

## ELECTRON-INDUCED TRAPS IN ZINC SULFIDE SINGLE CRYSTALS

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The thermoluminescence characteristic of single crystals of zinc sulfide was studied before and after room-temperature irradiation with monoenergetic electrons. A new trapping state with a threshold energy at 175-195 keV was observed and, in the same specimens, the production of a trapping state with a threshold energy of 235-245 keV was confirmed.

The thermoluminescence emission intensity of zinc sulfide has previously been used to study the annealing by energetic electrons of damage produced by deuteron irradiation<sup>1</sup> and to study the production of a trapping state by energetic electrons.<sup>2</sup> Identification of the radiation-sensitive defect in binary compounds is difficult,<sup>3</sup> particularly in those cases where only one of the atomic species can be displaced. After electron irradiation at room temperature of zinc sulfide single crystals two new peaks were produced in the thermoluminescence characteristic. One of these peaks revealed a new trapping state produced by electrons of energy greater than 175-195 keV, and the other resulted from a trapping state which was produced above a greater threshold electron energy.<sup>2</sup>

The single-crystal platelets of zinc sulfide were grown by the flow method from luminescent grade chlorine-free material. The platelets had a thickness of approximately 3-7  $\mu\text{m}$ . The irradiations with monoenergetic electrons in the range 100-400 keV were carried out in a vacuum of  $<5 \times 10^{-6}$  Torr, using a Van de Graaff accelerator having an electron-beam energy fluctuation of less than  $\pm 2$  keV.<sup>4</sup> The calibration of the electron-beam energy was performed using column-resistor measurements and, using aluminum-foil transmission techniques, was compared with other electron-beam energy calibrations in the literature. Using an E.M.I. 9502S photomultiplier, the thermoluminescence was observed after a zinc sulfide specimen had been cooled to 77°K, exposed to 3650-Å radiation from a mercury lamp, and warmed at a suitable heating rate. The heating rates used were selected from the range 1-2°C sec<sup>-1</sup> but all the results reported here were obtained with a heating rate of 2°C sec<sup>-1</sup>. A two-pen potentiometric recorder gave a simultaneous display of the thermoluminescence intensity and the crystal temperature. One of the difficulties in interpreting thermoluminescence data is the lack of consistency which may occur from sample to sample and also from experiment to repeated experiment.

Many crystals did not show any damage at all after electron irradiation. Because of this lack of consistency, samples from several different crystal-growth runs were investigated and the results presented here are considered to be typical of the majority of these crystals. Furthermore, after irradiation any change in the thermoluminescence properties which appeared to be permanent was removed (or almost removed) by a suitable annealing process. After irradiation and annealing the specimens could not be returned completely to their virgin as-grown condition, but they could be returned each time to a reproducible state suitable as an initial state for damage studies. The reproducible initial state was found to be slightly different from sample to sample.

In an effort to discover a second threshold energy for atomic displacement the thermoluminescence characteristic was studied as a function of electron energy for a series of zinc sulfide crystals of differing nonstoichiometry. To produce atomic displacement effects just above a threshold energy requires considerably greater electron doses than at higher energies. Thus the energy range below the previously observed threshold energy was investigated carefully with a large electron dose. The thermoluminescence curve for a typical zinc sulfide single crystal before and after irradiation with  $6.8 \times 10^{17}$  electrons cm<sup>-2</sup> at an energy of 229 keV is shown in Fig. 1. By varying the electron-beam energy a threshold of 175-195 keV was found for the production of the trapping state, giving rise to the new peak which occurred at  $195 \pm 5^\circ\text{K}$  for a heating rate of 2°C sec<sup>-1</sup> (Fig. 2). More precise location of the energy threshold must await the comparison of the experimental curve of Fig. 2 with a computed curve of the number of atomic displacements based on theoretical considerations.

Further irradiation of these specimens at higher electron energies shows the creation of another peak at  $235 \pm 5^\circ\text{K}$ . With a threshold energy of 235-245 keV this peak is clearly the same peak as that reported by Bryant and Cox.<sup>2</sup> Figure 3,

