First Principles Studies of the (001) Surface of Galena (PbS)

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ABSTRACT

Ab initio calculations of the surface structure and properties of the (001) surface of galena (PbS) have been performed using two complementary approaches. Both Gaussian and numerical basis functions have been utilized, as embodied within the programs CRYSTAL98 and SIESTA, with their associated implementations, in order to determine to what extent computational factors are influencing the results. Relaxations are presented based on calculations at the HF, B3LYP, LDA and GGA Hamiltonians. Significant relaxations are found to occur at the surface that decay into the bulk. The magnitude of the relaxations oscillates between layers, leading to pairing, with Pb ions being displaced outwards relative to S ions. We find that LDA, GGA and B3LYP Hamiltonians give results in reasonable agreement with each other but the structures computed using HF theory are vastly different and are physically unrealistic. The present calculations also predict a surface core level shift of 0.3 eV for the sulphur 2p level at the surface itself which is in excellent agreement with a recent experimental determination.

1. INTRODUCTION

Galena (PbS) is a mineral of considerable industrial importance both from the point of view of being the world's main source of lead and as a semi-conducting material. Furthermore, sulphide materials are of interest from the environmental perspective, being a major cause of the acidification of water systems after mining operations. Considerable effort has been devoted to understanding the physical and electronic properties of PbS, in particular the surface chemistry and underlying structure of the (001) termination. Surprisingly, despite the abundant availability of good single crystal mineral samples and its simple NaCl-halite structure, the surface structure of PbS (001) remains a controversial topic.

Early work on highly ionic, isostructural materials such as NaCl and MgO revealed that the surface is bulk terminated with very little relaxation or rumpling, consistent with simple bond length conservation arguments (Lafemina and Duke 1991). Subsequent theoretical investigations confirmed these results. However, the situation with less ionic, halite-structured materials, such as PbS, is less clear. Early tight binding calculations by Allan (Allan 1991), suggested that there could be a large relaxation of the top layer of the surface, explaining the very small observed surface core level shift (SCLS). Subsequent experimental measurements using low energy electron diffraction (LEED) on the PbS analogue, PbTe revealed a large relaxation at the surface with an inward 7% rumpling of the Pb ions relative to the Te sublattice and with an overall 4% contraction of the average separation of the first and second surface layers. A key finding of this work was that it showed that it is essential to allow the surface ions to rumple, a feature which was missing from the Allan work (Allan 1991) that assumed that the surface ions were rigid within a given layer.

Periodic Hartree-Fock calculations by Becker et al. (Becker and Hochella 1996) did allow for surface rumpling and showed that there is a small rumpling at the surface with the S ions displaced into the slab, in contrast to the PbTe experiments where the cations were seen to relax inwards. One issue concerning these calculations was the use of a relatively small slab units to model the surface structure which only allowed for four layers of PbS, the computational expense of the simulations precluding the use of larger, more realistic surface models.

The PbS (001) surface has been subjected to X-ray standing wave (XSW) experiments that determined that the surface is bulk terminated with little or no intra-layer rumpling or interlayer contraction (Kendelewicz et al. 1998). There have also been two recent theoretical studies of this surface, both of them performed using the plane-wave (PW) pseudopotential approach within the local density approximation (LDA) form of density functional theory (DFT). In the study by Satta et al. (Satta and De Gironcoli 2001), PbS and PbTe were studied with the PbS surface predicted to exhibit almost no rumpling, whereas the PbTe surface rumpled considerably, in agreement with the earlier LEED work (Lazarides et al. 1995). For both systems, an intralayer contraction between the top two layers and an expansion between the third and fourth layers was computed. Preobrajenski et al. (Preobrajenski and Chasse 2000) performed calculations on PbS using a very similar theoretical technique. They found agreement with Satta et al. with regards to the oscillatory contraction and expansion of the intralayer spacings, but with a significant rumpling (0.22 Å) of the top layer and with small rumplings seen further down the slab. Clearly, some controversy remains as to the surface structure of PbS (001).

We have chosen to tackle the problem using *ab initio* methods, taking great care to control our sources of error, such as limitations in the physical representation of the surface and technical

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parameters including the treatment of exchange and correlation and the basis set, drawing on our experience from a recent study of bulk PbS (Muscat and Klauber 2001).

In addition to using the LDA, we have used functionals based on the generalised gradient approximation (GGA) and the recently implemented hybrid functional techniques (Becke 1993;Stephens et al. 1994) that combine elements of HF and Density Functional Theory (DFT). These hybrid techniques have been shown to generally predict the electronic structure (Muscat et al. 2001), as well as the structural and elastic properties (Wilson and Muscat 2001), of a range of materials significantly more reliably than pure HF theory or DFT methods.

