficient of the optical band at 2.3 eV, concentration n (defects/cm^3) was obtained using Smakula's equation (see text).

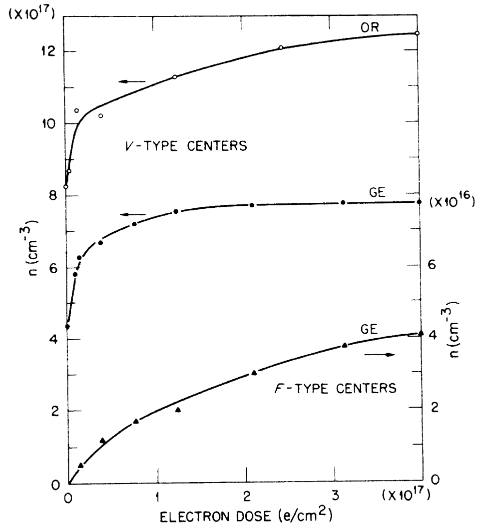

FIG. 12. Growth curves of V-type centers in two different crystals resulting from electron irradiation following a short initial ionizing γ irradiation. From the optical absorption of the optical band at 2.3 eV, concentration n (defects/cm^3) was obtained using Smakula's equation (see text). Also shown for comparison is the growth curve of the 5-eV optical-absorption F-band for the GE crystal. Note that the left ordinate is for the V-type centers, while the right ordinate is for the F-type centers.

Figure 11 illustrates the growth curve (absorption versus dose) of the 2.3-eV optical-absorption band upon irradiation with 2.0-MeV electrons from a Van de Graaff generator. The crystal was grown at Oak Ridge by Butler, Batch 061669, and the impurity analyses were reported in Ref. 25. Both irradiation and optical measurements were performed at 77 K in order to minimize thermal decay. These irradiations ($10^{12} e/\text{cm}^2$) are extremely low doses. The broad band at 2.3 eV is taken to represent V-type centers in the crystal, which in this case consisted of primarily V_{Al}[7,10] and V_{OH}.[4,5] Numerical concentrations were calculated using Smakula's equation $n = 6\times 10^{15} \alpha\omega f^{-1}$, where α is the absorption coefficient (cm^{-1}), ω is the half-width (~1.0 eV), and f is the oscillator strength (~0.1) for V-type centers.[3,5,26] Using the linear slope of the initial growth curve, the defect formation cross section $\sigma(E) = N^{-1}(\Delta n/\Delta\phi)$, where n is the concentration of defects produced in a material of atomic density N and ϕ is the integrated flux of incident particles, corresponds to $\sim 4\times 10^6$ b. A cross-section of this large magnitude is compatible with the notion that electron-hole pairs were being created and holes were being trapped at existing vacancies forming V_{Al} and V_{OH} centers. EPR and ENDOR measurements verified that these were primarily the centers formed. As can be observed, the curve is essentially saturated at an electron dose $\phi \sim 1\times 10^{13} e/\text{cm}^2$.

For some crystals, but not all, irradiation with higher electron dose produces the V^- center. Figure 12 exhibits the growth curves from two such

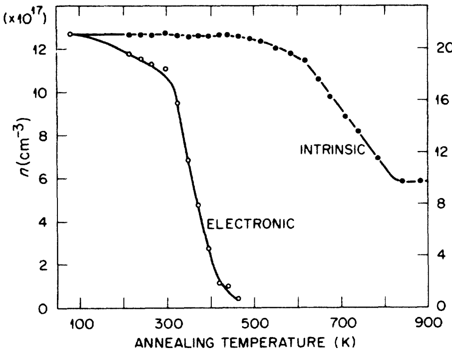

FIG. 13. Isochronal annealing of V-type centers of a crystal electron irradiated to a dose in excess of 10^{18} e/cm^2, and γ irradiated and therefore, initially containing V^-, V_{Al}, and V_{OH} centers. The lower curve (open circles) which describes the thermal stability of the hole trapped at these centers, was obtained by optical measurement after each isochronal anneal. The upper curve (solid circles) was obtained by repopulating the centers with holes by a short ionizing irradiation following each isochronal anneal and therefore portrays the thermal stability of vacancies which can trap holes. This particular crystal, containing the stable V^- center, was the same one loaned by the authors for the work cited in Ref. 23.

