PHYSICAL REVIEW B VOLUME 11, NUMBER 2 15 JANUARY 1975

Role of hydrogen and deuterium on the V^--center formation in MgO[†]

Y. Chen, M. M. Abraham, L. C. Templeton, and W. P. Unruh*
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 20 May 1974)

The formation of the V^- center in MgO by ionizing radiation is found to be contingent on the presence of an impurity: hydrogen. The attainable V^- concentration is dependent upon the initial V^-_{OH} concentration detected by the 3296-cm^{-1} infrared absorption band. A similar dependence on the V^-_{OD} concentration (2445-cm^{-1} band) in deuterated crystals is also observed. Photographs illustrate that the V^- density distribution for a given crystal is identical to that for the V_{OH} center in the same crystal. Quenching crystals, as compared with slow cooling, leads to larger V^-_{OH} or V^-_{OD} bands and, upon intense electron irradiation, results in larger V^- concentrations. As the V^- concentration is enhanced by electron irradiation, the V_{OH} and V^-_{OH} concentrations diminish and ultimately vanish at doses of $\sim 1\times 10^{18}$ e/cm^2. Hydrogen-free (or deuterium-free) crystals are immune to V^--center formation, regardless of thermal treatment. The experimental evidences can be understood on the basis of a formation mechanism which involves the displacement of hydrogen from the V^-_{OH} site by ionizing radiation. The enhancement of the infrared absorption bands at 3700 and 2723 cm^{-1} in certain crystals due to electron irradiation indicates that some of the displaced hydrogen and deuterium ions form Mg(OH)$_2$ and Mg(OD)$_2$ precipitates, respectively.

I. INTRODUCTION

Recently, it was shown conclusively by an electron-nuclear-double-resonance (ENDOR) study of MgO crystals[1] that the ionization-induced center previously believed to be the V^- center[2,3] was actually an Al^{3+} charge-compensated vacancy which we denoted as the V_{Al} center. Furthermore, it was demonstrated that another center, whose thermal stability[4] was consistent with that of an intrinsic V^- center (a magnesium vacancy with a trapped hole) can coexist with the V_{Al} center and possesses the same set of g values: $g_{\parallel}=2.0033(2)$ and $g_{\perp}=2.0386(2)$. In a study of proton-irradiated MgO powder, Tench and Duck[5] arrived at the conclusion that there were two "V^- centers" involved, by virtue of the apparently different formation mechanisms and thermal stabilities, and they correctly postulated that impurity charge compensation was involved with one of the centers.

Halliburton *et al.*[6] provided evidence that the g values of one of the centers average ($g_{\perp}-g_{\parallel}$ decreases) with rising temperatures toward an isotropic value (a characteristic of centro-symmetric centers such as [Li]^0, [Na]^0, and [K]^0 centers in the alkaline-earth oxides[7–9]), whereas the g-values of the other center do not. Investigation of the magnetic hyperfine structure of the more-stable center gave further evidence for the localized nature of the hole at low temperatures.[10] A study of the formation and thermal stability of both centers in MgO single crystals were reported[11]: The cross sections for the production of the V^- center in various crystals were found to be incompatible with a knock-on displacement of a magnesium ion, and the lack of energy dependence by photon irradiations confirmed an ionization mechanism. Further, it was shown that not all MgO crystals are susceptible to V^--center formation and this observation was attributed to an impurity dependence. In the present work, using electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR), infrared, and optical broad-band measurements, we demonstrate that the V^-_{OH} center, described by the configuration OH$^-$-(Mg vacancy)-O^{--}, is the precursor of the V^- center. All the experimental evidence supports the thesis that the V^- center is formed by the removal of the hydrogen from the V^-_{OH} site by ionizing radiation.

II. EXPERIMENTAL PROCEDURES

The crystals used in the present work were grown from powder obtained from the Kanto Chemical Co., Tokyo, Japan, by the arc-fusion method.[12,13] Crystals used were from three separate boules grown in this laboratory: (i) boule No. 010270, most of which was slightly cloudy; (ii) boule No. 032670, also slightly cloudy, in which deuterium had been introduced by presoaking the powder in D$_2$O (this is the same batch used for earlier investigations on deuteroxyl ions[14,15]); and (iii) boule No. 020171, which was totally clear in the bulk. The first two boules were grown by Butler *et al.*[12] and the third by an improved version of the arc-fusion method.[13] A fourth boule, labeled OR-18, grown by W.E. Spicer, Ltd., Winchcombe, Gloucestershire, England, was a source of crystals used in an earlier investigation.[14]

The irradiating sources were: a ^{137}Cs γ source (1.2×10^6 R/h, average energy of 0.66 MeV), and a 2.0-MeV Van de Graaff electron accelerator. γ irradiations were performed at both 77 and 295 K. Electron irradiations were carried out either in a specially designed irradiation chamber, at intensities typically of 10 $\mu A/cm^2$, using water as a coolant, or at 5 $\mu A/cm^2$ in a custom made liquid-nitrogen cryostat. Optical-absorption measurements in the photon energy region of 1–6 eV were taken on a Cary model 14R spectrophotometer and at lower energies with both a Perkin-Elmer 621 and a Beckman IR-10 spectrophotometer. An X-band homodyne spectrometer with 100-kHz field modulation was used for EPR measurements. The spectra were observed at 90 K by means of a Varian variable temperature Dewar system. The absolute concentrations of the various centers in the samples were determined by comparing the resonance line of the centers to that of the Cr^{3+} signal from a small Cr-doped MgO single crystal. The spin concentration of this MgO: Cr standard was compared with the Varian weak- and strong-pitch samples, with a phosphorus-doped silicon standard,[16] and with a second MgO: Cr powder sample, supplied by Strand Laboratories, which had been calibrated against oxygen-gas resonance lines. It was also analyzed for total chromium content by neutron activation analysis, performed by the Analytical Chemistry Division at this laboratory. Thus, the values of absolute concentrations reported in this paper are believed to be accurate within ±25%. ENDOR measurements were made with an X-band superheterodyne spectrometer at liquid-helium temperatures. A coil was wound on the outside of the TE_{102} rectangular cavity and a 0.050 inch slot in the cavity wall permitted entry of the radio-frequency magnetic field. Direct signal averaging of the video spectrometer output was employed,[17] using frequency sweep rates appropriate for the relaxation times encountered for the ENDOR transitions under consideration.

A Sentry Model 7AV furnace was used for heat treatments at temperature up to 1850 K in air. For higher-temperature work, a vacuum furnace made in this laboratory using a cylindrical tantalum heating element provided heating capabilities up to ~2500 K. MgO crystals were suspended with rhenium wire and centered in the heating zone. Another custom-made Marshall vacuum furnace was used for rapid quenching. It possessed a cylindrical tantalum heater fed by an 8-kW saturable reactor, with a bath containing diffusion pump oil 45 cm directly below the heat zone.

