

Band offsets in Eu-containing lead chalcogenides and lead chalcogenide superlattices from spectroscopic data

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Abstract. The results of an experimental study of the optical and photoelectrical properties of Eu-containing lead chalcogenides and superlattices are presented. From both sets of experiments band offset data for the lead chalcogenide–europium chalcogenide heterojunction are derived. The results are compared with the data obtained from a linear interpolation of the band structures between those of the binaries.

1. Introduction

Lead chalcogenide mixed crystals containing europium have found applications as confinement layers and active layers in diode lasers and as barriers in quantum well structures. For these applications one needs knowledge of the band-offsets between the binary lead chalcogenides PbS or PbSe (which are direct narrow-gap semiconductors) and the mixed crystals $Pb_{1-x}Eu_xS$ and $Pb_{1-x}Eu_xSe$ as well as between the binary lead salts and the binary europium chalcogenides EuS and EuSe (which are indirect materials). It is the aim of this paper to combine estimates of the band offsets obtained from experiments with mixed crystals ($Pb_{1-x}Eu_xSe$ and $Pb_{1-x}Eu_xS$) with results obtained from superlattices built up by the relevant binaries. These experimental data are compared with estimations derived from a linear interpolation of band structure between the binaries.

There exist a number of unsolved questions:

(i) Can we use the band created by the 4f levels of the europium as energetic reference for the prediction of band offsets in heterojunctions as Langer and Heinrich [1] proposed with respect to deep-level impurities (especially 3d levels of transition metal substitutional impurities such as Ti, Cr, Fe, Co, Ni, Cu)? In the light of the theoretical arguments for the Langer and Heinrich proposal given by Tersoff and Harrison [2] this question seems to be a very interesting one.

(ii) Will the extrapolation of the band structure of the

mixed crystals (with small Eu content) to EuSe and EuS deliver band offsets which fit the data obtained from spectroscopic measurements for superlattices?

2. Band structure interpolation

In order to get an idea of the band structure of $Pb_{1-x}Eu_xS$ and $Pb_{1-x}Eu_xSe$ we made a linear interpolation of published theoretical band structures of the binaries [3–5] for the relevant points within the first Brillouin zone (BZ). The result of this procedure is plotted in figure 1. The position of the 4f levels at the L point of the BZ was chosen as zero in both the europium salts and the lead salts with small europium content. (A justification for this assumption for the L point given in [6] where the extrapolation of the level positions meets the valence band edge.) Further, we assume that the position of these levels does not depend on the composition of the mixed crystal. From this picture we determined the composition dependences of the energy gap, the conduction band edge and the valence band edge by assuming that states at L define both bands in the whole region where the mixed-crystal system was investigated ($0 < x < 0.1$). These data are printed in table 1 in bold (first row).

Applying this simple model we would expect the position of the valence band formed by the partially filled 4f levels of europium to be close to the valence band formed by the anion (S, Se); compare the gradients quoted in table 1.

