

Inversion of Conduction and Valence Bands in $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ Alloys

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Single-crystal films of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys with rocksalt structure ($0 \leq x \leq 0.33$) have been deposited by evaporation on cleaved (100) faces of KCl substrates. The energy gap E_g at $T=300, 195,$ and 77°K has been determined by measuring the optical transmission between 2 and $25 \mu\text{m}$. As x increases or T decreases, E_g decreases for sufficiently low values of x , but increases for $x > 0.2$ and $T = 77^\circ\text{K}$. The sign reversal in the composition and temperature dependence of E_g shows that the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys exhibit the inversion in band structure recently proposed for the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys. If E_g is assigned negative values for samples in which the conduction and valence bands are inverted from those in PbSe, the data are well represented by the equation $E_g = 0.13 + (4.5 \times 10^{-4} \text{ deg}^{-1}) T - 0.89x$ eV. The inversion point, at which $E_g = 0$ because the L_6^+ and L_6^- band extrema are degenerate, is $x = 0.19$ at 77°K and $x = 0.30$ at 300°K .

INTRODUCTION

THIS paper reports the results of electrical and optical measurements on single-crystal films of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys with rocksalt structure ($0 \leq x \leq 0.33$), whose semiconductor properties have not been investigated previously. The composition dependence of the magnitude and temperature coefficient of the optical energy gap (E_g) shows that the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys exhibit the inversion of conduction and valence bands recently proposed¹ for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys on the basis of less conclusive evidence.

Since PbSe has the cubic rocksalt structure, whereas SnSe has the orthorhombic $B29$ structure, these compounds do not form a complete series of pseudobinary solid solutions. On the basis of x-ray diffraction studies on annealed powders, Krebs, Grün, and Kallen² have reported that the rocksalt structure is obtained for $0 \leq x \leq 0.43$. The results of similar experiments in our laboratory indicate that the maximum value of x for the rocksalt region is a little less than 0.4. Therefore the present investigation has been restricted to samples with x below 0.35.

PREPARATION, MICROPROBE ANALYSIS, AND X-RAY DATA

Epitaxial films, usually 5–15 μm thick, were deposited on freshly cleaved (100) faces of KCl substrates by means of an evaporation technique generally similar to those used to obtain single-crystal films of PbS, PbSe, and PbTe,³ $\text{PbSe}_x\text{Te}_{1-x}$ alloys,⁴ and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys.⁵ A single alloy source⁵ was employed, rather than separate sources⁴ of PbSe and SnSe. Source ingots were prepared by sealing appropriate quantities of the semiconductor grade elements in evacuated quartz ampoules, melting at about 1100°C for 2–4 h, and air quenching.

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¹ J. O. Dimmock, I. Melngailis, and A. J. Strauss, *Phys. Rev. Letters* **16**, 1193 (1966).

² H. Krebs, K. Grün, and D. Kallen, *Z. Anorg. Allgem. Chem.* **312**, 309 (1961).

³ J. N. Zemel, J. D. Jensen, and R. B. Schoolar, *Phys. Rev.* **140**, A330 (1965).

⁴ R. F. Bis and J. N. Zemel, *J. Appl. Phys.* **37**, 228 (1966).

⁵ E. G. Bylander, *Mater. Sci. Eng.* **1**, 190 (1966).

(Before weighing, the Pb and Sn were melted under flowing H_2 for about 6 h at about 600°C to remove oxides.) Just before evaporation, the source ampoule was opened and placed in a resistance-heated boron nitride furnace located about 15 cm below a second resistance-heated boron nitride furnace containing six substrate crystals. During deposition, which was carried out in a conventional vacuum evaporator with a glass bell jar, the source and substrate temperatures were in the ranges 770 – 780°C and 235 – 280°C , respectively. In most runs, each temperature was kept constant to within $\pm 5^\circ\text{C}$ or less. The deposition rate was usually about $750 \text{ \AA}/\text{min}$. After deposition was completed, the films were allowed to cool to room temperature under vacuum and then removed from the bell jar and stored in air.

