Photoconductivity of Gallium Selenide Crystals

RICHARD H. BUBE AND EDWARD L. LIND
RCA Laboratories, Princeton, New Jersey
(Received April 10, 1959)

Single crystals of GaSe have been prepared by reaction of the elements, followed by gradient freeze crystallization. Crystals as grown were *p*-type, probably because of Cu acceptors, with hole mobility of 15 cm^2/volt sec, hole concentration of 10^{16} cm^{-3}, and acceptor ionization energy of 0.12 ev. In many ways the properties of GaSe crystals are very similar to those of ZnTe crystals. The absorption edge of GaSe is at 6310 A, corresponding to a band gap of 1.97 ev; the temperature coefficient of band gap is about -4×10^{-4} ev/deg. Insulating and photosensitive GaSe crystals can be prepared by compensating the acceptor impurities by incorporated donors from Groups VII or IV. Rectification tests indicate *p*-type photoconductivity. Thermal quenching of photoconductivity corresponds to an ionization energy of about 0.5 ev, whereas optical quenching corresponds to an ionization energy of about 1.0 ev; thus a large Franck-Condon shift is indicated. Below the temperature at which thermal quenching of photoconductivity occurs, the sensitivity is within the range of sensitive CdS or CdSe crystals.

INTRODUCTION

A LARGE portion of the detailed measurements of photoconductivity to date have been concentrated on Group II–Group VI compounds[1] which show either the zincblende (cubic) or the wurtzite (hexagonal) crystal structure. In both these structures, a given atom is tetrahedrally bonded with four nearest-neighbor atoms of the other type. High photosensitivity has been associated with electron conduction, and the presence in the crystals of negatively charged centers which have a large capture cross section for photoexcited holes, but a subsequent small cross section for photoexcited electrons. The investigation of Group III–Group VI compounds, such as gallium selenide, affords the opportunity of observing photoconductivity effects in a crystal structure quite different from those of the Group II–Group VI compounds. In addition, since both GaSe and Ga_2Se_3 can be prepared, there is the opportunity of detecting differences produced by different valence states of the crystal cation. This report is concerned primarily with the results found with GaSe crystals; investigations of the Ga_2Se_3 form and of solid solutions of GaSe·GaS are in a preliminary state and will be described in a later publication.

Polycrystalline GaSe was prepared by Klemm and von Vogel[2] by reaction of the elements. Schubert and Dörre[3] showed that the crystal structure of GaSe was the same as that reported for GaS by Hahn and Frank,[4] i.e., a hexagonal layer structure. Figure 1 compares the basic atomic arrangement in CdS with that in GaSe. In GaSe, each Ga atom is bonded to three Se atoms and to another Ga atom; the layers occur with weak bonding between Se atoms, as indicated by easy cleavage perpendicular to the *c* axis. The valence of Ga in the Ga—Ga bond is best represented as Ga_2^{+4}. Since it is believed that Ga does not exhibit a +2 valence state, it is likely that the Ga—Ga bond consists mainly of a covalent double bond with contributions from ionic configurations. Electron spin and nuclear magnetic resonance experiments should help clarify this point. The crystal structure of Ga_2Se_3, on the other hand, has been shown by Hahn and Klinger[5] to be the same as that of zincblende with $\frac{1}{3}$ of the cation sites randomly vacant.

Photoconductivity measurements on polycrystalline GaSe and Ga_2Se_3 have been reported by Goryunova *et al.*,[6] who found a band gap of 1.95 ev for GaSe and of 1.75–1.9 ev for Ga_2Se_3. Fielding, Fischer, and Mooser[7] have also investigated GaSe, primarily from the standpoint of its thermoelectric properties. They reported *p*-type GaSe, with acceptor ionization energy of 0.2 ev, hole mobility of 20 cm^2/volt sec at 500°K, band gap of 2.01 ev at 300°K and of 2.09 at 78°K, giving a temperature coefficient of band gap, β, of -3.6×10^{-4} ev/deg. They reported the photoconductivity maxima, however, as being at 6550 A at room temperature and at 6050 A at liquid nitrogen temperature, between 0.05 and 0.1 ev lower energies than the band gaps.

