

second virial coefficient of the gas. A difference of this order of magnitude can, however, not play a rôle in the problem of crystal stability. The three-atom difference in crystal energy is one order of magnitude larger than that obtained on the basis of pair potentials.

We have undertaken the present analysis principally with the aim of verifying that the Gaussian effective-electron model does not lead to divergent results in passing from clusters of three atoms to four-atom configurations. In view of the large values of nearest-neighbor overlap integrals for the heavy rare-gas solids obtained with the Gaussian effective orbitals, such a verification is important within the framework of the model itself. The large overlap results from the manner in which the Gaussian parameter  $\beta$  is determined, namely, adapted to the long- and the short-range components of the pair potentials between near atoms and then extrapolated to the heavier rare-gas atoms. The postulatory basis for this procedure is the assumption that *relative* many-atom interactions can reliably be calculated in this way. Recent criticisms of the Gaussian

effective-electron approach, in particular those formulated by Swenberg,<sup>27</sup> must be viewed in this light.<sup>28</sup>

We have also found that, for *isolated* quadruplets of atoms, the four-atom interactions may in some cases (e.g., a square configuration) be of the same magnitude as the three-atom energy. Finally, the results of this analysis as applied to the stacking-fault energy in solid Ar and solid Xe seem to be in reasonable agreement with estimates obtained from observations on thin films of these crystals.<sup>12</sup> Definite conclusions must here await the development of more accurate methods for measuring the stacking-fault energy.

#### ACKNOWLEDGMENTS

We wish to thank Professor Henry Margenau for sending us the manuscript on four-atom first-order interactions by himself and Dr. J. Stamper prior to publication. Our thanks are also due to J. P. Eckmann of the Federal Institute of Technology in Zürich and to R. Ritter for essential help with the numerical calculations.

<sup>27</sup> C. E. Swenberg, *Phys. Letters* **24A**, 163 (1967).

<sup>28</sup> L. Jansen and E. Lombardi, *Chem. Phys. Letters* **1**, 33 (1967).

### Radiation Damage in ZnO Single Crystals\*

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The radiation and additive coloration of Li-doped and "pure" ZnO crystals have been investigated. The radiation coloration is enhanced by the presence of Li impurity when the radiation temperature is in the range 80–330°K, but the additive coloration is suppressed in Li-doped specimens. The defect production rate, as measured by the increased optical absorption of the samples, is a linear function of electron irradiation intensity and decreases with irradiation energy. The energy dependence of the electron coloration suggests that the defect giving rise to the coloration is produced by the displacement of zinc ions. For a given dose of radiation, fast neutrons (>1 MeV) produce about 30 times as many defects as do energetic electrons. In irradiated crystals the coloration anneals out around 250°C, whereas in additive colored samples the annealing-out temperature is about 900°C.  $\gamma$  irradiation during and after annealing indicates that in both cases annealing is complete and not due only to the loss of electrons or holes from the defect center. It is concluded from the study that radiation damage in ZnO occurs primarily as a result of elastic collisions, and that the photochemical processes prevalent in alkali halides contribute very little, if any, to the damage.

#### INTRODUCTION

THE electrical and optical properties of zinc oxide have been the subject of a number of investigations during the last two decades, and a comprehensive review of these studies up to the year 1958 has been presented by Heiland, Mollwo, and Stöckmann.<sup>1</sup> A

more recent survey by Kroger<sup>2</sup> gives a complete list of references as well as a discussion of defect models. The primary obstacle to understanding the effect of defects on the optical and electrical properties of this material appears to be that until recently only a few measurements had been made on single crystals; therefore, since these properties vary greatly when the chemical and mechanical purity of specimens is not high, it is difficult to make a consistent interpretation of all the available results. Our work involves the use of ZnO single crystals and so we will emphasize the experiments done on single

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<sup>1</sup> G. Heiland, E. Mollwo, and F. Stöckmann, *Advan. Solid State Phys.* **8**, 191 (1959).

<sup>2</sup> F. A. Kroger, *The Chemistry of Imperfect Crystals* (North-Holland Publishing Co., Amsterdam, 1964).

crystals in our discussion, although some reference will be made to work on ZnO powder when it is relevant.

It is possible to give transparent ZnO crystals a yellow color by increasing their optical absorption in the region of 2–3 eV through heat treating them in Zn vapor.<sup>3</sup> This additional absorption produced near the edge of the fundamental band has been labeled as *b* band absorption,<sup>1</sup> but it is not yet clear what defect is responsible for this band. It has been attributed to interstitial zinc or defects associated with interstitial zinc,<sup>1,3,4</sup> to oxygen-ion vacancies,<sup>5,6</sup> or to other defects such as chemical impurities.<sup>7</sup> Moreover, this same uncertainty exists regarding the importance of interstitial zinc atoms and oxygen vacancies in conduction processes.<sup>1,8</sup> The presence of interstitial zinc in ZnO was for a long time inferred from chemical methods where the amount of excess zinc was determined by dissolving crystals in the presence of an oxidizing agent and finding the amount of this oxidizing agent which reacts with the reducing agent in the crystals by back titration. Thomas<sup>7</sup> has pointed out that this method will detect almost any reducing agent including oxygen vacancies and, therefore, is not a good test for excess interstitial zinc. However, the work of Thomas<sup>7,8</sup> and Mohanty and Azaroff<sup>4</sup> certainly indicate that interstitial zinc is present in crystals which have been heat-treated in zinc vapor. In fact, Mohanty and Azaroff find that the actual number of interstitial zinc atoms present in a ZnO crystal doped by heating in zinc vapor is about 1000 times greater than the number deduced from conductivity measurements. They proposed that two types of zinc interstitials exist in the lattice with the bulk of them electrically neutral. This would explain the observation of Thomas who found that when a ZnO sample was heat-treated in zinc vapor it acquired an increased conductivity and a red color. The excess conductivity could be annealed out in air at 600°C, but the color was stable up to temperatures of around 900°C. Moreover, the results of Heiland *et al.*<sup>1</sup> on the easy coloration of preheat-treated crystals compared to untreated ones can also be explained on this basis. Nonetheless, discussion about the defect responsible for the coloration of ZnO still exists as is illustrated by the recent papers of Van Craeynest *et al.*<sup>5</sup> and Maenhout-Van der Vorst and Van Craeynest.<sup>9</sup> They propose models of *F*-type centers (oxygen vacancies with trapped electrons) associated with Zn<sup>+</sup> and Zn<sup>2+</sup> to explain the yellow coloration of heat-treated ZnO powder.

