

Radiation Damage in MgO†

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The radiation production of F centers in Fe-doped and "pure" MgO crystals has been investigated. The coloration is enhanced by impurities when the radiation temperature is in the range 80–330°K. Unlike the more ionic alkali halides, the F -center production rate is a linear function of electron-irradiation intensity and decreases with irradiation energy. For a given dose of radiation, fast neutrons produce about 50 times as many F centers as do energetic electrons. It is concluded from the study that radiation damage in MgO occurs primarily as a result of elastic collisions, and, that the photochemical processes prevalent in the alkali halides contribute very little, if any, to the damage.

INTRODUCTION

IT has been known for some time that crystals, such as alkali halides, which have highly ionic bonding are very easily damaged by radiation.^{1–3} Recent experiments have shown that radiation damage in these crystals is extremely sensitive to electron-hole recombination processes^{4,5} and there is some indication that the V_K center, a self-trapped hole, may be the precursor to vacancy-interstitial formation.^{6,7} These observations raise the question of whether the easy production of defects in crystals is associated with their ionicity. One way in which this question can begin to be answered is to investigate the radiation production of defects in materials which have somewhat less ionic character than do the alkali halides. One compound which is ideally suited for such a study is MgO, since the crystal structure is the same as the alkali halides and the ionicity less.

The recent assignment of the absorption band at 250 nm in neutron-irradiated MgO crystals to the F center,^{8–11} which is an oxygen vacancy with one trapped electron, has made possible a comparative study of the rates of formation of color centers in MgO and some of the alkali halides. The first step in this study was to determine the effect of ionizing radiation in MgO.¹² It was found that although there were considerable changes in the impurity states of the crystals investigated there was no evident production of defects such as F centers.

Radiation defects in alkali halides appear to be pri-

marily due to ionization, but in semiconductors and III-V compounds they result from elastic collisions or "knock-on" processes. It is intriguing, therefore, to inquire what mechanism prevails in some of the II-VI oxides. In general, the cross section for ionization damage, if it occurs in a material at all, is several orders of magnitude greater than that for damage by elastic scattering. The neutron, because of its large mass and neutral charge, produces damage primarily by the latter process, whereas the electron gives both ionization and knock-on damage. Hence a comparative study of the damage induced by electrons and neutrons affords a meaningful characterization of the production mechanism. In a supplementary manner, a study of the energy and intensity dependence of the damage rate can also shed some light on the mechanism. The damage rate for ionization processes should be relatively insensitive to variations in energy of the incident particles, but for elastic collisions a marked energy dependence should be evident. In fact, for elastic collisions there is a threshold energy below which no damage occurs.

The purpose of this paper is to report the effect of radiation type, temperature, energy, and intensity on F -center production in MgO. Moreover, since the photochemical coloration of ionic crystals generally is extremely sensitive to impurity concentration,^{4,13} we felt it was imperative to also study the effect of impurities on F -center production in MgO.

EXPERIMENTAL PROCEDURE

The single crystals used in this investigation were usually less than 1 mm thick and were obtained from several different sources. Their impurity concentrations have been reported previously.¹² The samples were placed in a special water- and air-cooled holder for electron irradiation at temperatures above 300°K. At first the specimens were irradiated in light-tight holders, but several experiments indicated that optical bleaching by white light produced no decrease in the F band and this practice was discontinued. Nonetheless, care was still taken to irradiate in the dark and to handle the samples only in subdued light. When the samples were irradiated

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¹ J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The MacMillan Company, New York), 1962.

² J. J. Markham, *Solid State Physics* (Academic Press Inc., New York, 1966), Suppl. 8.

³ J. H. Crawford, *Advances in Physics* (to be published).

⁴ W. A. Sibley, E. Sonder, and C. T. Butler, *Phys. Rev.* **136**, A537 (1964).

⁵ J. W. Mathews, W. C. Mallard, and W. A. Sibley, *Phys. Rev.* **146**, 611 (1966).

⁶ D. Pooley, *Solid State Commun.* **3**, 241 (1965); *Proc. Phys. Soc. (London)* **87**, 245 (1966); **87**, 257 (1966).

