

Electronic and structural anomalies in lead chalcogenides

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The rocksalt-structure PbS, PbSe, and PbTe semiconductors and their alloys exhibit a series of electronic-structure anomalies relative to the II-VI system, including the occurrence of direct gaps at the L point, anomalous order of band gaps and valence-band maximum energies versus anions, negative optical bowing, and negative band-gap pressure coefficients. We show that these anomalies result from the occurrence of the Pb s band below the top of the valence band, setting up coupling and level repulsion at the L point. Furthermore, we find that the topology of the frustrated octahedral structure leads to the occurrence in the random alloy of two distinct bonds for each anion-cation pair and to the predicted stabilization of *bulk* ordered Pb₂STe CuPt-like phase. ©S0163-1829-97!05120-5#

I. INTRODUCTION

The rocksalt-structure lead chalcocenide narrow-gap semiconductors PbS, PbSe, PbTe, and their alloys have been applied in long-wavelength imaging,¹

III. RESULTS AND DISCUSSION

Figure 1 depicts relativistic band structures of PbS, PbSe, and PbTe, while Fig. 2 compares band structures of PbSe calculated scalar-relativistically -a! and fully relativistically -b!. Table II gives some important band-structure parameters discussed in the following sections. Figures 1 and 2 show that the band structure of rocksalt PbX is distinguished from that of the zinc-blende II-VI and III-V semiconductors by having a Pb s band -dashed lines in Figs. 1 and 2! inside the valence band. This leads to strong-level repulsion at the L point between the two equal symmetry L_{1v} states @Fig. 2-a!#: the lower one being predominantly Pb s and the upper one being anion p . The electronic structure anomalies noted in the Introduction can be explained as follows.

(a) *Why does the VBM occur at the L point?* Of the high-symmetry states that could become the VBM (L_{1v} , L_{3v} , G_{15v} , X_{48v} , X_{58v} , see Fig. 2!, only the $L_{1v}^{(1)}$ -we chose the cation sites as origin! has a counterpart inside the valence band with the same symmetry ($L_{1v}^{(2)}$ at ~ -9 eV!. Since states with the same symmetry repel -in inverse proportion to their energy separation and in direct proportion to the coupling strength!, the higher of the two L_{1v} states ($L_{1v}^{(1)}$) becomes the VBM. On the other hand, the valence states at G and X have equal symmetry counterparts only in the *conduction band* -e.g., G_{15v} with G_{15c} !, so they are repelled *downwards*, being thus removed from the competition to become the VBM.

(b) *Why does the CBM occur at the L point?* Of the high-symmetry states that could become the CBM, the states at G (G_{15c}) and X (X_{48c} , X_{58c} !) are repelled *upwards*, thus being

removed from competition to become CBM. On the other hand, at the L point, L_{28c} is pushed down by -equal-symmetry! higher-lying conduction states. This is further enhanced by the spin-orbit coupling: once the spin-orbit interaction is turned on, the L_{28c} derived L_{6-} state is pushed downwards by the equal-symmetry L_{38c} derived L_{6-} state, thus becoming the CBM.

(c) *Why do the band gaps have the order $E_g(\text{PbS}) > E_g(\text{PbTe}) > E_g(\text{PbSe})$?* Sulphur has the deepest p -orbital energy among the three chalcogen anions: the calculated LDA atomic valence p -orbital energies are -7.2 , -6.7 , and -6.2 eV for S, Se, and Te, respectively. Thus, in the absence of level repulsion, the VBM of PbX will be the deepest. Opposing this effect is the fact that PbS also has the largest p - s repulsion in the three PbX compounds. This results from the closeness of the S p orbital to the Pb s -orbital energy and from the shortness of the Pb-S bond.

band gaps with $E_g(\text{PbS}) > E_g(\text{PbTe}) >$

while the band-edge state L_{6-c} and L_{6+v} have different symmetries -hence, they can cross when pressure is applied!, the states away from the L point -e.g., L_6 ! have identical symmetries -thus, cannot cross!. Therefore, when pressure is applied to PbX , the band gaps will initially decrease, approaching zero at $P=P_c$, and then they will increase. We predict that the pressure coefficient of the band gap will change signs at a critical pressure P_c when E_g vanishes. Using the experimental band gaps and the pressure coefficient given in Table II, we estimate the transition pressure $P_c=32, 20$, and 16 kbar for $PbS, PbSe$, and $PbTe$, respectively.

