PHYSICAL REVIEW B, VOLUME 63, 033302

Surface structure and core-level shifts in lead chalcogenide (001) surfaces

Alessandra Satta[1] and Stefano de Gironcoli[2]
[1]*Istituto Nazionale per la Fisica della Materia (INFM) and Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, 09042 Monserrato (CA), Italy*
[2]*Istituto Nazionale per la Fisica della Materia (INFM) and Scuola Internazionale Superiore di Studî Avanzati (SISSA), via Beirut 2-4, 34014 Trieste, Italy*

(Received 1 August 2000; published 22 December 2000)

We study the geometrical structure, the relaxation, and the surface core-level shifts of PbS and PbTe (001) surfaces via *ab initio* pseudopotential calculations. In both systems, an oscillatory relaxation of the surface-layer separations is predicted and this feature is expected to be present in other polarizable ionic rocksalt compounds. In agreement with experiment, PbTe displays a large surface rumpling that is absent in PbS. Reasons for these similarities and differences are addressed. Our results compare well with most available experimental data. Partial disagreement with a recent x-ray standing wave investigation in PbS is discussed. Core-level shifts in PbS are very small and are not sensitive to surface relaxation. Therefore, they are not a useful tool to investigate surface geometry in these compounds.

DOI: 10.1103/PhysRevB.63.033302 PACS number(s): 68.35.−p, 71.15.Mb, 71.20.Nr

I. INTRODUCTION

Lead chalcogenides are narrow gap semiconductor compounds with strong ionic character that crystallize in the cubic NaCl (rocksalt) structure. They have been intensively studied in the last decades due to their importance in various domains of both fundamental and environmental science. In particular, lead sulfide—naturally occurring as the mineral galena—constitutes the main reservoir of lead in water-rock interaction and a thorough study of its surface reactivity would provide a better understanding of many weathering mechanisms occurring in the Earth's surface.

The typical cleavage face of these compounds is the (001) and an accurate description of the atomic geometry and the electronic structure of this surface is therefore a prerequisite to further analysis of surface reactivity. Simple qualitative arguments based on *bondlength-conserving* atomic relaxation would predict, for close-packed ionic systems such as the rocksalt structure, very small surface relaxation.[1] These simple arguments apply satisfactorily for prototype ionic solids, such as MgO, but their validity for the more polarizable PbS and PbTe compounds is not well established.

The experimental situation is still controversial. On one hand, Kendelewicz *et al.*,[2] via x-ray standing wave (XSW) experiments on PbS (001) surface, found no evidence of a significant relaxation. This result was supported by a Hartree-Fock theoretical study,[3] that confirmed the absence of significant *rumpling* of the surface (evaluated to be of the order of 0.1 Å). On the other hand, low-energy electron diffraction (LEED) analysis of (001) surface of PbTe, naively expected to be very similar to PbS, indicates a relevant oscillatory relaxation together with a large (7%) *rumpling* of the surface[4] with the top-layer Pb atoms sinking below the plane containing the anions.

To add to the confusion, measurements[5,6] of the photoemission spectrum of the Pb $5d$ core level in the (001) PbS surface show negligible, <0.1 eV, surface core-level shifts (SCLS) that have been interpreted by Allan,[7] on the basis of linear chain tight-binding calculations, as due to a strong inward relaxation of the top surface layer, as large as $\approx 15\%$. This result is at variance with the recent XSW measurements by Kendelewicz *et al.*[2] that, on the other hand, confirmed the absence of surface shift in PbS (001) for both $4f$ Pb and $2p$ S core excitations.

Therefore, an accurate theoretical investigation of PbS and PbTe (001) surfaces is needed to understand the reasons for their different behavior and for a consistent interpretation of the results of surface core-level spectroscopy[2,5] and other structural analysis[2,4] in these compounds.