⁷ H. N. Hersh, *Phys. Rev.* **148**, 928 (1966).

⁸ J. E. Wertz, G. S. Saville, L. Hall, and P. Auzins, *Proc. Brit. Ceramic Soc.* **1**, 59 (1964).

⁹ B. Henderson and R. D. King, *Phil. Mag.* **13**, 1149 (1966).

¹⁰ W. Primak and J. Luthra, *Phys. Rev.* **150**, 551 (1966).

¹¹ J. C. Kemp and V. I. Neeley, *Phys. Rev.* **132**, 215 (1963).

¹² Y. Chen and W. A. Sibley, *Phys. Rev.* **154**, 842 (1967).

¹³ E. Sonder and W. A. Sibley, *Phys. Rev.* **140**, A539 (1965).

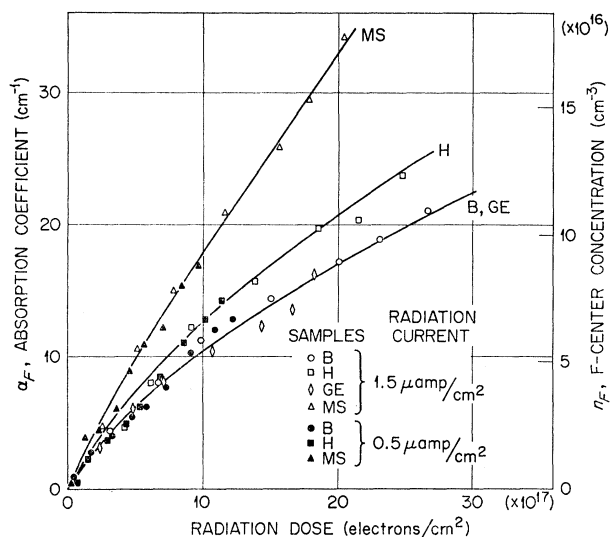


FIG. 1. A plot of the absorption coefficient at the peak of the F band versus electron dose. The ordinate on the right side of the figure shows the F -center concentration as calculated from Eq. (1). The open symbols represent data for irradiations at $1.5 \mu\text{A}/\text{cm}^2$, and the full symbols are data points for irradiations at $0.5 \mu\text{A}/\text{cm}^2$. All samples (H, B, GE) are pure (10-ppm Fe) except the Muscle Shoals, MS, specimens which contain 60-ppm Fe.

at liquid-nitrogen temperature, a Sulfrin liquid-helium cryostat with rotatable base was used. A Van de Graaff electron accelerator was utilized for most of the work and the irradiations were made with 1.6-MeV electrons and current densities ranging from 0.5 to $1.5 \mu\text{A}/\text{cm}^2$. The radiation intensity was calibrated by means of Ag-doped glass dosimeters.¹⁴ The irradiation temperature of the samples (when mounted in the water-cooled holder) was measured with a fine copper-constantan thermocouple sandwiched between two dummy MgO crystals, and it was found that when the current density was $1.5 \mu\text{A}/\text{cm}^2$ the lowest sample temperature obtainable was $60^\circ\text{C} \pm 5^\circ$. Therefore, all irradiations in this holder were controlled at this temperature regardless of radiation intensity. Warm water was circulated through the holder when low-intensity irradiations were made. The thermal conductivity of MgO at liquid-nitrogen temperature is quite high¹⁵ and for this reason an estimate of the sample temperature during irradiation could be obtained by simply measuring the temperature of the copper block on which the sample was mounted in the cryostat. This measurement was made with a platinum resistance thermometer and indicated that the irradiation temperature was about 80°K .

Samples were also neutron irradiated in the ORR hydraulic tube system No. 1-F-8-tube 12. The specimens were wrapped in 10 mils of Cd foil to reduce the thermal neutron flux and were cooled with water from the reactor pool which was at a temperature of about 34°C . The radiation temperature was less than 80°C and

probably between 40 and 60°C .¹⁶ The neutron flux in this facility was measured to be 3×10^{13} neutrons/ cm^2 sec for neutrons with energy greater than 1 MeV .¹⁶ After neutron irradiation it was sometimes necessary to either clean the sample surfaces or to reduce their thickness in order to obtain an accurate measurement of the optical density. This was done by etching the crystals with hot phosphoric or nitric acid (care was taken not to exceed 110°C since F centers have been reported to bleach out at 300°C)⁹ and then rinsing them with benzene and acetone.