<sup>3</sup> E. Sharowsky, Z. Physik **135**, 318 (1953); E. Mollwo, Z. Angew. Phys. **6**, 257 (1954).

<sup>4</sup> G. P. Mohanty and L. V. Azaroff, J. Chem. Phys. **35**, 1268 (1961).

<sup>5</sup> F. Van Craeynest, W. Maenhout-Van der Vorst, and W. Dekeyser, Phys. Status Solidi **8**, 841 (1965).

<sup>6</sup> S. E. Harrison, Phys. Rev. **93**, 52 (1954).

<sup>7</sup> D. G. Thomas, J. Phys. Chem. Solids **3**, 229 (1957).

<sup>8</sup> D. G. Thomas, *Semiconductors* (Reinhold Publishing Corporation, New York, 1959), pp. 269–312.

<sup>9</sup> W. Maenhout-Van der Vorst and F. Van Craeynest, Phys. Status Solidi **9**, 749 (1965).

TABLE I. Impurity analysis of ZnO.

Element	ORNL $\mu\text{g/g}$		3M <sup>a</sup>	Element	ORNL $\mu\text{g/g}$		3M <sup>a</sup>
	Pure	Li-doped	Pure		Pure	Li-doped	Pure
Ag	<0.5	<0.5	<1	Pb	<3	<3	...
Cu	2	10	8	Cr	<5	<5	<1
Ti	<10	<10	...	Ni	<5	<5	1
V	<5	<5	<1	Si	...	...	<5
Ca	...	...	<1	Sb	<5	<5	...
Sn	<3	<3	1.5	Mg	3	1–10	<1
Mo	<3	<3	...	Mn	<1	<1	...
Be	<0.5	<0.5	...	B	≤1	≤1	5 <sup>b</sup>
Al	≤5	≤5–10	<3	Ba	<3	<3	...
Bi	<2	<2	...	Li	<1	20–190	<1
Ge	<1	<1	...	K	...	...	<3
Fe	...	...	<1	Na	1	1	3

<sup>a</sup> These data were kindly supplied by the 3M Company.

<sup>b</sup> Samples ground in B<sub>4</sub>C mortar and pestle.

One area of research on ZnO which has been neglected is that of the effect of radiation, high-energy electrons and neutrons, on the optical properties of this material. Since irradiation of single crystals normally results in the production of vacancy-interstitial pairs, it appeared that the information obtained from a study of this type might help us to understand the primary defects produced in ZnO both by additive coloration and irradiation. Therefore, it is the purpose of this paper to report on the coloration of ZnO crystals by radiation and to compare the radiation-induced coloration with that created by heating crystals in zinc vapor at high temperatures. Furthermore, since ZnO is intermediate in its chemical bonding between polar alkali halides and the more covalently bonded semiconductors it is important to determine whether the radiation-damage mechanism is primarily photochemical in nature, as it is for the alkali halides,<sup>10</sup> or mostly due to elastic collisions as is the case for more covalently bonded materials.<sup>11</sup>

## EXPERIMENTAL PROCEDURE

The crystals used in this investigation were grown by the Minnesota Mining and Manufacturing Co. and furnished in the form of *Z*-axis wafers cut 0.3–1.0-mm thick. The impurity analyses of these crystals are shown in Table I. The data in the second column were kindly supplied by the 3M Company and the numbers in the other columns were obtained at this laboratory by means of mass spectroscopy. Our analyses were done on three pure single crystals from different batches and three Li-doped samples.

Optical-absorption measurements were made with a Cary model 14R spectrophotometer. The absorption edge in ZnO is at 3.15 eV at room temperature so that measurements could be made only in the visible and infrared portions of the spectrum. The surfaces of the samples were not completely transparent due to sample preparation, and some effort was made to

<sup>10</sup> J. H. Crawford, Advan. Phys. (to be published).

<sup>11</sup> W. A. Sibley and Y. Chen, Phys. Rev. **160**, 712 (1967).