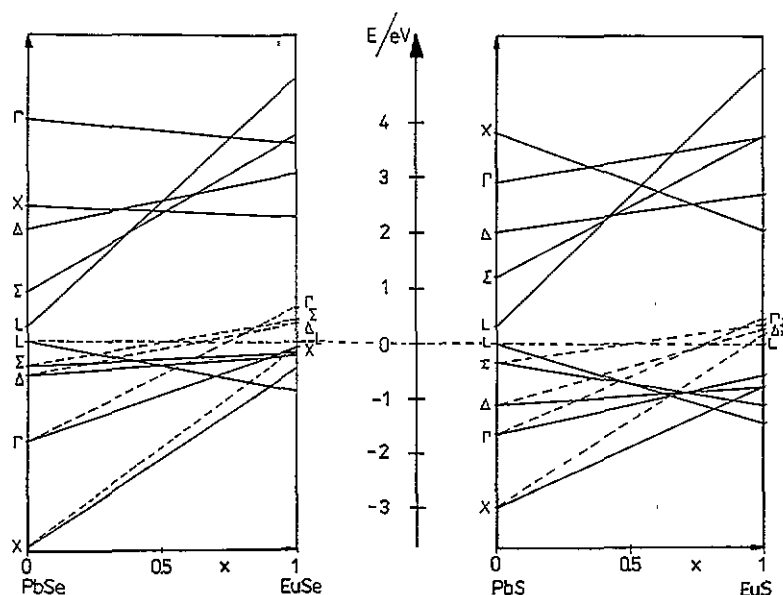


Figure 1. Linear interpolation of the band structures of PbSe [4] and EuSe [3] (left) as well as PbS [5] and EuS [3] (right). Full lines denote valence and conduction bands at different points of the kz . The broken line denotes the position of the valence band created by the partially filled 4f levels of europium.

Table 1. Band structure parameters of Eu-containing mixed-crystal systems estimated from the linear extrapolation of band structures calculated for the edge components PbS [5], PbSe [4], EuS [3] and EuSe [3] (see figure 1 also). Bold numbers are estimated from figure 1 for L-like bands whereas the other data are determined by our experiments ($T = 10$ K).

	(Pb, Eu)Se	(Pb, Eu)S
dE_g/dx (eV)	5.7	6.4
	4.1	5.9
	4.0	
dE_c/dx (eV)	4.8	5.0
	1.8	
	2.0	
$-dE_v/dx$ (eV)	0.9	1.4
	2.3	
	2.0	

3. Experiment

The samples investigated during this study were deposited by molecular beam epitaxy (MBE) or by a modified hot-wall apparatus. Substrates cleaved from (111)-oriented BaF_2 crystals were used.

(i) Two sets of $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ ($0 < x < 0.2$) samples grown with different MBE apparatus were investigated. A detailed description of sample preparation was given in [7]; the electrical and optical properties were published in [8].

(ii) $\text{Pb}_{1-x}\text{Eu}_x\text{S}$ ($0 < x < 0.01$) samples were grown by hot-wall molecular epitaxy as described in [9].

(iii) PbS-EuS and PbS-PbSe superlattices were deposited in a modified hot-wall system at a pressure of about 10^{-5} – 10^{-4} Pa [10]. The superlattices investigated in this study consist of ten layers of each component.

All samples were investigated by infrared photoluminescence (PL) and exhibited an efficient luminescence behaviour inclusive of the transition to stimulated emission at high excitation levels. A more detailed description of this technique with reference to $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ is given in [8]. Furthermore, steady-state photoconductivity (PC) and transient PC after picosecond excitation were measured from liquid-helium temperature up to room temperature. Details of these experiments were published in [6].

4. Results and discussion

The mixed crystals (sulphides and selenides) were investigated by PL, PC and transmittance. With increasing Eu contents we observed:

- (i) decreasing luminescence efficiencies;
- (ii) a softening of the interband edge (increasing Urbach parameter); and
- (iii) an increasing small signal PC lifetime.

It was possible to find an $E_g(x)$ dependence which fits the experimental data obtained by the different methods mentioned in a unique manner. The slopes dE_g/dx are given in table 1 as experimental data (second row). From the tailing in the PC spectra we estimated the position of the band generated by the 4f levels. By assuming that this band has an x -independent distance to the vacuum level or the character of a reference level as introduced by [2] we were able to split dE_g/dx into contributions

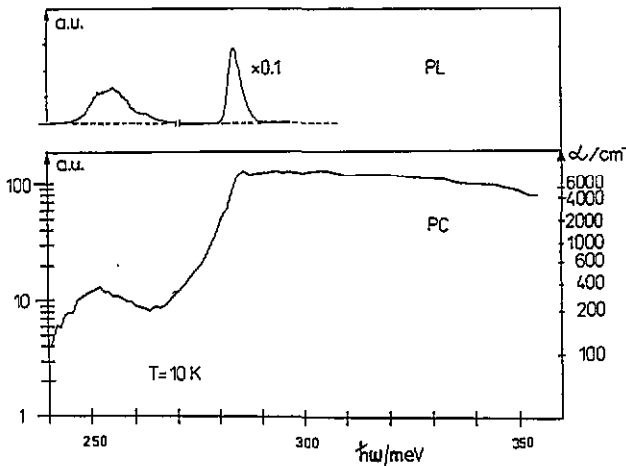


Figure 2. Photoluminescence (top) and photocurrent spectra (bottom) from a $\text{Pb}_{0.955}\text{Eu}_{0.045}\text{Se}$ mixed-crystal sample at $T = 10\text{ K}$. The right absorption coefficient scale was determined by using the lifetime obtained by transient photoconductivity. The gap of this sample was determined at about 280 meV (transmittance, luminescence).