In order to obtain the energy dependence of F -center formation in MgO it was necessary to use an accelerator which could produce a stable beam of low-energy electrons (300 keV – 700 keV). Through the courtesy of J. W. MacKay it was possible to use the Purdue accelerator to take these data. Again the radiation temperature was kept below 60°C , and the radiation intensity was monitored.

RESULTS

As mentioned above all irradiations were performed either at 80°K or at 330°K . In the course of the experiment, however, we did find that when samples were irradiated at temperatures greater than 90°C F -center annealing occurred during the radiation. Figure 1 portrays the effect of electron-radiation intensity and impurities on F -center production in MgO at 60°C . Even though the radiation intensity is varied over a factor of 3 it can be seen that for a given crystal purity the F -center concentration depends only on the radiation dose. Moreover, it is evident that the Muscle Shoals samples labeled MS, which contain about 60 ppm Fe, color faster than the purer samples (5–10 ppm Fe) obtained from Harwell, Bristol University, and General Electric, which are labeled H, B, and GE, respectively. In order to make a graph such as that shown in Fig. 1 the optical absorption at 250 nm before and after irradiation must be compared. Since ionizing radiation changes the absorption of a previously unirradiated crystal,¹² we found it necessary to always give the specimens to be investigated a short irradiation initially and use the absorption in these crystals as our baseline.

The effect of impurities on the neutron production of F centers is shown in Fig. 2. Again it is found that impurities enhance the F -center growth rate just as in the case of the electron irradiation.

The energy dependence of the F -center production is shown in Fig. 3 where the absorption coefficient at the peak of the F band, α_F , is plotted versus radiation dose. The ordinate on the right side of each of the figures shows the concentration of F centers. This concentration is calculated using Smakula's equation in its Gaussian form^{2,17} with $\epsilon_{1/2}$ the bandwidth at half-

¹⁶ R. R. Tucker, Oak Ridge National Laboratory Report No. ORNL-TM-1583, 1966 (unpublished).

¹⁷ D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 353.

¹⁴ V. H. Ritz and C. H. Cheek, *Radiation Res.* **25**, 537 (1965).

¹⁵ G. A. Slack, *Phys. Rev.* **126**, 427 (1962).

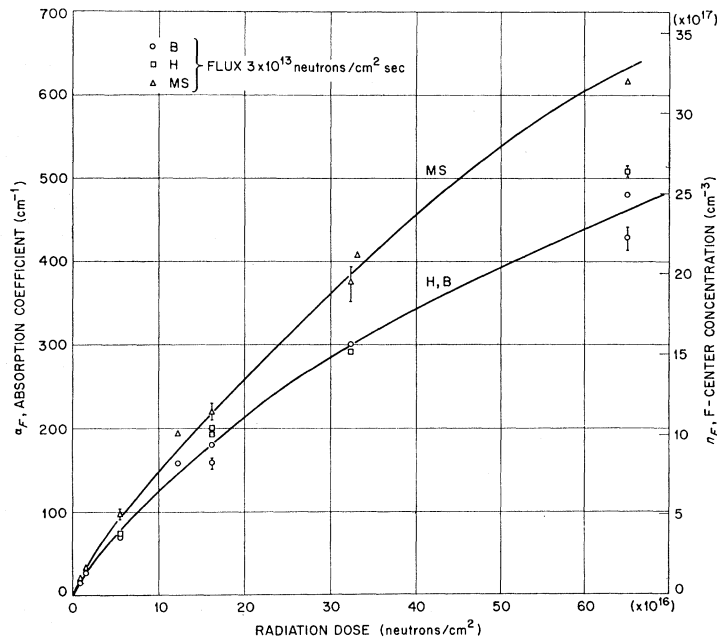


FIG. 2. A plot of the absorption coefficient at the peak of the F band versus neutron dose for pure and Fe-doped samples.

