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Inversion of conduction levels in $PbSe_{1-x}Te_x$ compounds

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The photovoltaic effect on p-n junctions, made with ternary compounds $PbSe_{1-x}Te_x$, has been used to measure the gap of these alloys, as a function of the temperature. The gap as a function of x exhibits a curvature towards high energies. This particular behavior of the gap supports the model of the inversion of $L_6^-(L_3^-)$ level (conduction band of PbTe) and of the $L_6^-(L_2^-)$ level (conduction band of PbSe), according to the results of some band-structure calculations for PbSe and PbTe. A simple theoretical model is proposed to take into account the effect of this inversion. This model reproduces the observed variation of the gap as a function of composition.

I. INTRODUCTION

Whereas mixed compounds based on lead and tin chalcogenides have been extensively studied, very little work has been reported on the $PbSe_{1-x}Te_x$ compounds. However a controversy on the relative band ordering around the optical gap in PbSe and PbTe has developed recently.[1,2] The conclusion was that further experimental investigation was necessary to clarify this subject. The most obvious information needed is that of the gap of these compounds and the purpose of this paper is to bring information about it. The three members of the family PbS, PbSe, PbTe exhibit very similar physical properties. Restricting ourselves to optical properties near the fundamental-absorption-edge energy, we can say that these compounds have a small direct gap at the L point of the Brillouin zone, positive temperature coefficient of the gap ($\simeq 4.4\times10^{-4}$ eV/°K), and a negative pressure coefficient of the gap ($\simeq -8\times10^{-6}$ eV/bar). However if the gap decreases from PbS to PbSe, it increases from PbSe to PbTe. Furthermore the effective-mass anisotropy of the order of 2 for PbS and PbSe increases up to 10 for PbTe.[3] Also the discontinuity of the refractive index near the absorption edge is significantly larger for PbTe than for the two other compounds.[4,5] Then it is clear that a difference in the position of the bands around the L point should exist between PbSe and PbTe. Some band-structure calculations[6,7] have tried to explain these anomalies with an inversion of two conduction levels in the neighborhood of the L point. The model suggested for this inversion is reproduced Fig. 1: the L_2^- and L_3^- levels would be reversed in both salts so that the L_6^- level of the first conduction band would originate from L_2^- in PbSe and L_3^- in PbTe. With this scheme it is possible to explain the anomalies reported above.[7] However Glosser *et al.*[1] have cast some doubt on

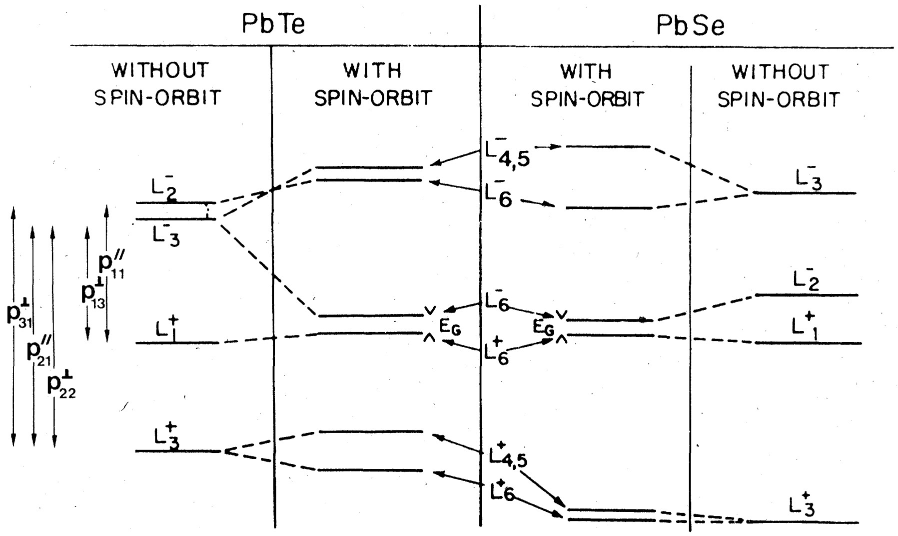

FIG. 1. Band ordering around the L point, proposed for PbTe and PbSe in Ref. 2. The nonzero matrix elements of the momentum are schematically drawn using the notations of Ref. 8.

this scheme claiming that they have not been able to see the optical transition, allowed by selection rules, between the valence L_6^+ level and the upper L_6^- level in PbTe.