II. METHOD

Our theoretical calculations have been performed within the framework of density-functional theory in the local-density approximation (DFT-LDA),[8] using norm-conserving[9] and ultrasoft[10] pseudopotentials for S and Te, and for Pb, respectively. For the latter element, $5d$ states are included in the valence region. We used the Ceperley-Alder[11] exchange-correlation potential as parametrized by Perdew and Zunger.[12,13] A kinetic energy cutoff of 28 Ry and a 10 k-points Monkhorst-Pack[14] grid in the bulk, or an equivalent density of points in the Brillouin zone (BZ) for larger systems, were found to be sufficient to converge all the quantities of interest.

The PbS and PbTe (001) surface were modeled in the supercell geometry by periodically repeated slabs of up to nine atomic layers separated by 5–6 equivalent vacuum layers. We will refer to a supercell as $N+M$ when the system contains N atomic layers separated by M equivalent vacuum layers. In the (1×1) surface unit cell, each layer contains one cation and one anion that keep, by symmetry, their bulk position in the x-y plane, while along the z direction, perpendicular to the surface, the equilibrium atomic positions are not fixed by symmetry and, in particular, can be different for different atomic species, thus inducing a surface *rumpling*. During relaxation, the in-plane lattice parameters of the slab were fixed by the bulk values of the two compounds, and all atoms in the supercells were allowed to relax until the inter-

TABLE I. Equilibrium bulk parameters for PbS and PbTe.

	PbS			PbTe		
	a_0 (a.u.)	B (GPa)	B'	a_0 (a.u.)	B (GPa)	B'
Present work	11.03	64	4.87	12.08	49	4.51
Expt.[a]	11.20	53–70		12.18	40	
Others[b]	11.16	66.3	4.38	12.17	51.7	4.52

[a] Reference 15.

[b] Reference 16.

atomic forces vanish. No remarkable change in the total energy and surface geometry was found by increasing the vacuum distance between slabs up to six equivalent layers. From the study of convergence with respect to the slab thickness in the case of PbS, we found that the $7+5$ supercell was sufficient to obtain converged results, while thinner slabs were not sufficient.

III. RESULTS AND DISCUSSION

PbS and PbTe form naturally in the rocksalt structure. Theoretical structural parameters have been determined by fitting our calculations to the Murnaghan equation of state. Lattice parameters and bulk moduli agree within a few percent with experimental data[15] and previous theoretical calculations[16] (see Table I).

In order to quantify the amount of surface rumpling, we define the rumpling parameter as the distance, for each layer, between the vertical position of cations and anions, scaled to the bulk distance d_0:

$$\Delta z_i = \frac{z_i^{(\mathrm{S,Te})} - z_i^{\mathrm{Pb}}}{d_0} \qquad (1)$$

where z_i^X refers to the position of the X ($X=$S,Te, or Pb) atoms along the z direction in a given layer i. Another parameter describing the surface relaxation is the average separation Δd_{ij} between two layers, again scaled to the bulk value:

$$\Delta d_{ij} = \frac{d_i - d_j}{d_0}, \quad d_i = \frac{1}{2}[z_i^{(\mathrm{S,Te})} + z_i^{\mathrm{Pb}}]. \qquad (2)$$

A. Surface relaxation

Our theoretical results for the average layer relaxation and for the surface *rumpling* of PbS and PbTe (001) surfaces are reported in Table II.

The calculations, in agreement with recent experiments,[2,4] predict no rumpling in the case of PbS (001) surface and a large positive rumpling of the first surface layer for PbTe (i.e., top-layer Pb atoms sink with respect to Te atoms) together with an opposite, smaller, effect for the second layer. The theoretical value of 5% for the topmost-layer rumpling in PbTe surface is in good agreement with the value of 7% measured by Lazarides *et al.*[4] These results demonstrate the accuracy of our calculation and show that simple ‘‘bond-length-conservation’’ arguments[1] cannot be applied in general.

TABLE II. Surface layer rumpling Δr_1 and interlayer distances Δd_{ij} for PbS and PbTe (001) surfaces. The thickness of the slabs in the supercell is $N+5$. (See text for explanation.)