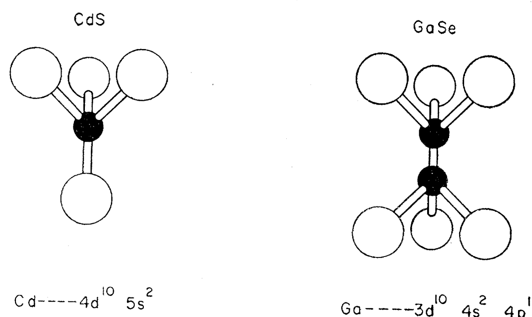

FIG. 1. Basic atomic arrangements in CdS and in GaSe crystals.

[1] R. H. Bube, Proc. I.R.E. **43**, 1836 (1955).
[2] W. Klemm and H. U. von Vogel, Z. anorg. u. allgem. Chem. **219**, 45 (1934).
[3] K. Schubert and E. Dörre, Naturwiss. **40**, 604 (1953).
[4] H. Hahn and G. Frank, Z. anorg. u. allgem. Chem. **278**, 340 (1955).
[5] H. Hahn and W. Klinger, Z. anorg. u. allgem. Chem. **259**, 135 (1949).
[6] Goryunova, Gregorieva, Konozalenko, and Ryvkin, J. Tech. Phys. U.S.S.R. **25**, 1675 (1955).
[7] Fielding, Fischer, and Mooser, J. Phys. Chem. Solids **8**, 434 (1959).

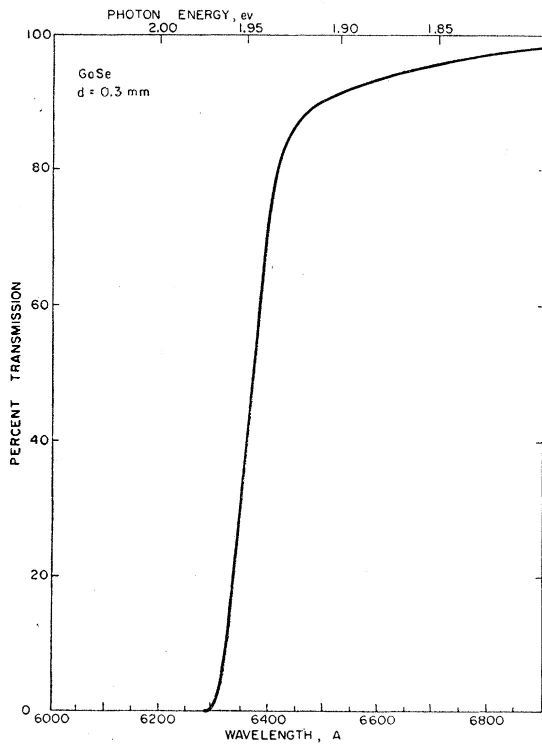

FIG. 2. Transmission of a 0.3-mm thick crystal of GaSe.

The results of the present investigation on photoconductivity in GaSe crystals indicate that the phenomena encountered are similar to those found in CdS and CdSe crystals. The chief differences are that *p*-type photoconductivity rather than *n*-type photoconductivity appears to be involved, and that the optically measured quenching energy is about twice the thermally measured energy.

EXPERIMENTAL

Crystals of GaSe were grown from reaction between the elements followed by gradient freeze crystallization. Alcoa Ga and American Smelting and Refining Se were placed in a graphite crucible, subsequently sealed in a quartz ampoule at about 10^{-5} mm Hg. Reaction was carried out at 600°C for about 15 hours, after which the temperature was raised to 970°C, 10° above the melting point of GaSe, and held for 24 hours. The sample was then slowly cooled in a furnace with a temperature gradient (externally measured) of about 40° over the 3-in. length of the tube, to 900°C in 20 hours, and then to 450°C in a second 20-hour period. For impurity compensation experiments, about 0.5% of either $GaCl_3$ or of metallic Sn was added to the initial materials. The grown crystals without added impurity were analyzed[8] and were found to contain about 3 ppm Cu, presumably the cause of the high *p*-type conductivity found.

Photoconductivity measurements were made with melted In contacts, tested to insure Ohmic behavior, in an atmosphere of He gas between the temperatures of liquid nitrogen and about 100°C. Excitation was primarily by a Bausch and Lomb grating monochromator, using neutral wire-mesh filters to alter the light intensity.

RESULTS

Transmission

The transmission measured through a 0.3-mm crystal of GaSe is shown in Fig. 2. The absorption edge is at about 6310 A, corresponding to a band gap of 1.97 ev at room temperature.