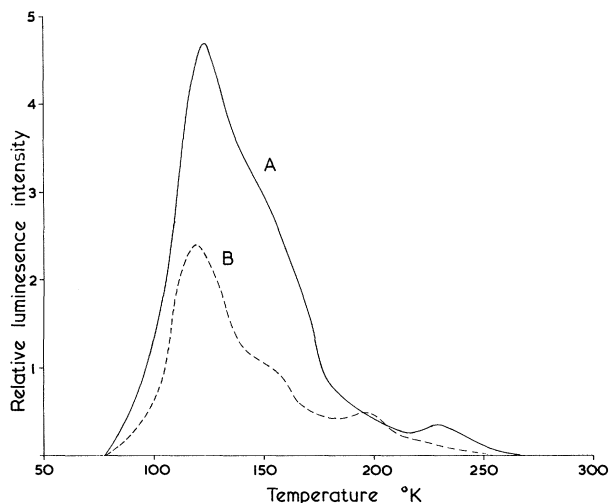


FIG. 1. Thermoluminescence intensity curves for a single crystal of zinc sulfide excited at 77°K by 3650-Å radiation. *A*, before electron bombardment; *B*, after bombardment at room temperature with  $6.8 \times 10^{17}$  electrons  $\text{cm}^{-2}$  of 229-keV energy.

the thermoluminescence curve before and after irradiation at 267 keV, shows the creation of both the 195 and 235°K peaks in the same single-crystal specimen. Very few crystals were found to show the emergence of both peaks. Some crystals showed emergence of only the 195°K peak and some the emergence of only the 235°K peak.

Electron irradiation below the threshold energies for enhancement of the two thermoluminescence peaks is found to produce a decrease in the whole of the thermoluminescence spectrum, presumably because of a change in the defect or defects responsible for fluorescence in these samples or because of changes in defects which compete nonradiatively with the luminescence center. For irradiation above a threshold energy, enhancement of an individual peak in the presence of a reduction in the intensity of the remainder of the thermoluminescence characteristic indicates the production of a trapping state. Careful examination of the glow curves prior to electron bombardment in Figs. 1 and 3 suggests the presence of both trapping states prior to irradiation, but it should be remembered that both curves labeled *A* are not glow curves for unirradiated samples but for samples which have been brought to a reproducible condition by successive irradiation and annealing. The roughly comparable areas under curves *A* and *B* in Fig. 3 might suggest the possibility of trapped-charge redistribution as opposed to trapping-site creation, but many results have been obtained in which the area under curves *A* and *B* differ by a factor of up to 3.

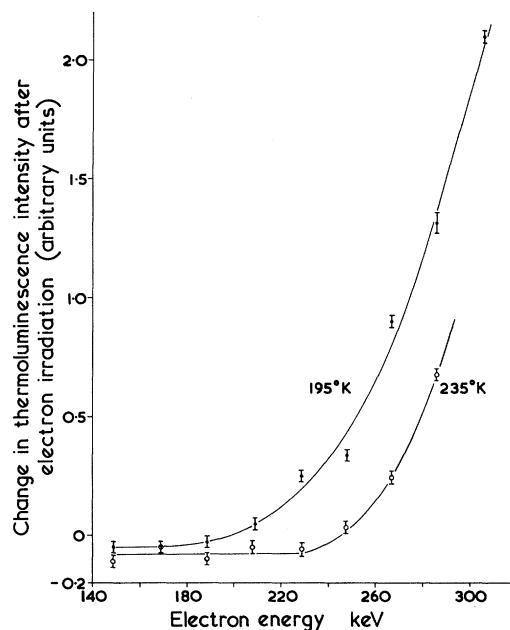


FIG. 2. Changes in the thermoluminescence intensity of a single crystal of zinc sulfide as a function of the energy of the incident electrons. (After each irradiation with  $6.8 \times 10^{17}$  electrons  $\text{cm}^{-2}$  the crystal was annealed by moderate heat treatment until it returned to approximately the same starting conditions.)

The possibility of trapped-charge redistribution occurring is made even less likely by the fact that for the damaged samples successive glow curves are almost completely reproducible over a long period of time. 170 days after electron irradiation the intensity of the peak at 195°K is

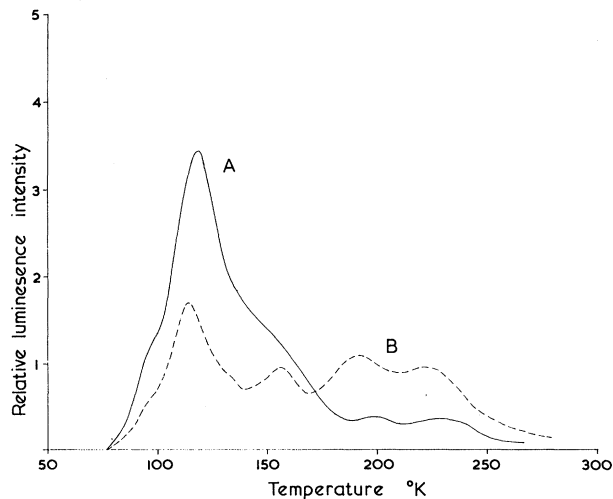


FIG. 3. Thermoluminescence intensity curves for a single crystal of zinc sulfide excited at 77°K by 3650-Å radiation. *A*, before electron bombardment. *B*, after bombardment at room temperature with  $6.8 \times 10^{17}$  electrons  $\text{cm}^{-2}$  of 267-keV energy.

still 48% of its intensity immediately after its creation. Moderate heat treatment is required to restore samples to a condition resembling their initial state. There is no thermoluminescence glow curve from material which is irradiated with electrons at room temperature unless it is exposed to ultraviolet radiation at low temperature. It seems clear that the results reported here are due to a selective increase in concentration of trapping states and not to redistribution of trapped charge among already existing sites.

