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The PbSe metastable phase: II. The energy gap of the CsCl-type phase of PbSe and PbSe doped with Cd

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Abstract. The transmittance and reflectance spectra of films of PbSe and PbSe doped with 2 mol% Cd grown by two different non-equilibrium growth techniques, laser-assisted deposition and electron-beam evaporation, on KCl and BaF₂ substrates are measured from 400 to 4000 cm⁻¹ in the temperature range 80–300 K. The energy gaps of the metastable CsCl-type phases of PbSe and PbSe: Cd and their temperature coefficients are determined from the interference spectra. The energy profiles of the films are also obtained.

1. Introduction

The structural and optical investigations of the films of PbSe and PbSe doped with 2 mol% Cd produced on KCl and BaF₂ substrates by non-equilibrium growth techniques, as reported in part I, show that they represent two-layer structures (figure 2, part I). The sublayers grown in the initial stage of growth, adjacent to the substrate, consist of the CsCl-type metastable phase and have considerable thickness d_m of about 1 μm for PbSe films grown on KCl substrates and of about 3 μm for the films grown on BaF₂ substrates. Thus we are able to investigate the optical properties of the CsCl-type metastable phase at different temperatures without applying hydrostatic pressure. From these investigations the energy gap and its temperature coefficient in the CsCl-type metastable phase, representing a new material, can be obtained. The aim of the work is (i) to determine the energy gaps and the energy-gap temperature coefficients of the CsCl-type metastable phases of PbSe and PbSe doped with 2 mol% Cd and (ii) to obtain the energy profiles of the films, representing heterophase junctions, a new type of semiconductor structure. On the other hand the optical investigations confirm by other means the presence of the metastable phases in the films and their heterophase junction nature.

2. Experimental details

The films under investigation are characterized in part I and the data on them are given in tables 1 and 2, part I.

The interference transmittance T and reflectance R spectra are measured at different temperatures between 80 K and 320 K in the range from 400 to 4000 cm⁻¹ using a UR-20 double-beam spectrometer. Three spectra are shown in figure 5, part I.

From the interference spectra the dispersions of the refractive indexes $n(E)$ are calculated in order to determine the energy gap of the metastable phase and to obtain the films energy profiles. In the case of thick films ($d > 2.5 \mu\text{m}$) the energy dependence of

the refractive index $n(E)$ is calculated from the minima and the maxima in the transmittance spectra. The energy dependence of the refractive index $n(E)$ in the thin films is determined from the reflectance R and transmittance T spectra, by solving numerically the equations for the dependences of T and R on the real and imaginary parts, n and k , of the refractive index, respectively, the wavelength of light, the film thickness d , the substrate thickness and its refractive index, using the method described by Nilsson [1]. In both methods of calculation of $n(E)$ we assume a one-layer model. Our calculations based on the assumption of a two-layer model [2] have shown that the calculations of $n(E)$ assuming a one-layer model give correct values for the energies of the transitions taking place in a given film. The values of the refractive index when the different phase quantities are comparable are the ones that are inaccurate. Thus, to determine the transition energies in a film it is enough to find the $n(E)$ dependence assuming a one-layer model. The complicated procedure of fitting the experimental T and R spectra to the calculated spectra on the basis of a two-layer model can be avoided.

The energy dependence of the refractive index $n(E)$ is determined for a number of PbSe and PbSe:Cd samples with various thicknesses deposited on different substrates. Typical $n(E)$ dependences of PbSe films (K170S, K189S, K20S*) at 320 K with different thicknesses are shown in figure 1. From figure 1 it is seen that in the thicker films (K20S*) the maximum in $n(E)$ at 320 K is at 0.29 eV, which corresponds to the direct energy gap of the FCC PbSe phase [3]. The maximum value of the refractive index is $n_{\infty} = 4.9$, in good agreement with the results of Zemel *et al* [3]. With decreasing thickness the behaviour of the refractive index changes and in the thinnest film (K170S) the absolute maximum in $n(E)$ is already at 0.19 eV, where $n \simeq 6.0$. The maxima in the $n(E)$ dependence additional to the one of the FCC phase, which are hardly seen in the dispersion of the refractive index of the thicker films, become clearly resolved in the thinner ones. Apart from the peaks at 0.29 eV and 0.19 eV, which appear at the same energy position in all samples, maxima whose energies change from sample to sample are seen. In the $n(E)$ dependence of sample K170S, for example, they are at 0.07, 0.12, 0.22 and 0.41 eV, while in the one of sample K189S, they are at 0.06, 0.14 and 0.24 eV (see figure 1).

