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Surface core-level shifts and relaxation of group-IVA-element chalcogenide semiconductors

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The (100) surface core-level shifts of PbS, PbSe, PbTe, GeTe, and SnTe are calculated with use of a simple molecular model. For the unrelaxed surface, the calculated values are quite large and increase with the compound ionicity. This discrepancy with the available experimental result for PbS suggests a large (100) surface relaxation annealing the effects of the surface on core-level shifts.

INTRODUCTION

Most semiconductor studies concern diamond- and zinc-blende-structure semiconductors. These materials certainly are the most commonly used in the fabrication of electronic devices. Semiconductors with the wurtzite structure are less studied and only a few papers deal with the group-IVA-element chalcogenides with the rocksalt structure, although PbS has been used for a long time as a solid-state radiowave detector. Due to their small band gaps, all these materials are still used to make infrared detectors. As we shall see below, their surface properties are quite different from the well-known zinc-blende-structure semiconductor band structure: For example, no surface state occurs in the band gap.

In the first section we give a brief description of their bulk band structure and we develop a very simple model completely analogous to the molecular model for zinc-blende-structure semiconductors. It notably gives a good description of the increasing ionicity from GeTe to PbSe as a function of a single band parameter, which is the difference between the cation and anion p-state energies. This simple model is also used to calculate the compound cohesive energy.

In Sec. II the zero-charge-transfer approximation is used to calculate the (100) surface core-level shifts. This approximation has been previously used near zinc-blende-structure (110) surfaces where it gives a good agreement with experiment.[1] Our simple band model easily explains the large values that we get for the (100) surface. We find that the surface-atom ionicity is larger than the bulk one due to the smaller coordination number of surface atoms. This gives rise to a larger charge transfer between anions and cations close to the surface. This charge transfer is screened by an electrostatic potential which shifts the valence- and the core-electron states. In this model, the surface core-level shift is due to the electron-charge reorganization and not only to the change of the Madelung energy near the surface. The value that we calculate for an unrelaxed perfect surface completely disagrees with the measured value for PbS. For this semiconductor, the Pb surface core-level shift is less than 0.1 eV.[2]

In Sec. III, we explain this discrepancy by an inwards surface relaxation which strengthens the backbonds of surface atoms. This relaxation cancels the reduction of the surface-atom coordination number.

I. GROUP-IVA-ELEMENT CHALCOGENIDE BULK BAND STRUCTURE

The chalcogenides GeTe, SnTe, PbTe, PbS, and PbSe have the rocksalt structure. Their band structure can be accurately described using the tight-binding approximation with a sp_3d_5 basis including spin-orbit coupling.[3] For example, the PbS energy dispersion along the high-symmetry directions in the bulk Brillouin zone is recalled on Fig. 1. The two lower bands mainly correspond to the s anion and cation states. The main component of the next three bands comes from the three-anion p states. In the perfect crystal these five bands are filled. The band gap arises at point L and is small (0.15–0.20 eV). The next three bands are mainly p cation states. We shall now try to simplify this band structure.

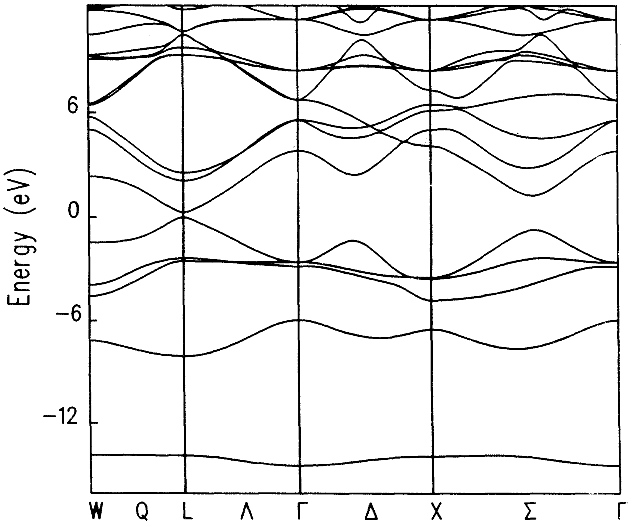

FIG. 1. PbS energy dispersion along symmetry directions in the Brillouin zone.

TABLE I. Comparison of the anion electronic charges with and without spin-orbit coupling.