III. RESULTS AND DISCUSSION

A. Selective V^- and V_{OH} formation in as-grown crystals

Figure 1, illustrating the visual observation of coloration (2.3-eV absorption band) due to γ and electron irradiations in a crystal from boule No. 010270, provided all the necessary clues to identify the impurity associated with the V^--center formation. For our purpose, γ irradiations, corresponding to approximately 10^{13}–10^{14} Compton-electrons/cm^2, produce enough ionization to fully populate existing vacancies with holes, whereas electron irradiations of doses $\gtrsim 1\times10^{17}$ e/cm^2 are capable of altering the type of existing vacancies and/or generating new ones.[11] Figure 1(a) is a photograph, taken against a dark background with light penetrating from one of the sides of the crystal (bottom), showing the voids in the crystal. Both the apparent size and the concentration of the voids are vastly exaggerated by the scattering of the incident light. These voids were shown by Briggs and Bowen[18] to contain high-pressure hydrogen gas, produced either from sorbed water, or $Mg(OH)_2$ in the powder from which the MgO was chemically processed. Two of the sides (right and bottom in the figure) were located near the ingot edge, which readily served as sinks for these voids at high temperatures. Figure 1(b), a photograph taken against a white background, illustrates the coloration of the crystal after a short γ irradiation. The contrast in coloration gives a reasonable facsimile of the void density pattern and was subsequently found to be due to differences in concentrations of the V_{OH} center, a hydrogen-compensated cation vacancy with a trapped hole, described by the configuration OH^-–(Mg vacancy)–O^-. The half-life of this center is known to be of the order of hours.[2,3] The coloration due to V_{OH} was unstable, as evidenced by the near depletion after a two day anneal at room temperature in the dark [Fig. 1(c)], leaving behind a somewhat more stable and uniform coloration, shown to be the V_{Al} center[1] which has the configuration O^-–(Mg vacancy)–O^{--}–Al^{3+}. In the neutral V_{OH} center, the proximity of the hydrogen ion is expected to render the hole more susceptible to leakage than in the V_{Al} center, where the Al^{3+} is farther away and shielded by an O^{--} ion. Figure 1(d), portrays the coloration immediately after an electron irradiation of ~1×10^{17} e/cm^2. Selective coloration was again observed, and unlike that due to the γ irradiation, did not vanish even after long periods of time in the dark at room temperature [Fig. 1(e)]. This persistent center was easily identified as the V^- center, which is stable up to many years at room temperature.[1,4] Further irradiation to a total fluence of ~1×10^{18} e/cm^2 somewhat enhanced the V^- concentration.

The similarity between the patterns for the void density [Fig. 1(a)], the V_{OH} [Fig. 1(b)], and V^- [Fig. 1(e)] distributions elucidates relationships between these three observations. That the hydrogen at the V_{OH} site stemmed from a high concentration of dissolved hydrogen originating from the high-pressure hydrogen gas and that the edges of

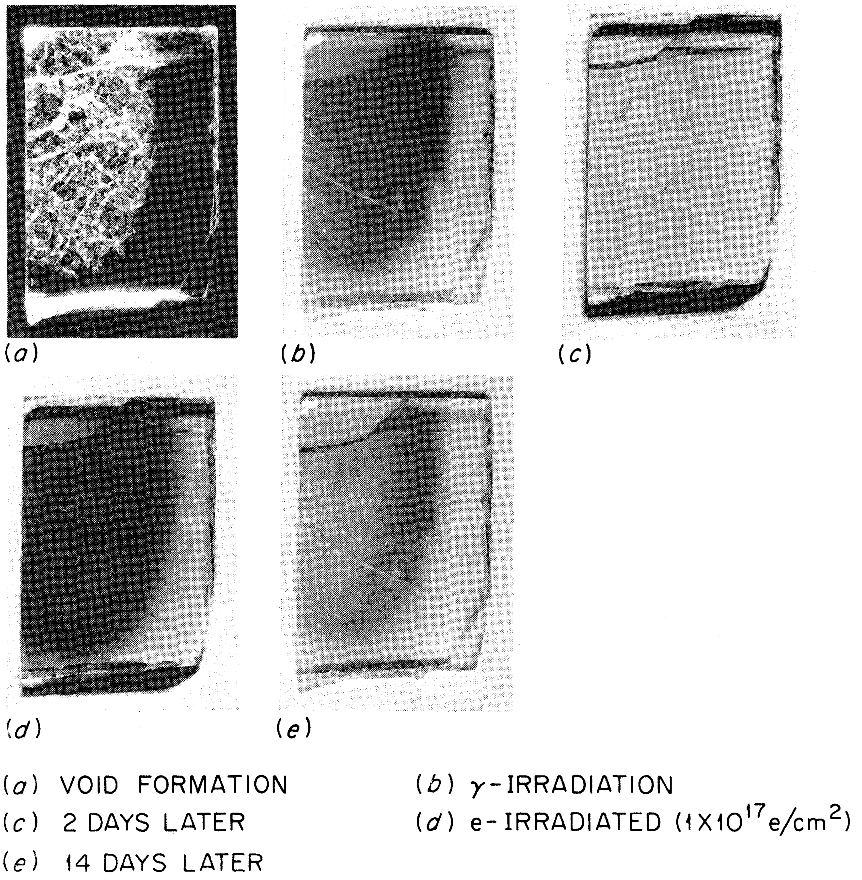


FIG. 1. Selective coloration of an MgO crystal due to γ and electron irradiations. (a) Scattering of incident light by voids formed during crystal growth; (b) immediately after γ irradiation; (c) 2 days after γ irradiation; (d) immediately after electron irradiation to a dose of 1×10^{17} e/cm^2; and (e) 14 days after the electron irradiation.

the ingot served as sinks for hydrogen gas and voids, is self-evident. However, the similarity between the V^- and V_{OH} distribution patterns must be regarded as more than a mere coincidence. This is particularly so, when we consider that this pattern was valid, without exception, for several other crystals. Figure 1 illustrates that even the fine details of the V_{OH} density are reproduced by that of the V^-. Figure 2 exemplifies an interesting departure from Fig. 1, in that the V_{OH} density [Fig. 2(b)] does not appear to match that of the voids [Fig. 2(a)], but it is again a replica version of that of the V^- center [Fig. 2(c)]. Actually, a closer examination of Fig. 1 reveals that the V_{OH} and V^- densities, while resembling one another, actually extend somewhat beyond the periphery occupied by the voids. Hence, evidence indicates that the source of hydrogen in the V_{OH} center is the hydrogen-laden void and that the V^- center is related to the V_{OH} center, or the concomitant hydrogen.

Two small samples of identical mass were chipped from this crystal· one from a high-coloration area (cloudy portion at the center of the crystal) and the other from a low-coloration area (clear portion at lower right-hand corner). The two samples were then heated at 1500 K to anneal the defects formed by electron irradiation, thereby restoring the crystals to their pre-irradiated condition. They were again subjected to a sequential γ and electron irradiation. Curves a and b of Fig. 3 illustrate the EPR spectra observed following γ irradiation. The striking difference between the two crystals, denoted "clear" and "cloudy," is that the latter contained a sizable concentration of V_{OH} center, which was responsible for the darker coloration noted in Fig. 1(b). The traces in Fig. 3(c) and 3(d) were recorded 14 days after electron irradiation to a fluence of 1×10^{18} e/cm^2, so that primarily the stable V^- center survived. A significant amount of V_{OH} centers was still present immediately after electron irradiation to a fluence of 1×10^{17} e/cm^2, but none was observed immediately after irradiation to $\sim1\times10^{18}$ e/cm^2, nor even after a subsequent γ irradiation at 78 K. The additional structures observed in Fig. 3(d) are magnesium satellite lines associated with the V^- center. The net result of the electron irradiation demonstrates that the cloudy crystal, in which the V_{OH} was prevalent, was more conducive to V^- center formation than the clear crystal, as was noted in Fig. 1(e).