We shall develop a model for the band inversion in the compounds $PbSe_{1-x}Te_x$ in Sec. II and obtain the calculated variation of the gap as a function of x. We discuss in Sec. III the procedure of growing and characterization of our samples. Experimental results and comparison with theory are given in Sec. IV. Section V is devoted to the discussion of the results.

II. LOCAL MODEL FOR THE INVERSION OF CONDUCTION LEVELS

As it has already been shown,[8] a six-band model around the L point of the Brillouin zone, is necessary to explain and reproduce the values of the effective masses in these salts. We shall consider three conduction levels to fix our model. These three levels originated from two levels L_2^- and L_3^- in the scheme without spin-orbit interaction (Fig. 1). These two levels have p character around the lead cation, and s and d character around the Se or Te anion. Table I contains a quantitative decomposition in s, p, d character of the levels around the L point for the upper valence band and the first three conduction bands. These values have been computed using the band structure calculations of Ref. 2. The spin-orbit splitting is mainly due to the lead, and then can be assumed as a constant for all compounds (except a slight correction due to the variation of the volume of the unit cell). So we are lead to assume a model for the band crossing in absence of the spin-orbit interaction and then diagonalize the Hamiltonian with the spin-orbit interaction. We use the procedure and notation given by Mitchell and Wallis.[9] For each compound the Hamiltonian matrix has the form shown on Table II. The zero in energy in the Hamiltonian for the set of levels is taken at the position of the L_3^- level neglecting spin-orbit coupling. Then ϵ_0 is the position of the L_2^- level with respect to the L_3^- level. Δ_1 characterizes the spin-orbit splitting of the L_3^- level and $\sqrt{2}\,\Delta_2$ the mixing strength between the $L_6^-(L_3^-)$ and $L_6^-(L_2^-)$ levels. Solving the secular equation, we get three solutions for the energies, each of them being twofold degenerate due to the time-reversal and space-inversion symmetries.

TABLE I. Calculated fractional charges at L point (in percent) inside touching spheres around anions and cations in terms of $l=0,1,2$ atomic angular functions, for the upper valence band and the first three conduction bands of PbSe and PbTe.

		Around Pb			Around Te or Se		
		s	p	d	s	p	d
PbTe	$L_6^+(L_1^+)$	61	0	3	0	36	0
	$L_6^-(L_3^-)$	0	82	0	4	0	14
	$L_6^-(L_2^-)$	0	70	0	13	0	17
	L_{45}^-	0	75	0	0	0	25
PbSe	$L_6^+(L_1^+)$	74	0	2	0	24	0
	$L_6^-(L_2^-)$	0	72	0	13	0	14
	$L_6^-(L_3^-)$	0	72	0	6	0	22
	L_{45}^-	0	74	0	0	0	26

TABLE II. Matrix elements of the Hamiltonian including spin orbit are given for the L point.

	$L_6^-(L_2^-)$	$L_6^-(L_2^-)$	$L_6^-(L_3^-)$	$L_6^-(L_3^-)$	L_4^-	L_5^-
$L_6^-(L_2^-)$	ϵ_0	0	0	$-\sqrt{2}\Delta_2$	0	0
$L_6^-(L_2^-)$	0	ϵ_0	$\sqrt{2}\Delta_2$	0	0	0
$L_6^-(L_3^-)$	0	$\sqrt{2}\Delta_2$	$-\Delta_1$	0	0	0
$L_6^-(L_3^-)$	$-\sqrt{2}\Delta_2$	0	0	$-\Delta_1$	0	0
L_4^-	0	0	0	0	Δ_1	0
L_5^-	0	0	0	0	0	Δ_1

The L_4^- and L_5^- levels have an energy $\epsilon_3 = \Delta_1$ and the two L_6^- levels are located at

$$\epsilon_{1,2} = \tfrac{1}{2}(\epsilon_0 - \Delta_1) \pm \left| (\epsilon_0 + \Delta_1)/\cos 2\theta \right| \; . \tag{1}$$

The angle θ characterizes the mixing of the levels and is defined as

$$\tan 2\theta = 2\sqrt{2}\,\Delta_2/(\epsilon_0 + \Delta_1) \; . \tag{2}$$

We use the results of the band-structure calculations[2] for defining all parameters for PbTe and PbSe. They are given in Table III where the energies noted as E are now given with the zero at the top of the valence band L_6^+. The simplest approximation is to assume a linear behavior of L_2^- and L_3^- levels energies as a function of x in the mixed compounds. Δ_1 and $2\sqrt{2}\,\Delta_2$ are also assumed

TABLE III. Parameters used for the model described in the text. All energies are given in eV.

