PHYSICAL REVIEW B **82**, 125308 (2010)

Ab initio study of stabilization of the misfit layer compound $(\mathrm{PbS})_{1.14}\mathrm{TaS}_2$

Evgeniya Kabliman, Peter Blaha, and Karlheinz Schwarz
Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria

(Received 28 May 2010; published 8 September 2010)

In the present work we perform *ab initio* electronic-structure calculations of the $(\mathrm{PbS})_{1.14}\mathrm{TaS}_2$ misfit layer compound in order to understand the basic mechanism of its stabilization. Density-functional based calculations were carried out in commensurate unit cells containing 74 or 296 atoms using the WIEN2K code. The two experimentally predicted mechanisms of stabilization, namely, metal cross substitution (interchange of Pb and Ta atoms in the PbS and TaS_2 layers) and nonstoichiometry (substitution of Pb by Ta), were investigated. The results show clearly that the nonstoichiometry mechanism plays the significant role. When Pb inside the PbS layer is substituted by Ta with concentrations around 0.13–0.19, a stabilization is found with respect to the parent PbS and TaS_2 compounds. These results are explained by an analysis of partial densities of states. The calculated x-ray photoemission spectroscopy core-level shifts are in reasonable agreement with experiments.

DOI: 10.1103/PhysRevB.82.125308 PACS number(s): 71.15.Mb, 71.15.Nc, 71.20.−b, 73.40.Vz

I. INTRODUCTION

The misfit layer compounds[1] form a class of materials which consists of hexagonal transition-metal dichalcogenides (TX_2) and bilayers of cubic monochalcogenides (MX), see Fig. 1. They can be described by the general formula $(MX)_{1+x}(TX_2)_m$, where M is a metal atom such as Sn, Pb, Bi, Sb, or a rare-earth element; X represents a chalcogen atom (S or Se), and T is a transition-metal atom (Ti, V, Cr, Nb, or Ta). The subindex m ($m=1,2,3$) denotes the number of hexagonal TX_2 layers alternating with one pseudocubic MX double layer. Because of the different crystal symmetries of the two subsystems, the lattice constants can match only along one direction (with $b_{TX_2}*\sqrt{3}=b_{MX}$) and a periodic structure is formed along b. Perpendicular to this commensurate direction the ratio a_{TX_2}/a_{MX} is irrational and thus an incommensurate structure is formed along a. The subindex $x=(2a_{TX_2}/a_{MX})-1$, which typically is $0.08<x<0.26$, defines the approximate stoichiometry of the misfit compound.[2,3]

The transition-metal dichalcogenides forming the TX_2 layers attract attention because of the occurrence of superconductivity and the possibility of intercalating foreign atoms and molecules.[1] This intercalation leads to new properties such as fast ion conduction of the intercalated ions and a change in the electronic properties of the host structure due to charge transfer. Instead of single atoms (molecules) it is possible to insert a double layer of cubic semiconductors MX (or metallic rare-earth sulfides), a process that forms the misfit layer compounds.[1] The interest in the latter originates from their properties and potential applications as small-scale thermoelectric and insulating materials.[4]

The stability and interlayer chemical bonding mechanism of the misfit layer compounds as well as the effect of incommensurability on their properties are not yet fully understood.[1,2,5,6] Based on previous experimental studies,[3,7] two possible bonding mechanisms were postulated.

(a) The first mechanism was proposed by Moëlo *et al.*[3] based on electron probe microanalysis of the $[(\mathrm{Pb},\mathrm{Sn})\mathrm{S}]_{1+x}[(\mathrm{Nb},\mathrm{Ti})\mathrm{S}_2]_m$ misfit layer compounds. They found a systematic (Pb,Sn) depletion and interpreted it as a partial (Ti,Nb) substitution into the pseudocubic MX layers of (Pb,Sn)S. It was argued that such a substitution may provide changes in the charge balance that is needed for a stabilization of the misfit layer compounds. In this model *nonstoichiometry* is a necessary condition for interlayer bonding. According to that review[3] three types of nonstoichiometry can be distinguished: (1) changes in the x coefficient, which is usually fixed by the incommensurability of the layers; (2) insertion of a low concentration of Nb atoms (9–10 at. %) between two adjacent NbS_2 layers in Nb bilayer and trilayer compounds; and (3) a systematic cationic substitution of M ions by T atoms within the MX layer, which varies from compound to compound.

(b) Recently Kalläne *et al.*[7] suggested an alternative mechanism when analyzing their photoelectron microscopy measurements on the $(\mathrm{PbS})_{1.13}\mathrm{TaS}_2$ compound. These authors suggested that Ta atoms substitute some Pb atoms in the PbS layer, in accordance with previous findings,[3] but in addition also Pb atoms substitute Ta atoms in the TaS_2 layer and called this a novel *metal cross-substitution* mechanism. In contrast to Moëlo *et al.*[3] they suggested that even formally stoichiometric misfit layer compounds can be stabilized by this mechanism. They generalized their findings stating that the metal cross substitution is of fundamental importance for all misfit layer compounds while nonstoichiometry is not necessary.