Furthermore, in order to validate our results, we have used two independent *ab initio* techniques for comparison. This allows the influence of implementational factors to be assessed in case the final results are particularly sensitive to any of them. Here we have chosen two approaches that are both based on localized orbitals, one of which utilizes Gaussians and one numerical orbitals. In the case of density functional results, comparisons are made using the same functionals for compatibility. One feature of the calculations performed using the numerical orbital approach is that it is necessary to generate pseudopotentials directly for use in the specific program, rather than employing standard tabulations. As a consequence, it is possible to generate pseudopotentials of both the small- and large-core forms, and furthermore to use a potential that is consistent with the density functional being used for the valence electrons.

1. **METHOD**

The calculations have been performed using the CRYSTAL98 (Dovesi et al. 1998) and SIESTA (Ordejon et al. 1996;Sanchez-Portal et al. 1997), *ab initio* software packages, both of which are described below with pertinent details for the present study.

CRYSTAL98 is based on the periodic, linear combination of atomic orbitals (LCAO) formalism where the Bloch orbitals of the crystal are expanded using atom centred Gaussian orbitals with s, p or d symmetry. A variety of treatments of exchange and correlation have been employed, including Becke's three parameter hybrid functional (B3LYP) (Becke 1993), HF theory, the local density approximation (LDA) (Dirac 1930;Perdew and Zunger 1981), and the generalised gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) (Perdew et al.).

Due to the computational expense required to describe the large number of electrons and the problems associated with treating relativistic effects in the core shells for heavy elements, such as lead, the core electrons up to, and including, the 5p shell have been replaced with a pseudopotential. However, recent studies have shown that the pseudopotential approximation can be a source of significant error (Muscat et al. 1999). We have examined the influence of the pseudopotential on the computed results by performing calculations using the Hay and Wadt (Hay and Wadt 1985) and the Durand (Barthelat and Durand 1978) type pseudopotentials. The sulphur ions have been treated using an all-electron basis set. In the current work, we have used basis sets that have been developed and optimised for use in recent studies of PbS (Mian et al. 1996) incorporating d-symmetry polarization functions on the S ions. Sampling of K-space has been performed using a Pack-Monkhurst grid (Dovesi et al. 1998;Pack and Monkhorst 1977) of shrinking parameter of 8, yielding 29 symmetry inequivalent K-points for bulk PbS. Tests reveal

that increasing the number of K-points produces no significant difference in the computed structure or energy of the crystals (the total energy of the bulk crystals is converged with respect to K-points to within about 10^{-5} eV, i.e. well below thermally significant energies).

CRYSTAL98 computes the matrix elements of the Coulomb and exchange terms by direct summation of the infinite periodic lattice. The truncation of these summations is controlled by five Gaussian overlap criteria, details of the control of these parameters is available elsewhere (Dovesi et al. 1998;Pisani et al. 1988). The values of the overlap criteria chosen in the current study were high (ITOLS parameters set to 10^{-8}, 10^{-8}, 10^{-8}, 10^{-8} and 10^{-16}) in order to converge numerical errors to about 3 meV in the total energy (Dovesi et al. 1992).

The structural optimisations within CRYSTAL98 were converged to a tolerance of 0.01 Å in cell parameters and 10^{-4} eV in the total energy using a modified Broyden-Fletcher-Goldfarb-Shanno minimisation algorithm (Zhu et al. 1994).

In the present study, for calculations based on the CRYSTAL98 program, the surface is modelled as a two dimensional slab, periodic in the [001] and [010] directions, but finite in the [001] direction (see Figure 1). This obviates the need to converge calculations with respect to the inter-slab vacuum distance introduced in the three dimensional supercell models of surface structures. The thickness of the slab used to model the surface is an important approximation. We have performed tests on slabs ranging from 3 to 17 layers using B3LYP to establish the convergence of the surface structure with respect to slab thickness. We find that the surface displacements are converged to around 0.02 Å at a slab thickness of around 9 layers (see Figure 2). We have performed similar tests with LDA or GGA and find that the computed decay of the ionic displacements with depth into the slab is faster with LDA or GGA than with B3LYP.

For comparison with the results obtained from the above calculations based on CRYSTAL, we have also examined the same problem using the methodology embedded within the program SIESTA. The aim of this latter code is to be able to tackle especially large system sizes, and to this end both the construction of the Hamiltonian and the solution of the self-consistent field (SCF) problem can be performed in a linear scaling fashion with respect to both computer time and memory. In the case of this study, we choose to use conventional matrix diagonalization within the SCF procedure, thus sacrificing the O(N) properties. However, the prefactor for this part of the calculation is small for the size of system concerned and allows sampling of the Brillouin zone to be performed with the same K-point grid as used within the rest of the present study.