from the valence band and the conduction band (as done below).

After proposing this model for the band structure of the mixed-crystal systems for small Eu contents we repeated all measurements on a second set of $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ samples grown with an improved MBE apparatus with reduced rest gas pressure. In these samples we observed for the first time separate band-like levels within the forbidden gap producing absorption coefficients of several 100 cm^{-1} . Figure 2 displays typical PL and PC curves.

The absorption coefficient scale was determined from transient PC data obtained with selective excitation. Employing the spectra from the second set of $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ samples we repeated our determination of the slopes (see third row in table 1). If these slopes are extrapolated to $x = 1$ (this is a rather risky estimate since it neglects bowing) one finds the conduction band edge at L closer to the conduction band minimum at X than expected from figure 1 and it follows

$$E_{cL}(\text{EuSe}) - E_{vL}(\text{EuSe}) = E_{cL}(\text{PbSe}) - E_{vL}(\text{PbSe}) + 4\text{ eV}. \quad (1)$$

As an independent approach to the determination of the band offsets we investigated luminescence spectra from PbS–EuS superlattices. In figures 3 and 4 PL spectra from two samples with different superlattice periods are given. The spectra are attributed to transitions between PbS well states. The arrows mark the calculated energetical positions for the onset of the *allowed optical transitions* ($\Delta n = 0$, equal subband numbers) assuming a conduction band offset of

$$\Delta E_c = E_g(\text{EuS}) - E_g(\text{PbS}) \quad (2)$$

and a valence band offset $\Delta E_v = 0$.

The subband energies were calculated by solving the

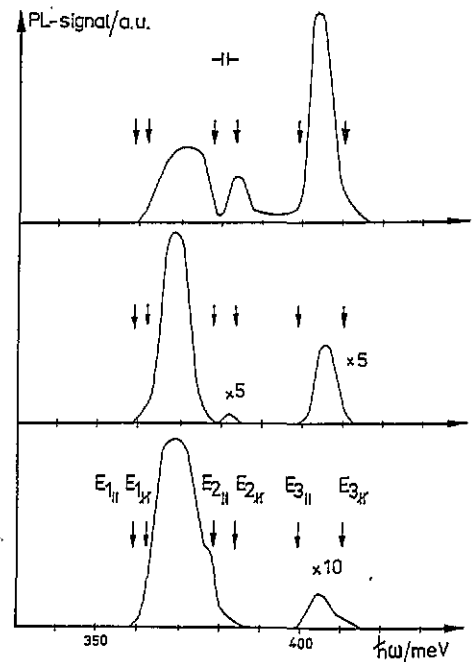


Figure 3. Photoluminescence spectra from a PbS–EuS superlattice with 50 nm period (25 nm PbS/25 nm EuS) at $T = 80\text{ K}$. The excitation densities are 20 kW cm^{-2} , 70 kW cm^{-2} and 200 kW cm^{-2} (from the bottom to the top). The arrows mark the positions calculated for the onset of transitions between well states.