(f) *Why is the optical bowing coefficient of the $PbSe_xTe_{1-x}$ alloy negative?* We have analyzed b by decomposing it into physically distinct additive-contributions:²³ -1! volume deformation -VD!, -2! charge exchange -CE!, and -3! structural relaxation -SR!. The VD term represents changes in the band gaps due to compression or dilation of the constituents from their individual equilibrium lattice constants to the intermediate alloy value $a(x)$. The CE term is the change in band gaps in bringing together the constituents, both already prepared at $a=a(x)$, thus forming an alloy at $a=a(x)$ with all atoms assumed to be on ideal rocksalt lattice sites -unrelaxed SQS!. Finally, the SR term represents the change of band gaps upon passing from the atomically unrelaxed to the relaxed alloy at $a(x)$ -relaxed SQS!. By construction, the total bowing is $b [b_{VD} + b_{CE} + b_{SR}$. Table III shows the breakdown of bowing for the three random alloys. We observe the following: -i! by definition, b_{VD} is proportional to the lattice mismatch and to the difference in the deformation potentials between PbX and PbY . Since the magnitude of the deformation potential is reduced in the series $PbS \rightarrow PbSe \rightarrow PbTe$ -Table II, line 6!, b_{VD} is negative in the alloys. -ii! b_{SR} is positive, partially canceling the effect of volume deformation. The total bowing is thus determined mostly by -iii! b_{CE} which is negative in these systems. In a previous study,²⁴ the negative bowing in $PbSe_xTe_{1-x}$ was attributed to the reversal of the order of the L_{38c} and L_{28c} states in $PbTe$ relative to $PbSe$, predicted from empirical pseudopotential calculations.^{25,13,26} Because of this level reversal, the CBM on one end of the alloy composition traces a line towards a state with energy higher than the CBM on the other end of the alloy composition. Consequently, the CBM of the alloy would be higher in energy than the weighted average, thus $b < 0$. However, our self-consistent calculations show that although $PbTe$ has a much smaller energy difference $De(L_{38c} - L_{28c})$ than $PbSe$ and PbS -Table II, line 3!, the level order in all three compounds is the same. We find instead that due to the closeness of the energies of L_{38c} and L_{28c} in $PbTe$, these two states are strongly coupled -through the spin-orbit interaction!. This

leads to negative b_{CE} , thus to negative total bowing in $PbSe_xTe_{1-x}$. Our calculated $b = -0.09$ eV for $PbSe_xTe_{1-x}$ is in good agreement with experimental data $b; -0.1$ eV.^{14,15}

(g) *Why does $PbS_{0.2}Te_{0.8}$ show two different Pb-S bond lengths?* Atoms in a covalent alloy relax to attain as much as possible ‘‘ideal’’ bond lengths $R^0(Pb-X)$ and $R^0(Pb-Y)$ and bond angles.²⁷ Our total energy and force calculations show that in the PbX_xY_{1-x} alloys energy is lowered primarily by bond-stretching relaxation, while the effect of bond-bending relaxation on the total energy is small -a consequence of ionicity!. Further, we find that bond relaxation occurs here primarily through displacement of the *common* sublattice atom -i.e., Pb !. These features are similar to that found in zinc-blende alloys.²⁷ What is different here is that in the Pb centered ideal X_nY_{6-n} $-n=0-6$! octahedra, since any two cation-anion bonds are either parallel or orthogonal to each other, to first order, displacement of Pb can make only *some* of the bonds $R_r(Pb-X)$ relax $-r$! towards their ideal $R^0(Pb-X)$ values. The remaining bonds R_{ur}

played by ferroelectric transition in the system, the bimodal distribution of the Pb-S bonds is an intrinsic behavior of rocksalt alloys. The short Pb-S bonds are the more relaxed ones while the long Pb-S bonds correspond to the more unrelaxed ones. The ratio between the number of relaxed and unrelaxed bond is predicted to be 4 to 1 at $x=0.2$. On the other hand, at small composition x , the relaxed and unrelaxed Pb-Te bonds have similar lengths, hence may not be distinguished in the experimental analysis.¹⁶ Further study is needed to clarify this issue.

(h) *Predicted spontaneous CuPt ordering.* We have studied the formation energies $DH(S, Pb_2XY) = E(S, Pb_2XY) - @E(PbX) + E(PbY)\#$ of several ordered and disordered rocksalt Pb alloys at $x=0.5$. The configurations S which we

mation of the binding energy of the Pb s band -similar to the LDA error in the band gap!, thus to an underestimation of the p - s level repulsion. If one adjusts the Pb s band to lower binding energy -Refs. 22 and 13!, the calculated magnitude of the deformation potential becomes larger.

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