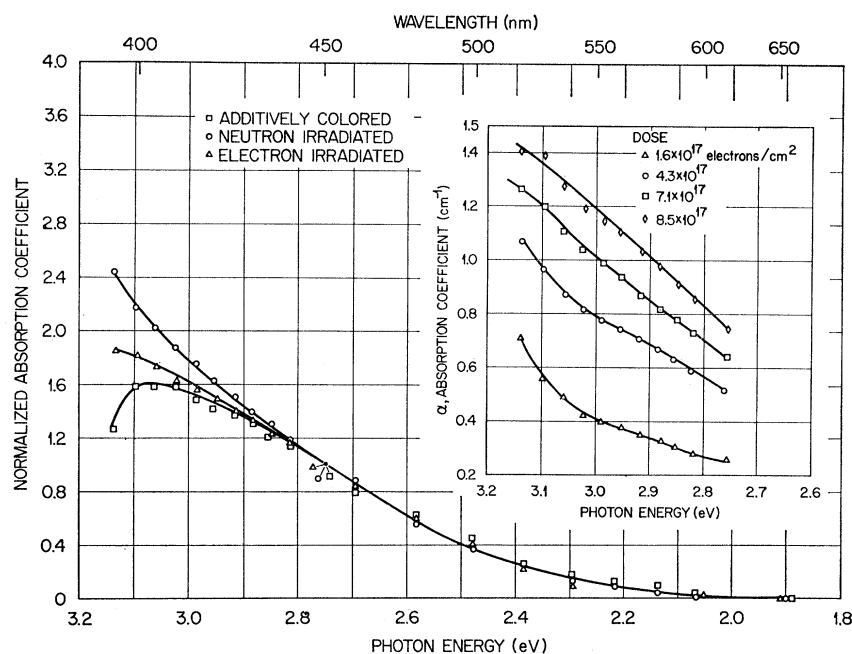


FIG. 1. A plot of the normalized absorption coefficient versus photon energy which shows the induced-absorption spectra for samples colored in different ways. The data are normalized to the absorption coefficient at 450 nm (2.755 eV). The inset shows the change in character of the absorption with dose for an electron-irradiated specimen.

improve the optical quality of the specimens. It was found that warm phosphoric acid etched away polishing damage but left a surface coating which could not be completely removed without further polishing. The optical absorption of this film was a function of both time and treatment of the crystal. Therefore, we employed a standard etching procedure consisting of a 2-min etch in warm (50°C) phosphoric acid followed by a benzene rinse and light polishing. Later it was found that a fine polish, without etching, followed by heating in air to 650°C, and cooling at a rate of 50°C/h gave more reproducible results than the etching process for pure crystals. For Li-doped samples, however, the heat treatment resulted in an increased absorption near the band edge which could not be annealed out.

Several crystals were colored by heating them in Zn vapor in an apparatus of the Van Doorn type.<sup>12</sup> There were three features of this apparatus which proved especially useful: (i) The pressure of the Zn vapor is determined by the pressure of an inert gas (nitrogen in our case) sealed in the system with metallic zinc and the ZnO crystal. The pressure of the nitrogen and, therefore, the pressure of the Zn vapor can be easily and accurately adjusted and measured. (ii) The samples can be removed quickly for quenching in liquid nitrogen; and (iii) it is possible to heat the metallic Zn in a vacuum to just above its melting point so that any dissolved water vapor or hydrogen in the Zn can be removed at a temperature of less than 500°C. This is particularly important since the presence of hydrogen in the system at temperatures above 500°C results in rapid reduction of ZnO crystals.<sup>13</sup>

<sup>12</sup> C. Z. Van Doorn, *Rev. Sci. Instr.* **32**, 755 (1961).

<sup>13</sup> D. F. Anthrop and A. F. Searey, *J. Phys. Chem.* **68**, 2335 (1964).

The electron irradiations were performed with a Van de Graaff accelerator at current densities of 0.75 and 1.5  $\mu\text{A}/\text{cm}^2$  and energies of 0.60 and 1.7 MeV. The current densities at the samples were determined by measurements with Ag-doped glass dosimeters.<sup>14</sup> A Sulfrian liquid-helium cryostat with optical windows was used for low-temperature irradiations and a water- and air-cooled holder was utilized for the room-temperature irradiations (actually, the crystal temperature was about 60°C). These holders and the radiation procedure have been described previously.<sup>11</sup> Several attempts were made to bleach the irradiation-induced coloration in the ZnO samples with white light at room temperature, but no measurable changes were noted in the absorption. Therefore, the crystals were not always kept in total darkness except when the specimens were at low temperature in the cryostat. In any case the samples were always kept in subdued light.

A series of samples were irradiated in the Oak Ridge Reactor hydraulic tube system No. 1-F-8-Tube 12. Each specimen was wrapped in 30 mils of Cd foil to reduce the thermal neutron flux and irradiated in a fast ( $>1$  MeV) neutron flux of  $3 \times 10^{13}$  neutrons/cm<sup>2</sup> sec at a temperature of about 60°C.<sup>11</sup>

After coloration the crystals were annealed in air in a controlled temperature furnace. The temperature was measured with a Chromel-Alumel thermocouple and controlled to within  $\pm 1^\circ\text{C}$  of the desired temperature. The samples were brought to the desired annealing temperature in a few seconds, held at that temperature for 10 min, and then quenched to room temperature for measurement. The annealing was done in 25°C steps.

The x-ray-induced luminescence of the crystals was

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

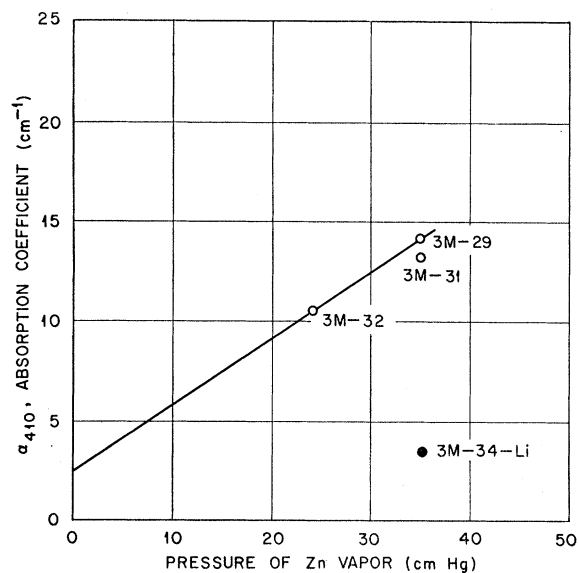


FIG. 2. This figure illustrates the relation between the Zn-vapor pressure and the amount of coloration in crystals held at 858°C for 10 h. Notice that the Li-doped sample, 3M-34-Li, does not color appreciably, whereas the pure ones do. Sample 3M-31 has been colored and annealed prior to this treatment.

also studied. The luminescence was measured using an EMI 9558 or RCA 7102 multiplier phototube cooled to dry-ice temperature in conjunction with a  $\frac{1}{2}$ -m Bausch and Lomb monochromator. This detection system was calibrated using a GE tungsten-filament quartz iodine standard lamp with calibration traceable to the National Bureau of Standards.