To follow the temperature behaviour of the energy gaps in the two phases the dependences $n(E)$ are obtained from the transmittance spectra, taken at different temperatures between 8K and 320 K. In figure 2 the $n(E)$ dependences of a PbSe film (K172S) at 320 K and 80 K are compared. Apart from the maximum at 0.19 eV in the $n(E)$ dependence at 80 K, which corresponds to the PbSe FCC phase band-to-band transitions [3], another two maxima are seen.

Typical dispersions of the refractive indexes $n(E)$ of PbSe:Cd films (K2C73S, B2C61S, K2C21S) with different thicknesses are shown in figure 3. In figure 4 are shown the $n(E)$ dependences of a PbSe:Cd film (K2C22S) at 320 K, 190 K and 80 K. In the case of the thicker PbSe:Cd films the absolute maximum of the refractive index is at 0.34 eV at 320 K, which corresponds to the direct energy gap of the FCC phase of $\text{Pb}_{0.98}\text{Cd}_{0.02}\text{Se}$ [4,5]. The maximum value $n_{\infty} = 4.6$ of the refractive index is in good agreement with previous results [4]. At 320 K, as well as the maximum at 0.34 eV, another one, at 0.24 eV, which remains unchanged in all samples, is clearly resolved not only in the thin samples but also in the thicker ones. In the dispersions of the refractive indexes maxima that change their positions in the different films also appear. In the $n(E)$ dependence of sample B2C61S, for instance, they are at 0.14 eV and 0.42 eV, while in sample K2C22S at 320 K an additional maximum appears at 0.17 eV (see figures 3 and 4).

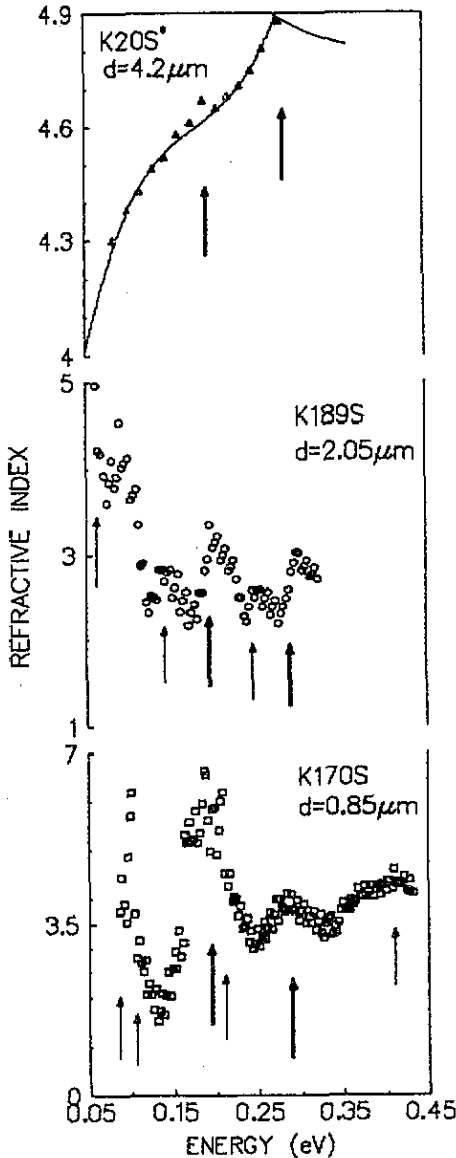


Figure 1. The dispersion of the refractive index of PbSe films with different thicknesses at 320 K. The bold arrows indicate the interband transitions at 0.29 eV in the stable FCC phase and at 0.19 eV in the metastable CsCl-type phase. The fine arrows indicate the transitions across the heterophase junctions: $E_p^{\text{CsCl}} - E_p^{\text{FCC}} = 0.12$ eV and 0.14 eV, $E_n^{\text{CsCl}} - E_n^{\text{FCC}} = 0.22$ eV and 0.24 eV, for samples K170S and K189S, respectively; the transition $E_p^{\text{CsCl}} - E_n^{\text{FCC}} = 0.41$ eV is seen only in sample K170S. The dispersion of the refractive index of sample K20S* calculated from the transmittance spectrum at 320 K is compared to that calculated according to equation (1) with $E_g = 0.29$ eV (full curve).