crystals. One crystal, from General Electric (GE), courtesy of Hansler, had an impurity content comparable to that of the crystal used in obtaining the data shown in Fig. 11, while the second crystal, one of the first crystals grown in our laboratory (Oak Ridge) was less pure, and had 20-ppm Fe. Electron irradiations of the GE crystal were carried out at 77 K to minimize possible interstitial-vacancy recombination. Doses in excess of $\sim 10^{16} e/\mathrm{cm}^2$ normally introduce surface contamination which is not conducive to optical measurements. Hence, after each electron irradiation, the sample was warmed to room temperature, and cleaned in nitric acid. It was then γ irradiated in the ^{60}Co source (3.6×10^6 R/h)[27] for 15 min, which was the minimum dose to assure the population of all existing centers, but not sufficient to create appreciable amounts of new defects. Measurements were made immediately thereafter. The initial point, of course, represents the concentration after γ irradiation only, while the increase represents the growth above and beyond that incurred by trapping holes at existing vacancies. The initial slope yields a displacement cross section $\sigma = 500$ b. Saturation occurred at about $\phi = 1\times 10^{17} e/\mathrm{cm}^2$. For comparison, the growth curve of the F-type (F^+ and F) centers in the same GE crystal, as determined by the optical absorption band at 5.0 eV,[6,28,29] is illustrated in the bottom curve. The corresponding cross section for the F-type-center formation is about two orders of magnitude lower than that of the V^- center, and saturation has been reported[30] to occur at $\phi \sim 10^{20} e/\mathrm{cm}^2$.

Similar curves were obtained from other crystals. The cross sections, as determined from the initial slopes, had a spread in the range 300–800 b. The Oak Ridge crystal, which was irradiated and measured at room temperature (illustrated in Fig. 12), was studied in greater detail. Optical absorption and EPR measurement, with occasional ENDOR checks, were made after each electron irradiation so that the trapped-hole centers could be monitored individually. The V^- center concentration increased in proportion to the optical curve. The V_{OH} concentration decreased rapidly at first and somewhat slower after a dose of $\sim 2\times 10^{16} e/\mathrm{cm}^2$.

2. *Thermal stability*

The thermal stability of the trapped-hole centers in this Oak Ridge crystal is illustrated in Fig. 13. The sample was irradiated to doses in excess of $10^{18} e/\mathrm{cm}^2$. The absorption coefficient, and therefore concentration, of the 2.3 eV band is plotted versus isochronal annealing temperature; that is, the sample temperature was raised to and maintained at a given temperature for 10 min before cooling down to the measuring temperature. Below the isochronal annealing temperature at 350 K, measurements were made at 77 K, while above that temperature the measuring temperature was 295 K. Initially, the crystal was given an ionizing radiation in the cryostat to saturate the centers. After an anneal a measurement was made and the concentration is indicated by a hollow circle in the lower curve. The sample was reirradiated to repopulate the vacancies with holes, and the resulting concentration is illustrated by the solid circle in the upper curve. This was followed by the next annealing temperature, and so forth. Hence, the curve described by the open circles portrays an electronic decay via a hole release process. Actually, the curve represents a composite decay of the stable V^- center and the relatively less stable V_{Al} and V_{OH}. The latter two centers did not survive an annealing temperature of 360 K, and it is apparent that the electronic decay of the stable V^- centers overlaps those of the less stable defects. However, at room temperature (295 K) the half-lives are quite different: the V_{Al} and V_{OH} have half-lives of the order of hours,[3] while the V^- has a half-life of the order of many months (perhaps years).[7] This produces the net effect of a room-temperature half-life of days (as reported in Ref. 6) for the total concentration of V-type centers, while the tail of the decay persists for years.