## RESULTS

### A. Additive Coloration

Five pure ZnO samples were additively colored and the induced absorption spectrum for one of these crystals is shown in Fig. 1. All of the induced absorption spectra shown in Fig. 1 were obtained by subtracting the absorption for an uncolored sample from the absorption after coloration. The shape of the absorption for additively colored specimens in Fig. 1 is in general agreement with that reported by Scharowsky.<sup>8</sup> Before additive coloration the crystals were polished and heat treated with no etching, as described previously. Crystals were colored at three different temperatures, 825, 858, and 1000°C, with the higher temperatures producing more coloration for a given pressure of Zn. Figure 2 shows the effect of Zn-vapor pressure on the coloration at a fixed temperature, 858°C. In this figure the induced-absorption coefficient at 410 nm,  $\alpha_{410}$ , is plotted as a function of Zn-vapor pressure. The absorption at 410 nm (3.02 eV) was chosen since it is near the peak of the *b* band,<sup>1</sup> as shown in Fig. 1, for the additively colored samples and is also a convenient measure of radiation-induced damage. The data shown in Fig. 2 for the three pure samples, 3M-29, 3M-31, 3M-32, are

for specimens held at 858°C for 10 hrs. Sample 3M-31 was actually colored twice. The first time at 828°C and then after annealing which removes most, but not all, of the *b* band absorption it was recolored at 858°C. It is noteworthy that this point falls so close to the one for 3M-29 which was colored for the first time. However, since the sample had been colored previously, the point could not be used in drawing the line shown in Fig. 2. It is very interesting that the intercept value on the ordinate in Fig. 2 is just that absorption induced by heat treating an as received crystal in air at high temperatures and then quenching to room temperature. Heiland *et al.*<sup>1</sup> mentioned that untreated crystals are more difficult to additively color than crystals which had a prior history of additive coloration. We have not attempted to confirm this observation. It should be noted that the Li-doped sample, 3M-34-Li (see Fig. 2), did not color appreciably even though it was heat-treated in Zn vapor simultaneously with the purer 3M-29. In fact, the total induced coloration in this crystal is no greater than that obtained when a sample is heated in air to the same temperature and then quenched. Moreover, it was not possible to anneal out what little coloration was induced by the treatment. The same effect was also observed in the case of another Li-doped specimen which was heated with a pure crystal in Zn vapor (64-cm Hg) at 1000°C for 15 min. The Li-doped sample did not color appreciably, but the pure one showed a yellow coloration. From our data in Fig. 2, it appears that the number of centers introduced by additive coloration is proportional to *P*, but the data are not sufficient for detailed discussion.

### B. Electron Irradiation

The shape of the optical absorption produced in a pure ZnO sample by electron irradiation is also shown in Fig. 1. It was found that the shape of the induced absorption varies somewhat in the vicinity of the absorption edge (3.1 eV) for different crystals. This variation could be due to the fact that the coloration by electrons occurs in two stages, and the amount of first-stage coloration is sample-dependent. Figure 3, which is a plot of the induced absorption at 410 nm versus radiation dose for samples irradiated with 1.7-MeV electrons at about 60°C, illustrates the two-stage coloration of the pure crystals and the fact that the amount of first-stage coloration varies from specimen to specimen. The inset of Fig. 1, which shows the growth of the absorption as a function of radiation dose, clearly indicates that the curve shape at low doses is markedly different from that at high doses.

Figure 3 also portrays the effect of impurities on the electron colorability of ZnO. It is readily seen that the presence of Li impurity enhances the coloration and that, unlike the case for the pure crystals, the data for the impure specimens form a straight line which passes through the origin. Most of the irradiations on both

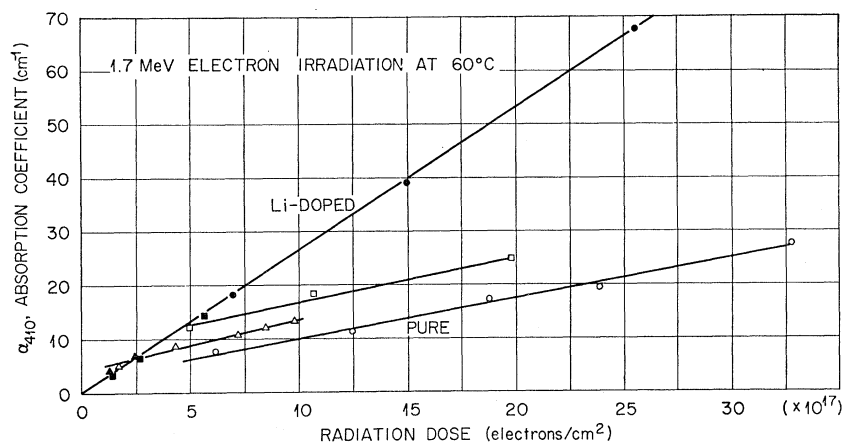


FIG. 3. A plot of the absorption coefficient at 410 nm versus electron-radiation dose for several "pure" and doped samples. The radiation energy was 1.7 MeV and the sample temperature was 60°C during irradiation.

the pure and doped crystals were made with intensities of  $1.5 \mu\text{A}/\text{cm}^2$ , but several experiments were performed using  $0.75 \mu\text{A}/\text{cm}^2$  in order to determine if there was an intensity dependence of the coloration. It was found that for the lower intensity of radiation the data points fell on the same lines as those shown in Fig. 3, indicating a linear dependence of the coloration on radiation intensity. Similarly, the energy of radiation was varied from 1.7 to 0.60 MeV and, rather surprisingly, it was found that essentially no coloration was induced at the lower-radiation energy in either the pure or doped crystals.