3. Discussion

In the earliest investigations, as already mentioned, the energy gap of the FCC PbSe was determined to be 0.29 eV at 320 K and 0.19 eV at 80 K from the maximum value of the refractive index [3]. The energy gap of FCC PbSe doped with 2 mol% Cd was determined to be 0.35 ± 0.01 eV at 320 K and 0.27 ± 0.01 eV at 80 K [4,5]. Hence the maxima at 0.29 eV (undoped PbSe films, figures 1 and 2) and 0.34 eV (PbSe: Cd films, figures 3 and 4) that appear in the experimental $n(E)$ dependences at 320 K correspond to the direct interband transitions at the L point of the Brillouin zone of the stable FCC phase. In the thicker PbSe and PbSe: Cd films, where the FCC phase prevails the maximum value of the refractive index is $n_\infty = 4.9$ and 4.6, respectively, in good coincidence with the values

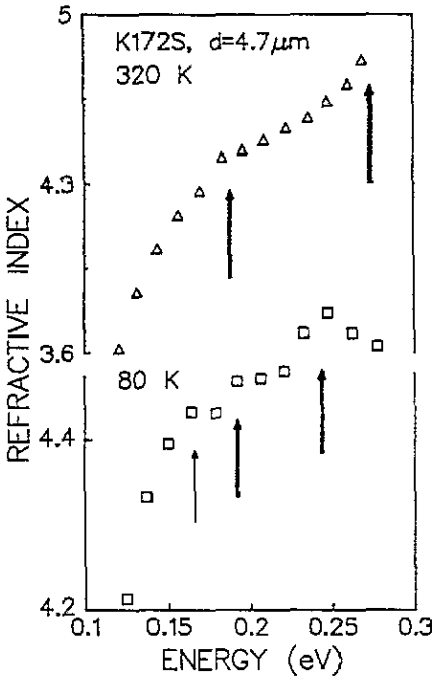


Figure 2. The dispersion of the refractive index of an undoped PbSe film (K172S) at 320 K and 80 K. The bold arrows indicate the interband transitions in the FCC phase—0.29 eV at 320 K and 0.19 eV at 80 K—and in the CsCl-type phase—0.19 eV at 320 K and 0.24 eV at 80 K. The fine arrow in the dispersion of the refractive index at 80 K indicates the transition $E_p^{\text{FCC}} - E_n^{\text{CsCl}} = 0.16$ eV.

reported in the literature [3, 4].

The refractive index energy dependence according to the classical dispersion theory can be written in the form:

$$n(E) = 1 + \frac{E_p^2(E_g - E)}{2E_g[(E_g - E)^2 + \gamma^2]} + \sqrt{1 + \frac{E_p^2}{E_g^2} \left(1 + \frac{E^2}{E_g^2}\right)} \quad (1)$$

where E_g is the energy gap, $E_p = \hbar\omega_p$, where $\omega_p^2 = 4\pi Ne/\epsilon_\infty m_\sigma$ is the plasma frequency, N is the carrier concentration, m_σ is the susceptibility effective mass, e is the electron charge and ϵ_∞ is the optical dielectric constant. In figures 1 and 3 the dispersions of n in the thicker films (K20S* and K2C21S) calculated from the interference spectra are compared to those calculated according to equation (1) with $E_g = 0.29$ eV at 320 K for the FCC PbSe phase, $E_g = 0.34$ eV at 320 K for PbSe: Cd and the corresponding carrier concentrations N (see table 1, part I). As is seen from this comparison the dispersion of the refractive index in these thicker films, in general, follows the dependence given by equation (1). In the case of the thinner films it evidently differs to a great extent. The lower values of the refractive index in the thinner films may be accounted for by the fact that these films contain comparable quantities of CsCl-type and FCC phases but nevertheless the peak at 0.29 eV (0.34 eV for PbSe: Cd) remains clearly resolved. Apart from this peak, which corresponds to the energy gap of the FCC phase, additional peaks are seen in $n(E)$ of all samples. As stems from the Kramers–Kronig dispersion relation, a maximum in the dispersion of the refractive index $n(E)$ corresponds to a sharp increase of the absorption coefficient. Then the maxima in $n(E)$ have to be attributed to the band-to-band CsCl-type phase transition as well as to transitions across the heterophase junction between the CsCl-type and FCC phases. At room temperature the highest value of the refractive index is at 0.19 eV in the thinner undoped films and at 0.24 eV in the doped films and we assign this peak to direct