Conductivity

GaSe crystals as grown were high-conductivity *p*-type. Hall effect measurements indicated a room-temperature hole mobility of 15 cm^2/volt sec with a hole concentration of 10^{16} cm^{-3}. Various attempts to prepare purer crystals did not succeed in lowering the hole concentration below 10^{15} cm^{-3}. An attempt to compensate for the *p*-type conductivity by dissociating a crystal of GaSe at high temperature in vacuum did not affect the type or the magnitude of the conduc-

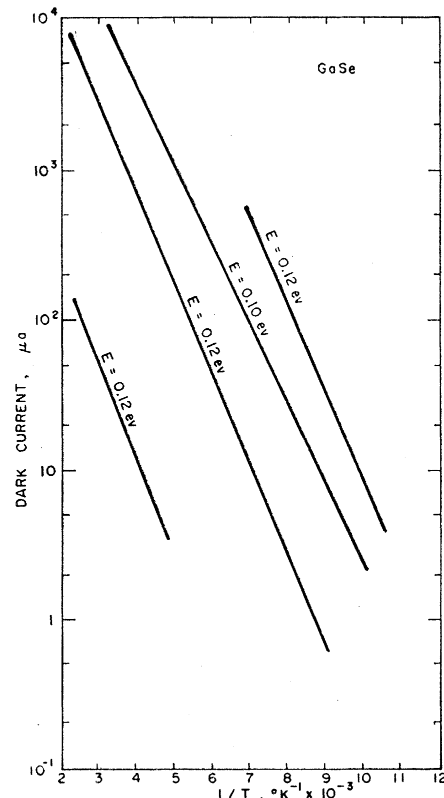

FIG. 3. Dark current as a function of temperature for several different samples of high-conductivity *p*-type GaSe, giving an acceptor ionization energy of 0.12 ev.

[8] Analysis by H. H. Whittaker.

tivity. The temperature dependence of the conductivity for several samples is shown in Fig. 3, indicating an acceptor ionization energy of 0.12 ev.

Ga_2Se_3 crystals, prepared from the same raw materials and by the same procedure as the GaSe crystals, were however highly insulating and photoinsensitive.

Photoconductivity Spectral Response

The *p*-type conductivity of the GaSe crystals could be compensated by incorporating impurities from Group VII or Group IV; specifically, Cl and Sn impurities were principally used. Spectral response curves for

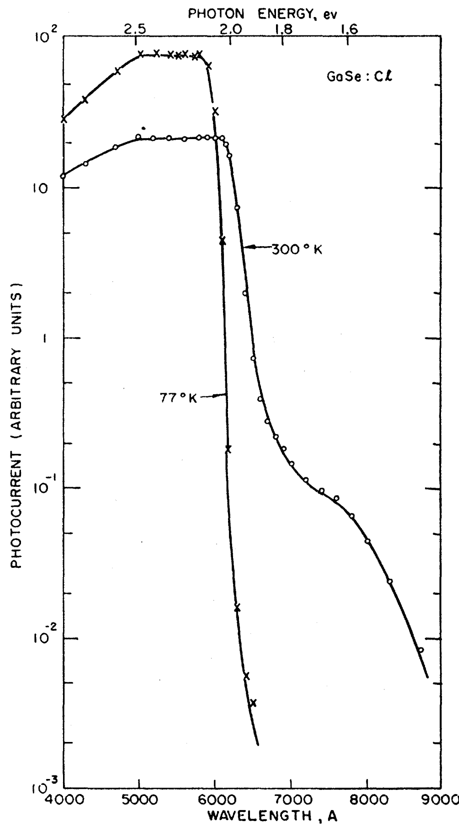

FIG. 4. Spectral response of photoconductivity at room temperature and at liquid nitrogen temperature, for GaSe:Cl, measured with the applied field perpendicular to the c axis.

GaSe:Cl and GaSe:Sn crystals are shown in Figs. 4, 5, and 6. All measurements in GaSe:Cl crystals were made with applied field perpendicular to the c axis; in GaSe:Sn crystals, measurements were made both with field perpendicular to and parallel to the c axis. A summary of the various energy values found from photoconductivity data is given in Table I. In the GaSe:Sn crystals a long-wavelength response was found at low temperatures, which was identified with stimulation of trapped charge by these wavelengths, rather than a bona fide excitation.