In the SIESTA approach, the core electrons are represented by a non-local pseudopotential of the separable Kleinmann-Bylander form. All pseudopotentials are generated in a consistent manner - i.e. with the same density functional that will be used to treat the valence electrons - and with inclusion of scalar relativistic correction. For Pb, we have used a small core pseudopotential (i.e. the 5d electrons are included in the valence shell) since the use of a large core pseudopotential was found to adversely affect the quality of the results. The basis set in this approach consists of numerical pseudo atomic orbitals (PAOs) that are the solutions to the pseudized atomic problem. Additional radial flexibility is then incorporated by smoothly dividing the orbitals into inner and outer regions. Here a basis set of double-zeta plus polarization (DZP) quality was employed for both atoms, with a radial confinement that corresponds to an energy shift in the orbitals of 0.005 Ry.

Calculation of the Hartree and exchange-correlation potentials in SIESTA is performed on a real space mesh. The maximum planewave kinetic energy representable on the mesh used in the current

work was 250 Ry. Because of the use of Fast Fourier Transforms on the mesh, it is necessary to use a 3-D supercell model for the surface in SIESTA, unlike CRYSTAL which is genuinely 2-D. However, because the density goes to zero at a controlled distance from the surface, it is easy to ensure that the interaction between slabs is negligible. Furthermore, the computational cost of empty space is small, unlike a planewave calculation, and therefore the use of large vacuum gaps is not an issue.

All details of the calculations pertaining to the structural model, other than that mentioned above, were chosen to be the same for the numerical PAO calculations as for those based on the Gaussian basis sets to maximize compatibility.

2. RESULTS

3.1 Structural Properties

The ionic displacements of the PbS (001) surface computed using the CRYSTAL98 package, based on the Hay and Wadt pseudopotential description of lead, for a 13 layer slab model are presented in Table **1**. The results from calculations performed using HF theory are not shown because they yielded physically unrealistic relaxations with ionic displacements of up to 1 Å at the surface and continuing large displacements even 6 or 7 layers into the slab. Possible reasons for this failure of HF theory are presented in the Discussion. Earlier HF calculations on PbS surfaces (Becker and Hochella 1996) were performed on very thin slabs (4 layers thick) which could have artificially constrained the full surface relaxation. Also included in **Table 1** are the comparable SIESTA results for the same system and density functionals. The different treatments of exchange and correlation yield similar results; the largest discrepancies are no more than 0.05Å for the top two layers. Calculations performed using SIESTA with the PBE functional yield almost the same

structure as the CRYSTAL98 calculations with the same GGA, indicating that computational parameters are well converged here. However, the results for the LDA are greater at quantitative variance. This may be influenced by the pseudopotential being consistently generated within SIESTA for the appropriate Hamiltonian, while the same Hay and Wadt pseudopotential has been utilized for all levels within CRYSTAL98. Tests performed with CRYSTAL98 using the Durand pseudopotential gave similar results to the calculations performed using the Hay and Wadt pseudopotential with moderate (about 0.05 Å) differences in the computed structures.

The main result of the calculations is that they predict significant relaxation of the surface, particularly in the top four layers, contrary to the XSW results. A couple of clear trends can be seen in the relaxation. Firstly, there is clear evidence of oscillating contraction and expansion of the interlayer spacing with depth, with the magnitude of these displacements decaying rapidly into the slab (see Table 2). Secondly, the current calculations predict a small, but clear rumpling of the surface with the Pb ions lying above the S ions along the (001) direction, (see Table 3). The contraction and expansion of the interlayer spacings has been reported in the recent plane-wave studies of Satta et al. (Satta and De Gironcoli 2001) and Preobrajenski et al. (Preobrajenski and Chasse 2000). Although the absolute magnitude of these contractions vary slightly with each study, all the calculations predict contractions up to the third or fourth layers, with a contraction between the first and second layers of between 5 – 8 %.

The situation in the literature with regards to the rumpling is less clear. In the current study, we find that there is a significant rumpling of the first few surface layers with the S moving towards the bulk by between 1 to 3% compared to the unrelaxed surface depending on the method used. Satta et al. predicted almost no rumpling (around 0.1 %) whilst calculations by Preobrajenski et al. gave over 7 %, twice as large as the largest rumpling found in our calculations. A 3 % rumpling of

the surface has been reported in previous periodic HF calculations, although the absolute magnitude of the rumpling may not be very reliable since the slab model used was only four layers thick (Becker and Hochella 1996).

3.2 Electronic structure

We have computed the densities of states (DOS) of the relaxed (001) surface, which are presented in Figure 3. Essentially, the DOS are very similar to those computed in a recent study of bulk PbS (Muscat and Klauber 2001), with the main features of the surface DOS, such as the valence band width and the position of the S 3s states, being identical to those of the bulk.