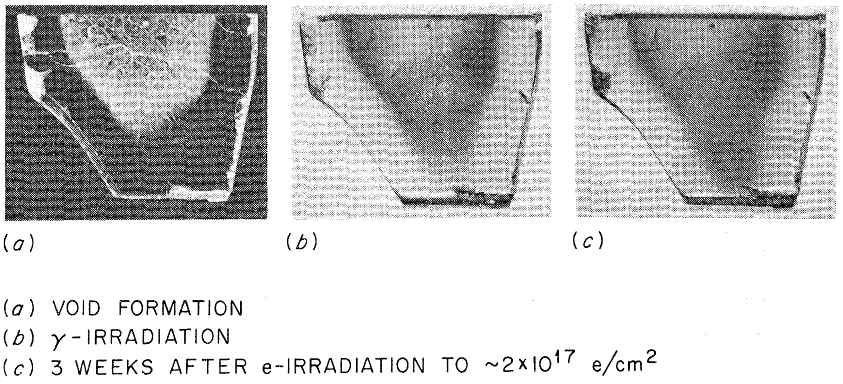


FIG. 2. Selective coloration of another MgO crystal induced by γ and electron irradiations. (a) Scattering of incident light by voids formed during crystal growth; (b) immediately after γ irradiation, soon after which the preferential coloration vanished; and (c) 21 days after electron irradiation to a dose of 2×10^{17} e/cm^2.

B. Effects of heat treatment on V^--center formation in hydrogenated and deuterated crystals

Broad-band optical absorption, EPR, and infrared studies were performed to determine the effect of quenching on the formation of V_{OH}^-, V_{OH}, and V^- centers. The known trapped-hole centers in undoped MgO (V_{Al}, V^-, V_{OH}, and V_F) all absorb in the vicinity of 2.3 eV. Hence, broad-band optical absorption measurements sample a conglomerate of trapped-hole centers. EPR can differentiate between these paramagnetic centers, but it is handicapped in being unable to quantitatively differentiate between the V^- and the V_{Al} center, since both centers have identical sets of g values.[1,11] For quantitave measurements, we simply permit a reasonable time (a few weeks) for the V_{Al} and the other neutrally charged centers to decay at room temperature. The surviving center is the stable V^- center, as verified by ENDOR.[11] Infrared measurements, on the other hand, can identify both the paramagnetic V_{OH} and the diamagnetic V_{OH}^- center.

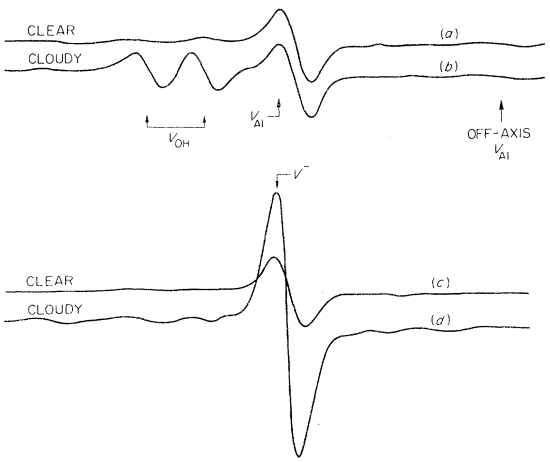


FIG. 3. EPR spectra of two crystals, one from the clear and the other from the slightly cloudy segment of the slab shown in Fig. 1. The crystals were heated at 1500 K to erase the defects formed by the earlier irradiations. The two top traces, (a) and (b), were taken immediately after γ irradiation. The two lower curves (c) and (d) represent spectra taken 24 days after electron irradiation to a dose of 1×10^{18} e/cm^2. All traces were taken at $\theta = 90°$.

1. Infrared

Three crystals were used to obtain the spectra shown in Fig. 4. The first two columns refer to two crystals obtained from the same slab of boule No. 010270, which was cut nearly in halves along the thickness of the crystal. The twin crystals were verified by EPR and infrared measurements to possess identical V_{OH}, V_{OH}^-, and paramagnetic impurity concentrations. The Fe^{3+} concentration, for example, was found to be 3 ppm. The slab, taken from a cloudy portion of the ingot, contained a sizeable

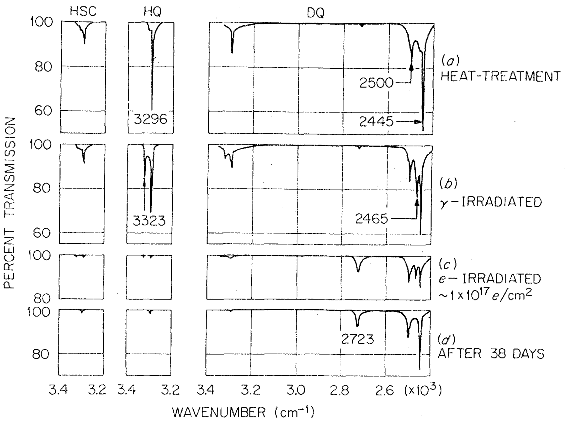


FIG. 4. Effects of γ and e irradiations on the infrared spectra of three crystals: HSC (slow-cooled crystal containing hydrogen), HQ (quenched crystal containing hydrogen), and DQ (quenched crystal containing deuterium). The thicknesses were 0.145, 0.133, and 0.181 cm, respectively.

concentration of the hydrogen charge-compensated centers ($\approx 10^{18}$ cm^{-3}). One of the crystals was slow cooled from 1500 K over a period of 2 days and is labeled HSC (hydrogen, slow cooled). The other crystal was quenched from the same temperature into a liquid-nitrogen bath and is denoted by HQ (hydrogen, quenched). The third crystal, DQ (deuterium, quenched), was obtained from a cloudy portion of boule No. 032 670, in which deuterium had been introduced ($\gtrsim 10^{18}$ cm^{-3}) by soaking the MgO powder in D_2O prior to crystal growth.

The effects of the heat treatments on these three crystals are illustrated by the infrared spectra shown in Fig. 4(a). The 3296-cm^{-1} band corresponds to the stretching frequency of the OH^- ion at the V_{OH} site[19–21] and its intensity is, therefore, a measure of the concentration of the V_{OH}^- center. The band in crystal HQ is much more intense than that in sample HSC, consistent with results shown previously.[22] In the deuterated crystal DQ, the 2445-cm^{-1} band is the OD^- analog at the V_{OD}^- site.[14] The V_{OH}^- center was also present, constituting only a fraction of the V_{OD}^- concentration. A low-intensity band is observed at 2723 cm^{-1}, which in all liklihood is the same band reported previously at 2727 cm^{-1}.[14] This band and one at 3700 cm^{-1} have been associated with the infrared active OD^- and OH^- stretching modes of the precipitates $Mg(OD)_2$ and $Mg(OH)_2$, respectively,[23] and we shall assume that the assignments are correct. The assignments were made on the basis that similar absorption peaks have been identified in the pure brucite materials, and the ratio of their frequencies corresponds to $[\mu(OD)/\mu(OH)]^{1/2} = 1.37$, where μ is the reduced mass of the radical. Precipitation is expected in a slow-cooled crystal; indeed, a slow-cooled deuterated MgO crystal yielded a much larger band at 2723 cm^{-1} than a quenched one. Surprisingly, the 3700-cm^{-1} band was not observed in crystal HQ or even HSC. No assignment has been proposed for the band observed at 2500 cm^{-1}.