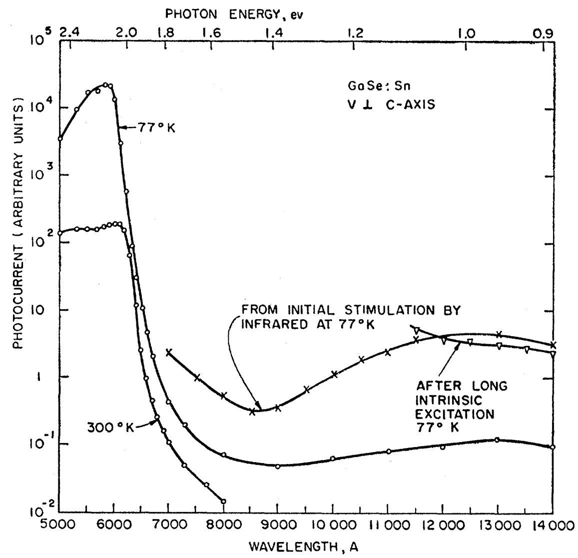

FIG. 5. Spectral response of photoconductivity at room temperature and at liquid nitrogen temperature, for GaSe:Sn, measured with the applied field perpendicular to the c axis. The long-wavelength response results from stimulation of trapped carriers previously excited by intrinsic excitation.

Sufficient preliminary preparation of Ga_2Se_3 was carried out to indicate the band gap and give the spectral response curve for photoconductivity shown

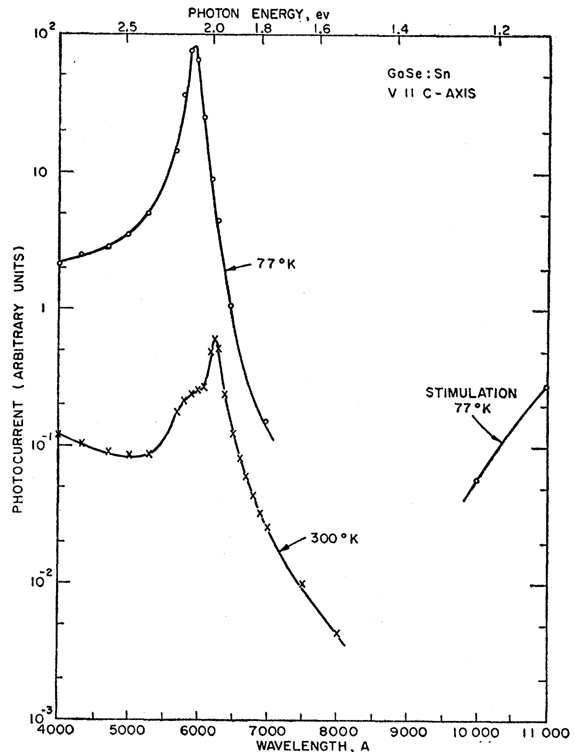

FIG. 6. Spectral response of photoconductivity at room temperature and liquid nitrogen temperature, for GaSe:Sn, measured with the applied field parallel to the c axis.

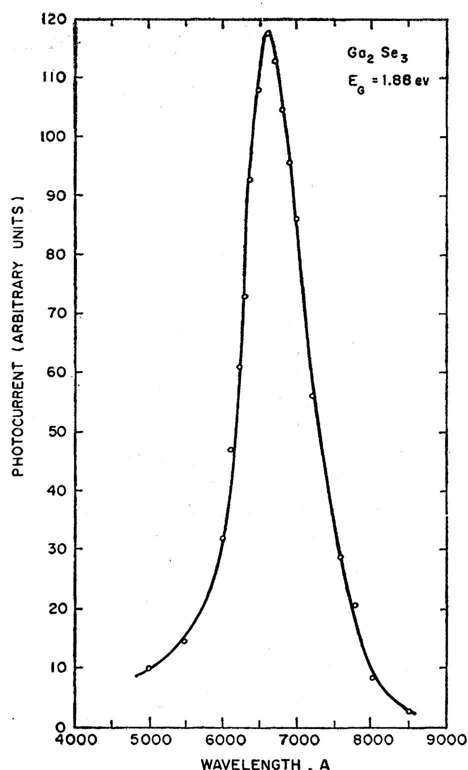

FIG. 7. Spectral response of photoconductivity at room temperature in Ga_2Se_3, giving a band gap of 1.88 ev.

in Fig. 7. A band gap of 1.88 ev is indicated from the photoconductivity maximum.