The aim of this paper is to study $(\mathrm{PbS})_{1.14}\mathrm{TaS}_2$ by *ab initio* electronic-structure calculations and explore which of the two experimentally predicted mechanisms for the stabilization of the misfit layer compound (metal cross substitution or nonstoichiometry) is likely to be correct.

II. COMPUTATIONAL DETAILS

In the present work the *ab initio* electronic-structure calculations were performed using the WIEN2K code[8] which utilizes the full-potential augmented plane wave+local orbitals method[9,10] for solving the density-functional theory (DFT) equations.[11,12] The exchange-correlation functional was evaluated within the generalized gradient approximation (GGA) proposed by Wu and Cohen[13] since this approxima-

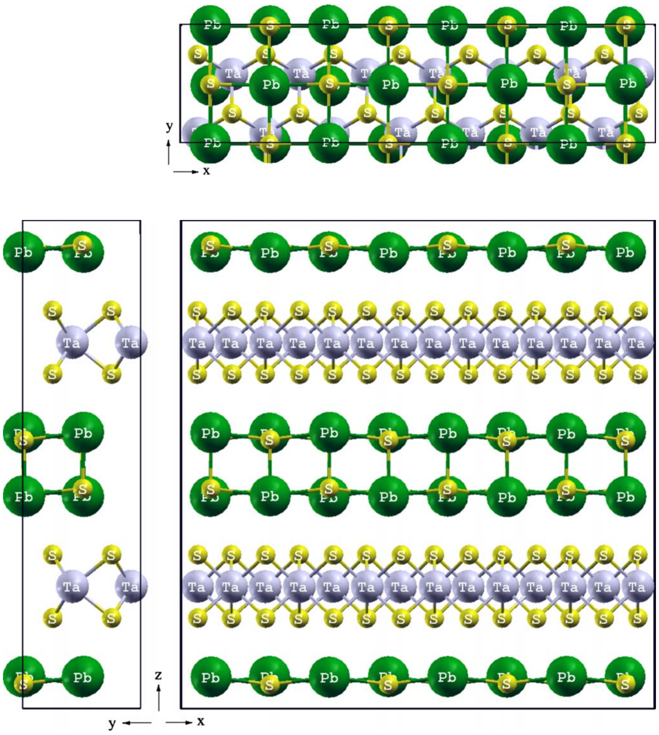

FIG. 1. (Color online) The conventional unit cell (with a periodic structure containing four PbS and seven TaS_2 unit cells in the "incommensurate" direction) of the stoichiometric misfit layer compound $(PbS)_{1.14}TaS_2$ with relaxed atomic coordinates.

tion gives in general more accurate lattice parameters in solids than the standard PBE-GGA.[14] In particular, nearly perfect agreement was obtained for the parent compounds PbS and TaS_2 (see Table I). The atomic sphere radii R of the Pb, Ta and S atoms were chosen as 2.80 a.u., 2.13 a.u., and 2.07 a.u., respectively. The product of the smallest atomic sphere radius R times the largest reciprocal-lattice vector RK_{max} is taken equal to 6.0 and defines our plane wave basis set cutoff. To check the accuracy of the calculations the RK_{max} value was later increased to 7.0 for the final results. A k mesh of up to $2\times2\times5$ was used for the 74 atoms cell described below. The core states are recalculated in each self-consistent-field iteration in the given (spherical) potential by numerically solving the radial Dirac equation.[15] For the valence states only scalar relativistic effects (the Darwin s shift and the mass velocity term) were considered[16] and spin-orbit coupling is neglected.

TABLE I. The theoretically optimized structure parameters of TaS_2, PbS, and $(PbS)_{1.14}TaS_2$. Experimental values are given in parenthesis. The two experimental a lattice parameters of $(PbS)_{1.13}TaS_2$ indicate the incommensurability of the PbS and TaS_2 sublattices. Note that c of TaS_2 cannot be optimized in standard GGAs since the weak interlayer interactions are not properly modeled and thus the experimental value was taken.

Compound	Space group	Parameters (Å)
PbS	$Fm\bar{3}m$	$a_{cubic}=a_{PbS}=5.91$ (5.914^{a})
TaS_2	$P6_3/mmc$	$a_{hex}=a_{TaS_2}=3.30$ (3.314^{b})
		$c_{hex}=c_{TaS_2}=12.097$ ^{b}
$(PbS)_{1.14}TaS_2$	$Bb2b$	$a=23.19$ ($23.30/23.13)^{c}$
		$b=5.77$ ($5.78)^{c}$
		$c=23.88$ ($23.96)^{c}$

[a] Reference 18.
[b] References 19 and 20.
[c] Reference 17.