The spectra after γ irradiation are shown in Fig. 4(b). The irradiation-induced band at 3323 cm^{-1}, which is associated with the OH- stretching vibration perturbed by the presence of a trapped hole at the V_{OH} site,[19,20] was more intense in HQ than in HSC, as expected. A band appeared at 2465 cm^{-1} in the deuterated crystal, which has been designated as the OD^- analog of the 3323-cm^{-1} band by virtue of its radiation-induced origin and the proper frequency.[15] The ratio of the frequencies 3323:2465, identical to that of 3296:2445 at the V_{OH}^- and V_{OD}^- sites, yields 1.35, which is in excellent agreement with the theoretically predicted 1.37 for pure harmonic stretching bond. Hence, the band intensities at 3323 and 2465 cm^{-1} may be regarded as indicative of the V_{OH} and V_{OD} concentrations, respectively. Certainly, γ irradiation induced the bands at 3323 and 2465 cm^{-1} at the expense of those at 3296 and 2445 cm^{-1}, respectively. In the deuterated crystal, the 2500-cm^{-1} band appeared to be unaffected by the irradiation.

The effect of electron irradiation to a dose of 1×10^{17} e/cm^2 is shown in Fig. 4(c). The absorption bands identifying the V_{OH}^-, V_{OH}, V_{OD}^-, and V_{OD} centers in the three crystals decrease in intensity. That the OD^- bands decreased less dramatically than those of the OH^- may be reflection of the different masses of the D^+ and H^+ ions affecting their mobilities. In the deuterated crystal, the band at 2723 cm^{-1} was enhanced. After prolonged periods at room temperature in the dark, the disappearance of the 2465-cm^{-1} band was accompanied by the increase of the 2445-cm^{-1} line intensity. Upon further irradiation, to a fluence of 1×10^{18} e/cm^2, all signs of the hydrogen and deuterium charge-compensated defects disappeared (not illustrated in Fig. 4). In fact, with the exception of the 2723-cm^{-1} band in DQ, whose intensity increased further, the spectra in all three crystals vanished, and did not reappear even after several weeks, that is, no V_{OH}^-, V_{OH}, V_{OD}^-, and V_{OD} centers were detectable.

The infrared spectra of an OR-18 crystal, on which a previous investigation was based,[14] are portrayed in Fig. 5. After quenching from 1500 K into a liquid-nitrogen bath, the crystal possessed the spectrum illustrated in Fig. 5(a). The most dominant band appeared at 3296 cm^{-1}, attended by structures at 3477, 3465, 3372, and 3310 cm^{-1}. The band at 3310 cm^{-1} has been associated with OH^- ions charge compensated by trivalent impurities.[20] After a short γ irradiation, the band at 3323 cm^{-1} emerged, with a corresponding decrease of like intensity at 3296 cm^{-1} (not shown in Fig. 5). The intensity at 3310 cm^{-1} remained unaltered, while the band at 3372 cm^{-1} was barely detectable, and those at 3477 and 3465 vanished. Upon electron irradiation to a fluence of 1.2×10^{18} e/cm^2, all bands previously present disappeared. However, unlike crystals HQ and HSC, the band at 3700 cm^{-1} appeared in this crystal [Fig. 5(b)].

Upon heating this crystal at 1300 K such that practically all memories of previous irradiations were erased, and slow cooling to room temperature, the spectrum shown in Fig. 5(c) was obtained. The slow cooling resulted in the formation of the $Mg(OH)_2$ precipitates as illustrated by the emergence of the 3700-cm^{-1} band. The line intensity at 3296 cm^{-1} became substantially weaker than after the quenching [Fig. 5(a)]. Again irradiating the crystal to a dose of 1.2×10^{18} e/cm^2, the band at 3296 cm^{-1} vanished, and the band at 3700 cm^{-1} increased [Fig. 5(d)]. The stable 2.3-eV coloration due to the high-fluence electron irradiation was much less intense than that after the quenching. After reheating the crystal at 1500 K and requench-

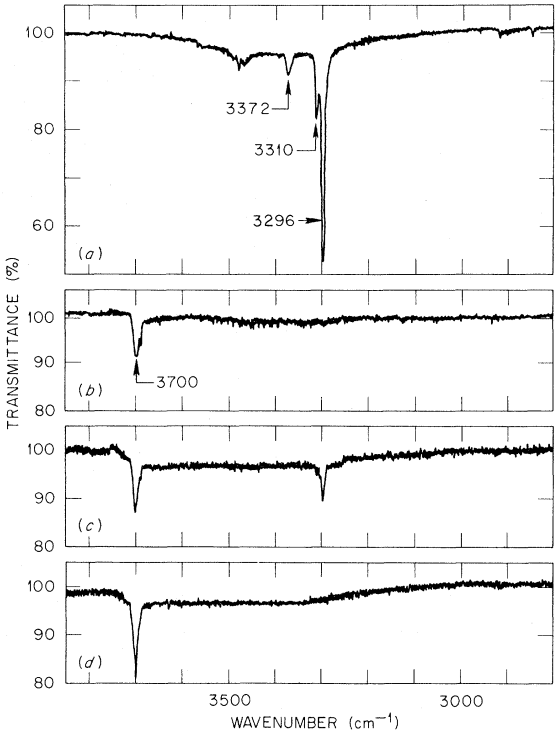


FIG. 5. Infrared spectra of a crystal from OR-18 (thickness = 1.72 mm) upon (a) quenching from 1500 K, (b) electron irradiation to a fluence of 1.2×10^{18} e/cm^2, (c) heating to 1300 K and slow cooling, and (d) electron irradiation to a fluence of 1.2×10^{18} e/cm^2.

ing, a spectrum identical to that shown in Fig. 5(a) was again obtained, confirming reversibility of the process and that no loss of hydrogen from the crystal was involved during these treatments.

Both Figs. 4 and 5 showed that, as a result of electron irradiations, most of the infrared bands, including those responsible for the V^-_{OH} and V^-_{OD} centers, were destroyed. In OR-18 and the deuterated DQ crystals, the bands associated with $\mathrm{Mg(OH)_2}$ and $\mathrm{Mg(OD)_2}$ prevailed either as a result of the electron irradiation or thermal precipitation by slow cooling. However, in crystals HSC and HQ (boule No. 010270), the 3700-cm^{-1} band was not observed under either condition, indicating the existence of another storage site for hydrogen. Indeed, comparing the spectra due to the two electron irradiations [Figs. 5(b) and 5(d)] in which only the 3700 cm^{-1} was observed, the intensity of the band corresponding to the quenched case [Fig. 5(b)] is notably weaker. Since the total concentration of hydrogen in the crystal remained intact, it is reasonable to assume that even in OR-18 crystals, at least some of the hydrogen ions exist in forms other than $\mathrm{Mg(OH)_2}$ precipitates.