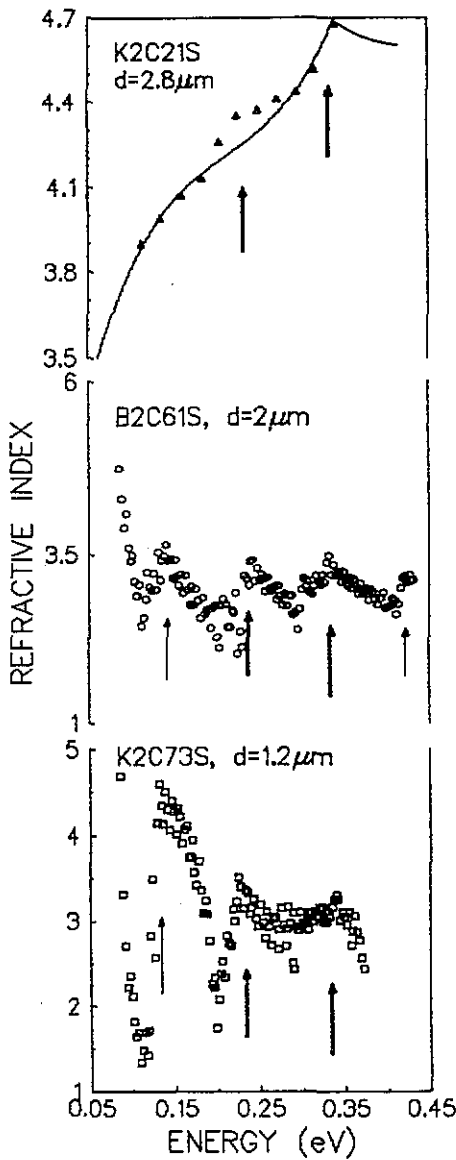


Figure 3. The dispersion of the refractive index of PbSe:Cd films with different thicknesses at 320 K. The bold arrows indicate the interband transitions at 0.34 eV in the stable FCC phase and at 0.24 eV in the metastable CsCl-type phase. The fine arrows indicate the transitions across the heterophase junctions: $E_p^{\text{CsCl}} - E_p^{\text{FCC}} = 0.13$ eV and 0.14 eV, for samples K2C73S and B2C61S, respectively, and the transition $E_p^{\text{CsCl}} - E_n^{\text{FCC}} = 0.42$ eV in sample B2C61S. The dispersion of the refractive index of sample K2C21S calculated from the transmittance spectrum at 320 K is compared to that calculated according to equation (1) with $E_g = 0.34$ eV (full curve).

band-to-band energy transitions in the CsCl-type phase. Apart from the peak at 0.29 eV (0.34 eV in PbSe:Cd) the peak at 0.19 eV (0.24 eV in PbSe:Cd) is the only one whose energy position remains unchanged in the $n(E)$ dependences of all samples. The energies of the other additional maxima change from one sample to another, which is only possible if they are due to junction transitions, whose energies depend on the Fermi level position which is different in the different samples. The energy profiles of an undoped PbSe sample K170S and a doped one K2C22S at 320 K are given in figures 5(a) and 6(a), respectively. In the figures, E_p^{CsCl} and E_n^{CsCl} are the energies of the valence band top and the conduction band bottom of the CsCl-type phase and E_p^{FCC} and E_n^{FCC} are the corresponding values for the FCC phase. As it is seen from figures 1 and 5(a) for undoped PbSe (figures 4 and 6(a) for PbSe:Cd) the peak in $n(E)$ at 0.12 eV (0.07 eV) corresponds to the transition E_p^{CsCl}