Until recently, it was believed that PbS surfaces do not exhibit a significant SCLS. Allan (Allan 1991) performed calculations of the SCLS of PbS and found that for the unrelaxed surface, there is a SCLS of around 0.25 eV. By contracting the surface layer, ie. both Pb and S ions, towards the bulk by 15 %, it was found that the SCLS is reduced to under 0.05 eV. Based on this information, Allan deduced that the surface of PbS must be significantly relaxed.

However, recent synchrotron XPS experiments observed a significant narrowing of the S 2p, Pb 5d and Pb 4f lines at low temperatures due to strong dependence of phonon broadening on temperature (Leiro et al. 1998). This narrowing made it possible to observe a SCLS, to lower binding energies in the S 2p states by around 0.3 eV. We have performed calculations of the binding energy of the S 2p states with respect to depth in the slab. Our calculations, the results of which are presented in Figure 4 do indeed reveal a small SCLS of about 0.3 eV in the binding energy of the 2p states at the surface. The magnitude of the computed SCLS gradually decreases with increasing depth into the slab until it converges to the bulk PbS value.

4 DISCUSSION

The results in the current study are generally in good agreement with recent theoretical studies, but appear to disagree with experimental observations that claim that the surface is not appreciably relaxed. Satta et al. suggest that the XSW technique may not be sensitive enough to detect the relaxation of the surface, particularly as it was assumed in the experiment that only thetop layer relaxes. From the simulations, it is clear that several layers actually undergo relaxation and that the contraction of the interlayer spacing for the top two layers occurs because both the layers move. In fact, our calculations predict that the second layer undergoes a larger relaxation than the top layer; the possibility of such a feature was completely neglected in the analysis of the XSW results.

With regards to the theoretical calculations of the surface, small discrepancies arise as to the magnitude of the relaxation and whether or not the surface is rumpled. However, most authors are agreed that the surface undergoes oscillating contraction and expansion, with the surface becoming bulk-like from depths of around four layers.

Based on our calculations which consistently predict the same trends, it seems likely that there is a rumpling of the surface, but that it is small, probably no more than around 1-2 %. Satta et al. computed it to be under 1 %, but the other recent plane wave study by Preobrajenski et al. predicted a somewhat larger rumpling. In all cases where rumpling is reported, it is the S ion that moves into the bulk.

In the previous section, we noted that the calculations performed using HF theory predicted physically unrealistic surface relaxations. HF theory has recently been shown to fail to give accurate structural parameters for bulk FeS_2 (Muscat et al. 2001) due to the neglect of electronic

correlation which is necessary to treat low spin Fe ions correctly. The lack of treatment of correlation effects in HF could be a cause of the failure of HF theory for PbS surfaces. The poor performance of HF theory could also be due to a lone pair effect on the Pb ions, similar to that reported recently in studies of PbO (Watson and Parker 1999;Watson et al. 1999). Watson et al. have shown that the stabilisation of the ?-PbO structure over the CsCl structure is the result of mixing of Pb 6p states with filled O 2p and Pb 6s states. HF theory may be tending to overstabilise an ?-PbO type structure (as opposed to NaCl) for PbS which could lead to large distortions at the surface. Similar distortions would not have been seen in calculations of bulk PbS due to symmetry constraints imposed on the system.

The relaxation of the surface appears to be driven by electrostatic considerations. The ions at the surface are under-coordinated (5-fold coordination at the surface, compared to 6-fold in the bulk). Typically, the ions at the surface increase their effective coordination by relaxing into the bulk towards the second layer with the second layer relaxing upwards towards it. This in turn has the effect of reducing the effective coordination of the ions in the third layer. This layer now relaxes downwards with the fourth layer moving upwards in an analogous pattern to the top two layers. The magnitude of the contraction between even layers decays rapidly to zero by the fifth and sixth layers.

As described in the previous section, the current calculations predict a small SCLS in agreement with recent experiments. In the past, the presence or lack of a SCLS has been used to infer details as to the surface structure. For example, based on the lack of a SCLS, Allan suggested that the surface of PbS must undergo a large inward relaxation. However, tests performed in the current study on bulk terminated surfaces show that the SCLS does not appear to depend on whether or not the surface is relaxed. Satta et al. (Satta and De Gironcoli 2001) found similar results and pointed

out that it is difficult to assess the level of relaxation of the PbS surface from the SCLS since it is a property that is relatively insensitive to relaxation. The calculations in the current study support this view.

5 CONCLUSIONS

In the current article, we have presented the results of first principles calculations of the structure of the PbS (001) surface. Our results are in good agreement with previous first principles studies, with only relatively minor discrepancies present. In particular, we find that the surface does undergo significant relaxation in the (001) direction with oscillatory contraction and expansion of interlayer spacings down the surface. Some disagreement exists with regards to surface rumpling although our calculations concurr with most previous theoretical studies that predict a surface rumpling where the Pb ions lie above the plane of the surface S ions.