The room-temperature optical transmission of every film at wavelengths between 2 and $15 \mu\text{m}$ was measured with a Perkin-Elmer model 221 double-beam prism spectrophotometer. All other measurements were made only on selected films. All measurements were made without removing the films from their KCl substrates.

Determinations of composition by electron microprobe analysis show that most of the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ films are uniform in x , the mole fraction of SnSe, to within the experimental accuracy of the microprobe, which is estimated to be $\pm 3\%$ of x . Significant differences in composition are sometimes found between films deposited in different runs with the same source composition and between different films deposited in the same run. In most cases the mole fraction of SnSe is lower in the film than in the source ingot, although the vapor pressure at 770 – 780°C is reported to be at least twice as high for pure SnSe^{6,7} as for pure PbSe.⁸ For sources with $x = 0.1, 0.2,$ and 0.3 , respectively, the ranges of x for the analyzed films are 0.053 – 0.100 (8 films, 3 runs), 0.188 – 0.206 (3 films, 2 runs), and 0.293 – 0.322 (3 films, 1 run).

⁶ I. M. Nesterova, A. S. Pashinkin, and A. V. Novoselova, *Russ. J. Inorg. Chem.* **6**, 1031 (1961).

⁷ C. Hirayama, Y. Ichikawa, and A. M. DeRoo, *J. Phys. Chem.* **67**, 1039 (1963).

⁸ V. P. Zlomanov, B. A. Popovkin, and A. V. Novoselova, *Russ. J. Inorg. Chem.* **4**, 1231 (1959).

As in the case of single-crystal films of PbS, PbSe, and PbTe deposited on the (100) face of KCl or NaCl, the x-ray diffraction patterns for the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ films obtained with a diffractometer contain only the (200), (400), and (600) lines, the characteristic reflections for a (100) face in the rocksalt structure. The lattice parameter (a_0) values, which have been calculated from the position of the (600) line using the (600) line of the KCl substrate as an internal standard, decrease with increasing x . The data are well represented by the straight line $a_0(\text{\AA}) = 6.127 - (0.12)x$. This line has the same slope as Krebs, Grün, and Kallen² found in their measurements on annealed $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ powders, but the a_0 values are about 0.15% greater than those of Krebs *et al.* This discrepancy is apparently due to a systematic error in the results of Krebs *et al.*, since their a_0 value for pure PbSe is only 6.118 Å, compared with values of 6.124–6.129 Å reported in the literature.

ELECTRICAL MEASUREMENTS

Measurements of resistivity (ρ) and Hall coefficient (R_H) were made at room temperature and 77°K by conventional dc potentiometric techniques. Lead wires were soldered directly to the films, in some initial experiments with a solder melting at about 50°C and later with a solder which is liquid at room temperature. Because of differences in deposition conditions, there is considerable scatter in the results, but a number of general characteristics are apparent.

At 77°K, all the films measured have positive Hall coefficients, with hole concentrations calculated on a one-carrier model ($p = 1/R_H e$) between 8×10^{16} and $3 \times 10^{18} \text{ cm}^{-3}$. By analogy with PbSe, the acceptors are probably lattice defects (specifically, Pb and Sn vacancies) resulting from the presence of Se in excess of the stoichiometric composition. There appears to be no essential connection between net acceptor concentration ($N_A - N_D \approx p_{77}$) and Sn content, although the lowest concentrations were obtained for films prepared from sources with $x \geq 0.2$ because of a change in deposition conditions which occurred when the source furnace was replaced. (In contrast, the acceptor concentration in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys increases rapidly as x increases.⁵) Values of the Hall mobility (R_H/ρ) at 77°K range from 1×10^3 to $1 \times 10^4 \text{ cm}^2/\text{V sec}$, with some tendency to decrease as x increases. Hole mobilities of about $3 \times 10^4 \text{ cm}^2/\text{V sec}$ at 77°K are typical of bulk PbSe with concentrations of $1 \times 10^{18} \text{ cm}^{-3}$ or below.