maximum and n the index of refraction,

$$n_F = 0.87 \times 10^{17} n(n^2 + 2)^{-2} f^{-1} \alpha_F \epsilon_{1/2} = 5.0 \times 10^{15} \alpha_F \text{ cm}^{-3}. \quad (1)$$

A half-width of 0.67 eV, $n=1.74$, and an oscillator strength f of 0.8 as determined by Henderson and

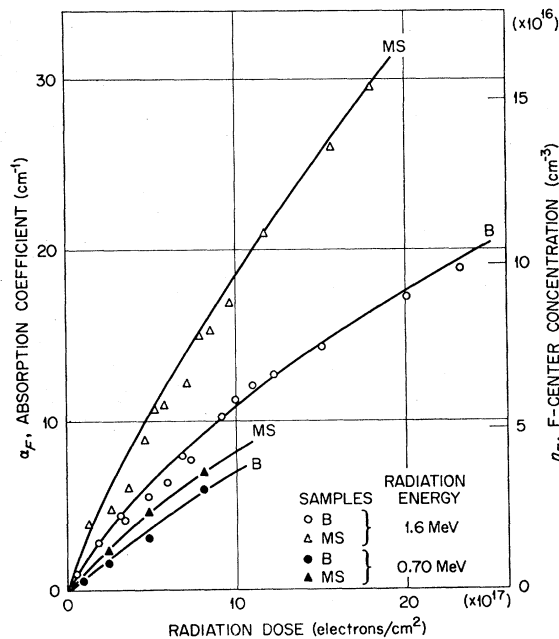


FIG. 3. The effect of radiation energy on the production of F centers by electrons. The open symbols show data for irradiations with 1.6-MeV electrons and the full symbols are data points for irradiations with 0.70-MeV electrons. Irradiation with 0.33-MeV electrons to a dose of $2 \times 10^{18} \text{ e/cm}^2$ produced few if any F centers.

King⁹ were used to determine the numerical coefficient in the last part of Eq. (1). It should be noted that electrons with energies of 330 keV produced few if any F centers even at doses of $2 \times 10^{18} \text{ e/cm}^2$ and thus these data could not be plotted in Fig. 3.

We felt that some idea of the importance of radiation temperature in the range 80–330°K should be obtained. Thus, the isochronal annealing of F centers created at 80°K was investigated. The measurements were made by warming the crystals (both pure and doped specimens) rapidly to the annealing temperature, holding at that temperature for 10 min, and then quickly recooling to liquid-nitrogen temperature to make the absorption measurement. The warming was done in increments of 25°K and the time necessary to reach the desired annealing temperature was always small compared to the annealing time. In neither case, pure or doped crystals, was there annealing, within our experimental accuracy of 5 percent, for the temperature range 80–330°K. In every liquid-nitrogen irradiation, however, there was a problem with surface contamination of the samples in the cryostat. This contamination occurred regardless of whether the irradiation was made with a static vacuum or a vacuum that was maintained at 2×10^{-6} Torr by pumping through an 80°K cold trap during irradiation. The result of this surface contamination was to increase the optical-absorption baseline in the range 200–300 nm, but since the contamination did not change during the annealing runs it could be treated simply as background absorption and subtracted.

DISCUSSION

The experimental results suggest that the photochemical ionization mechanism responsible for most of

the radiation damage in the alkali halides is not operative in MgO. It is known, however, that both energetic electrons and fast neutrons can produce displaced atoms in solids by means of elastic collisions and this may be the source of radiation damage in MgO. The relative effectiveness of electrons and neutrons in creating damage can be roughly estimated by comparing the maximum energy T_m which each can transfer to a lattice atom. For relativistic particles, such as electrons, the maximum kinetic energy transferable to a lattice atom is

$$T_m = \frac{2(E + 2mc^2)E}{M_2c^2}, \quad (2)$$

where E is the kinetic energy of the incident particle, m the electron mass, and M_2 the mass of the struck atom. In the case of neutrons,

$$T_m = \frac{4M_1M_2}{(M_1 + M_2)^2}E, \quad (3)$$

where M_1 is the neutron mass and the other symbols have the same meaning as in Eq. (2).