The upper curve described by solid circles illustrates an "intrinsic" effect; each of these points represents an isochronal annealing plus an ionizing irradiation at the given measuring temperature in order to repopulate existing vacancies with holes. The two plateaus, at < 600 K and > 800 K, demonstrate the existence of two types of hole-trapping sites and show that between 600 and 800 K, the intrinsic center was destroyed. Indeed, EPR and ENDOR measurements indicated that almost all of the stable V^- centers have vanished after anneals above 800 K. However, there is evidence among the few crystals studied which contained ~ 10^{17} V^- centers/cm^3 that, despite heating at 1500 K and a slow cooldown, there was still a remnant (~ 10^{14} cm^{-3}) of the V^- centers upon a short ionizing radiation. No remnant was observed for crystals that did not previously have V^- centers. Under this condition of preponderant $V_{\rm Al}$ centers, the EPR averaging technique was not dependable for identifying the presence of small concentrations of V^- centers, but the ENDOR technique could be, and in our experience clearly was, superior for this purpose.

It should be noted that part of the 7×10^{17} defects/cm^3 annihilated prior to the 850-K anneal were due to the thermal precipitation of the OH$^-$ ions[31] in the crystals, thereby reducing the concentration of the isolated $V_{\rm OH}$ centers. After heating the same specimen at 1500 K, thereby almost entirely destroying the intrinsic V^- center, a subsequent anneal at 850 K indicated that about 3×10^{17} centers/cm^3, primarily $V_{\rm OH}$ centers, vanished. Hence, we estimate that about 4×10^{17} V^- centers/cm^3 were present in the crystal prior to the anneal. This value is in reasonable agreement with the 5×10^{17} V^- centers/cm^3 created by electron irradiation shown in Fig. 12.

In the only other study to date on the formation and thermal stability of the centers, Tench and Duck[32] irradiated ultrapure MgO powder with protons and arrived independently at the conclusion that there were "two V^- centers." A significant point of their experiment was that they used ultrahigh purity powder which contained less than 1 ppm aluminum. γ irradiation of the virgin powder gave no EPR signals attributable to the trapped-hole centers. Furthermore, they found that the V^- center formed by proton irradiation has an activation energy of 1.6 ± 0.2 eV for thermal hole release, as compared to the 1.13 ± 0.05 eV obtained by Searle and Glass in x-irradiated crystals.[33] They therefore concluded that the larger value is associated with an isolated vacancy, and the smaller with a vacancy charge compensated by a tripositive cation or singly charged negative anion. It is reasonable at this time to believe that the defect created by protons is the same intrinsic V^- center that we reported.[7] At any rate, the two rather distinct activation energies are compatible with two centers with different stabilities, the smaller value being associated with the $V_{\rm Al}$ (and possibly some $V_{\rm OH}$) center, and the larger value with the V^- center.

Assuming that the defect produced in MgO powder by proton irradiation is indeed the V^- center, further comparisons can be made. In the present study, the formation of the V^- center was found to be impurity dependent (see Sec. III D). In the case of Tench and Duck's studies,[32] the nominal high purity of the powder makes it unlikely that impurities play an essential role in V^- center production, unless an impurity was present which was not detected. Furthermore, their results on powder of different particle sizes showed that although the surface area appears to affect the efficiency of V^--center production, the effect is unmistakably enhanced in the case of F^+- center formation. Clearly, the possibility of trapping sites at the surface is negligible for irradiations of single crystals. The concentration of the V^- center in this study was fully saturated at a dose of $<1\times10^{18}e/{\rm cm}^2$ before the buildup of anion vacancies (F-type centers) became appreciable (Fig. 12). The production curves for the powder studies were not drastically different from the present results in the sense that the V^- center reaches a saturation concentration at much lower dose levels than the F^+ center.

The efficient manner (σ~ 10^7 b) in which the V-type centers were formed, as typically shown in the growth curve of Fig. 11, is consistent with the idea that electron-hole pairs were being created and holes were being trapped at existing vacancies. EPR and ENDOR measurements on this crystal and others verified that the centers formed were charge-compensated V-type centers, such as $V_{\rm Al}$, $V_{\rm OH}$, and V_F centers.