The existence of two distinct threshold energies for the creation of two new trapping states is believed to indicate the displacement of each of the atomic species in the binary compound. Assignment of the atomic species displaced at each threshold energy is not easy because there has been no conclusive identification of the defects responsible for the 195 and 235°K peaks in these samples. The often quoted empirical rule<sup>3</sup> that the cation is always displaced at a lower displacement energy than the anion is of no use for the threshold energies quoted here because it is true for each of the two possible assignments. The close relationship which seems to exist between displacement energy and the bond energy of the lattice has already been pointed out by Bäuerlein.<sup>5</sup> Both elements in a binary compound would be expected to have similar displacement energies, particularly if the two elements of the compound are as similar to each other as possible. When the masses of the two elements are not similar we may associate the displacement of the lighter atom with the lower of the two observed threshold electron energies. Hence the 185-keV threshold electron energy is tentatively assigned to the displacement of sulfur (giving the sulfur atom a recoil energy of 15.0 eV at threshold) and the 240-keV threshold electron energy to the displacement of zinc (giving the zinc atom a recoil energy of 9.9 eV). This assignment is also strongly favored because it produces displacement energies which are less dissimilar than the alternative assignment which would yield a zinc displacement energy of 7.3 eV at 185 keV and a sulfur displacement energy of 20.2 eV at 240 keV. The measured value of approximately 15.0 eV for the displacement energy of sulfur confirms surprisingly well the estimate of 15 eV made by Curie.<sup>6</sup> The fact that the displacement energies observed in zinc sulfide are considerably greater than the displacement energies observed in other group II-VI

compounds (cadmium sulfide, cadmium selenide, zinc selenide, and cadmium telluride) is not surprising when it is realized that zinc sulfide has much the greatest formation enthalpy of these compounds.<sup>3</sup>

For each defect further efforts will be made to correlate curves of the theoretically evaluated number of defects per incident electron as a function of the incident electron energy with the dependence of the experimentally observed enhancement of thermoluminescence intensity on the incident electron energy. Similar correlations between theoretical curves and experimental curves have already been made by Bryant and Cox<sup>7</sup> using photoluminescence for cadmium telluride and cathodoluminescence for cadmium sulfide. However, electron irradiation at room temperature does not preclude the formation of complex defects and the analysis may not prove to be straightforward.

The trap which we observe at 195°K is not likely to have the same origin in our samples as the halogen traps which have been reported in this temperature region at the same heating rate.<sup>8</sup> Hoogenstraaten<sup>8</sup> has suggested that the defect responsible for the 235°K peak is a complex center consisting of a pair of sulfur vacancies  $[V_S^+]_2$ , but his alternative suggestion of a  $[V_S^+][V_{Zn}^-]$  complex for this peak could be more readily accepted with the tentative assignment which we have made. It is hoped that electron paramagnetic-resonance studies and experiments on crystals of widely differing stoichiometry will yield the exact nature of each radiation-induced defect.

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<sup>2</sup>F. J. Bryant and A. F. J. Cox, *Phys. Letters* **20**, 108 (1966).

<sup>3</sup>F. J. Bryant and A. F. J. Cox, *J. Phys. C: Phys. Soc. (London) Proc.* **1**, 1734 (1968).

<sup>4</sup>F. J. Bryant, A. F. J. Cox, and R. Kirbitson, *J. Nucl. Instr.* **63**, 195 (1968).

<sup>5</sup>B. Bäuerlein, in *Radiation Damage in Solids, Proceedings of the International School of Physics "Enrico Fermi," Course XVIII*, edited by D. S. Billington (Academic Press, Inc., New York, 1963), p. 358.

<sup>6</sup>D. Curie, *Luminescence in Crystals* (Methuen and Company, Ltd., London, England, 1962), p. 309.

<sup>7</sup>F. J. Bryant and A. F. J. Cox, to be published.

<sup>8</sup>W. Hoogenstraaten, thesis, University of Amsterdam, 1958 (unpublished).