	PbSe	PbTe
$E(L_{4,5}^-) - E(L_3^-) = \Delta_1$	0.573	0.604
$E(L_2^-) - E(L_3^-) = \epsilon_0$	−1.150	0.040
$2\sqrt{2}\,\Delta_2$	1.170	1.489
$\tan 2\theta$	−2.029	2.312
$\cos 2\theta$	0.442	−0.397
$E(L_3^-) - E(L_6^+(L_1^+))$	1.666	1.284
$E(L_2^-) - E(L_6^+(L_1^+))$	0.516	1.324
$E(L_{4,5}^-) - E(L_6^+(L_1^+))$	2.239	1.888
$E(L_6^-(L_3^-)) - E(L_6^+(L_1^+))$	1.457	0.191 (gap)
$E(L_6^-(L_2^-)) - E(L_6^+(L_1^+))$	0.152 (gap)	1.813

to vary linearly as a function of x. For each value of x, the angle θ is then calculated from (2) and energies deduced from (1). As expected the L_{45}^- level keeps its linear behavior, whereas the L_6^- levels repel each other giving an energy gap which exhibits a maximum between the PbSe and PbTe gaps. The results are very similar to those presented in the scale of Fig. 2.

Comparing these results with the experiment presented below, we shall see that the above effect is much less pronounced than the calculated one. We have been lead to assume a bowing in the energy dependence of the levels, keeping the linearity dependence for all other parameters. The introduction of a bowing in the energy dependence of gaps for semiconductor alloys is not unusual. This effect has already been shown experimentally for instance in $\mathrm{GaP}_x\mathrm{As}_{1-x}$ alloys.[10,11] From the theoretical point of view some attempts to explain it have been made. The bowing corresponds to a breakdown of the virtual-crystal approximation, and can be reproduced assuming a chemical disorder in the atomic potentials.[12,13] *A priori*, looking at the character of the wave function at L (Table I) there is no reason to include a bowing for the L_2^- level rather than for the L_3^- level. However from the results of band-structure calculations[6] on the three compounds PbS, PbSe, and PbTe, it appears that among the levels we are interested in, the L_2^- level exhibits the most important anomalous behavior. We tried, then to give a nonlinear variation in energy at this level, keeping the energy dependence of the L_3^- level linear. The results of this new approach are shown on Fig. 2. Using the parameters given in Table III, a less pronounced maximum in the gap dependence as a function of x is found. The variation of the energy of the L_2^- level is given by the relation

$$E(L_2^-)-E(L_6^+)=0.318\,x^2+0.490\,x+0.516\ (\mathrm{eV})\ .$$

The maximum departure of the energy dependence of the L_2^- level from the straight line is of 0.1 eV which is of the order of magnitude of that found for $\mathrm{GaP}_x\mathrm{As}_{1-x}$ alloys.[12]

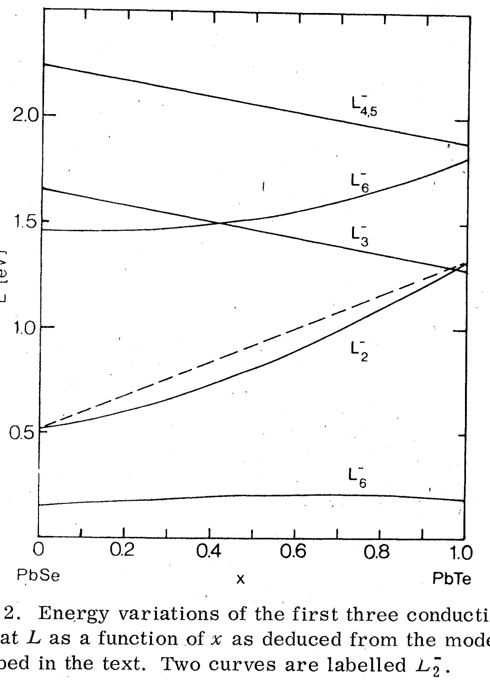

FIG. 2. Energy variations of the first three conduction levels at L as a function of x as deduced from the model described in the text. Two curves are labelled L_2^-. The dashed line represents the linear behavior of the L_2^- level as a function of x.