Both pure and doped specimens were irradiated at 80°K with 1.7-MeV electrons, and the results of these irradiations are shown in Figs. 4 and 5. The coloration rate is greater than that for the room-temperature irradiations, and in the case of the doped crystals the shape of the induced optical absorption is significantly different at low temperatures. It was observed, however, that when the doped crystal was warmed the absorption shape changed from that shown by the full triangle symbols of Fig. 5 to that illustrated by the full circles. This change in the absorption occurred at 150°K which is the same temperature at which some of the low-temperature radiation damage anneals out, as is shown in the inset of Fig. 5. The annealing procedure in this instance was to warm the sample quickly to the desired

temperature, hold at that temperature for 10 min, and then quench the crystals back to 77°K and measure the absorption spectrum. No annealing stages were found for the pure sample in the temperature range of 77–473°K.

### C. Neutron Irradiation

The results of fast neutron irradiation of ZnO crystals are shown in Figs. 1 and 6. It can be seen in Fig. 1 that there is a general absorption increase in the range 2.4–3.1 eV, but this increase is not the same as that for either the additively colored or the electron-irradiated samples. Figure 6 is a plot of the optical-absorption coefficient at 410 nm versus neutron dose and illustrates that doping a ZnO crystal with Li enhances the neutron colorability as well as the electron colorability. A comparison of the data shown in Fig. 6 with that of Fig. 3 suggests that there may be an early stage of coloration in the neutron-irradiated samples also. It should be remembered that the production of color centers by additive coloration is suppressed in the Li-doped specimens.

### D. Other Measurements

Many times it is possible to produce coloration in a crystal by ionizing radiation such as x rays or  $\gamma$  rays.

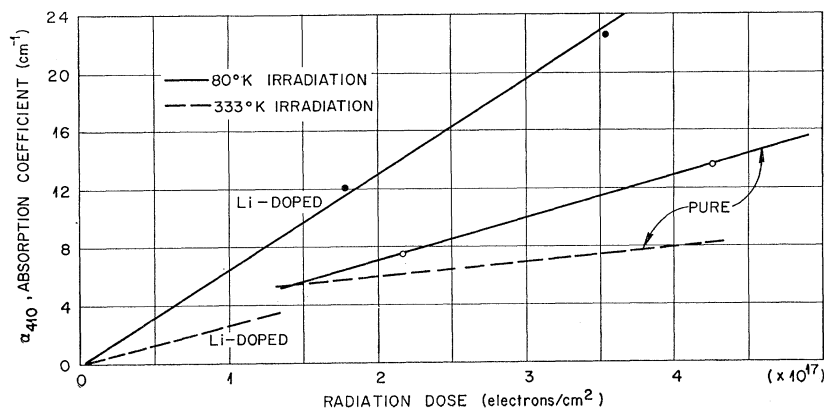
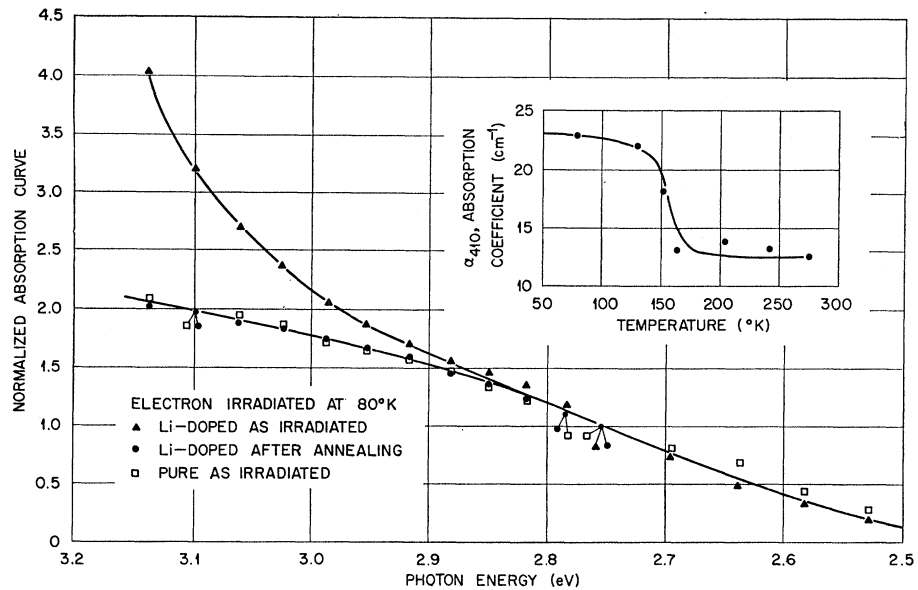


FIG. 4. A plot of the absorption coefficient at 410 nm versus electron-radiation dose for a "pure" and a Li-doped crystal. The radiation energy was 1.7 MeV and the sample temperature during irradiation was 80°K. For comparison the dashed lines show data from Fig. 3 for samples irradiated at 333°K.

FIG. 5. A plot of the induced normalized absorption coefficient, normalized at 450 nm versus photon energy for a pure and Li-doped crystal irradiated and measured at 80°K. The full circles show the spectrum of the doped specimen after it was pulse annealed above 170°K and then recooled to 80°K. The inset shows the annealing of the optical absorption at 410 nm as a function of temperature.



This coloration can be created by a photochemical defect-creation mechanism such as occurs in the alkali halides, by the filling of existing defects with either electrons or holes, or by the ionization of impurities. We  $\gamma$  irradiated our samples before any treatment whatsoever, after additive coloration, electron and neutron irradiation, and both during and at the end of thermal-annealing measurements. No detectable change was ever observed as a result of 30-min irradiations using a  $3.0 \times 10^6$  R/h  $^{60}\text{Co}$  source with the sample temperature  $32 \pm 1^\circ\text{C}$ .