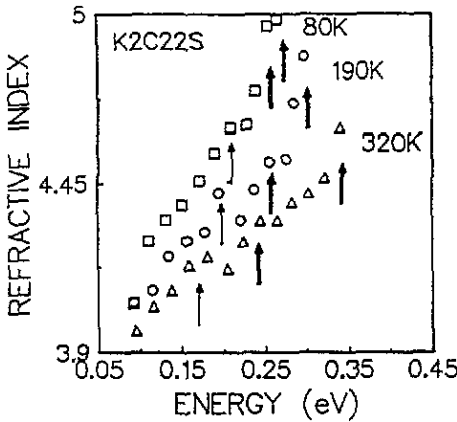


Figure 4. The dispersion of the refractive index of a doped PbSe: Cd film (K2C22S) at 320 K, 190 K and 80 K. The bold arrows indicate the interband transitions in the FCC phase—0.34 eV at 320 K, 0.30 eV at 190 K and 0.27 eV at 80 K and in the CsCl-type phase—0.24 eV at 320 K, 0.26 eV at 190 K and 0.28 eV at 80 K. The fine arrows indicate the transition $E_p^{FCC} - E_n^{CsCl} = 0.17$ eV at 320 K, 0.19 eV at 190 K and 0.20 eV at 80 K.

→ E_p^{FCC} , that at 0.41 eV (0.41 eV) to the transition $E_p^{CsCl} \rightarrow E_n^{FCC}$, and that at 0.22 eV (0.17 eV) to the $E_n^{CsCl} \rightarrow E_p^{FCC}$ transition. The heterophase junction transition energies change from sample to sample, indicating different carrier concentrations and as a result different Fermi level positions.

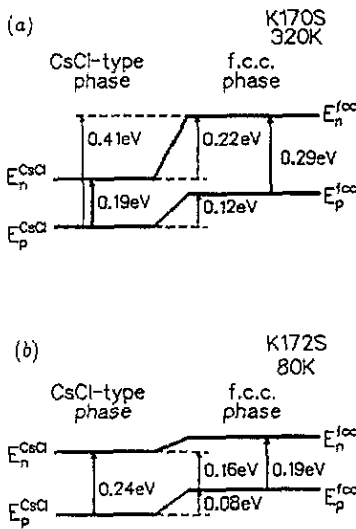


Figure 5. Schematic diagram of the energy profile of undoped PbSe films: (a) sample K170S at 320 K; (b) sample K172S at 80 K.

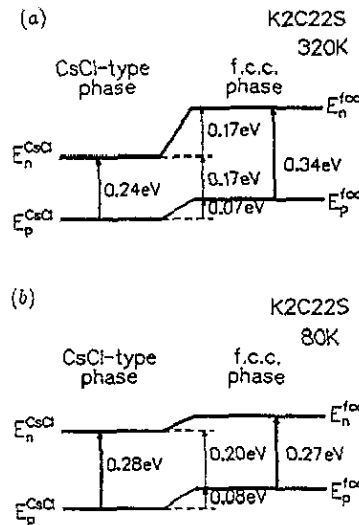


Figure 6. Schematic diagram of the energy profile of a PbSe film doped with 2 mol% Cd (K2C22S) at (a) 320 K and (b) 80 K.

The dispersions of the refractive index are obtained at different temperatures. In figure 2 $n(E)$ dependences of an undoped PbSe sample (K172S) at 320 K and 80 K are shown. It is known that the direct energy gap of the FCC PbSe is at 0.19 eV at 80 K [3]. The refractive index continues to increase at higher energies forming a clearly resolved maximum at 0.24 eV. It is reasonable to assign this to the direct energy gap of the CsCl-type phase at 80 K. The energy profile of sample K172S at 80 K is given in figure 5(b). The energy