2. EPR and ENDOR

The identification by EPR of the various trapped-hole centers induced by irradiations in crystals HQ, HSC, and DQ is shown in Fig. 6. The association of the V_{OH}, V_{OD} [$g_{\parallel}=2.0033(2)$, $g_{\perp}=2.0398(2)$], and the V_{F} [$g_{\parallel}=2.0032(2)$, $g_{\perp}=2.0390(2)$] with the hydrogen, deuterium, and fluorine nuclei, respectively, has been positively verified by ENDOR.[15,24–26] The concentration of the V_{F} center is not plotted, because its small signal was completely dominated by the neighboring V_{Al} or V^- line. After γ irradiation [Fig. 6(a)], the V_{OH} was clearly more prominent in sample HQ than in HSC, a finding consistent with the infrared data. The concentration of the V_{OD} center in DQ was greater than that of the V_{OH} in HQ. This is not surprising since deuterium was deliberately introduced into the crystal, whereas in crystals HQ and HSC the presence of hydrogen was an unavoidable consequence of the crystal growth process. It is noteworthy that, if the isolated Mg vacancy were created as a direct consequence of quenching,[6] the V^- center should be detectable after a γ irradiation. No V^- center was observed by our sensitive ENDOR technique.

After electron irradiation to a dose of 2×10^{18} e/cm^2, the V_{OH} and V_{OD} centers were undetectable. Since the V_{OH} EPR spectra nearly coincide with magnesium satellite lines of either the V_{Al} or V^- center [compare Fig. 3(b) with 3(d)] it is pointless to estimate the V_{OH} contribution to the very small signal. Hence, in Fig. 6, we merely represent an upper limit of the V_{OH} concentration with a dot, with the understanding that it was negligible. Clearly, in each case, the EPR signal corresponding to $V^- + V_{\mathrm{Al}}$ centers increased, more dramatically for the quenched crystals [Fig. 6(b)]. After 24 days in the dark at 297 K such that most

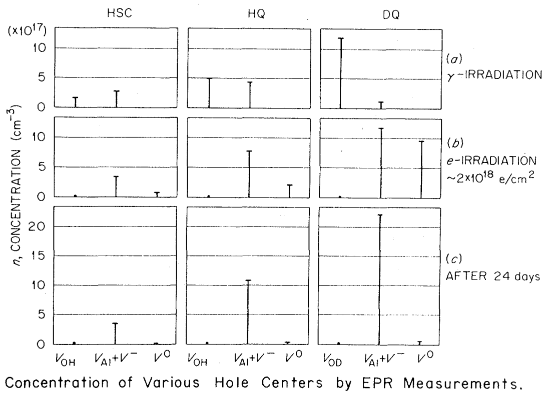


FIG. 6. Effects of γ and electron irradiations on the EPR concentrations of V_{OH} (V_{OD}), V_{Al} and V^-, and V^0 centers in HSC, HQ, and DQ crystals.

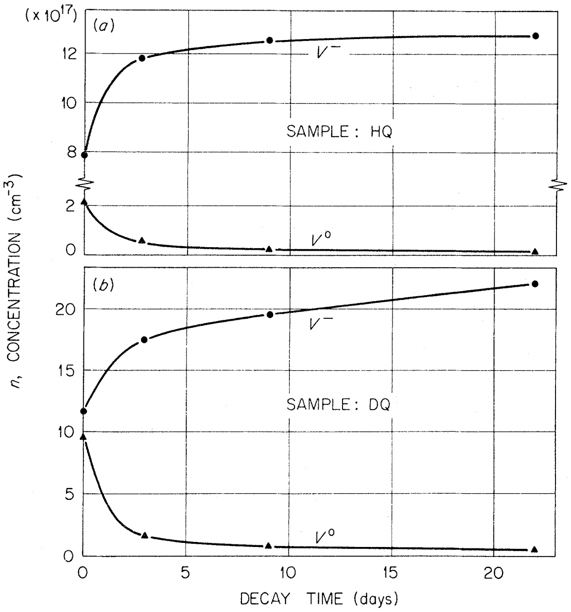


FIG. 7. Room-temperature decay of the V^0 center and the concomitant increase of the V^- center for crystals HQ and DQ.

V_{Al} centers decayed, crystal HQ clearly exhibited larger V^- concentration than crystal HSC [Fig. 6(c)].

An interesting phenomenon was observed: The paramagnetic V^0 center with effective spin $S = 1$ (previous notations: H_2, W, V_2),[27] which is normally induced by low-temperature irradiations and has not been known to survive even a short exposure to room temperatures, was actually produced by electron irradiation at 305 K! This defect usually occurs in small concentrations, $\sim 10^{16}$ cm^{-3}. In this study, concentration of 1×10^{18} cm^{-3} in crystal DQ was actually achieved! Our measurements yielded the following relevant EPR parameters for this center: $g_{\parallel} = 2.0033(2)$, $g_{\perp} = 2.0395(2)$, and $D = 212.61(5) \times 10^{-4}$ cm^{-1}. These values are in reasonable agreement with those obtained previously.[27]

After more than three weeks at 295 K in the dark, the V^0 center was still present in all three crystals and had decayed to approximately the 5% level. In crystal DQ, 0.5×10^{17} V^0 centers/cm^3 remained. The decay of the V^0 and other neutrally charged trapped-hole centers led to enhancement of the stable V^- centers in all three crystals, which in DQ approached a concentration of 2×10^{18} cm^{-3}. The decay of the V^0 centers and the corresponding increase of the V^- center for crystals HQ and DQ, are depicted in Fig. 7.

The significance of the infrared and the EPR results on quenched and slow-cooled crystals is that they show that the ability to create V^- centers does not depend on the total concentration of hydrogen in the crystal matrix, but on the V_{OH}^- concentration. Crystals HQ and HSC had the same hydrogen concentration, but the former had a greater V_{OH}^- concentration by virtue of the quenching. That the heat-treatment at 1500 K had no effect on the concentration of hydrogen as such could be demonstrated by alternate slow cools and quenches, by means of which one is able to obtain reproducibly the predictable small and large V_{OH}^- and V_{OH} signals, respectively. The treatment of the two crystals, HSC and HQ, were reversed. For example, HSC was subsequently quenched from 1500 K and electron irradiated. The V_{OH} and V^- concentrations obtained were approximately the same as those for sample HQ (see Fig. 6). It is clear that the V_{OH}^-, and undoubtedly also the V_{OD}^- centers, have a direct role in the formation of the V^- centers. The infrared results correlate with the EPR measurements.

3. Broad optical-absorption band

The 2.3-eV optical absorption band has been positively correlated with the axial V^- and V_{Al} centers using a combined EPR-MCD (magnetic circular dichroism) double-resonance technique.[28] While the behavior of the absorption coefficient α, shown for the three crystals is illustrated Fig. 8, these data alone are less useful than EPR and infrared data in exploring the parameters leading to V^--center formation. Nevertheless, the data illustrate several relevant points: It verifies that quenching enhances V^--center formation (Fig. 9) and that the presence of deuterium also can lead to V^- centers. It also demonstrates again that the coloration resulting from electron irradiation,

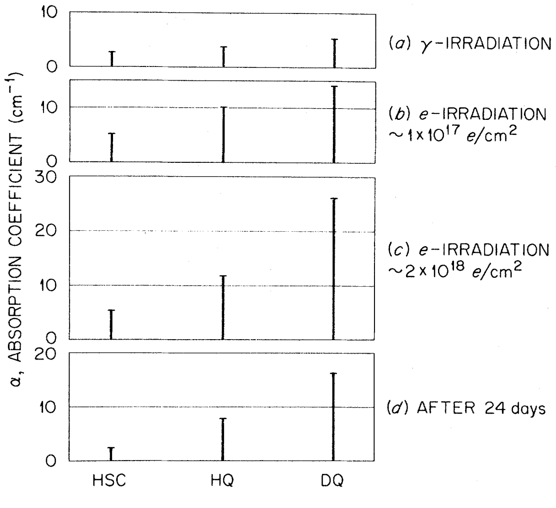


FIG. 8. Effects of γ and electron irradiations on the absorption coefficient of the 2.3-eV band in crystals HSC, HQ, and DQ.