The results of isochronal annealing in air of the various types of coloration are shown in Fig. 7. Additively colored samples exhibited the behavior indicated in Fig. 7(a). The annealing curve dropped rather sharply between 850 and 950°C. However, the annealing was not complete at 950°C in the sense that the absorption did not return to its initial precoloration value. In fact, the residual coloration could not be annealed up to temperatures of 1050°C and was not removed by slow cooling. Moreover, it was found that when a colored and annealed sample was recolorated the residual absorp-

tion continued to increase. The shape of the absorption curve for this residual absorption differed from that shown in Fig. 1 for additively colored crystals in that no peak was present near the absorption edge. We found that samples colored at different temperatures, 825 or 1000°C, showed no significant differences in their annealing behavior.

In Fig. 7(a) the full symbols representing the data on additively colored Li-doped samples show no annealing up to 1050°C. However, as was pointed out earlier, very little coloration could be induced in these samples, and the total amount of coloration was equivalent to what remained in the pure specimens after annealing to 950°C.

The electron-irradiated crystals fall distinctly into two groups. The pure samples anneal in a rather erratic fashion and, in some cases, exhibit long tails in the annealing curves which extend to above 600°C. The annealing behavior of three such samples is shown in Fig. 7(b). This behavior could be related to the two stages of coloration shown in Fig. 3. The Li-doped crystals, on the other hand, annealed sharply and

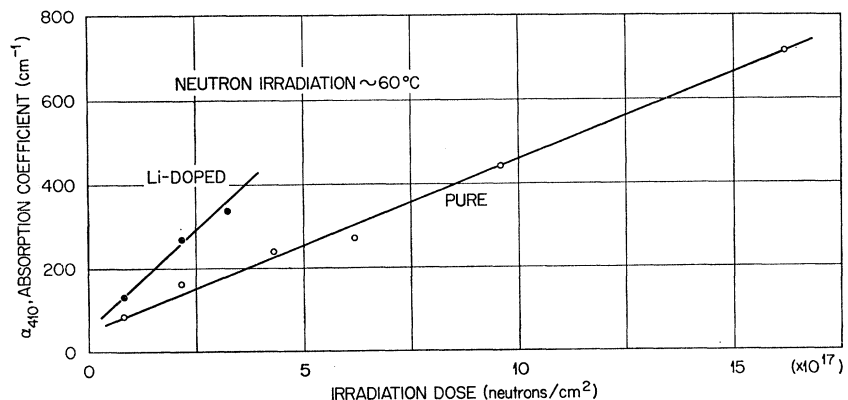


FIG. 6. A plot of the absorption coefficient at 410 nm versus fast neutron dose for pure and doped ZnO crystals. The sample irradiation temperature was about 60°C.

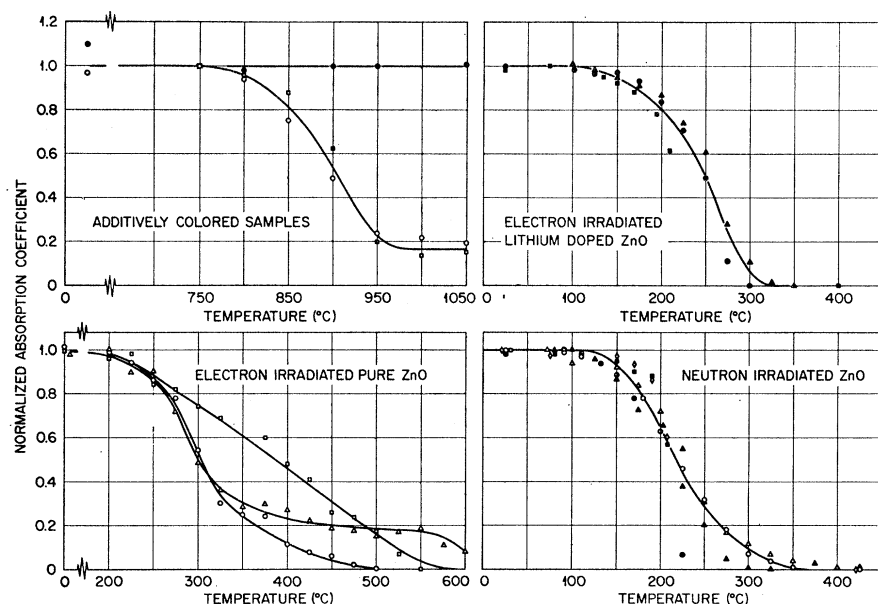


FIG. 7. Annealing data for pure and doped specimens colored by irradiation and heat treatment in Zn vapor. The data have all been normalized such that before annealing the induced absorption coefficient at 410 nm is one. The open symbols represent data on pure crystals while the full symbols are for data on Li-doped samples. (a) Additively colored samples, (b) electron irradiated pure ZnO, (c) electron irradiated doped ZnO, (d) neutron irradiated ZnO.

consistently at 250°C, as is shown in Fig. 7(c). Neutron-irradiated samples annealed at temperatures that were slightly lower than those for the electron-irradiated specimens, Fig. 7(d), and although in this case both pure and doped samples show the same general annealing curves it again appears that the doped crystals anneal more readily than the pure ones.

Figure 8 illustrates the effect of the various treatments on the luminescence properties of the crystals. The two primary bands are the same as reported previously for ZnO powder,<sup>1,5,8</sup> but it is interesting that the additive coloration process shifts the primary luminescence to the 400-nm band, and that electron irradiation tends to suppress the luminescence, as shown in the inset of Fig. 8. We found that heat treating a pure ZnO sample in hydrogen at 1000°C for 5 min enhanced the 400-nm band just as the additive coloration does. When specimens were cooled to liquid-helium temperature the 400-nm luminescence band sharpened and moved from 3.10 to 3.19 eV. The 530-nm band did not sharpen appreciably and the peak position shifted only slightly to a higher energy. The work of Solbrig and Mollwo<sup>15</sup> indicates that in the case of the 400-nm band self-absorption plays a major role in determining the apparent peak position.