At room temperature, all films prepared from sources with $x \leq 0.15$ have positive Hall coefficients, with values of R_{300} between 2 and 12 cm^3/C . For sources with $x \geq 0.2$, some films have positive Hall coefficients ($0.5 < R_{300} < 3$), and others have negative Hall coefficients ($-0.5 > R_{300} > -6$). For the latter, R_H changes from positive to negative between 77°K and room temperature. This change in sign shows that the ratio of electron to hole mobility (b) is greater than

unity for the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys, as it is for PbSe, PbTe and PbS. For samples with $N_A > N_D$, R_H becomes negative when the intrinsic carrier concentration (n_i) increases sufficiently to make the ratio of hole to electron concentration (p/n) less than b^2 .

Since p/n increases as $(N_A - N_D)$ increases, for a given alloy composition R_{300} should be negative for net acceptor concentrations below a certain maximum value, $(N_A - N_D)_{\text{max}}$, and positive for higher acceptor concentrations. The present results are consistent with this behavior, as shown by comparison of R_{77} and R_{300} for films prepared from sources with $x = 0.2, 0.25,$ and 0.275 . These are the only compositions for which both positive and negative values of R_{300} were obtained. Although the data are too limited to determine precise values of $(N_A - N_D)_{\text{max}}$, they show clearly that this quantity increases as the Sn content of the films increases. This composition dependence explains why negative values of R_{300} were not obtained for $x \leq 0.15$. The increase in $(N_A - N_D)_{\text{max}}$ shows that n_i at 300°K also increases as x increases, if it is assumed that b does not depend strongly on x . Such an increase in n_i is also indicated by the data for films with negative values of R_{300} . For these films, $n_{300} \equiv 1/eR_{300}$ increases from $1-2 \times 10^{18} \text{ cm}^{-3}$ for a source composition of $x = 0.2$ to about $1 \times 10^{19} \text{ cm}^{-3}$ for $x = 0.35$. [The ratio $n_i/n_{300} = (b-1)/(b+1)$ for an intrinsic sample.] An increase in n_i is also indicated by the fact that the resistivity at room temperature generally decreases as x increases, from greater than $10^{-2} \Omega\text{-cm}$ for pure PbSe to $2-3 \times 10^{-3} \Omega\text{-cm}$ for $x = 0.35$. An increase in n_i with increasing x is to be expected because the energy gap of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys at room temperature decreases with increasing Sn content, as discussed below.

OPTICAL MEASUREMENTS AND BAND STRUCTURE

Infrared transmission measurements made at room temperature with the model 221 spectrophotometer showed that many of the films were of sufficient uniformity and optical quality to exhibit high-contrast, regularly shaped interference fringes at wavelengths beyond the absorption edge. The transmission of selected films was measured with a single-beam, single-pass Perkin-Elmer model 12-C spectrophotometer equipped with NaCl and KBr prisms. The films were mounted with vacuum grease on the copper cold finger of a metal Dewar, which for low-temperature measurements was cooled either with a slurry of dry ice and methanol (195°K), liquid oxygen (90°K), or liquid nitrogen (77°K). The sample temperature was probably within 10°K of the refrigerant temperature. After the transmission measurements were made, the Sn content of each film was determined with the electron microprobe.

In order to evaluate the energy gap (E_g) in a consistent manner from the position of the absorption edge, E_g was taken to be the energy corresponding to the