	Rumpling (%)				Relaxation (%)			
	Δr_1	Δr_2	Δr_3	Δr_4	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}
				(001) PbS				
$N=5$	0.1	0.2			−4.7	2.3		
7	0.03	0.4	−0.2		−5.1	3.2	−0.4	
9	−0.1	0.4	−0.4	0.6	−5.2	3.5	−1.2	0.5
Expt.[a]	0.0				<1			
				(001) PbTe				
$N=7$	5.3	−3.5	1.4		−4.1	2.1	−0.1	
Expt.[b]	7				−4	2		

[a] Reference 2.

[b] Reference 4.

As for the average layer relaxation, calculations show a similar pattern for the two compounds with an oscillatory interlayer relaxation: the top-to-second layer distance contracts (by ≈5% and ≈4% for PbS and PbTe, respectively) and the second-to-third layer distance expands (by ≈3% and ≈2%). Deeper layers are practically unaffected by relaxation from their bulk positions. These theoretical results are in very good agreement with the LEED analysis[4] for PbTe, while they are at variance with the XSW study of PbS surface where no significant surface relaxation was reported.[2]

We believe that this disagreement is only apparent and is to be related to the fact that more than one surface layer participates to the relaxation, contrary to what was assumed in the experimental analysis. In fact, XSW experiments are sensitive to *displacements* of the surface atoms from their *bulk positions*, as determined by the bulk diffraction conditions, and, due to the oscillatory surface relaxation in PbS, in spite of the large ≈5 top-to-second layer contraction, the atomic displacements of surface atoms from their ideal positions are much smaller: ≈−2% and ≈+3%, for top and second layers, respectively. Moreover, signals from the two relaxing layers tend to compensate each other in the XSW yield in such a way that, we believe, the total surface contribution to the XSW signal is within the 1% noise level quoted in Ref. 2. In order to solve this issue, the reanalysis of the experimental data in Ref. 2 on the basis of the present results and/or the investigation of this surface with some surface technique more sensitive to *interlayer distances*, such as LEED, for instance, would be desirable.

Our calculations predict that both PbS and PbTe (001) surfaces display an oscillatory relaxation of the surface layers as a whole: the topmost layer tends to contract, the second one tends to expand, and so on. In addition to this layer relaxation, PbTe show a strong rumpling that is absent in PbS. Let us examine the reasons for these similarities and differences.

In the bulk, anions and cations occupy high-symmetry sites and the interacting forces among them vanish by sym-

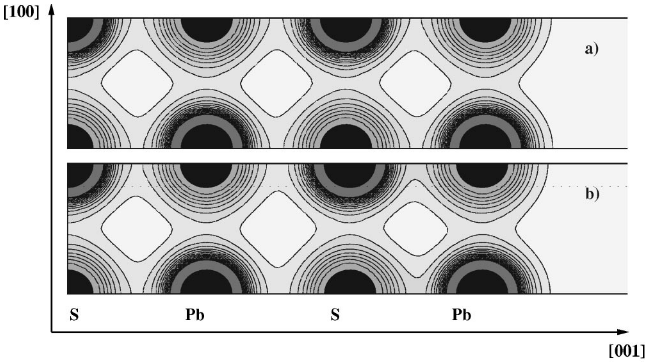

FIG. 1. PbS: contour of the electronic charge density on the plane (100), for the unrelaxed (a) and relaxed (b) geometry, respectively.

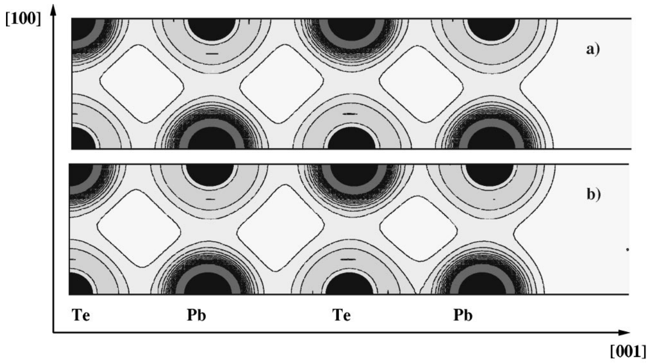

FIG. 2. PbTe: contour of the electronic charge density on the plane (100), for the unrelaxed (a) and relaxed (b) geometry, respectively.

metry. Due to the reduced symmetry, the relaxed geometry at the surface is dictated by the equilibrium between the long-range electrostatic interaction and the short-range Pauli repulsion between ionic cores. The electrostatic part can easily be calculated by the Ewald sum and the short-range repulsion can be, in first approximation, modeled in terms of two-body repulsive interaction between ions.