Kroger<sup>2</sup> has estimated the energy gap in ZnO from the data of Mollwo<sup>1</sup> as

$$(E)_{\text{opt}} = E^0 - \beta T = (3.5 - 10^{-3}T) \text{ eV.}$$

In measurements of the absorption edge as a function of temperature, we find very good agreement with Mollwo's<sup>1</sup> data. Also, it is found that the position of the edge remains constant at 3.30 eV for temperatures below 78°K.

<sup>15</sup> Ch. Solbrig and E. Mollwo, *Solid State Commun.* **5**, 625 (1967).

## DISCUSSION

The marked energy dependence, linear intensity dependence, and difficulty in producing defects by radiation all suggest that elastic collisions between the incident irradiating particles and the indigenous ions are the major source of damage in ZnO. In fact, no evidence at all was found for the photochemical type of damage produced in the alkali halide crystals. In elastic collisions between relativistic electrons and lattice ions the maximum kinetic energy transferable to a lattice ion by the electron is

$$T_m = 2(E + 2mc^2)E/Mc^2, \quad (1)$$

where  $E$  is the kinetic energy of the incident electron,  $m$  the electron mass, and  $M$  the mass of the struck ion. In order for a lattice ion to be displaced from its lattice site it must receive a certain amount of energy from the incident particle. The 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  $E$  such that  $T_m \geq T_d$ . Therefore, we can obtain an estimate for the displacement energy by decreasing the energy of the incident particles until no defect production is evident even for high-radiation doses. Since 0.60-MeV electrons did not give any appreciable coloration of either the pure or doped ZnO crystals, we will use this to estimate an approximate displacement energy. If the displacement of oxygen ions was the primary cause of coloration, then we would find from Eq. (1) a value  $T_d \approx 120$  eV but, if it is the displacement of Zn ions that induces the coloration, then  $T_d \approx 30$  eV. The value of 120 eV for a displacement energy seems to be rather high and we believe that the results suggest it is the displacement of Zn ions which gives rise to the colorability of ZnO in the case of electron irradiations.

Certainly this suggestion cannot be extended to either the neutron irradiation or additive coloration case.

As mentioned earlier, it is not known whether the coloration produced by heating crystals in Zn vapor is due to interstitial zinc ions or to negative-ion vacancies which have captured electrons.<sup>1-8</sup> In alkali halides and MgO it is known that the additive coloration process produces negative-ion vacancies with associated electrons such that the over-all electrical neutrality of the crystal is maintained. However, in ZnO, which has the wurtzite structure, it is possible that zinc interstitials

cause the coloration. Mohanty and Azaroff<sup>4</sup> have implied that the coloration produced in ZnO by heating in Zn vapor is due to interstitial-zinc atoms  $Zn_i^0$  whereas the conductivity increase is caused by interstitial-zinc ions,  $Zn_i^{2+}$  or  $Zn_i^{1+}$ , which act as donors. They explained Thomas's results, which showed that the excess electronic conductivity annealed out at around 500°C and that the coloration was stable up to about 900°C, in terms of the relative mobilities of interstitial atoms and ions. (The radius of  $Zn^{2+}$  is much less than that for  $Zn^0$ , and one might expect a higher