III. STRUCTURE

As mentioned above, the structure of the misfit layer compound consists of hexagonal TaS_2 slabs and a double layer of cubic PbS. It is commensurate along one of the axes (usually the b axis, which is equal to $a_{PbS}\approx a_{TaS_2}*\sqrt{3}$) but incommensurate along the a axis due to the irrational ratio a_{TaS_2}/a_{PbS} for the two subsystems[2](see Fig. 1). For the PbS-TaS_2 system, the misfit leads to an experimentally observed[7,17] stoichiometry of $(PbS)_{1.13}TaS_2$. In order to facilitate periodic boundary conditions for band-structure calculations, one must approximate this incommensurate ratio by some rational one, n_{PbS}/n_{TaS_2}, where n_{PbS} and n_{TaS_2} specifies the number of unit cells of each corresponding subsystem forming the a lattice parameter of the unit cell representing the misfit layer compound. In the present paper we investigate $(PbS)_{1.14}TaS_2$ with a ratio $a_{TaS_2}/a_{PbS}=4/7$ or $7*a_{TaS_2}\simeq4*a_{PbS}\simeq a$, which is very close to the actual experimental stoichiometry. In the unit cell projected perpendicular to the (x,y) plane (top of Fig. 1) one can see both, the hexagonal TaS_2 structure and how seven of these units match the four pseudocubic PbS units. The starting cell parameters of the misfit compound were deduced from the theoretically optimized PbS and TaS_2 lattice parameters (see Table I). The a parameter was derived as an average between $(7*a_{TaS_2})$ and $(4*a_{PbS})$, the b parameter is an average between $a_{TaS_2}*\sqrt{3}$ and a_{PbS} and the c parameter is equal to $(c_{TaS_2}+2*a_{PbS})$. This gave the following $(PbS)_{1.14}TaS_2$ starting structure parameters: $a=23.45$ Å, $b=5.83$ Å, and $c=23.93$ Å, which were optimized later on.

Fang *et al.*[2] showed in a study of the $(LaS)_{1.14}NbS_2$ and other misfit layer compounds that the commensurate misfit layer structure can be modeled in space group No. 37 ($Bb2b$). The unit cell contains 74 atoms which in the $(PbS)_{1.14}TaS_2$ case corresponds to four independent Ta (14 atoms) and seven independent S sites (28 atoms) in the TaS_2 layer; and four independent Pb and S sites (16 atoms each) in the PbS layer. Figure 1 shows the corresponding unit cell for which both, the lattice parameters as well as the internal coordinates were fully relaxed. The results are given in Table I and II and will be discussed in Sec. IV A.

The investigation of the two possible bonding mechanisms requires several different substitutions at various atomic sites. The compositions are summarized in Table III and the structures will be discussed in detail in the corresponding sections. Although the unit cell mentioned above contains 74 atoms, it is still too small because of the short dimension along the b direction, which would lead to highly

TABLE II. The atomic coordinates of the fully relaxed $(PbS)_{1.14}TaS_2$ unit cell (stoichiometric and without cross substitution) in the *Bb*2*b* space group with $a=23.19$ Å, $b=5.77$ Å, and $c=23.88$ Å.

Atom	Wyck. pos.	x	y	z
Ta (1)	4*c*	0.2500	0.5789	0.2500
Ta (2)	8*d*	0.0360	0.0789	0.2504
Ta (3)	8*d*	0.6069	0.0788	0.2500
Ta (4)	8*d*	0.1787	0.0790	0.2497
S (1)	8*d*	0.0353	0.7454	0.3152
S (2)	8*d*	0.1784	0.7454	0.3147
S (3)	8*d*	0.6074	0.7459	0.3152
S (4)	8*d*	0.4647	0.7457	0.3147
S (5)	8*d*	0.3216	0.7453	0.3149
S (6)	8*d*	0.8925	0.7460	0.3152
S (7)	8*d*	0.7500	0.7462	0.3153
Pb (1)	8*d*	0.3128	0.9824	0.5660
Pb (2)	8*d*	0.5629	0.9921	0.5648
Pb (3)	8*d*	0.8123	0.9955	0.5643
Pb (4)	8*d*	0.0620	0.9868	0.5654
S (8)	8*d*	0.3125	0.4854	0.5488
S (9)	8*d*	0.5624	0.4923	0.5503
S (10)	8*d*	0.8125	0.4947	0.5510
S (11)	8*d*	0.0626	0.4885	0.5495

ordered "rows" of impurity atoms. Therefore we have constructed a unit cell that has a four times larger b axis making all three cell parameters comparable and containing 296 inequivalent atoms. This allows to model various distributions of Ta atoms in the PbS layer as well as Pb atoms in the TaS_2 layer and to evaluate effects of impurity clustering or the dependence on the distances between impurities.