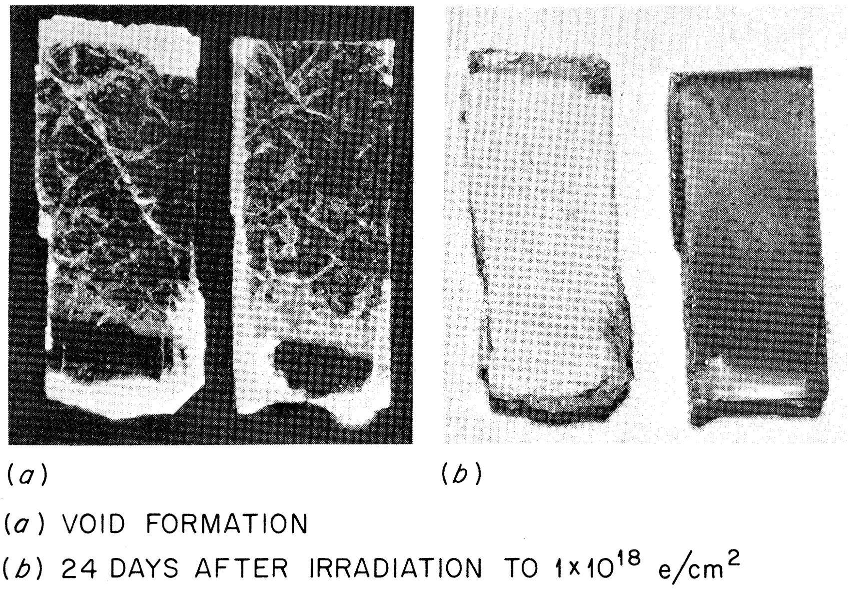


FIG. 9. Effect of slow cooling (HSC, left) and quenching (HQ, right) on V^--center formation in MgO. (a) Scattering of incident light by voids in MgO, and (b) V^--center coloration 24 days after electron irradiations of 1×10^{18} e/cm^2.

which is above and beyond that created by γ irradiation, can be equated with the V^- concentration[11]; that is, for all three crystals reported, the increase in α due to electron irradiation [Figs. 8(b) and 8(c)] corresponds to the concentration of the stable V^- center [Fig. 8(d)].

Some conclusions may also be drawn regarding oscillator strength: By relating the V^- concentration of crystals HQ and DQ [Fig. 6(c)] with the corresponding optical absorption coefficients [Fig. 8(d)] using Smakula's equation in its Gaussian form,[3] we obtain an oscillator strength $f\sim 0.05$. Somewhat lower f values are obtained by adding the V_{A1} plus V_{OH} EPR concentrations [Fig. 6(a)] and relating them to the optical bands [Fig. 8(a)]; accuracy here was handicapped by the broad band and the small intensity. These values are in reasonable agreement with the rough $f\approx 0.1$ quoted previously.[2,29,30] Relating the EPR intensities of V^- and V^0 centers for crystal DQ [Figs. 6(b) and 6(c)] with the optical data in Figs. 8(c) and 8(d), one can readily see that the oscillator strengths for the two centers are not the same. The number of V^- plus V^0 centers immediately after electron irradiation remained essentially the same after 24 days, even though the concentration of each has changed. But the optical absorption coefficient has decreased. On the assumption that the half widths of the two centers are approximately the same, the ratio of their oscillator strengths $f(V^0)/f(V^-)$ is certainly greater than unity.

C. Effects of hydrogen and deuterium removal at elevated temperature and in crystal growth

It was reported earlier that subsequent to the crystal-growth process, the clarity of the MgO crystals can be enhanced if the arc power is reduced to keep the temperatures hovering in the range of 2300–2800 K.[13] The result is that high-pressure hydrogen escapes to the surface of each ingot of the boule. The net effect is that the crystals become depleted of hydrogen. Indeed, infrared measurements (or EPR) reveal no detectable V_{OH}^- or V_{OH} centers ($<10^{16}$ cm^{-3}) in such crystals, regardless of subsequent quenching. A γ irradiation produced only the unstable charge-compensated centers (primarily the V_{F} and V_{A1}). Subsequent electron irradiation, even up to 5×10^{18} e/cm^2, produced no signs of the presence of V^- centers: no optical band growth at 2.3 eV beyond that incurred by the γ irradiation, no stable 2.3-eV coloration, and most important of all, no V^- ENDOR signal.

In a complementary fashion, for crystals in which hydrogen has been shown to be present in abundant concentration, such as from boule No. 010270, heating periods at temperatures in excess of 1700 K, either in vacuum or in air, tend to drive out the hydrogen or deuterium in the crystal. Such incubation for sufficiently long times (up to many days) renders the crystal free of V_{OH}^- centers. The dynamics of the hydrogen removal is being studied in greater detail by Harris and Crawford.[31] The consequence was that V^- centers were not observed upon electron irradiation. Hydrogen-containing crystals from several boules were given similar treatment and yielded identical results. In fact, the HQ crystal was heated in vacuum at 2200–2300 K for 2 h; V^- centers were not produced by subsequent electron irradiation regardless of whether or not the crystal was quenched from 1500 K. We conclude that thermal depletion of hydrogen renders the crystal immune to V^--center formation.

Intuitively, the idea that there exists an ideal combination of incubation period and temperature, whereby the hydrogen at a V_{OH}^- site has ample opportunity to diffuse away before a less mobile Mg^{++} ion recombines with the resulting vacancy, has been rather appealing. A cursory search for the proper conditions turned out to be fruitless.

Further evidence exists that quenching, as such, does not lead to V^--center formation. A 0.9-mm-thick hydrogen-free ($< 10^{16}$-cm^{-3}) crystal suspended by a platinum wire, was heated in a vacuum in the Marshall furnace. When the temperature of the crystal reached the melting point of platinum (~2000 K), the crystal was dropped automatically into a room-temperature diffusion-oil bath. This type of quenching is undoubtedly the fastest possible. The cracked sample was found to contain no detectable V^- centers upon a 77-K γ irradiation, as would be expected if isolated Mg vacancies were produced by quenching. No F^+ or F centers were detectable. Furthermore, no V^- centers were formed even after an extensive electron irradiation, again illustrating that in hydrogen-free crystals, V^- centers are not produced, regardless of quenching or irradiation.

The reverse procedure of introducing hydrogen into a grown hydrogen-free crystal is most appealing. Unfortunately, our attempts to perform this task by gaseous diffusion of hydrogen have been unsuccessful. Proton ion implantation combined with heat treatment, however, may prove fruitful.