Of the different treatments of exchange and correlation tested, LDA, GGA and the hybrid B3LYP method all give results in reasonable agreement with each other, irrespective of the computational techniques used as long as the calculations are performed on reasonably sized systems and care has been taken to use converged basis sets and numerical tolerances. Other approximations such as the type of pseudopotential used for Pb, have an effect on the computed structure, but these effects are fairly small and do not alter the basic physical picture of the system. HF theory fails to give a reasonable description of the surface structure of PbS and we have offered some suggestions as to the reason for this. However, this is a question that needs further investigation before it can be answered conclusively.

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We have also computed the surface core level shift, with the value predicted being in excellent agreement with recent synchrotron experiments. The current calculations also confirm that the surface core level shift of PbS is not particularly sensitive to whether or not the surface is relaxed or bulk terminated and hence is probably not a reliable method for inferring surface structure for this material.

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TABLES

Atom type (layer number)	CRYSTAL98			SIESTA	
	B3LYP	LDA	GGA	LDA	PBE
Pb (1)	0.00	0.05	0.01	-0.01	-0.02
S (1)	-0.07	-0.04	-0.04	-0.02	-0.05
Pb (2)	0.14	0.09	0.12	0.15	0.12
S (2)	0.22	0.16	0.16	0.17	0.16
Pb (3)	-0.04	0.04	0.02	0.02	0.00
S (3)	-0.09	0.00	0.00	0.00	-0.02
Pb (4)	0.02	0.02	0.02	0.05	0.04
S (4)	0.06	0.04	0.04	0.06	0.05
Pb (5)	-0.04	0.01	0.00	0.01	0.00
S (5)	-0.06	0.00	0.02	0.01	0.00
Pb (6)	-0.01	0.00	0.00	0.01	0.01
S (6)	0.00	0.00	0.00	0.02	0.01

Table 1   The computed relaxation, from bulk terminated positions of the PbS (001) surface in Å

Layer No	CRYSTAL98			SIESTA	PW-LDA (Satta and De Gironcoli 2001)	PW-LDA (Preobrajenski and Chasse 2000)
	B3LYP	LDA	GGA	PBE		
1-2	-7.9	-4.1	-5.2	-5.8	-5.2	-8.5
2-3	8.4	3.6	4.3	5.0	3.5	3.6
3-4	-3.8	-0.3	-0.7	-1.8	-1.2	-1.3
4-5	3.0	0.8	0.7	1.5	0.5	
5-6	-1.5	0.2	0.3	-0.3		

Table 2   Computed % interlayer relaxations (relative to bulk)

Layer No	CRYSTAL98			SIESTA	PW-LDA (Satta and De Gironcoli 2001)	PW-LDA (Preobrajenski and Chasse 2000)
	B3LYP	LDA	GGA	PBE		
1	-2.6	-3.0	-1.7	-1.0	-0.1	-7.4
2	2.6	2.4	1.3	1.3	0.4	5.7
3	-1.6	-1.4	-0.7	-0.7	-0.4	-2.4
4	1.3	0.6	0.7	0.3	0.6	
5	-0.7	-0.3	0.7	0.0		
6	0.1	0.0	0.0	0.0		

Table 3   The computed % rumpling of the surface layers (relative to bulk)

FIGURES

Figure 1   The PbS (001) surface.

Figure 2   Convergence of ionic displacements with slab thickness computed using B3LYP.

Figure 3   The density of states of the clean PbS (001) surface computed for a 13 layer slab using B3LYP. Solid lines represent DOS for the surface Pb and S ions (layer 1), dashed lines refer to ions in the centre of the slab (layer 7).