IV. RESULTS AND DISCUSSION

Since the present misfit layer compound has a complex structure, any Ta or Pb atomic substitution causes substantial displacements of the adjacent atoms. Therefore, all calculations were done including a full relaxation of the internal parameters. The energy of formation with respect to the parent compounds TaS_2, PbS and bulk Ta was obtained by the general formula,

$$\begin{aligned} E_{form} = E_{total}^{n_{\mathrm{Ta}_{imp}}}((\mathrm{PbS})_{1.14}\mathrm{TaS}_2) - [7 * E_{total}^{bulk}(\mathrm{TaS}_2) \\ + 4 * E_{total}^{bulk}(\mathrm{PbS}) - n_{\mathrm{Ta}_{imp}} * E_{total}^{bulk}(\mathrm{Pb}) \\ + n_{\mathrm{Ta}_{imp}} * E_{total}^{bulk}(\mathrm{Ta})], \end{aligned} \tag{1}$$

where $n_{\mathrm{Ta}_{imp}}$ is the number of Ta impurities substituting Pb atoms in the PbS layer. Only for metal cross substitution $n_{\mathrm{Ta}_{imp}}$ is zero but otherwise it ranges from $n_{\mathrm{Ta}_{imp}}=1-8$ for the nonstoichiometric models.

A. Stoichiometric and ideal structure

The real misfit layer compound has a complex and incommensurate structure which we model by a commensurate cell. The effect of incommensurability can be estimated from the structural data (Table I) with an experimentally determined misfit of less than half a percent compared to the assumed commensurate structure. Thus such a commensurate model should be realistic and fairly reliable. The full theoretical structure relaxation of the misfit layer compound implies not only the optimization of the internal positions but also of the a, b, and c cell parameters. In the present work the following cell parameters for the $(PbS)_{1.14}TaS_2$ structure were found: $a=23.19$ Å, $b=5.77$ Å, and $c=23.88$ Å which compare perfectly with the experimental data (see Table I). In comparison to the assumed lattice parameters derived from the averages of the parent compounds PbS and TaS_2 ($a=23.43$ Å, $b=5.83$ Å, and $c=23.93$ Å) only a 1% reduction in a (the "incommensurate") and b (the short commensurate direction) was obtained while c has changed even less. This indicates that bonding effects between the two subsystems of the misfit layer compound must be weak. The corresponding energy gain of the optimized with respect to the original $(PbS)_{1.14}TaS_2$ structure (unrelaxed with cell parameters derived directly from the parent PbS and TaS_2 compounds) is fairly small and about 64 mRy/unit cell (74 atoms). Also the formation energy compared to the parent PbS and TaS_2 compounds is about zero (Table IV), which would

TABLE III. Number of Pb and Ta atoms in various model structures. There are always 16 (64) and 28 (112) S atoms in the PbS and TaS_2 layers of the 74 (296) atoms unit cells.

	PbS layer		TaS_2 layer		
	Pb	Ta	Ta	Pb	Total
Ideal	16		14		74
Cross substitution	15	1	13	1	74
	60	4	52	4	296
Nonstoichiom.	$16-n$	n	14		74
	$64-4n$	$4n$	56	4	296
Cross substitution+nonstoichiom.	$15-n$	$1+n$	13	1	74
	$60-4n$	$4+4n$	52	4	296

TABLE IV. The formation energies of the $(PbS)_{1.14}TaS_2$ misfit layer compound (mRy/atom). The optimized structure parameters of the unit cell: $a=23.193$ Å, $b=23.884$ Å, and $c=5.765$ Å.

Structural model	N_{at}	E_{form} (Ry/74 atoms unit cell)
Original structure	296	0.005
Metal cross substitution	74	0.113
Metal cross substitution	296	0.095
Nonstoichiometry	74	−0.289
Nonstoichiometry	296	−0.396
Met. cross subst.+nonst.	74	0.010
Met. cross subst.+nonst.	296	−0.028

indicate that the idealized stoichiometric $(PbS)_{1.14}TaS_2$ structure itself is not stable. Since experimentally these misfit layer compounds form easily, one needs to understand what really stabilizes them.