III. PREPARATION OF SAMPLES AND CHARACTERIZATION

The samples have been grown using a phase vapor transport technique. Starting from purified (6N) elements one gets two syntheses of PbSe and PbTe. We then melt a third synthesis of a mixture of the chosen ternary compound. This mixture is put in a quartz ampoula sealed under a vacuum of 10^{-6} Torr. This ampoula is introduced in a vertical furnace. The temperature profile is a plateau followed by a gradient of the order of 1–2 °C/cm. The temperature of the plateau ranges from 970 °C for PbSe to 910 °C for PbTe. The ampoula is then pulled down at a speed of 0.2 mm per h. Monocrystals with a section of 1 cm^2 and to 1–2 cm length are obtained after four days. Their carrier concentrations are measured by Hall effect and ranges typically from 1 to 5×10^{18} carriers/cm^3. They are obtained n or p type depending on the departure from stoichiometry we chose for the synthesis. Attempts to get samples with the Bridgmann method have been done but the homogeneity in x is very poor with this method, the segregation coefficient being apparently important.

On samples prepared by phase vapor transport we determined the x values by measuring the lattice parameter of the compound. These compounds are solid solutions whose lattice parameter has a linear behavior as a function of x.[14] These indirect measurements give an uncertainty on the x value of ± 0.02. From all measurements we did not find any significant change in x on a plane perpendicular to the growing axis. The relative variation of the value of x along the growing direction, has been found to be of the order of 10% per centimeter.

To determine the gap of these alloys we have been led to measure the photovoltaic effect on p-n structures made with them. We did not try to measure directly the absorption coefficient because we need for that large samples which are difficult to grow homogeneous. Furthermore, it is difficult to deduce the gap with a good precision from absorption coefficient in lead salts due to tail states and Burstein shift effects which induce corrections typically of the order of 30 meV on the measured values.[8] On the other hand the photovoltaic effect can give correct values of gaps to within 2 meV as has been shown.[15] So we prepared diodes to study this effect. These *p*-*n* structures are made by diffusion of Se or Te on *n* substrates, or exodiffusion of lead on *p* substrates with the same method used in Ref. 16. The diffused slabs are cleaved to make diodes of $\simeq 100\times 200\times 500$ μm^3 sizes. Two diodes around the one used for experiment are kept for x-ray measurements giving the x value. The diodes were electrolytically gold covered on the *p*-type side. Good ohmic point contacts on the illuminated *n*-type surfaces were made by the Hg-In alloy solder and gold wire.

IV. EXPERIMENTAL RESULTS

A. Principle of measurements of the gap

At low temperatures, below 150 °K, the photovoltaic spectrum of diodes illuminated perpendicular to the junction plane exhibits two peaks. The interpretation of the spectrum has been done by I. Chambouleyron *et al.*[15] The two parts of the diode far from the junction are degenerated and have an optical gap larger than E_G by at least the Fermi energy. Then all photons the energy of which are closed to E_G are directly absorbed in the transition region, giving electron-hole pairs which are dissociated without any diffusion process. Just above E_G the process has to involve diffusion and becomes less efficient. At low temperatures the efficiency of the radiative recombination is quite important provided the material is of good quality. Far from the junction when a photon with an energy larger than E_G+E_F is absorbed the electron-hole pair can recombine radiatively giving a photon of energy E_G for which the material is transparent until it reaches the transition region. This process which can be efficient only far from the junction gives the second peak of the photovoltaic spectrum. The interesting point is that the extremum of the first peak gives the energy-gap value of the intrinsic material within ± 2 meV which is demonstrated by comparison with all results obtained by other methods.[15]

B. Experimental setup

The experiments have been done using an infrared S. V. Coderg spectrophotometer with a resolution of 0.5 meV. The experiment is done under a vacuum common to the spectrometer and the circulation cryostat used to vary the temperature of the diode. The chopping frequency is of 2400 Hz, and the photovoltaic response is compared to that of a Golay detector.