IV. CONCLUSIONS

In principle, for a quenching process, the supersaturation of point defects due to thermal equilibrium at high temperature results in Schottky defects with concentrations determined by the Boltzmann factor $e^{-E/kT}$. In reality, to our knowledge, the creation of Schottky pairs in ionic crystals by quenching has never been observed, in part due to the low thermal conductivity of insulators at high temperatures. Positive ion vacancies have been observed as a consequence of quenching but were found to be the result of impurities behaving as charge compensators for vacancies.[32] Any implication[6] that isolated cation vacancies are created in MgO as a direct result of quenching from 1500 K is premature: Certainly in the previously cited study on MgO,[6] there was no report of the observation of concomitant F or F^+ centers as a direct result of quenching. Furthermore, if quenching from 1300 K indeed generates Schottky defects, one would expect a much enhanced concentration by quenching from higher temperatures. It has been demonstrated in this study that quenching a hydrogen-free crystal from 2000 K did not yield detectable isolated cation or anion vacancies. Indeed, the yield of trapped hole centers as a function of quenching temperatures has been adequately reported in the past.[2,3,20,29,33] Above 1200 K, no further increase in the absorption coefficient at 2.3-eV band has been observed. The increase in α from 800 to 1200 K has, in fact, been properly attributed by Henderson and Sibley[14] to the dissolution of hydroxide precipitates leading to a high concentration of V_{OH}^- (V_{OH}) center, with saturation occurring above 1200 K.

We now consider a model which involves the displacement of hydrogen at the V_{OH}^- site by intense ionizing radiation:

$$V_{OH}^- + \text{hole} \rightarrow V_{OH} \rightarrow V^- + H^+ .$$

Certainly, it is compatible with all the following experimental evidences: (i) The identical match between the V_{OH} and V^- density patterns (Figs. 1 and 2) attests to a relationship between the two centers. (ii) The attainable V^- concentration varies with the initial V_{OH}^- concentration. This fact eliminates the possibility of a direct dependence of V^--center formation on the hydrogen concentration alone. (iii) As the V^- concentration is enhanced by electron irradiation, the V_{OH} and V_{OH}^- concentrations diminish correspondingly. (iv) V^- production is undetectable in crystals from which hydrogen has been removed either during the growth process, or by heat treatment at ~2000 K. (v) The removal of a hydrogen ion at the V_{OH}^- site by ionization is compatible with the large cross section, shown previously be 10^2–10^3 b. Ionization-induced mobility of the hydrogen ion in crystals is not without precedent; in germanium, the production of defects at 77 K involving the relocation of hydrogen ions by an ionization process had been demonstrated.[34] These experimental evidences can easily explain the observation that ionizing x irradiation of a quenched crystal[6] can lead to V^--center production. The criterion is, of course, that the crystal contain a large V_{OH}^- concentration!!

It is certain that during electron irradiation the displaced hydrogen ions ultimately form various complexes. The enhancement of the 3700- and 2723-cm^{-1} bands in selected crystals is convincing evidence that the hydrogen or deuterium ions can form $Mg(OH)_2$ and $Mg(OD)_2$ precipitates, respectively. In some crystals, the annihilation of the V_{OH}^- center and the absence of the 3700-cm^{-1} band make a strong case for other existing sites for the displaced hydrogen ions. Although the presence of atomic hydrogen in an oxide matrix is of low probability, using EPR a search at low temperature for atomic hydrogen[36] was performed but no signals were observed. This implies that the relocated hydrogen ions exist in diamagnetic states. The possibility that they were in H_2 or H_2^+ molecular forms in the matrix appears unlikely since one would intuitively expect an ionization-induced equilibrium between these and the V_{OH}^- center; a molecular form nevertheless cannot be ruled out at this time.

So far we have found no evidence of V^- formation in single crystals by γ, electron or neutron irradiation via a competing mechanism—specifically, the knock-on displacement of magnesium ions. Similarly, Evans *et al.*[35] in a study of MgO bombarded with energetic $^{20}Ne^+$ ions found no evidence for the formation of V^- centers. This indicates that magnesium interstitial-vacancy pairs are unstable and recombine. An investigation is presently being undertaken to determine if the mechanism of V^--center formation in CaO is similar to that reported here. Preliminary results indicate that the V^- center, which is stable in CaO at 295 K, only occurs in crystals which contain V_{OH} or V_{OD} centers.

---

†Research sponsored by the U.S. Atomic Energy Comission under contract with Union Carbide Corp.

*Guest Scientist. Permanent address: Dept. of Physics, University of Kansas, Lawrence, Kan. 66044.

[1] W. P. Unruh, Y. Chen, and M. M. Abraham, Phys. Rev. Lett. 30, 446 (1973).

[2] B. Henderson and J. E. Wertz, Adv. Phys. 17, 749 (1968).

[3] A. E. Hughes and B. Henderson, in *Defects in Crystalline Solids*, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1972).

[4] Y. Chen, J. L. Kolopus, and W. A. Sibley, Phys. Rev. 186, 865 (1969).

[5] A. J. Tench, and M. J. Duck, J. Phys. C 6, 1134 (1973).

[6] L. E. Halliburton, L. A. Kappers, D. L. Cowan, F. Dravnieks, and J. E. Wertz, Phys. Rev. Lett. 30, 607 (1973).

[7] H. T. Tohver, B. Henderson, Y. Chen, and M. M. Abraham, Phys. Rev. B 5, 3276 (1972).

[8] M. M. Abraham, Y. Chen, J. L. Kolopus, and H. T. Tohver, Phys. Rev. B 5, 4945 (1972).

[9] M. M. Abraham, Y. Chen, J. T. Lewis, and F. A. Modine, Phys. Rev. B 7, 2732 (1973).

[10] L. E. Halliburton, D. L. Cowan, W. B. J. Blake, and J. E. Wertz, Phys. Rev. B 8, 1610 (1973).

[11] M. M. Abraham, Y. Chen, W. P. Unruh, Phys. Rev. B 9, 1842 (1974).

[12] C. T. Butler, B. J. Sturm, and R. B. Quincy, Jr., J. Cryst. Growth 8, 197 (1971).

[13] M. M. Abraham, C. T. Butler and Y. Chen, J. Chem. Phys. 55, 3752 (1971).

[14] B. Henderson and W. A. Sibley, J. Chem. Phys. 55, 1276 (1971).

[15] B. Henderson, J. L. Kolopus, and W. P. Unruh, J. Chem. Phys. 55, 3519 (1971).

[16] The P-doped Si standard was obtained from and calibrated by E. A. Gere, Bell Laboratories.

[17] W. P. Unruh, L. G. Nelson, J. T. Lewis, and J. L. Kolopus, J. Phys. C 4, 2992 (1971).

[18] A. Briggs and D. H. Bowen, Natl. Bur. Std. (U.S.) Spec. Publ. 296, 103 (1968).

[19] P. W. Kirklin, P. Auzins, and J. E. Wertz, J. Phys. Chem. Solids 26, 1069 (1965).

[20] A. M. Glass and T. M. Searle, J. Chem. Phys. 46, 2092 (1967).

[21] T. M. Searle, J. Phys. Chem. Solids 30, 2143 (1969).

[22] W. A. Sibley, C. M. Nelson, and Y. Chen, J. Chem. Phys. 48, 4582 (1968).