	GeTe	SnTe	PbTe	PbS	PbSe
With *L*-*S* coupling	5.74	6.00	6.43	6.74	7.00
Without *L*-*S* coupling	5.75	6.01	6.48	6.69	7.05

The inclusion of the spin-orbit coupling is necessary to correctly describe the band gaps. Only intra-atomic spin-orbit terms are considered, and their influence on the atomic charges, which is the central point of our calculation, is limited, as one can see in Table I. The *d* states here are used to improve the behavior of the bulk conduction band. The *d* energy levels are higher than the *p* anion and cation states, and so their effect on the valence band and on the atomic charges is also quite small. In the same way, the influence of *s* states which are much lower in energy than the *p* anion states can be neglected. We are then left with only *p*-state interactions in the rocksalt structure. Among the interactions between *p* states,[4] the hopping integral $I_{pp\pi}$ is much smaller than $I_{pp\sigma}$ and, as we shall see below, can also be neglected. All these approximations lead to a simple description of the valence band in terms of *p* states along independent orthogonal linear chains with two atoms per unit cell [Fig. 2(a)].

The local atomic charges calculated with this simplified band model, which could seem rather crude, are in fact in very good agreement with the ones obtained by a more complete calculation. It can be shown[5] that this small difference is only due to coupling between the *p* bonding and the *s* states with the *p* antibonding and the *d* states. As the energy difference between these two groups of orbitals is large, the effect of the coupling on the local atomic charges is small.

In this simplified model, the local densities of states are analytic but this is still too complex for our purpose, which is the calculation of atomic charges. These atomic charges are obtained by integration of the local density of valence states and such a procedure does not depend very much on details of the density of states. A rough description of the density of states can be obtained using the moment method. We consider three exact moments for the local electronic density on each atom. For a bulk anion whose *p* atomic level is equal to E_A, these moments are equal to

$$\begin{aligned} \mu_A^0 &= 1 , \\ \mu_A^1 &= E_A , \\ \mu_A^2 &= E_A^2 + 2I_{pp\sigma}^2 , \\ \mu_A^3 &= E_A^3 + 4I_{pp\sigma}^2 E_A + 2I_{pp\sigma}^2 E_C , \end{aligned} \tag{1}$$

where E_C is the cation *p*-state energy. We find similar formulas for the cation states if we exchange E_A and E_C. If one takes into account the $I_{pp\pi}$ integrals, $I_{pp\sigma}$ must be replaced by $I_{pp\sigma}(1+2I_{pp\pi}^2/I_{pp\sigma}^2)^{1/2}$. As the ratio $I_{pp\pi}/I_{pp\sigma}$ is small (~ 0.2),[3] we can neglect the $I_{pp\pi}$ integrals in calculations of the atomic charges.

These moments (1) are equal to those of the two-atom chain shown in Fig. 2(b) if in this chain the hopping integral between the *p* anion and cation states is taken equal to $I_{pp\sigma}\sqrt{2}$. Then we can replace the infinite linear-chain valence band by the two-atom-chain bonding state E_B

$$E_B = \frac{E_A+E_C}{2} - \left[\left[\frac{E_c-E_A}{2} \right]^2 + 2I_{pp\sigma}^2 \right]^{1/2} . \tag{2}$$

In this model, the *p* orbital anion occupancy is equal to $1+f$ ($1-f$ for the cation one) if we set

$$f = \frac{\Delta}{(\Delta^2 + 2I_{pp\sigma}^2)^{1/2}} \tag{3}$$

and $\Delta = (E_C - E_A)/2$. As the *s* states are filled, the anion local electronic charge is equal to $5+3f$, whereas the cation one is $5-3f$, where f is always positive. This model is equivalent to the molecular model often used for diamond and zinc-blende-structure semiconductors. Here the interactions occur between *p* states instead of sp_3 orbitals for the usual molecular model. As one can see on Fig. 3, the charges calculated with this simple model agree quite well with those obtained using the complete relativistic band structure. Assuming now that the free-atom orbital energies are equal to the bulk ones, we can calculate the contribution of one anion and one cation *p* orbital to the crystal cohesive energy:

$$\begin{aligned} E_{\text{coh}} &= 2 \left[\frac{E_C+E_A}{2} - (\Delta^2 + 2I_{pp\sigma}^2) \right]^{1/2} - \frac{4E_A}{3} \\ &\quad - \frac{2E_c}{3} + 4C , \\ E_{\text{coh}} &= \frac{2\Delta}{3} - 2(\Delta^2 + 2I_{pp\sigma}^2)^{1/2} + 4C . \end{aligned} \tag{4}$$