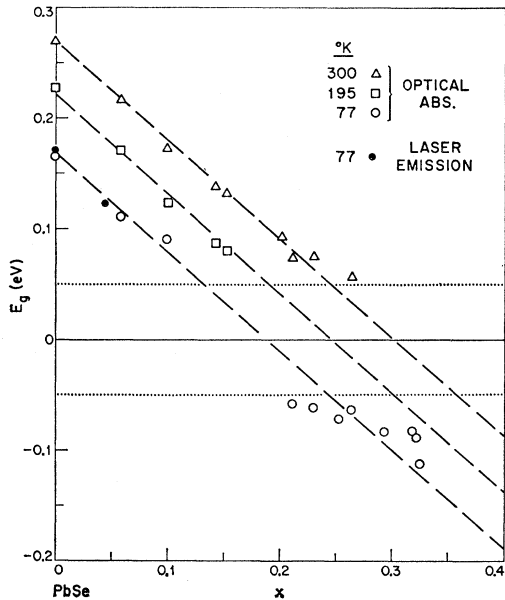


FIG. 1. Variation of energy gap (E_g) with composition and temperature for $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys with rocksalt structure. The dotted lines drawn at $+0.05$ and -0.05 eV indicate that no values of E_g could be obtained between these limits.

wavelength at which the absorption coefficient (α) was $1.5 \times 10^3 \text{ cm}^{-1}$. In determining α from the transmission data, the reflectivity was assumed to be 0.45, a representative value based on measurements below the absorption edge on films of several compositions. The sample thickness was assumed to be the same as the thickness measured with a Talysurf instrument for another film deposited during the same evaporation run. The films ranged in thickness between 5.7 and 16 μm , so that $\alpha = 1.5 \times 10^3 \text{ cm}^{-1}$ corresponds to transmission values between 2.8 and 13.4%.

The variation of E_g with Sn content in the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys is shown in Fig. 1 for nominal sample temperatures of 300°, 195°, and 77°K. Dotted lines have been drawn at $+0.05$ and -0.05 eV to indicate that no values of E_g could be obtained between these limits, since transmission measurements were not made beyond 25 μm . (The significance of the negative sign adopted for certain values of E_g is discussed below.) The present values are seen to be in good agreement with values of E_g at 77°K corresponding to the emission wavelengths of diode lasers prepared from PbSe (Ref. 9) and $\text{Pb}_{0.96}\text{Sn}_{0.04}\text{Se}$ (Ref. 10). For pure PbSe at 77°K, the present value of 0.165 eV is intermediate between the values of 0.159 and 0.176 eV obtained from interband magnetoabsorption data for epitaxial films before and after removal from NaCl substrates, respectively.¹¹

Films with sufficiently low Sn content exhibit the positive temperature coefficient of E_g which is characteristic of PbSe, PbTe, and PbS.

As shown in Fig. 1, E_g for the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys initially decreases as x increases. The present investigation was undertaken primarily in anticipation of observing such a decrease, which was expected¹ because the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys exhibit a similar decrease,^{1,5,12,13} at an initial rate of about 0.6 eV/100 mole % SnTe. In the present case, E_g becomes so small with increasing x that the absorption edge shifts beyond 25 μm , the limit of the present measurements, at each of the temperatures investigated. When x exceeds 0.2, however, the absorption edge at 77°K once more becomes measurable and moves to shorter wavelengths. In this region of composition and temperature, therefore, E_g increases as x increases. The data also show that in this region (where E_g is assigned negative values in Fig. 1) E_g decreases with increasing temperature, since E_g at 195°K is too small to be measured for any value of x above 0.15. This temperature dependence is confirmed by the results of transmission measurements made at 90°K on four samples with x between 0.25 and 0.33. In each case E_g at 90°K is smaller than at 77°K but still measurable. Thus for samples with sufficiently high values of x both the composition and temperature dependence of E_g at low temperatures are opposite in sign to those for PbSe. This sign reversal shows that the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys exhibit the inversion of conduction and valence bands proposed¹ for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys.

According to the band-inversion model, as represented schematically in Fig. 2 of Ref. 1, the conduction and valence band extrema of PbTe are L_6^- and L_6^+ states, respectively. With increasing Sn content, these states approach each other, become degenerate at a value of x which increases with increasing temperature, and then interchange. Beyond the inversion point, the L_6^+ state forms the conduction band edge and the L_6^- state forms the valence band edge.