[23] S. S. Mitra, Solid State Phys. 13, 1 (1962).

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

[25] J. E. Wertz, and P. Auzins, Phys. Rev. 139, A1645 (1965).

[26] W. P. Unruh, Y. Chen, and M. M. Abraham, J. Chem. Phys. 59, 3284 (1973).

[27] J. E. Wertz, P. Auzins, J. H. E. Griffiths, and J. W. Orton, Discuss. Faraday Soc. 28, 136 (1959).

[28] E. H. Izen, R. M. Mazo, and J. C. Kemp, J. Phys. Chem. Solids 34, 1431 (1973).

[29] Y. Chen, and W. A. Sibley, Phys. Rev. 154, 842 (1967).

[30] W. A. Sibley, J. L. Kolopus, and W. C. Mallard, Phys. Status Solidi 31, 223 (1969).

[31] E. F. Harris and J. H. Crawford, Jr. (private communication).

[32] J. H. Crawford, Jr., Adv. Phys. 17, 93 (1968).

[33] E. Sonder, and W. A. Sibley, in Ref. 3.

[34] Y. Chen, and J. W. MacKay, Phys. Rev. 167, 745 (1968).

[35] B. D. Evans, J. Comas, and P. R. Malmberg, Phys. Rev. B 6, 2453 (1972).

[36] Observation of atomic hydrogen in CaO was reported by B. Henderson and H. T. Tohver [Phys. Status Solidi 51, 761 (1972)].

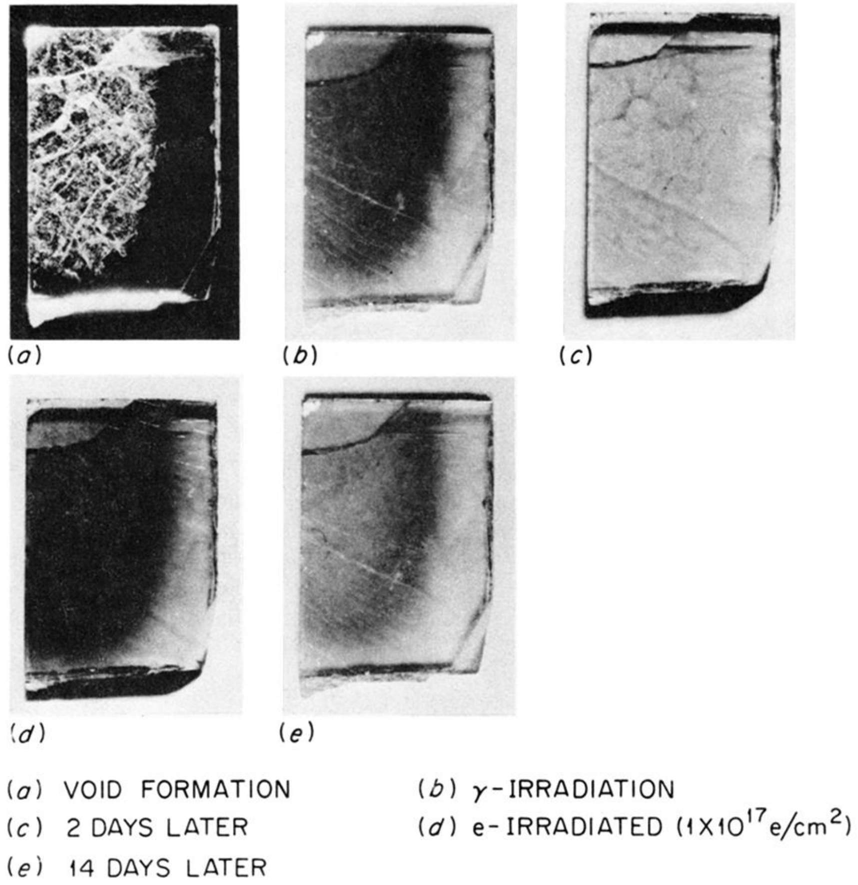
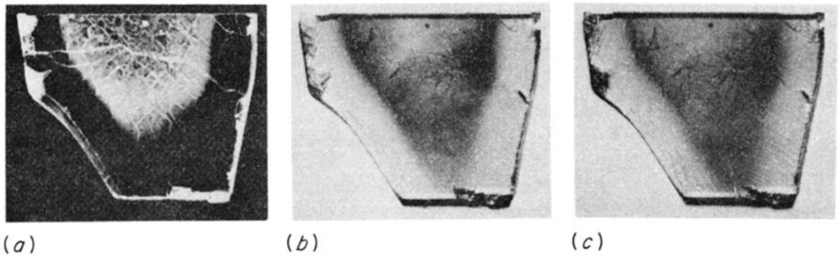
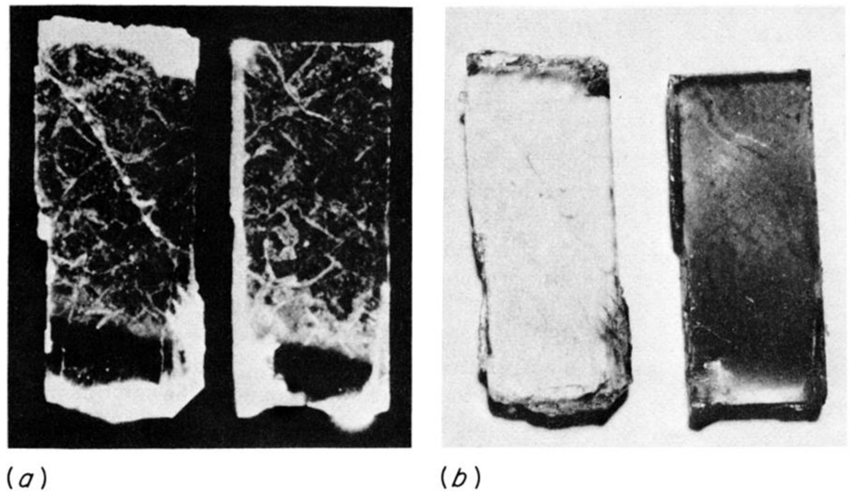


FIG. 1. Selective coloration of an MgO crystal due to γ and electron irradiations. (a) Scattering of incident light by voids formed during crystal growth; (b) immediately after γ irradiation; (c) 2 days after γ irradiation; (d) immediately after electron irradiation to a dose of 1×10^{17} e/cm^2; and (e) 14 days after the electron irradiation.



(a) VOID FORMATION
(b) γ-IRRADIATION
(c) 3 WEEKS AFTER e-IRRADIATION TO $\sim 2 \times 10^{17}$ e/cm^2

FIG. 2. Selective coloration of another MgO crystal induced by γ and electron irradiations. (a) Scattering of incident light by voids formed during crystal growth; (b) immediately after γ irradiation, soon after which the preferential coloration vanished; and (c) 21 days after electron irradiation to a dose of 2×10^{17} *e*/cm^2.



(a) VOID FORMATION

(b) 24 DAYS AFTER IRRADIATION TO 1×10^{18} e/cm^2

FIG. 9. Effect of slow cooling (HSC, left) and quenching (HQ, right) on V^--center formation in MgO. (a) Scattering of incident light by voids in MgO, and (b) V^--center coloration 24 days after electron irradiations of 1×10^{18} e/cm^2.