The relaxation of the $(PbS)_{1.14}TaS_2$ structure allows us to compare distances between atoms in the parent PbS and TaS_2 structures and $(PbS)_{1.14}TaS_2$. The most pronounced differences stem from a movement of the S atoms of the PbS double layer along the z direction because they are strongly repelled by the adjacent sulfur atoms of the TaS_2 slabs (Fig. 1 and Table V). These sulfur atoms move about 0.2 Å toward the Pb atoms below/above them, thereby reducing the Pb-S distance by 0.2 Å and the S-S distances within the PbS double layer by about 0.35 Å. These S-S distances (around 3.72 Å) are still significantly larger than those between the sulfur atoms of PbS and TaS_2 (about 3.53 Å). The movements of the Pb atoms are much smaller and the nearest Pb-Pb distances vary between 4.05 Å (within one PbS layer) and 4.22 Å (between different PbS layers), values which are similar to the Pb-Pb distance in pure PbS (4.18 Å). The closest distances between Pb and S of the TaS_2 layer range from 3.24–3.29 Å and are much larger than the Pb-S distances within the PbS layer. The experimentally determined distortions[17] are qualitatively very similar with a larger movement of Pb atoms toward the adjacent TaS_2 layers, whereby the distance between the two Pb planes increased from 2.97 Å in bulk PbS to 3.28 Å. The theoretical increase of this distance (about 3.10 Å) is smaller. On the other hand, the experimentally determined change in the S position is smaller and thus the decrease of the Pb-S distance in the PbS layer (2.83 Å) is smaller than in theory (2.74 Å). In contrast to the flexible PbS double layer, the TaS_2 slabs are fairly rigid and the Ta-S distances hardly change in comparison to pure TaS_2. The shortest S-S distance along z reduces slightly indicating a small compression of the TaS_2 sandwich slab while the S-S distances within one layer hardly change. Experimentally (Ref. 17) a characteristic splitting of the Pb-S distances (2.44 and 2.52 Å) was found which we do not find in the "ideal" structure but with metal cross substitution (see below, Sec. IV B and Table V). It should be mentioned, that in the x-ray diffraction refinements neither nonstoichiometry nor antisite atoms have been taken into account, although their sample could hardly be taken as ideal.

B. Metal cross-substitution model

As mentioned above, the ideal stoichiometric structure has about zero formation energy with respect to the parent compounds. In this section we will investigate how much metal cross substitution (as suggested in a recent experimental study[7]) will influence the stability. In order to model this situation we exchange one Pb atom from one of the PbS layers with one Ta atom from the TaS_2 layer (Table III). Since the $(PbS)_{1.14}TaS_2$ structure is quite complicated and has many nonequivalent sites, there are many different possibilities to arrange such cross substitutions. While we cannot test all possible combinations, 26 different arrangements of the substituted atoms were chosen. They differ mainly in the distance of the exchanged atoms (as close as possible vs as far as possible) but also by choosing different inequivalent Pb sites (Wyckoff positions) in the PbS layer. All 26 calculated structures have positive formation energies ($0.113 < E_{form} < 0.129$ Ry/74 atoms unit cell). The most stable energy is shown in Fig. 3 (inverted triangles) and the cross-substitution model structures are clearly less stable than the ideal structure (Table IV). Since such substitutions lead to

TABLE V. The atomic distances (Å) in bulk PbS and TaS_2 and the $(PbS)_{1.14}TaS_2$ compound. The letter in parenthesis gives the direction of the neighbor.

	PbS	TaS_2	PbS layer (ideal)	TaS_2 layer (ideal)	PbS layer (exch.)	TaS_2 layer (exch.)
Pb-S	2.957		2.74(z), 2.92(xy)		2.74–3.04	2.69–2.76
			3.24–3.29[a]		3.07–3.71	
Pb-Pb	4.182		4.05–4.22		3.79–4.39	
Ta-S		2.467		2.46–2.47	2.26–2.46	2.44–2.50
Ta-Ta		3.297		3.32–3.33		3.15[d]–3.60
S-S	4.182	3.137(z), 3.297(xy)	3.71–3.76	3.09(z), 3.31(xy)	3.33[c]–3.72	3.03[d]–3.45
			3.52–3.58[b]		3.20–3.86[b,c]	

[a] Pb(PbS)-S(TaS_2).

[b] S(PbS)-S(TaS_2).

[c] Ta(exch) is nearest neighbor (nn).

[d] Pb(exch) is nn.

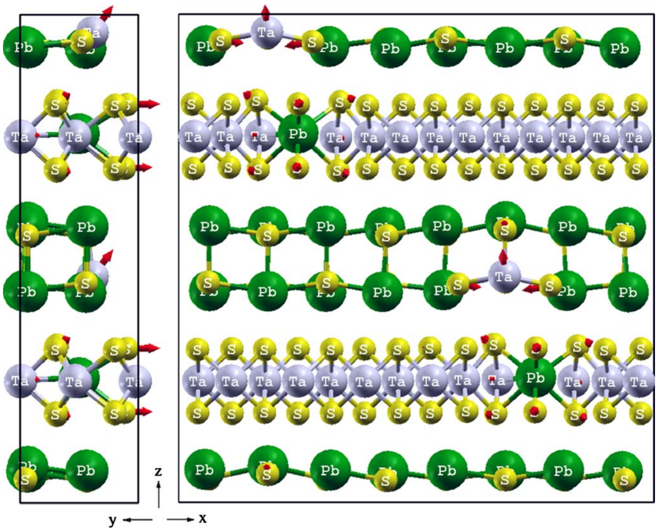

FIG. 2. (Color online) The conventional unit cell of the stoichiometric misfit layer compound $(PbS)_{1.14}TaS_2$ in the lowest energy relaxed structure after a metal (Pb,Ta) cross substitution with a fairly small distance between the exchanged atoms. The arrows indicate the atomic movements due to the cross substitution.

relative short distances between the antisite atoms along the short *b* axis, we have also used a four times larger supercell (Table III) with 296 atoms/cell, which allows a better separation of the antisite atoms. This slightly reduces the calculated formation energy to about 0.095 Ry /74 atoms cell (Fig. 3 and Table IV) but E_{form} is still clearly positive and unfavorable. It should be mentioned, that the distance between the antisite atoms is not necessarily the determining parameter for the total-energy variations but shorter distances tend to give lower energies.