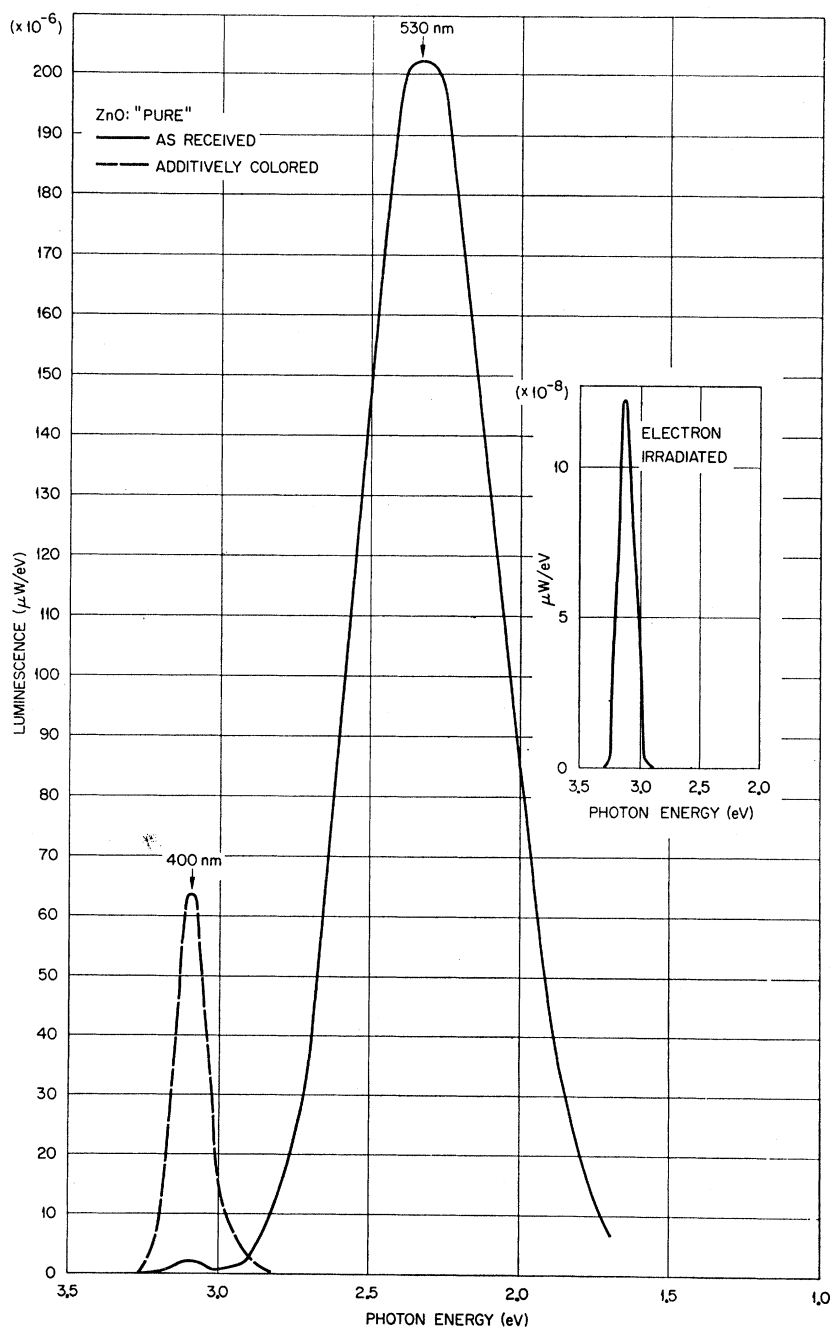


FIG. 8. A plot of luminescence intensity versus photon energy which illustrates the effect of various treatments on the luminescence properties of pure ZnO. The inset portrays the effect of electron irradiation on the luminescence.



mobility for the  $Zn^{2+}$ .) That is, ionized Zn interstitial donors can be removed from the crystals by heat treatment (thus eliminating the enhanced conductivity) more readily than  $Zn_i^0$  interstitials.

Our results can be explained in terms of this model, although other possibilities exist. Radiation produces both vacancies and interstitials simultaneously as Frenkel pairs, whereas in the additive coloration process only one type of defect is formed. The energy dependence we observe suggests that displaced Zn atoms are most likely responsible for the coloration produced by electrons. Within the framework of the Mohanty and Azaroff proposal, our data could be explained in the following manner: The radiation displaces zinc atoms into interstitial sites with  $Zn_i^0$  interstitials producing the coloration. Hole traps, such as impurities or positive-ion vacancies are available to stabilize the interstitial in this charge state, as long as the radiation temperature is low enough, and thus enhance the colorability. In fact, Lander<sup>16</sup> and Kasai<sup>17</sup> have investigated the reactions of Li impurity in ZnO and determined that it can be either a donor or an acceptor. If it acts as a hole trap, still assuming the model of Mohanty and Azaroff,<sup>4</sup> it is easy to see how the total radiation coloration of the crystals could be increased by the presence of more  $Zn_i^0$  due to these hole traps, and hole trapping impurities could also explain the early-stage coloration in the pure samples. Since Li impurity is said to form a donor center if the atmosphere surrounding the crystal is reducing, the lack of coloration in the Li-doped samples when they are heat-treated in Zn vapor could be due to the reduced probability of forming  $Zn_i^0$ .

The annealing results for the irradiated crystals shown in Fig. 7 could be due to the thermal ionization of hole traps with the holes returning to the interstitial- $Zn_i^0$  atoms and forming  $Zn_i^{1+}$  or  $Zn_i^{2+}$  species which could be mobile and might recombine with vacancies at temperatures as low as 200–300°C. Even though our data can be made consistent with the suggestion of Mohanty and Azaroff, other possibilities exist. Furthermore, the complexity of the optical spectra shown in Figs. 1 and 5 indicates that absorption centers other than  $Zn_i^0$  may be present in the irradiated crystals.

Another explanation for our data that must be considered is that of the possible formation of negative-ion vacancies and, hence,  $F$ -type centers by additive coloration and irradiation. In alkali halide single crystals and in MgO, both the additive coloration process and irradiation produce negative-ion vacancies and these centers give rise to the predominant absorption bands in these materials. Van Craeynest *et al.*<sup>5</sup> have interpreted the yellow coloration of heat-treated zinc-oxide powder in terms of  $F$  centers. The enhanced irradiation production of  $F$  centers induced by doping a sample with impurity, such as is shown in Figs. 3, 4, and 6, has also been observed in KCl irradiated at low temperature<sup>18</sup> and in MgO.<sup>11</sup> The simplest explanation of this enhancement is that the impurities act to trap mobile interstitials, thus reducing the amount of vacancy-interstitial recombination occurring during radiation and resulting in more stable defects. This would explain the two stages of coloration shown in Fig. 3 for the pure crystals. The differences in the absorption spectra shown in Figs. 1 and 5 and the annealing results illustrated in Fig. 7 are not inconsistent with the concept that  $F$  centers are the entity responsible for the coloration. However, the displacement energy calculated from the energy dependence of defect formation by electrons is not very satisfying if one considers only oxygen-ion displacement. The rather complete suppression of additive coloration in the Li-doped samples is also surprising if the defect responsible for the increased coloration is an  $F$ -type center. Even if Li were an electron trap, one would expect some  $F$ -center coloration to be produced by additive coloration. Nonetheless, one cannot on the basis of our data eliminate the possibility that  $F$  centers contribute to the coloration of ZnO.

In conclusion, we think it is important to note that radiation damage in ZnO apparently occurs primarily as a result of elastic collisions and the photochemical processes prevalent in the alkali halides contribute very little to the damage. Moreover, our data are more consistent with the idea that the coloration is produced by zinc defects, probably zinc interstitials, but the possibility of negative-ion vacancies being responsible for the coloration cannot be ruled out.

<sup>16</sup> J. J. Lander, *J. Phys. Chem. Solids* **15**, 324 (1960).

<sup>17</sup> P. H. Kasai, *Phys. Rev.* **130**, 989 (1963).

<sup>18</sup> E. Sonder and W. A. Sibley, *Phys. Rev.* **140**, A539 (1965).