The band-inversion model should be directly applicable to the $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ alloys with rocksalt structure, since PbSe has essentially the same band structure as PbTe. According to the model, the composition and temperature dependence of E_g must both change sign when the conduction and valence bands are inverted. The observation of such a simultaneous reversal for alloys with x between 0.2 and 0.35 at low temperatures therefore constitutes strong evidence for the validity of the model. In the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ system, E_g data have been obtained for pure SnTe but not for alloys containing enough Sn to have the inverted band structure, since alloys in this composition range have extremely

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¹⁰ J. F. Butler, A. R. Calawa, and T. C. Harman, *Appl. Phys. Letters* **9**, 427 (1966).

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the Seventh International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie., Paris, 1964), p. 325.

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¹³ I. Melngailis and A. R. Calawa, *Appl. Phys. Letters* **9**, 304 (1966).

high carrier concentrations due to deviations from stoichiometry.

For the $Pb_{1-x}Sn_xTe$ alloys, the change in band structure with composition has been attributed to the influence of relativistic effects on the energies of the conduction and valence bands.¹ It is probable that the changes in $Pb_{1-x}Sn_xSe$ band structure are also due principally to the difference between the relativistic energy shifts of the Pb and Sn atomic valence states. Approximate calculations¹⁴ indicate that the rate of decrease in E_g from this source would be 0.7 eV/100 mole % SnSe, compared with the observed rate of about 0.9 eV/100 mole % SnSe.

In Fig. 1, negative values of E_g have been assigned to those sample compositions and temperatures for which the energy bands are inverted from those in PbSe. Adopting this convention makes it possible to represent the data by straight lines satisfying the equation $E_g = 0.13 + (4.5 \times 10^{-4} \text{ deg}^{-1}) T - 0.89x$ eV.

¹⁴ J. O. Dimmock (private communication).

According to this equation, band inversion occurs at 77°, 195°, and 300°K for $x=0.19, 0.25,$ and $0.30,$ respectively. The deviations from the straight line at 77°K for samples with $x=0.21, 0.23,$ and 0.25 may be due to the presence of hole concentrations large enough to place the Fermi level inside the valence band and therefore to shift the absorption edge to shorter wavelengths (Burstein effect¹⁵). The relatively large deviations at 77°K for 2 samples with $x=0.32$ have the wrong sign to be explained in this way.

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Raman Scattering by Coupled Plasmon-Longitudinal-Optical-Phonon Modes in Zinblende-Type Crystals*

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A phenomenological theory of Raman scattering by the $q \approx 0$ coupled plasmon-(LO) longitudinal-optical-phonon modes, which takes into account the electro-optic effect of the longitudinal electric fields associated with the coupled modes, is presented. Estimates of the scattering efficiency of the plasmon-like mode at high carrier densities, for which the major contribution comes from the electro-optic effect, are obtained using values of the electro-optic coefficient derived from second-harmonic light-generation data. For n -type GaAs with a carrier density of $3 \times 10^{18}/\text{cm}^3$, the scattering efficiency of the plasmon-like mode is found to be 1×10^{-6} . The theoretical treatment is also applicable to Raman scattering by the collective cyclotron excitation modes of free carriers in a magnetic field and by their coupled modes with LO phonons.

THERE has been considerable interest in recent years in the scattering of electromagnetic (EM) radiation by plasmas in semiconductors, and theoretical expressions have been derived for the contributions to the scattering cross section arising from intraband processes^{1,2} and from interband processes.³ In the case of polar semiconductors which lack a center of symmetry, such as those with ZnS-type structures, it was

suggested⁴ that the two $q \approx 0$ coupled plasmon-(LO) longitudinal-optical-phonon collective modes would participate in first-order Raman scattering via mechanisms analogous to those involved in scattering by the $q \approx 0$ LO phonons in the absence of free carriers. The first-order Raman scattering of EM radiation by the $q \approx 0$ coupled plasmon-LO-phonon modes in GaAs was recently reported by Mooradian and Wright.⁵ Their spectra, which were obtained for samples with different carrier densities, clearly exhibit two Raman lines due to the coupled plasmon-LO-phonon modes as well as the Raman line due to the $q \approx 0$ transverse-optical (TO) phonons. In their discussion of the relative intensities of

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