From the bulk electronic energy equal to $2E_B$, we have

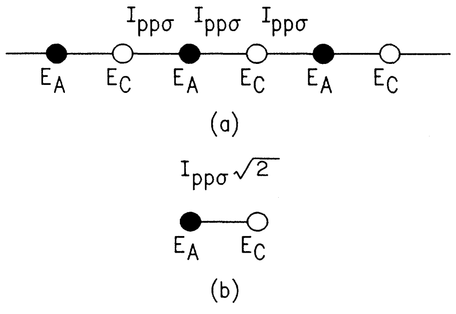

FIG. 2. (a) Two-atom linear chain. The *p* states (whose energies are E_A and E_C) interact through $I_{pp\sigma}$ hopping integrals. (b) If we consider only three exact moments, this is equivalent to the two-atom chain. The interaction between the *p* states is now $\sqrt{2}I_{pp\sigma}$.

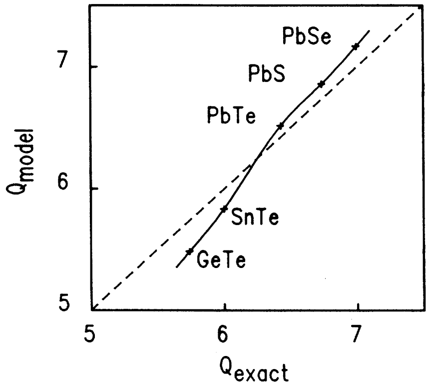

FIG. 3. Variation of the anion atomic charges (in electrons) calculated by the molecular model as a function of the charges given by the complete relativistic tight-binding calculation. The charge transfer between cations and anions is opposite in GeTe and in the three other chalcogenides PbTe, PbS, and PbSe. In this model, it is almost zero for SnTe.

subtracted the free-atom p electron energy and we have also taken into account the repulsion C between the atoms. The hopping integral $I_{pp\sigma}$ and the atom repulsion C vary with the interatomic distance:

$$I_{pp\sigma}(\delta R)=I_{pp\sigma_0}\exp(-q\delta R) , \tag{5}$$

$$C=C_0\exp(-p\delta R) , \tag{6}$$

where δR is the deviation from the bulk interatomic equilibrium distance R_0. The cohesive energy is minimal for the bulk interatomic distance ($\delta R=0$),

$$\left[\frac{\partial E_{\text{coh}}}{\partial \delta R}\right]_{\delta R=0}=0 . \tag{7}$$

This gives a relation between p, q, $I_{pp\sigma_0}$, and C_0,

$$pC_0=\frac{qI^2_{pp\sigma_0}}{(\Delta^2+2I^2_{pp\sigma_0})^{1/2}} . \tag{8}$$

For this kind of material $p \sim 2q$.[6,7] This is sufficient to calculate the cohesive energy E_{coh} (Table II). The charge transfer and the cohesive energy depend on $\Delta/I_{pp\sigma_0}$. As $I_{pp\sigma_0}$ is nearly constant for all the materials we consider, the only difference comes from Δ.

TABLE II. Cohesive energies of the group-IVA-element chalcogenides (in eV per neutral atom).

	GeTe	SnTe	PbTe	PbS	PbSe
E_{coh}	4.32	4.37	4.67	5.45	6.13

II. UNRELAXED SURFACE CORE-LEVEL SHIFTS

The Pb core-level shift has been recently measured for the (100) PbS surface.[1] Due to the large compound ionicity, a large value was expected but in fact the Pb core-level shift was surprisingly small (less than 0.1 eV). Let us apply our simple molecular model to calculate the surface-atom charges. In a first step, we neglect the screening potential due to different charge transfers between the surface and the bulk atoms. The first moments of the x orbital local density of states on a (100) surface anion are

$$\begin{aligned}
&\mu_A^0=1 ,\\
&\mu_A^1=E_A ,\\
&\mu_A^2=E_A^2+I^2_{pp\sigma_0} ,\\
&\mu_A^3=E_A^3+2I^2_{pp\sigma_0}E_A+I^2_{pp\sigma_0}E_c .
\end{aligned} \tag{9}$$

Similar formulas can be found for the cation p state. The surface valence-band state occurs at a different energy from the bulk one. However their energy difference is small. This is quite different from the usual molecular model as it does not give rise to a strongly localized surface state in the band gap when one takes into account all the s-, p-, and d-band parameters.