Figure 2 displays the cross-substituted structure with the lowest energy and the arrows show the movements of the atoms after Pb-Ta exchange. The Pb atom is much larger than Ta and thus the sulfur atoms in the TaS_2 layer move away from the antisite Pb atom. However, since the TaS_2 sandwich is fairly rigid, these movements are limited and the Pb-S distances (ranging between 2.69–2.76 Å) remain smaller than the Pb-S distances in the PbS layer (2.74 and 2.92 Å) and are energetically unfavorable (Table V). Of course the large Pb atom can lead to fairly small Ta-Ta and S-S distances in the vicinity of the impurity and also the Ta-S distances may become unequal. On the other hand, the small Ta ion in the PbS layer moves a lot toward the sulfur above it, making the Ta-S distance along z only 2.26 Å while in xy direction the neighboring S atoms come also closer establishing the usual Ta-S distances of about 2.46 Å. Due to this large relaxation, also all other distances in the vicinity of the Ta impurity are affected.

The obtained results demonstrate that the metal (Pb-Ta) cross substitution in $(PbS)_{1.14}TaS_2$ is not energetically favorable in comparison to the formation energy of the original structure and thus we conclude that the metal cross-substitution mechanism cannot stabilize the stoichiometric misfit layer compound.

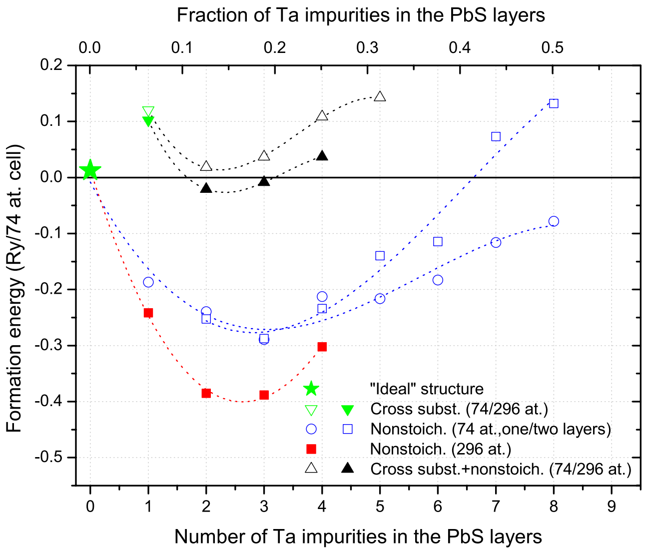

FIG. 3. (Color online) The formation energy (Ry/74 atoms unit cell) of the misfit layer compound $(PbS)_{1.14}TaS_2$ as function of the Ta impurity concentration using 74 atoms (open symbols) and 296 atoms (filled symbols) cells. The green star corresponds to the ideal structure, the inverted triangles to the cross-substitution model, the triangles correspond to a combined model of metal cross substitution with one Pb atom in the TaS_2 slab and additional nonstoichiometry, while squares and circles indicate nonstoichiometry only, with Ta impurities in both or only one PbS layer, respectively.

C. Nonstoichiometric model

In Ref. 7 it was argued, that metal cross substitution should be the driving force for the stabilization of these misfit layer compounds but even there the authors found a significantly larger concentration of Ta that is substituted into the PbS layer ($x=0.18\pm0.05$) than of Pb into TaS_2 ($y=0.08\pm0.05$). This is in good agreement with Moëlo *et al.*,[3] who found that nonstoichiometry is a necessary condition for the stability of these compounds. In order to test this model, n Pb atoms in the PbS layer have been substituted by n Ta impurities, where $n=1-8$ per 74 atoms unit cell, which corresponds to fractional impurity concentrations of $x=0.0625-0.50$ (Table III). A single Ta impurity can occupy four different inequivalent Pb sites in the 74 atoms cell. We have tested all of them but the energies are almost the same (within 3.5 mRy) and only one data point (open circle at 1 Ta impurity) is shown in Fig. 3. We immediately notice a significant stabilization (about 200 mRy) of such structures compared to the stoichiometric compound while the specific site of substitution plays a minor role. Encouraged by this result we continued and substituted up to 8 Ta atoms into the PbS layer. With multiple substitutions, many possible arrangements for the Ta impurities become possible. We have tested several of them, in particular, restricting the substitutions to only one (empty squares in Fig. 3) or distributing them into both PbS layers (empty circles in Fig. 3) but also varying the distance between impurities as much as possible. Due to the strong lattice relaxation around the small Ta impurities it is more favorable to separate the impurities as far as possible from each other. For instance, for two Ta impurities (one in each PbS layer) the formation energy is about 44 mRy higher for a short vs a large distance between these impurities. For even higher concentration it is advantageous to put them into just one PbS layer (empty squares in Fig. 3) because the relaxations in different layers will be hampered. As shown in Fig. 2 a single Ta impurity in one PbS layer shifts mainly along z toward the other PbS layer. Therefore, when two or more Ta impurities belong to different PbS layers but are close to each other, they will repel in contrast to a common movement along z when they are only in one PbS layer. Figure 3 and Table IV clearly shows that a Ta impurity concentration between $x=0.13-0.19$ is energetically most favorable which is in excellent agreement with the experimental findings quoted above.