Sign of the Photocarriers

Rectification tests were performed at room temperature to determine the sign of the photocurrent carriers in GaSe. Currents were measured in the direction of the *c* axis with one contact being a broad-area melted In contact and the other being a sharp Cu point contact. With CdS, as expected, the forward direction was with the point contact positive, indicating *n*-type photoconductivity. With GaSe, the forward direction was definitely for the point contact negative, indicating *p*-type photoconductivity. At the same time measurements were made on ZnTe:In and ZnTe:Al samples reported in a previous paper[9] where there had been some doubt of the sign of the photocarriers; tentative indications were for *p*-type photoconductivity in ZnTe:In and *n*-type photoconductivity in ZnTe:Al.

TABLE I. Energy values from photoconductivity measurements.

	E_G, ev		Quenching	
	300°K	90°K	E_{opt}, ev	E_{therm}, ev
GaSe:Cl				
($V \perp c$-axis)	2.02	2.10	1.05	0.39
GaSe:Sn				
($V \perp c$-axis)	2.02	2.09	1.05	0.54
($V \parallel c$-axis)	1.99	2.08	0.95	0.62
Temp. coeff. of band gap, $\beta_{Av} \approx -3.8 \times 10^{-4}$ ev/degree				

[9] R. H. Bube and E. L. Lind, Phys. Rev. **105**, 1711 (1957).

Thermal Quenching

All photosensitive GaSe crystals showed a temperature quenching of photoconductivity which set in at about −70°C. Typical curves measured for a GaSe:Sn crystal are given in Fig. 8. If, following a rate equation analysis previously reported,[10] the photocurrent at the breakpoint is plotted as a function of the reciprocal temperature at the breakpoint a straight line should be obtained, as indicated in Fig. 9, with slope giving the thermal ionization energy of the sensitizing centers and intercept giving the capture cross-section ratio for these centers. The thermal quenching energies given in Table I are obtained in this way.

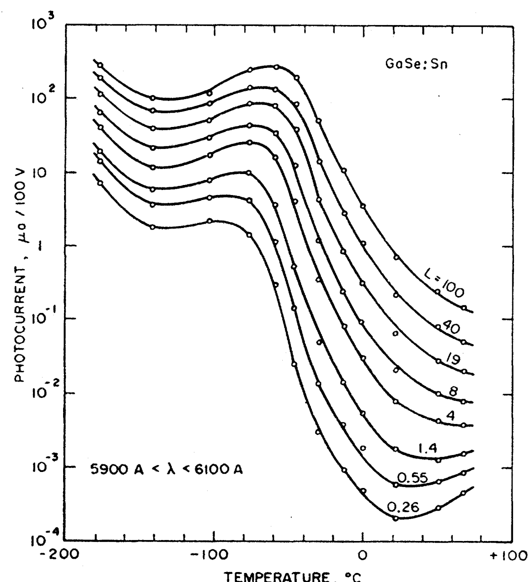

FIG. 8. Photocurrent as a function of temperature for different levels of light intensity for GaSe:Sn, measured with the applied field perpendicular to the *c* axis. The excitation was by a band of radiation lying between 5900 A and 6100 A.

Optical Quenching

At liquid nitrogen temperature, the photoconductivity can also be optically quenched. Figure 10 gives three typical optical quenching curves indicating optical ionization energies for the sensitizing centers of about 1 ev. The temperature dependence of the optical quenching process is traced in Fig. 11 for a GaSe:Cl crystal, indicating that the process of optical quenching ceases as the process of thermal quenching sets in, as would be expected if the same center were involved in both processes.

[10] R. H. Bube, J. Phys. Chem. Solids **1**, 234 (1957).

Trapping Centers

Both GaSe:Cl and GaSe:Sn crystals showed considerable density of trapping centers, although optical stimulation out of trapping centers was prominent only in crystals with Sn impurity. Thermally stimulated current curves are given in Fig. 12. The decrease in free-carrier lifetime with temperature above −80°C, as indicated by the temperature dependence of photocurrent in the figure, makes the determination of deep trap densities difficult. Estimates from the curves indicate minimum trap densities of 5×10^{16} cm^{-3} in GaSe:Cl and 10^{18} cm^{-3} in GaSe:Sn, with trap depths in the range between 0.2 and 0.4 ev.