In this simplified picture, the oscillatory layer relaxation can be traced back to the electrostatic part of the cohesive energy: for the ideal unrelaxed surface, the electrostatic forces acting on ions display an oscillatory behavior with the topmost layer pushed toward the bulk and the second layer pulled toward the vacuum, exactly as required by an oscillatory relaxation to occur. This is a generic feature in rocksalt ionic crystal due to the geometrical arrangement of atoms in the (001) surface and to the electrostatic nature of the interaction. The extent to which these oscillatory forces are converted into relaxation depends on the stiffness of the short-range repulsion. Very stiff cores will not relax much, softer and more polarizable cores will relax more. This is why the amount of relaxation found in the strongly polarizable lead chalcogenides is larger than that encountered in other ionic compounds such as MgO or NaCl.

The electrostatic interaction is invariant for exchange of anion and cation charges, and cannot be held responsible for the rumpling of the surface since the electrostatic forces are the same for both kinds of atoms on a given unrelaxed surface layer. The asymmetric relaxation present in PbTe, and absent in PbS, implies that in the former case an asymmetry between anion and cation exists in the short-range part of the interaction that is absent in the latter. This is consistent with the assumption that in PbS, the dominant contribution to the short-range repulsion comes from Pb-S first-nearest-neighbor interaction, which is symmetric for anion-cation exchange. In PbTe, a sizable contribution comes also from the Te-Te next-nearest-neighbor repulsion in such a way that Te sublattice in PbTe tends to remain closer to the ideal geometry, while lead atoms in the first few surface layers relax more, inducing the surface rumpling. This picture is supported by literature values[17] of ionic radii for the two anions $[r_i(\mathrm{S}^{2-}) = 1.84$ Å, $r_i(\mathrm{Te}^{2-}) = 2.21$ Å$]$: The experimental Te-Te next-nearest-neighbor distance in PbTe is only 3% larger than twice $r_i(\mathrm{Te}^{2-})$ while the S-S distance in PbS is more than 13% larger than twice $r_i(\mathrm{S}^{2-})$.

The difference between these two surfaces is evident from the charge-density distribution, in the ideal and relaxed geometries, shown in Fig. 1 and Fig. 2 on a (100) plane through the slab. In the ideal geometry, the charge density of PbTe outside the core region is clearly asymmetric for Pb and Te exchange, with Te atoms more extended than Pb ones. Upon relaxation the anion sublattice remains almost unrelaxed but Pb atoms have more room to move at the surface than in the bulk. The resulting surface rumpling determines charge profiles that appear more symmetric in the first surface layers. In PbS, the charge density is rather symmetric for Pb and S exchange already in the ideal geometry and it remains symmetric after relaxation.

B. Surface core-level shifts

A piece of experimental evidence that is not controversial is the small value of the surface core-level shifts in PbS that have been reported both in early[5] and recent[2] studies. However, from the absence of SCLS, Allan[7] predicted, on the basis of tight-binding calculations, a very large, 15%, surface contraction not found in experiments and in the present first-principle calculations.

To clarify this issue, we computed the SCLS for PbS and PbTe in the first-principle final-state approach[18] that accounts also for the valence electron screening of the hole created in the core region by photoemission. In this scheme, the surface core-level shift is simply the energy difference between the energy of the slab containing an isolated core-ionized atom on the surface layer and that of a slab where the excited atom is in the central, bulk layer. In practice the isolated excitation is approximated by a (super) periodical arrangement of excited atoms in the desired layer. In order to describe the core-excited Pb atom, while adopting the pseudopotential approach, a pseudopotential has been generated from an atomic configuration with one $4f$ electron removed from the core. No significant dependence of the calculated SCLS on the atomic valence configuration used in the pseudopotential generation has been found.