Figure 4   The computed S 2p surface core level shift as a function of depth into the slab, computed using B3LYP for a 13 layer slab of PbS (001). The Fermi energy has been set to 0 eV and the peak corresponding to S ions in the top layer is shown filled. Relativistic effects are not being treated explicitly in the current calculations and hence the small splitting in the 2p binding energy peaks is due to differences between the energies of the p_x, p_y (large peaks) and the p_z orbitals.
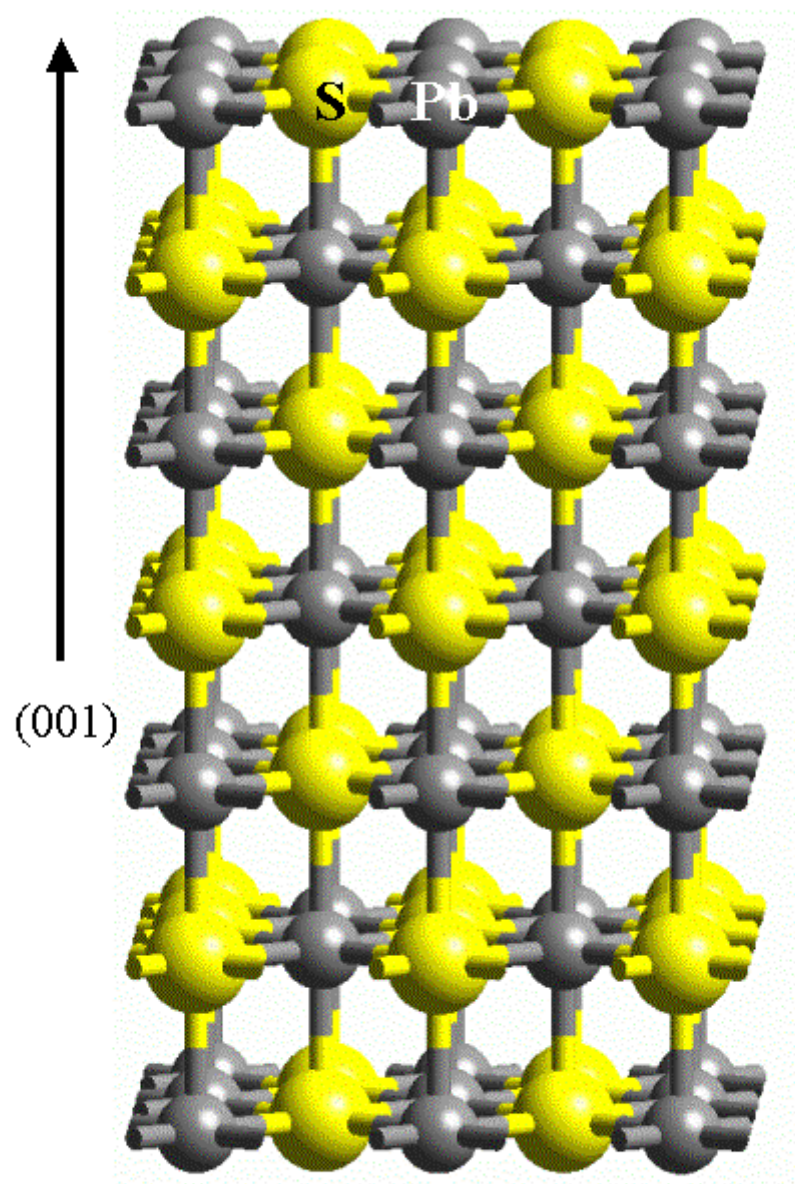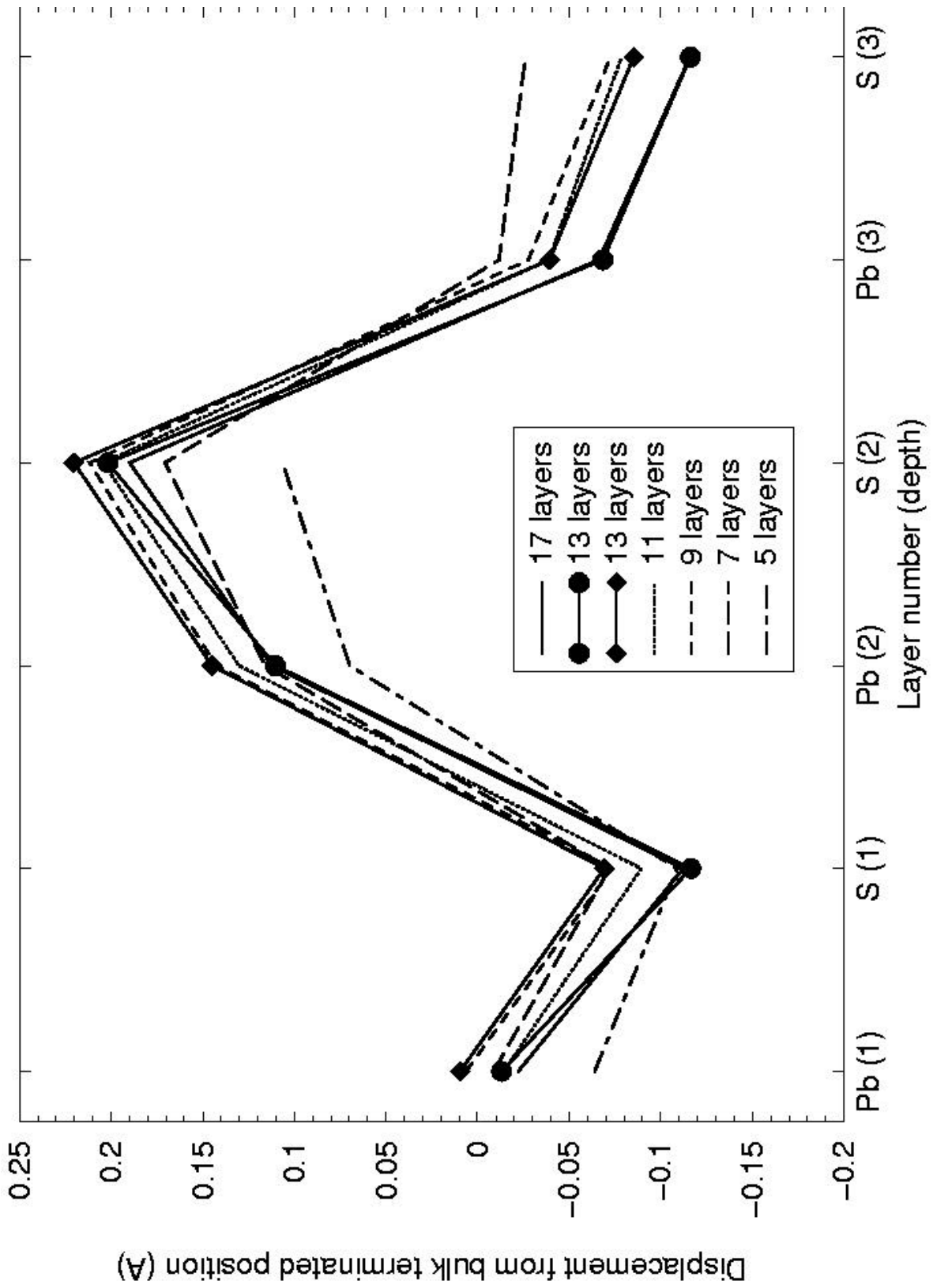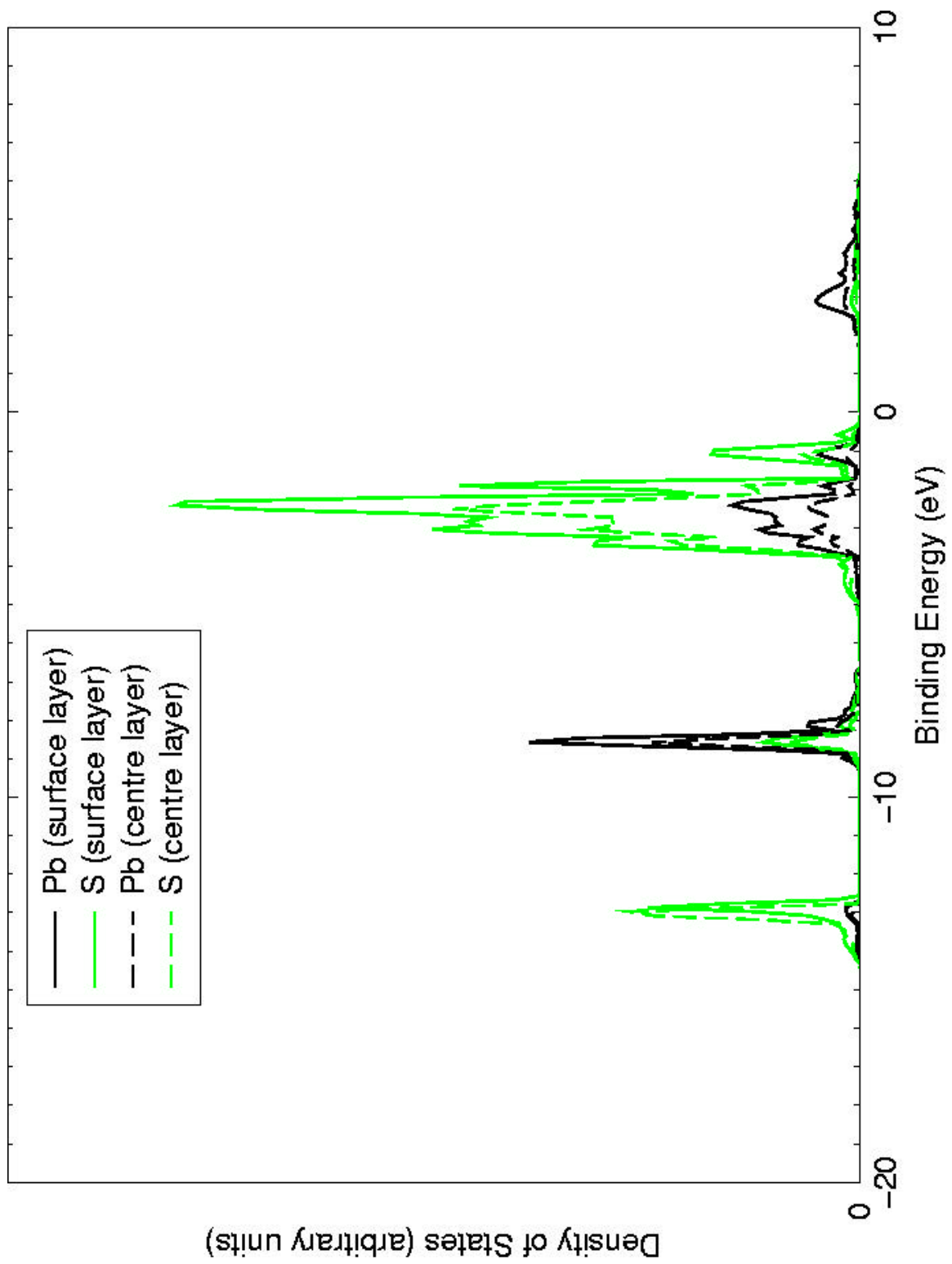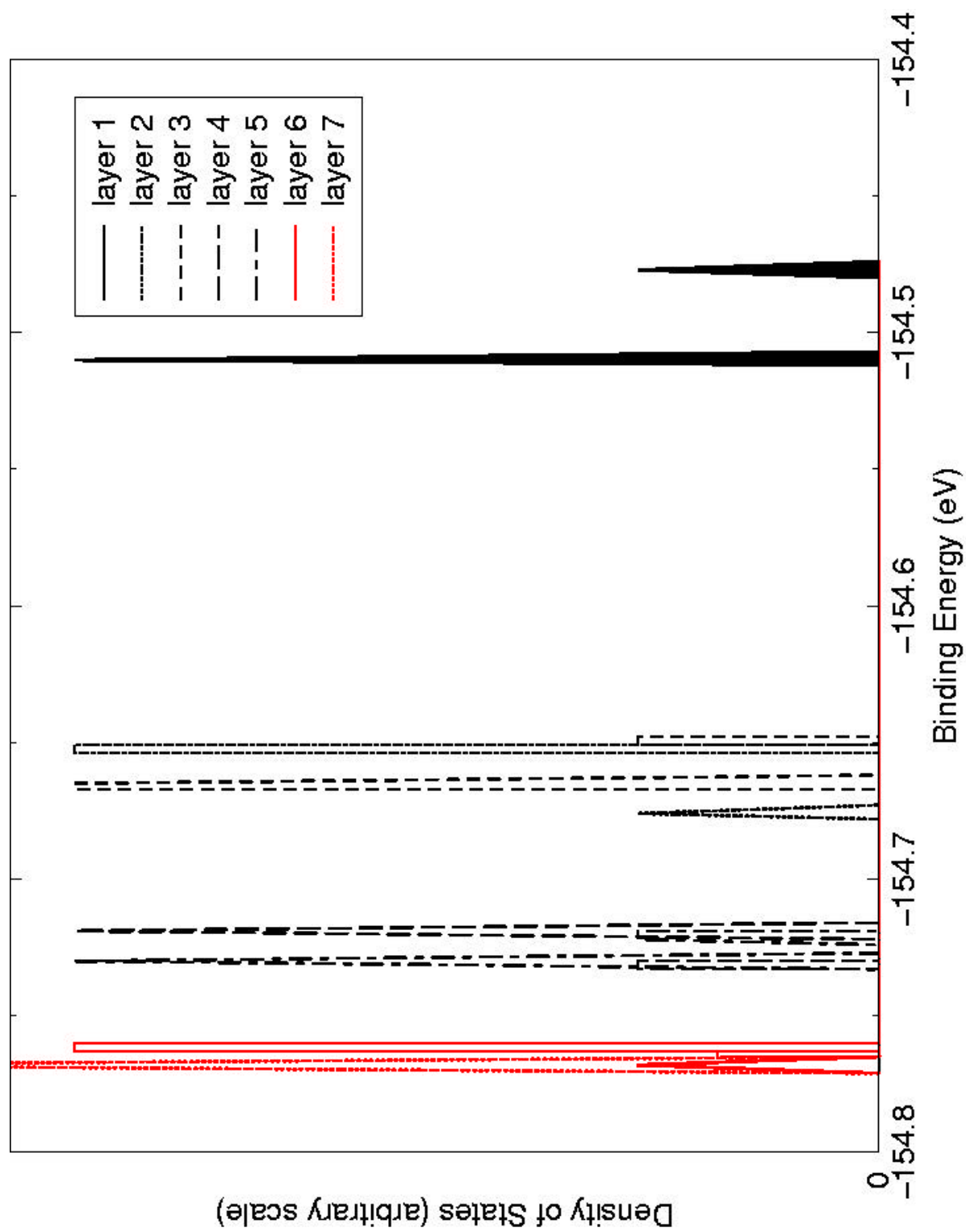
Figure 1

Figure 2

Figure 3

Figure 4