For irradiation $>10^{17}e/{\rm cm}^2$, EPR and ENDOR indeed verified that the defect called the V^- center was created. The initial rate of production of the V^- center (Fig. 12) far exceeds that for the F-type center. The corresponding cross-section of ~ 500 b for the V^- center is far too large to be attributable to a knock-on process based on a displacement energy T_d of 60 eV, which was determined for the oxygen ion.[25] The theoretical cross section for 2-MeV electrons based on a Mg-ion displacement energy of 60 eV is 10 b.[34] Due to interstitial-vacancy recombination, experimentally observed cross sections are normally lower, typically by one or two orders of magnitude. Clearly, the large cross section for V^--center formation is incompatible with a displacement energy near 60 eV. In fact, if one is persuaded to believe that the displacement process is indeed due to a knock-on process, a cross section of 500 b would predict a T_d considerably less than 5 eV. A smaller T_d value for the Mg ion compared to that of the O ion is not unreasonable since the Mg ion is much smaller. However, such a large difference has no precedent in other binary compounds, namely, InSb,[35] ZnO,[36] CdS,[37,38] CdTe,[38] InP,[39] InAs,[39] and GaAs.[39] Hence, it is unlikely that a knock-on process is involved and certainly an ionization mechanism[40,41] warrants further consideration.

3. *X and γ irradiations*

X and γ irradiations have certain advantages over electron irradiations–uniformity of defect production and penetration depth. The latter is particularly crucial for low-energy irradiations. The primary process by which energy is transferred to the lattice is via photoelectric and Compton electrons. As the energy of the incident photons decreases, photoelectrons become more predominant. For this study, we used one crystal, namely, the Oak Ridge crystal which had previously been electron irradiated (see Figs. 12 and 13), to study the effect of photon irradiations in the following sequence: (a) 20-kV x rays (20 mA; $\sim 1\times 10^6$ R/h) and irradiated for one week; (b) γ rays from ^{137}Cs source ($\overline{E}=0.66$ MeV; 1.2×10^6 R/h) and irradiated for one week; (c) γ rays from the ^{60}Co source ($\overline{E}=1.25$ MeV; 1.8×10^6 R/h) and irradiated for five days; and (d) 10-kV x rays (20 mA; $\sim 1\times 10^6$ R/h) and irradiated for one week. Prior to each of these studies, the crystal was heated at 1500 K for one hour to anneal out V^- centers. The experimental procedure typically was as follows. For (a), after annealing, the specimen was subjected to 20-kV x irradiation. After 20 min of irradiation, an optical absorption measurement was made; ENDOR indicated that only a trace of V^- centers was present. After one week of exposure, an ENDOR measurement indicated that a large concentration of V^- centers was formed. The increase in optical absorption coefficient corresponded to $\sim 4\times 10^{17}$ new centers per cm^3. This same value was also obtained by a later optical absorption measurement on the same exposed portion of the crystal. A period of three weeks transpired between the two optical measurements so that the V_{A1} and V_{OH} centers had adequate time to decay. Thus, we conclude that while the initial irradiation ($< 10^6$ R) simply populated existing charge-compensated vacancies with holes, the extended irradiation ($\sim 2\times 10^8$ R) resulted in isolated Mg^{++} ion vacancies, corresponding to the observed increase in concentration of the stable V^- center. The concentrations of the V^- center formed by the above four irradiations were (a) 20-kV x rays, 4×10^{17} cm^{-3}; (b) ^{137}Cs γ rays, 3×10^{17} cm^{-3}; (c) ^{60}Co γ rays, 3×10^{17} cm^{-3}; and (d) 10-kV x rays, $\approx 4\times 10^{17}$ cm^{-3} for the region within the penetration depth.