Results of the calculations are reported in Table III for $7+5$ surface slabs. For PbS (001) surface, we checked that

TABLE III. The $4f$ Pb surface core-level shifts for the relaxed surfaces computed in the supercell approach with different periodicity of the core-exitations.

$\Delta\xi$ (eV)	(1×1)	$(\sqrt{2}\times\sqrt{2})$	Expt.[a]
PbS (001)	0.18	0.18	0.0 ± 0.1
PbTe (001)	0.06		

[a] Reference 2.

supercells where the excited atoms have (1×1) and $(\sqrt{2}\times\sqrt{2})$ surface periodicy give identical results, within 10 meV, so that (1×1) supercell is already sufficient for the present purpose.

Both PbS and PbTe display very small surface shifts, PbTe in particular. Although the theoretical value for core-level shift in PbS, 0.18 eV, is outside the quoted experimental error bar we estimate that an agreement with experiment within ≈ 0.1 eV is rather successful, in view of the various approximations involved in the calculation—pseudopotentials, slab thickness, exchange-corelation functional used—and it is comparable to what is obtained in other materials.[18]

Since in Ref. 7 the absence of SCLS was used to draw conclusions on the amount of surface contraction, we evaluated the influence of the relaxation on the SCLS in PbS by computing the shift also in the ideal unrelaxed surface. The obtained value of 0.14 eV, differing from the relaxed value by only 0.04 eV, indicates that core levels are very insensitive to relaxation in PbS and their value cannot be easily used to address structural issues in this compound.

IV. CONCLUSIONS

The structural relaxation of PbS and PbTe (001) surfaces and a calculation of their surface $4f$-Pb core-level shifts have been presented. Comparison with experimental data, as well as similarities and differences in the behavior of the two compounds, have been discussed. The oscillatory surface relaxation present for both systems can be traced back to the electrostatic part of the atomic interaction while the surface rumpling, when present, is related to an asymmetry in the short-range Pauli repulsion between ionic cores. Simple bond-length-conserving arguments do not apply to these materials. SCLS are insensitive to surface relaxation in these materials and are of little help in the structural determination.

ACKNOWLEDGMENTS

We acknowledge edifying discussions with P. Zuddas and G. De Giudici. This work has been done within the *Iniziativa Trasversale Calcolo Parallelo* of INFM. S.dG. has been supported in part by MURST under COFIN99. A.S. is indebted to P. Ruggerone and A. Geddo Lehmann for valid support.

---

[1] J.P. La Femina and C.B. Duke, J. Vac. Sci. Technol. A **9**, 1847 (1991).
[2] T. Kendelewicz, P. Liu, G.E. Brown, Jr., and E.J. Nelson, Surf. Sci. **395**, 229 (1998).
[3] U. Becker, S.P. Greatbanks, K.M. Rosso, I.H. Hillier, and D.J. Vaughan, J. Chem. Phys. **107**, 7537 (1997).
[4] A.A. Lazarides, C.B. Duke, A. Paton, and A. Kahn, Phys. Rev. B **52**, 14 895 (1995).
[5] G. Paolucci and K.C. Prince, Phys. Rev. B **41**, 3851 (1990).
[6] U. Becker and M.F. Hochella, Jr., Geochim. Cosmochim. Acta **60**, 2413 (1996).
[7] G. Allan, Phys. Rev. B **43**, 9594 (1991).
[8] R. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
[9] G.B. Bachelet, D.R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
[10] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[11] D. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[12] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[13] D.R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
[14] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).
[15] G. Nimtz, in *Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, Landolt Börnstein, New Series, Group III, Vol. 17f (Springer, Berlin, 1983), p. 15.
[16] S.-H. Wei and A. Zunger, Phys. Rev. B **55**, 13 605 (1997).
[17] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976), p. 386.
[18] E. Pehlke and M. Sheffler Phys. Rev. Lett. **71**, 2338 (1993).