C. Experimental results

Figure 3 shows typical spectra obtained on a diode with $x=0.42$. The double peak structure is clearly apparent at low temperatures and vanishes at higher temperatures when the homogeneous material on both sides of the junction becomes less degenerated and when the efficiency of the absorption-reemission process decreases. We restrict ourselves to results at low temperatures.

Assuming the value of the energy gap is given by the energy of the maximum of the first peak we plotted in Fig. 4 the variation of the gap with temperature for six types of diodes. For PbSe and PbTe the results are in very good agreement with all values found in literature.[4,15] The variation of E_G with temperature is found practically the same for all compounds:

$$\frac{\partial E_G}{\partial T} \simeq (4.4\pm 0.2)\times 10^{-4}\ \text{eV}/^\circ\text{K}\ .$$

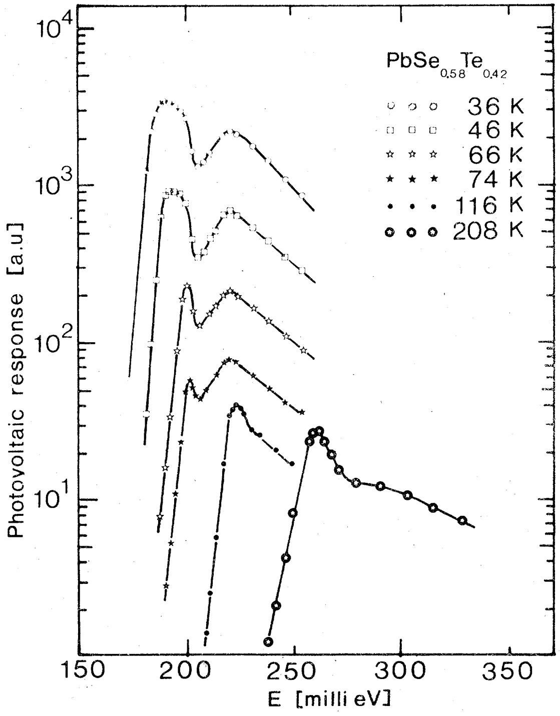

FIG. 3. Photovoltaic response of a diode with $x=0.42$, for different temperatures, as a function of the incoming photon energy.

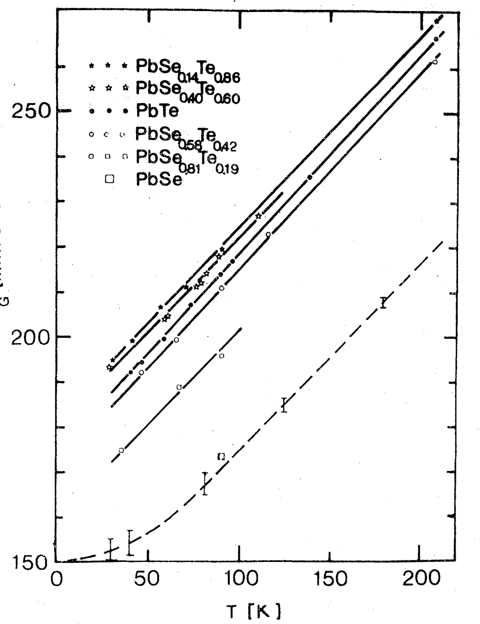

FIG. 4. Variation of the energy of the first maximum of the photovoltaic response with temperature, for different compositions alloys. The dashed curve and error bars reproduce the experimental results of Ref. 15.