One can easily calculate the expression of the exact density of p states on atoms in a linear chain. It can be obtained by the recursion method. At least without any surface potential, it is easy to show that no surface bound state exists.

As there is also no modification of the y and z orbitals in the surface plane, the charge variation on a surface anion is then just equal to f_x-f, where

$$f_x=\frac{\Delta}{(\Delta^2+I^2_{pp\sigma_0})^{1/2}} . \tag{10}$$

Let us remark that this charge transfer in this simple model is limited to surface atoms and is due to their smaller coordination number. The f_x-f maximum occurs when $\Delta/I_{pp\sigma_0}$ is close to 0.9 (which is nearly the case of PbTe and PbS) and is equal to 0.13 electrons. Let us compare with the (110) III-V compounds.[1] In that case, the cation dangling-bond electrons are transferred to the anion dangling-bond orbital and then the unscreened charge transfer between the anion and the cation surface atoms is close to 0.75 electron. So even if the group-IVA-element chalcogenides are more ionic than the III-V semiconductor compounds, the unscreened charge transfer between the surface anions and cations is much smaller.

Let us now estimate the value of the self-consistent potential near the surface. The charge transfer between planes parallel to the surface is screened by the material dielectric constant[8] and then, except in the surface plane, the corresponding potential is small and can be neglected. The screening of the charge transfer between atoms in the same plane parallel to the surface is less efficient (the corresponding dielectric constant is smaller), but it is sufficient to reduce the charge transfer as in the (110) III-V semiconductor surface.[1] So a good approximation to calculate this potential is to use a zero-charge-transfer model. That means that the surface atoms have the same charges as the bulk ones.

Let us call V the potential shift on the surface anion states. Due to symmetry, the potential on the cation states is equal to $-V$. The first moments of the x state, surface anion, local density of states can be obtained from (9) if we replace E_A by E_A+V. Let us now consider the y and z orbitals on surface anions. The first moments of the local density of states are now obtained from (1), where we replace E_A by E_A+V and E_C by E_C-V.

The total electronic charge on a surface anion is $5+f_x+2f_y$, where f_x is given by (10) if we replace Δ by $\Delta_x=(E_C-E_A-V)/2$. On the other hand, f_y is given by (3) if we replace Δ by $\Delta_y=(E_C-E_A-2V)/2$.

Using the zero-charge-transfer condition ($f_x+2f_y=3f$), one can get a good approximation of the self-consistent anion surface potential (Fig. 4). In this model, the cation surface potential is opposite to the anion one. This potential is of the same order of magnitude as in the case of the III-V compound (110) surface,[1] but it is larger than the experimental value[2] which is less than 0.1 eV for Pb atoms in the PbS (100) surface. Such a discrepancy is not due to our simplified band structure. We have checked that a more complete calculation, taking into account all the s and p interactions and only neglecting the d states, gives, for the (100) PbS surface, Pb and S core-level shifts equal, respectively, to -0.17 and $+0.37$ eV. This discrepancy between the result for the perfect surface and the experimental one can be better explained by a large (100) surface contraction.

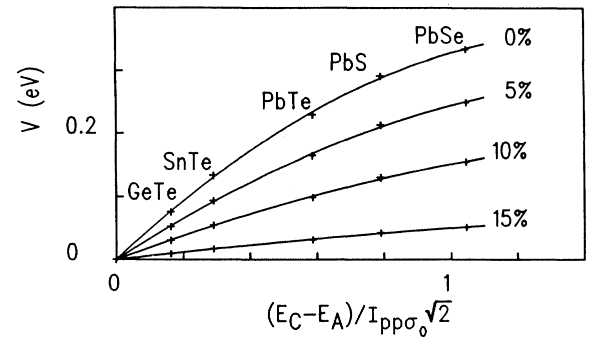

FIG. 4. Anion surface core-level shift as a function of the chalcogenide ionicity for different surface-layer contractions.

III. (100) SURFACE RELAXATION

The cohesion of the crystal in the [100] direction is ensured by the x states. When one creates a (100) surface, one suppresses one neighbor of the surface atom and this perturbation is large, as a bulk atom has only two nearest neighbors along the x chain. So one can expect a large surface relaxation.