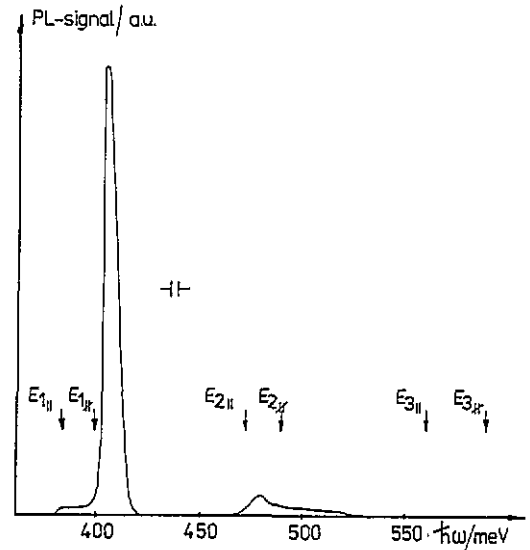


Figure 4. Photoluminescence spectrum from a PbS–EuS superlattice with 14 nm period (7 nm PbS/7 nm EuS) at $T = 80\text{ K}$. The excitation density is 70 kW cm^{-2} . The arrows mark the positions calculated for the onset of transitions between well states.

eigenvalue equation with a Kronig–Penney potential. For the band edge masses m_0 of PbS we took

$$m_{0||} = m_{0l} \quad (3)$$

$$m_{0X} = 9 * (1/m_1 + 8/m_2) \quad (4)$$

The subscripts ‘||’ (parallel) and ‘X’ (antiparallel) refer to both valley groups in the BZ which have to be

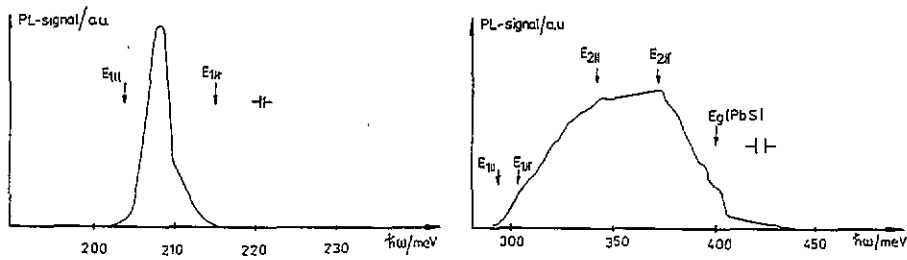


Figure 5. Photoluminescence spectra for a PbSe–PbS superlattice with 27 nm period (13 nm PbSe/14 nm PbS) at $T = 80$ K (left) and $T = 260$ K (right). The excitation density is about 20 kW cm^{-2} . The arrows mark the positions calculated for the onset of transitions between well states.

distinguished for (111)-oriented samples ($l =$ longitudinal, $t =$ transverse). The energy dependence of m according to the Kane band structure was used; all parameters were taken from [11]. For the assessment it is necessary to have observed the transition between higher n subbands. For the strain-induced gap shift (partially relaxed built-in and thermally induced strain) we took the empirical value $\Delta E_g = +30 \text{ meV}$ (from experiments with single layers of comparable thickness).

The good agreement between the arrows and the onset of PL lines as visible in figures 3 and 4 indicates that a vanishing valence band offset produces a reasonable fit. That means that the $4f$ levels of Eu at Γ actually define the valence band edge of the EuSe, and that their distance to the vacuum level is similar to that of the $4p$ levels of the PbSe defining the valence band edge. Aside from the mixed-crystal analysis this is a second hint that the valence band edge of the europium chalcogenides should be lower than expected from figure 1 by 0.5–1 eV.

For the independent determination of the band offset between the binary lead salts PbS and PbSe the PL spectra of this kind of superlattice were investigated. Figure 5 displays spectra at different temperatures. The fit (as described above) confirms the data (valence band offset 90 meV) obtained by [12].

5. Conclusions

The valence band offset between PbSe and EuSe as well as between PbS and EuS was determined near to zero by considering the valence band of the lead salt and the valence band formed by the $4f$ levels of the europium. Therefore the PbS–EuS superlattice is a particular type-I lattice.

We have reason to assume that with increasing Eu content the band formed by the $4f$ levels of the Eu moves faster and more towards midgap (between the conduction band and the p-level valence band) than expected from the linear interpolation of the band structures of the binaries following the theoretical computations by [3–5].

Further investigations by other methods are needed in order to prove our hypothesis.

Acknowledgments

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