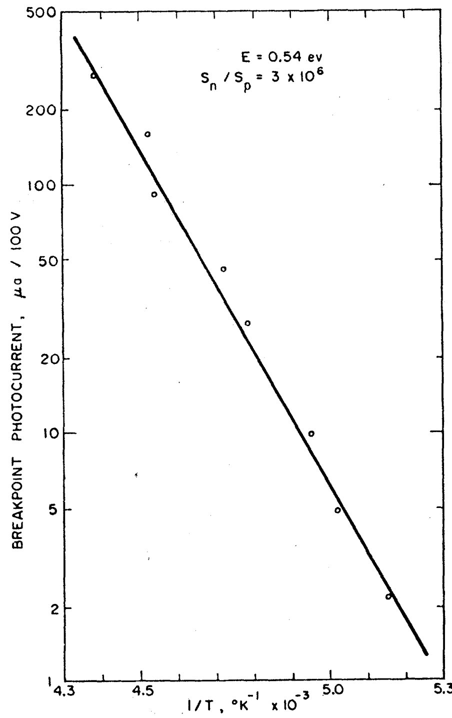

FIG. 9. The photocurrents for the sensitivity break-points in Fig. 8 as a function of the temperature at the breakpoints. The slope of the line gives the ionization energy of the sensitizing centers, 0.54 ev, and the intercept on the photocurrent axis gives the capture cross-section ratio of these centers, 3×10^6.

DISCUSSION

The work on GaSe has pointed up how strikingly similar two different materials can be in spite of different crystal structures. GaSe and ZnTe[9] are almost identical in (1) band gap, (2) acceptor ionization energy, (3) difficulty of preparing low-conductivity samples without compensation, (4) hole mobility, (5) occurrence of *p*-type photoconductivity, i.e., ZnTe:In data, and (6) thermal quenching energy. The two compounds illustrate a general rule of many compounds that similar properties are obtained, at least as far as band

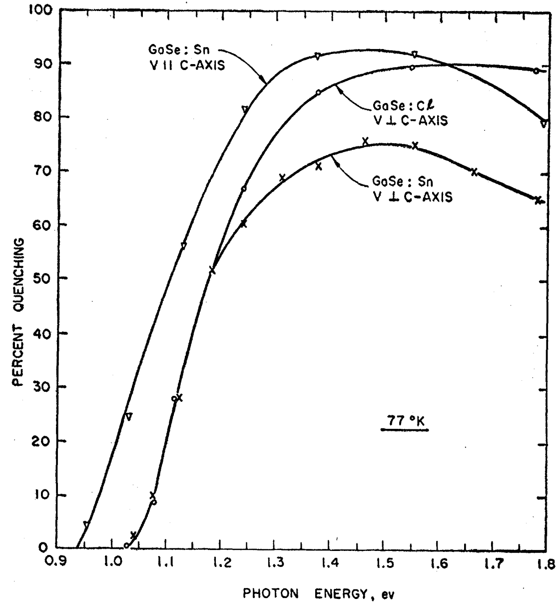

FIG. 10. Infrared quenching spectra at liquid nitrogen temperature for GaSe:Cl and GaSe:Sn crystals.

gap is concerned, if[11]

$$\Delta G_M+\Delta P_M+\Delta P_X-\Delta G_X=0, \quad (1)$$

where ΔG_M is the difference between the groups of the cations in the two compounds (the group being determined by the effective valence of the cation), ΔP_M is the difference between the periods of the cations in the two compounds, ΔP_X is the difference between the

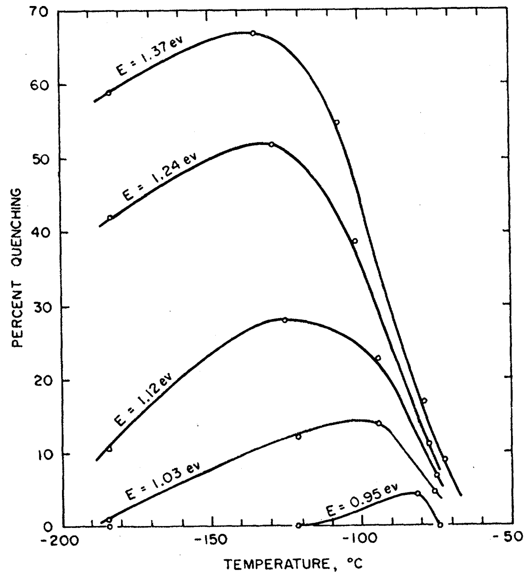

FIG. 11. Temperature dependence of infrared quenching for a number of different wavelengths in the quenching region. There is a slight shift of the low-energy cutoff of the quenching spectrum to lower energies with increasing temperature.