To calculate the surface relaxation, we neglect the variation of the potential near the surface as it contributes only to second-order terms in the linear chain total energy.[9] This is justified by the fact that the potential values calculated in the preceding section are small and will still be reduced by the relaxation itself. Let us call d_{ij} the variation of the distance between atoms i and j due to the surface relaxation. Using the same approximation as above, only the x orbital bonding-state energy varies with the surface relaxation. If we assume that the relaxation is the same for the cations and the anions in the same ith plane parallel to the (100) surface, it is obvious to calculate the contribution to the linear chain total energy of a cation and anion atom pair,

$$E^i_{\text{coh}}=\frac{2\Delta}{3}-2\{\Delta^2+I^2_{pp\sigma_0}[\exp(-2qd_{i,i+1})+\exp(-2qd_{i,i-1})]\}^{1/2}+2C_0[\exp(-pd_{i,i+1})+\exp(-pd_{i,i-1})]\ . \tag{11}$$

The surface atoms ($i=1$) have a different contribution equal to

$$E^1_{\text{coh}}=\frac{2\Delta}{3}-2[\Delta^2+I^2_{pp\sigma_0}\exp(-2qd_{1,2})]^{1/2}+2C_0\exp(-pd_{1,2})\ . \tag{12}$$

In the harmonic approximation, each pair of atoms in the ith plane has a contribution to the relaxation energy equal to

$$\frac{\delta E^i_{\text{coh}}}{2|I_{pp\sigma_0}|}=q\left[\sum_j d_{ij}\right]\left[\frac{1}{\left[\dfrac{\Delta}{I^2_{pp\sigma_0}}+N_i\right]^{1/2}}-\frac{1}{\left[\dfrac{\Delta^2}{I^2_{pp\sigma_0}}+2\right]^{1/2}}\right]+\left[\sum_j d^2_{ij}\right]\left[\frac{-q^2}{\left[\dfrac{\Delta^2}{I^2_{pp\sigma_0}}+N_i\right]^{1/2}}+\frac{pq/2}{\left[\dfrac{\Delta^2}{I^2_{pp\sigma_0}}+2\right]^{1/2}}\right]+\left[\sum_j d_{ij}\right]^2\frac{q^2/2}{\left[\dfrac{\Delta^2}{I^2_{pp\sigma_0}}+N_i\right]^{3/2}}\ , \tag{13}$$

where N_i is the ith atom coordination number and the summation over j is extended to its neighbors. Expression (13) is similar to the one obtained near transition-metal surfaces.[10] The first-order term, which is different from zero only for the surface atom, is positive and leads to a surface contraction.

The surface relaxation also decreases when the ionicity increases. For example, with $q=2$ and $p=4.2$ (the bulk crystal is unstable for $p<2q$), we find a 12% contraction of the first GeTe layer and 9% of the PbSe one. The relaxation is, as usual, oscillatory and its amplitude exponentially decreases away from the surface. With the same p and q values as above, the second GeTe layer is 9% expanded (5% for PbSe). Similar results have been found by other authors also using tight binding but a slightly different method to calculate the crystal energy.[11]

Using again the expression (8) where we replace E_A by E_A+V and $I_{pp\sigma_0}$ by $I_{pp\sigma_0}\exp(-q\delta R)$, we can calculate the surface potential as a function of the first-layer relaxation. In Fig. 4, one can see that the surface core-level shifts become less than 0.1 eV for a relaxation larger than 10%. Such a value seems consistent with the usual p and q values. In fact, the relaxation strongly increases the hopping integral between a surface atom and its neighbor in the plane below the surface. This effect counterbalances the smallest surface-atom coordination number. One can also remark that the anion core-level shift always has the same sign whatever the sign of the charge transfer between anions and cations. A model considering only the change of the Madelung energy would give opposite anion core-level shifts for GeTe and PbSe. We have also checked that we get similar results when we exactly take into account of all the s and p interactions. For example, in this more accurate band-structure model, a 10% surface contraction reduces the Pb and S surface core-level shifts, respectively, to -0.06 and $+0.12$ eV in good agreement with the results shown in Fig. 4.

CONCLUSION

We have shown that a simple molecular model accurately describes the ionicity and the bulk charge transfer between anions and cations in group-IVA-element chalcogenides. Even if these materials are assumed to be more ionic than the III-V semiconductor compounds, for a perfect unrelaxed surface, the core-level shifts would be of the same order of magnitude. The discrepancy with the available measurement is easily explained by a large inwards surface relaxation. Core-level-shift measurements for other materials together with low-energy electron-diffraction (LEED) experiments are needed to support this effect.

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