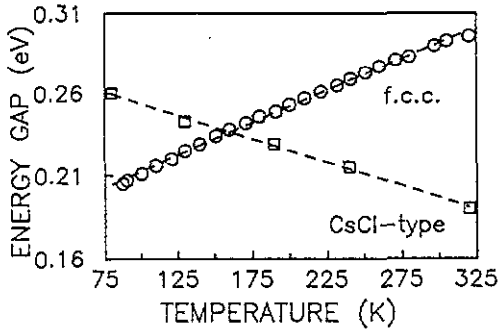


Figure 7. The temperature dependence of the energy gap of PbSe stable FCC [6] and metastable CsCl-type phases.

of the heterophase junction transition $E_p^{\text{FCC}} \rightarrow E_n^{\text{CsCl}}$ in this sample, as follows from the dependence $n(E)$ (figure 2) is at 0.16 eV.

The energy gap of the metastable PbSe phase is determined at different temperatures in the interval from 80 K to 320 K. In figure 7 the temperature dependence of the energy gap of the metastable phase is compared to that of the stable PbSe FCC phase [6]. It is seen that the energy gap of the metastable CsCl-type phase has an opposite temperature behaviour to that of the stable FCC phase. The energy gap of the CsCl-type phase varies from 0.19 eV at 320 K to 0.24 eV at 80 K with a negative temperature coefficient $dE_g^{\text{CsCl}}/dT = -2 \times 10^{-4} \text{ eV K}^{-1}$ opposite to the positive $dE_g^{\text{FCC}}/dT = 4 \times 10^{-4} \text{ eV K}^{-1}$ one of the stable FCC phase.

The analysis of the dependence $n(E)$ of the doped samples at different temperatures, three of which—at 320 K, 190 K and 80 K—are shown in figure 4 (sample K2C22S), gives the following results. The PbSe: Cd metastable CsCl-type-phase energy gap temperature coefficient is also negative and its value is lower than that of the undoped material: $dE_g^{\text{CsCl}}/dT = -1.7 \times 10^{-4} \text{ eV K}^{-1}$. The temperature coefficient of the stable FCC phase energy gap of the doped material also is lower than that of the undoped material; for PbSe: Cd $dE_g^{\text{FCC}}/dT = 2.9 \times 10^{-4} \text{ eV K}^{-1}$ against $dE_g^{\text{FCC}}/dT = 4 \times 10^{-4} \text{ eV K}^{-1}$ for PbSe.

In our recent investigations of the metastable phases of PbTe [2] we have obtained the following values for the PbTe CsCl-type phase: the energy gap $E_g^{\text{CsCl}} = 0.23 \text{ eV}$ at 320 K and the energy gap temperature coefficient $dE_g^{\text{CsCl}}/dT = -2.9 \times 10^{-4} \text{ eV K}^{-1}$. As can be expected the CsCl-type-phase energy gap of PbSe is smaller than that of PbTe (0.19 eV against 0.23 eV) analogous to the stable FCC phases (0.29 eV against 0.32 eV). The energy-gap temperature coefficients of both PbSe and PbTe CsCl-type metastable phases are negative ($dE_g^{\text{CsCl}}/dT = -2 \times 10^{-4} \text{ eV K}^{-1}$ and $dE_g^{\text{CsCl}}/dT = -2.9 \times 10^{-4} \text{ eV K}^{-1}$).

4. Conclusion

The growth of PbSe films and sublayers with the metastable CsCl-type phase enabled us to study the optical properties of this pressure-induced phase without applying any hydrostatic pressure. (i) The value of the CsCl-type-phase energy gap is determined to be $E_g = 0.19 \text{ eV}$ at 320 K with temperature coefficient $dE_g^{\text{CsCl}}/dT = -2 \times 10^{-4} \text{ eV K}^{-1}$. The energy gap of the PbSe CsCl-type phase is smaller than that of the FCC phase and its temperature coefficient is of opposite sign, as in the case of PbTe. (ii) The influence of the doping on the energy gap of the metastable phase is the same as that on the energy gap of the

stable phase. The doping of PbSe with 2 mol% Cd leads to a significant broadening of the metastable CsCl-type-phase energy gap—from 0.19 eV (320 K) for PbSe to 0.24 eV (320 K) for PbSe doped with 2 mol% Cd. For the stable phase this change is from 0.29 eV to 0.34 eV at 320 K.

Acknowledgment

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