Hence, we must regard the more energetic γ rays as no more efficient in producing V^- centers than the lower-energy x rays. The ability of photoelectrons with energy less than 10 keV to create V^- centers in such concentration clearly shows that there is an essentially zero-energy threshold for the production of V^- centers. Therefore, the V^- center is formed by an ionization process and not by a knock-on process. Furthermore, in view of the apparent lack of energy dependence, we conclude that the ionization process of V^--center production is the dominant one. This conclusion appears to differ from that drawn in a recent electron microscopy study[42] and with previous suspicions.[7,14] Certainly, the production of V^- centers by means of electron or neutron irradiation is the result of the intense ionization accompanying both irradiation methods, rather than a direct result of knock-on processes. In the case of neutron irradiation, the neutron flux of 2.3×10^{13} neutrons cm^{-2} sec^{-1} in the Oak Ridge Reactor is accompanied by an overwhelming γ intensity of 2×10^9 R/h! There is no evidence at this time that V^- centers can be produced by a knock-on process using electrons or neutrons in single-crystal MgO. In fact, while neutrons are conducive to the formation of F-type centers, it appears that the V^- center cannot survive high doses of neutrons. V^- centers can be produced, however, by low doses of neutrons, due presumably to the concomitant large γ fluxes. Additional evidence for V^--center formation seems to exist in the work of Searle and Bowler,[24] who measured the temperature dependence of optical bleaching of the 2.3-eV absorption band generated by 30-kV x rays. They found that the decay rate constant progressively increased for cumulative x-ray doses of many hours but that a brief anneal at ~ 1000 K (presumably to annihilate Mg^{++} ion vacancies) before each x irradiation was necessary to give reproducible results. Their dose-dependent results probably reflect the presence of a mixture of V^- and V_{A1} centers in samples that were not annealed after each irradiation.

D. Impurity dependence

The formation of the V^- center in single-crystal MgO was found to be strongly sample dependent. In certain crystals, V^- centers could not be produced under electron or neutron irradiations regardless of dose (up to $10^{19} e/\mathrm{cm}^2$). For other crystals, a concentration gradient of the V^- center could be observed visually in various portions of the crystal. Subsequent repeated thermal annihilations and rejuvenations by high-dose electron irradiations at 80 K produced the same concentration gradient, indicating impurity dependence as being the cause. Certainly, it cannot be attributed to nonuniform thermal annealing over the crystal, since the temperature of irradiation was well below the annealing temperature of the V^- center, and indeed far below room temperature. Furthermore, the procedure was repeated each time at somewhat different geometric positions under the condition of uniform electron flux.

Investigations are being undertaken to determine the impurity which makes possible the formation of the V^- center. Preliminary results indicate that the V_{OH} (and V_{OH}^-) center is a precursor of the V^- center. It appears that the production of the V^- center is achieved not by the displacement of the Mg ion, but by the removal of the hydrogen ion at a V_{OH} (or V_{OH}^-) site by ionization.

IV. CONCLUSION

It is shown here that in spite of the virtually identical EPR and optical spectra of the V_{Al} and V^- centers, a distinction between the two centers can be made by means of the ENDOR. The presence of a charge-compensating impurity may be inferred from the absence of EPR thermal averaging but only the ENDOR can directly identify the tripositive aluminum impurity. It should be reiterated that the absence of thermal averaging does not necessarily imply the presence of aluminum, but may be due to some other charge-compensating impurity as yet unobserved. Actually the simplest and most obvious way to separate and distinguish between the V_{Al} and the V^- centers follows from their different production rates and thermal stabilities.

The V^- center cannot be produced in all MgO crystals and its formation is probably contingent upon the presence of an impurity: hydrogen. In summary, the predominant formation mechanism is that of an ionization rather than a knock-on process for the following reasons: First, the 10^2–10^3-b cross section for V^--center production by 2-MeV electron irradiation was much larger than the few barns for its antimorph, the anion vacancy. This large cross section is compatible only with a displacement energy of considerably less than 5 eV for the Mg ion, which is unlikely in view of the 60 eV reported for the O-ion displacement energy. Second, the relative ease with which V^- centers were formed by low-energy x rays indicates that an essentially zero-energy threshold is involved. Third, irradiation with both low-energy x rays and higher-energy γ rays showed that there is no energy dependence for the V^--center formation.

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