In order for a lattice atom to be displaced from its lattice site it must receive a certain amount of energy from the incident particle. This energy, in the case of a collision process, is referred to as the displacement energy and denoted by T_d . For a displacement to result, the incident particle must have sufficient kinetic energy such that $T_m \geq T_d$. Therefore, the displacement energy can be determined experimentally by decreasing the energy of the incident particles until no defect production is evident even for high radiation doses. In any material of atomic density N the concentration of displaced atoms n produced by a given integrated flux φ of particles with energy E is related to the displacement cross section $\sigma(E)$ in the following way:

$$n = \varphi N \sigma(E). \quad (4)$$

Oen,¹⁸ using the differential scattering cross section given by Mott¹⁹ and the Kinchin and Pease multiple-displacement theory,²⁰ has calculated values of $\sigma(E)$ for magnesium and oxygen.

In our experiment, if we assume that most of the negative-ion vacancies created by radiation trap electrons and become F centers, n is measurable and the cross section can be estimated. As a result of our inability to produce, even at high radiation doses, an appreciable number of defects using 0.33-MeV electrons we can estimate T_d from Eq. (2) as roughly 50 eV. Fortuitously or not this is close to the value of T_d obtained

by Compton and Arnold for Al_2O_3 .²¹ If 50 eV is taken as the displacement energy for oxygen in MgO then a comparison of the experimental and theoretical cross sections can be made. The theoretical calculations indicate that for an incident particle energy of 1.6 MeV the displacement cross section is 11.6 b. The data given in Fig. 1 show that for the doped samples, which show the highest coloration rate, at a dose $\varphi = 10^{18}$ e/cm^2 the F -center concentration is 9×10^{16} cm^{-3} . From Eq. (4) with $N = 5.2 \times 10^{22}$ cm^{-3} the experimental cross section then is found to be 1.7 bs. This value can be corrected for energy degradation and multiple scattering of the electrons as they traverse the samples.²² The correction, however, is very small (less than 10%) for our conditions and is not important to our conclusions. Moreover, when it is considered that the theory does not make allowance for defect recombination and that in the experiment some recombination probably occurs at the radiation temperatures used, the result suggests that an experimental determination of T_d at 4°K is necessary. Nevertheless, this comparison gives some credence to the idea that defect production in MgO occurs primarily as a result of elastic collisions.

Radiation damage in copper is thought to occur primarily by knock-on processes²³ and it is interesting from this point of view to compare radiation effects in copper and MgO. In copper the damage ratio of fast neutrons to 1.4-MeV electrons can be obtained by comparing the resistivity increases for doses of 10^{17} n/cm^2 and 10^{17} e/cm^2 . The ratio is found to be about 10.²³⁻²⁵ In the case of MgO a comparison of the data shown in Figs. 1 and 2 yields a ratio of ~ 50 for neutron to electron damage for both pure and Fe-doped samples. The observation that impurities enhance F -center production in MgO is also consistent with data taken on copper.^{23,26,27} This increased damage in impurity-doped samples has been explained as being due to trapping of interstitials by impurities. That is, interstitials, when they become mobile, wander into the neighborhood of an impurity atom and form an association with some binding energy due to lattice strains around the impurity.

There is a definite discrepancy between the number of F centers per neutron we obtain and that determined by Henderson and King.⁹ This difference could be due

²¹ W. D. Compton and G. W. Arnold, *Discussions Faraday Soc.* **31**, 130 (1961).

²² J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Chap. II, Suppl. 7.

²³ D. K. Holmes, *The Interaction of Radiation with Solids* (North-Holland Publishing Company, Amsterdam, 1964).

²⁴ J. W. Corbett, R. B. Smith, and R. M. Walker, *Phys. Rev.* **114**, 1452 (1959); **114**, 1460 (1959).

²⁵ R. R. Coltman, C. E. Klabunde, D. L. McDonald, and J. K. Redman, *J. Appl. Phys.* **33**, 3509 (1962).

²⁶ T. H. Blewitt, R. R. Coltman, C. E. Klabunde, and T. S. Noggle, *J. Appl. Phys.* **28**, 639 (1957).