In order to verify our results we have again cross-checked them using a four times larger supercell (Table III). Qualitatively we obtained the same trend as above but the stabilization is even a bit stronger since in the large cell the impurities can be more evenly distributed in the PbS layers (filled squares in Fig. 3). By using the large supercell we estimate a final stabilization of about 0.4 Ry/74 atoms cells for an impurity concentration of about $x=0.13-0.19$ (see Table IV) and thus can conclude that nonstoichiometry, or more specifically, the presence of Ta impurities in the pseudocubic PbS layers is necessary for the stabilization of the $(PbS)_{1.14}TaS_2$ compound.

D. Metal cross-substitution+nonstoichiometry model

In order to test whether both suggested bonding mechanisms may actually occur simultaneously and lead to further stabilization, we have also tested these possibilities (Table III). As can be seen from Fig. 3 (open and filled triangles) metal cross substitution has no energetic advantage over nonstoichiometry, at least not in the $(PbS)_{1.14}TaS_2$ compound. Nevertheless, a minimum occurs at $x=0.16$ and $y=0.06$, which is in perfect agreement with experimental estimates given in Ref. 7. Because the energy differences are not very large, it may happen that under the harsh growth conditions and finite tempering times most samples will show both, large nonstoichiometry and also some cross substitutions into the TX_2 layers.

E. Density of states and core-level shifts

In this section we will analyze how the density of states (DOS), charge distribution, and bonding mechanism are responsible for the stabilization of the misfit layer compound. In addition we will discuss the core level shifts and compare them with experiment. The calculated total and partial DOS of the parent compounds PbS and TaS_2 as well as that of the stoichiometric misfit layer compound $(PbS)_{1.14}TaS_2$ in the ideal structure and after metal cross substitution are shown in Fig. 4. It should be noted that there are significant differences in the DOS compared to earlier linear muffin-tin orbital calculations.[5]

Comparing the DOS of the parent compounds [Fig. 4(a)] with ideal $(PbS)_{1.14}TaS_2$ [Fig. 4(b)] we notice some similarity but also significant and important differences indicating that the misfit layer compound is not just a superposition of the parent compounds. Bulk PbS is found to be an insulator with a tiny gap of about 0.2 eV at the L point but the DOS around E_F is very small for about 1 eV because of very steep parabolic bands. The Pb s band (with the main peak around