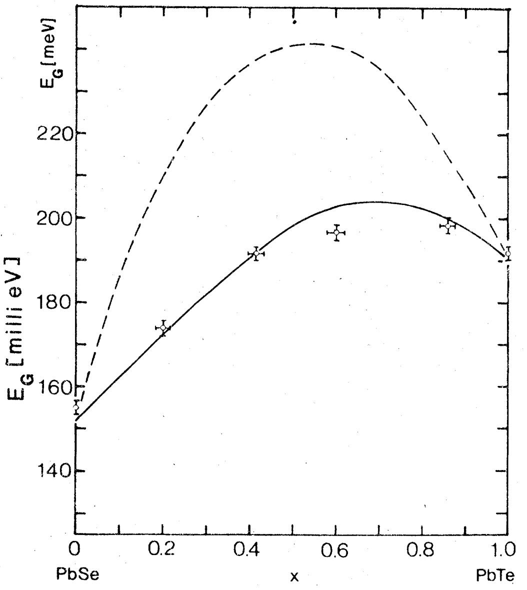

FIG. 5. Comparison between experimental values of the energy gap and those deduced from the linear model (dashed line) and the one including the bowing of the L_2^- level (full line).

Clearly for all temperatures we see that the gap of $PbSe_{0.4}Te_{0.6}$ is larger than that of PbTe indicating a bowing of this gap in the sequence $PbSe_{1-x}Te_x$. Similarly to what has been found for the binary compounds, the linear dependence of E_G with temperature vanishes below 30–35 °K in such a way that gaps at 4 °K are smaller than gaps at 30 °K by no more than 2 or 3 meV. So the comparison between the model and the experiment can be done at 30 °K.

We have gathered our results for two temperatures and all diodes we used in Fig. 5. Each experimental point represents the mean value of results. This figure shows the results of the two models we have made with a linear and nonlinear behavior of the L_2^- level energy. The agreement between theory and experiment is satisfactory for the model including a bowing of this level, and clearly poor with the linear model. The discrepancy found with the diodes made from material with $x = 0.6$ is not understood. For all these diodes we always found an energy a little bit smaller than that we would expect from a smooth variation of the energy gap as a function x. The rather bad values of the mobility found in this material could explain this anomaly as being due to different processes involved in the photoresponse and/or to a poor definition of the junction barrier.

V. DISCUSSION OF THE RESULTS

From this experiment we can think that the model proposed for the conduction bands of PbSe and PbTe is reasonable. The origin of the controversy[1] came from the fact that some optical transitions allowed by symmetry, such as the ones involving the L_6^+ and $L_6^-(L_2^-)$ levels in PbTe have not been seen in electroreflectance experiments, whereas the $L_6^+ \rightarrow L_6^-(L_3^-)$ transition in PbSe appears. What we would like to point out is that the two transitions do not involve the same matrix elements. In fact the $L_6^+ \rightarrow L_6^-(L_2^-)$ transition involves a matrix element which is essentially $P_{11}^{\parallel}$ and the $L_6^+ \rightarrow L_6^-(L_3^-)$ transition $P_{13}^{\perp}$ according to the notation of Mitchell and Wallis.[9] These are shown on Fig. 1. From band structures calculations $(P_{13}^{\perp})^2$ appears to be typically ten times larger than $(P_{11}^{\parallel})^2$ for both salts and this property explains the difference in the anisotropy of masses between PbSe and PbTe, because through the $\vec{k}\cdot\vec{p}$ theory the same matrix elements appear in the expression for the masses. The difference between the index of refraction jump near the gap originates also from this property.[7] So we expect for PbTe to see a transition at high energy ten times smaller than that of PbSe. Furthermore the symmetries of matrix elements are not the same and it is not evident that the electric field enhances in a same way transitions involving $P^{\parallel}$ and $P^{\perp}$. So we think that the electroreflectance experiment may not infirm the model reproduced in Fig. 1. The crossing of bands involved in the model is not local (at L) in the Brillouin zone. An inspection of the band structure for both salts shows that the first optical transition at Σ is also modified going from PbSe to PbTe. This is what reflectivity measurements on these compounds showed. Belle[16] observed an anomalous behavior of this transition as a function of x for the E_1 peak in the reflectivity spectrum. So the change in the band structure for these two compounds involves a rather important volume of the Brillouin zone.

VI. CONCLUSION

The variation with the composition of the gap of the ternary alloys $PbSe_{1-x}Te_x$ has been measured as a function of temperature. For a given temperature the variation of this gap can be reproduced with a simple model involving a band inversion of the conduction levels for PbSe and PbTe. The introduction of a bowing parameter has been necessary to reproduce the nonlinear dependence of the gap but not to explain it. So we think that this work supports the band scheme proposed, for the conduction levels of PbSe and PbTe, by the authors of Refs. 6 and 7.

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