[11] R. H. Bube, *Photoconductivity of Solids* (John Wiley and Sons, Inc., New York, to be published), Chap. 7.

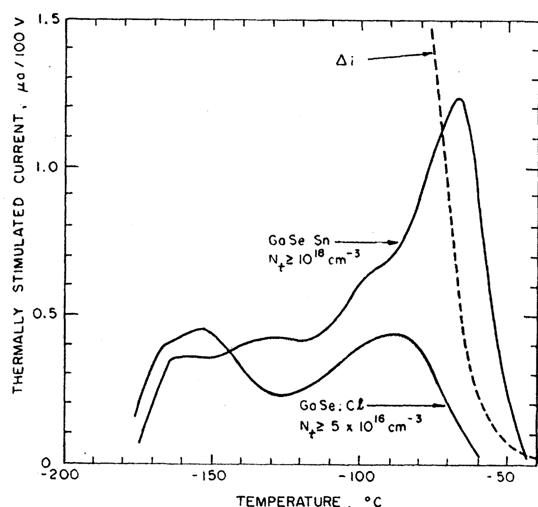

FIG. 12. Thermally stimulated current curves for GaSe:Cl and GaSe:Sn crystals, measured with a heating rate of 0.5°/sec. The dashed curve shows the actual photocurrent as a function of temperature for a light intensity of proper intensity to give currents of the same magnitude as the thermally stimulated currents.

periods of the anions in the two compounds, and ΔG_X is the difference between the groups of the anions in the two compounds. This is just a re-statement of the concept of electronegativity. For example, the decrease in period of the anion between ZnTe and GaSe is compensated by the increase in the group of the cation.

The measurements on GaSe indicate an acceptor level lying 0.12 ev above the top of the valence band, and a sensitizing level for hole photoconductivity with capture cross section for electrons some 10^6 time greater than the subsequent cross section for holes, lying about 0.5 ev thermally and 1.0 ev optically below the bottom of the conduction band.[12] The identity of these sensitizing centers, possibly selenium vacancies, is expected to be suggested by the behavior of the ionization energies in the GaSe·GaS solid solutions. The reason for the large Franck-Condon shift may lie in the crystal structure itself, and might be expected to manifest itself through measurements of dielectric constant. In CdS, where hole ionization is involved in thermal and optical quenching,[1] no appreciable difference between optical and thermal energies are found; the low-frequency dielectric constant is 11.6,[13] and the high-frequency dielectric constant is 6.3 from the index of refraction. Measurements by MacDonald have given a low-frequency dielectric constant of 7±1 for GaSe, and a high-frequency dielectric constant of 4.7 for GaSe without added impurity and for GaSe: Cl, and of 3.4 for GaSe: Sn.[14] Considerations by Mott and Gurney[15] show that the energy difference between thermal and optical ionization energies in an ionic crystal should be proportional to $(1/\epsilon_\infty - 1/\epsilon_0)$, where ϵ_0 is the low-frequency dielectric constant and ϵ_∞ is the high-frequency dielectric constant. The ratio of the low- and high-frequency dielectric constants in GaSe is not appreciably different from that in CdS, but if the value of ϵ_∞ for GaSe:Sn is taken, the quantity $(1/\epsilon_\infty - 1/\epsilon_0)$ is twice as large in GaSe as in CdS.

At low temperatures and low light levels, the photosensitivity of GaSe:Sn crystals is the same as that of sensitive CdS:Cl:Cu and CdSe:I:Cu crystals, i.e., about 10^{-1} mho cm^2/watt.

ACKNOWLEDGMENTS

The authors are indebted to Dr. R. Williams for assistance in making the rectification measurements, and to Dr. W. E. Spicer for helpful discussions.

[12] The possibility that *n*-type photoconductivity is involved at low temperatures, leaving *p*-type photoconductivity after the *n*-type photoconductivity has been quenched, cannot be overlooked and will be tested further.

[13] Kröger, Vink, and Volger, Philips Research Repts. **10**, 39 (1955).

[14] H. E. MacDonald (unpublished).

[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), p. 162.