²⁷ A. Sosin and H. H. Neely, *Phys. Rev.* **127**, 1465 (1962).

¹⁸ O. S. Oen, Oak Ridge National Laboratory Report No. ORNL 3813, 1965 (unpublished); (private communication).

¹⁹ N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1949), 2nd ed., Chap. IV.

²⁰ G. H. Kinchin and R. S. Pease, *Repts. Progr. Phys.* **18**, 1 (1955).

to many factors but probably occurs because of the difference in radiation temperature. When specimens which had previously been irradiated at 60°C were electron irradiated at temperatures higher than 90°C there was a noticeable decrease in the total F -center concentration. This suggests that radiation annealing is important at temperatures in excess of 90°C.

Mention should perhaps be made at this point of a somewhat puzzling result of the investigation. Even though it was possible to produce measurable quantities of F centers by electron and neutron irradiation there was no evidence for the creation of a corresponding number of positive-ion vacancies even though magnesium should have a larger displacement cross section than oxygen. In the past, positive-ion vacancies which have trapped holes, V_1 centers, have been identified in lightly irradiated MgO crystals,^{12,28} and it was hoped that the production of positive-ion vacancies could be monitored optically as was the creation of the negative-ion vacancies. However, it was found that for electron irradiation the absorption band due to V_1 centers grew rapidly at very low doses and then saturated long before there was any evidence of F -center absorption.

²⁸ J. E. Wertz, G. Saville, P. Auzins, and J. W. Orton, *J. Phys. Soc. Japan* **18**, Suppl. II, 305 (1963).

CONCLUSION

The strong temperature and radiation intensity dependence of the coloration in alkali halide crystals is well documented.¹⁻³ This as well as the energy dependence of F -center production in these materials²⁹ indicates that the dominant radiation damage mechanism is not one of elastic collisions. On the other hand, the results presented above for MgO are very consistent with the idea that the primary damage mechanism is that of elastic collisions. Therefore, we are drawn to the tentative conclusion that crystal ionicity or crystal bonding may make a significant difference in the mechanism of radiation damage.

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²⁹ V. Ritz, *Phys. Rev.* **133**, A1452 (1964).

Ionic-Model Theory of Polar Molecules*

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A simple extension of the current models of lattice dynamics is used to evaluate the binding energy, the internuclear distance, the electric dipole, and the vibrational frequency of the alkali-halide molecules from solid-state properties. An extensive comparison with experimental data suggests that the models may be useful as an empirical scheme of interpolation between the perfect crystal and the molecule. A polarization catastrophe in the standard ionic theory is discussed.

QUALITATIVE considerations suggest that the classical theory of ionic systems should provide a reasonably accurate first-order description of the properties of the alkali-halide molecules. Thus, the observed electric dipoles are quite close to their polarized-point-ion value and, as in the solid, the interpenetration of the ions still affects only the tails of the outer electron shells. These considerations have prompted investigations of these molecules by the classical theory,^{1,2} which have, however, found it necessary to postulate a very sizeable stiffening of the short-range potential appropriate to the solid in order to fit such molecular properties as the internuclear distance and the vibrational frequency. In

this note we show that the difficulty arises from the treatment of induced dipoles and that the discrepancy between the solid and the molecule is largely removed by the inclusion of short-range polarization.

In a tight-binding approach one may express the Hamiltonian of the ion pair through the multipole expansion, including short-range couplings between the various poles in addition to the classical electrostatic couplings. We write the potential energy of the ion pair, as a function of the internuclear distance r and of the electronic dipoles m_+ and m_- , as follows:

$$U(r, m_+, m_-) = -\frac{e^2}{r} - (m_+ + m_-) \frac{e}{r^2} - \frac{2m_+ m_-}{r^3} + \frac{m_+^2}{2\alpha_+} + \frac{m_-^2}{2\alpha_-} + m_- B(r) + \varphi(r). \quad (1)$$

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

¹ E. J. W. Verwey and J. H. de Boer, *Rec. Trav. Chim.* **55**, 431 (1936).

² E. S. Rittner, *J. Chem. Phys.* **19**, 1030 (1951).