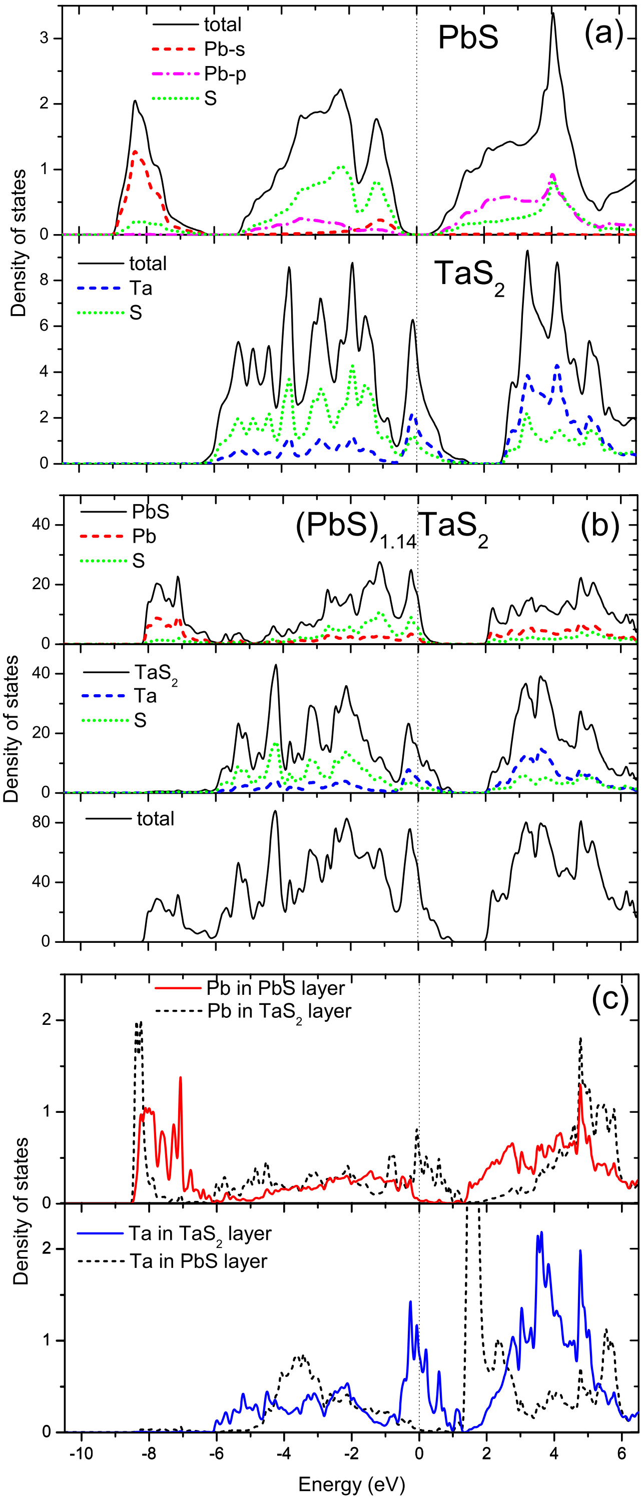

FIG. 4. (Color online) The total and partial DOS of (a) the parent compounds PbS and TaS_2; (b) the ideal misfit layer compound $(PbS)_{1.14}TaS_2$ with the total DOS as well as the partial DOS of the PbS and TaS_2 layers; and (c) the partial DOS of the nonstoichiometric model, showing the Ta and Pb DOS in both layers.

TABLE VI. The atomic (Pb,Ta,S) charges in bulk TaS_2 and PbS and $(PbS)_{1.14}TaS_2$ compound.

System	Pb	S	Ta
PbS bulk	80.21	14.05	
TaS_2 bulk		14.17	69.52
$(PbS)_{1.14}TaS_2$ (ideal)			
PbS domain	80.24	14.07	
TaS_2 domain		14.19	69.58
$(PbS)_{1.14}TaS_2$ (exch.)			
PbS domain	80.22(2)	14.07[a]–14.15[b]	69.53
TaS_2 domain	80.55	14.14[c]–14.21[d]	69.59

[a] Only Pb is nn.

[b] Ta(exch) is nn.

[c] Pb(exch) is nn.

[d] Only Ta is nn.

−8 eV) is separated from the S(Pb) *p* band by about 0.8 eV and one should note that at the top of the valence band there is again a significant Pb *s* contribution.

In $PbS_{1.14}TaS_2$ [Fig. 4(b)], however, the DOS from the atoms of the PbS layer is shifted upward with respect to the Fermi energy (E_F) and thus the top of the PbS valence band becomes unoccupied and the layer is metallic. Note, that such a change in the DOS indicates a charge transfer from the PbS layer into the TaS_2 layer. This charge transfer, however, is not directly visible in the total charges inside the corresponding atomic spheres (see Table VI) because the diffuse Pb 6*sp* orbitals have most of their charge outside the sphere. On the other hand the corresponding conduction band starts at about 2 eV above E_F so that the effective separation between valence and conduction bands has been enlarged. Furthermore the low-lying Pb *s* band has broadened and there is no gap between the *s* and *p* bands anymore.

When we compare the DOS of the TaS_2 states in the bulk [Fig. 4(a)] and the misfit layer compound [Fig. 4(b)] we find a small downward shift (for PbS we noticed an upward shift) of the TaS_2 states in the misfit compound. E_F is not so close to the top of the characteristic Ta *d* peak anymore, which is of mixed d_{z^2} and $d_{xy}+d_{x^2-y^2}$ character as found before,[21] but not only of d_{z^2} character as was quoted in other literature.[5,22] In accord with this observation the Ta and S charges in the TaS_2 layer increased slightly in comparison to bulk TaS_2 (Table VI). Otherwise the DOS has not changed much, a result that is in agreement with the small structural changes described above, where the TaS_2 layer was found to be fairly rigid in contrast to the PbS double layer, where much larger relaxations were found.

In summary the DOS of the misfit layer compound indicates some charge transfer from the PbS toward the TaS_2 layer which might be of vital importance for the stability. In addition a broadening of the PbS DOS is found while the DOS originating from the TaS_2 layer has not changed much compared to bulk TaS_2.

As mentioned above, metal cross substitution is one of the suggested stabilization mechanisms that was put forward in Ref. 7. In Fig. 4(c) we show the partial DOS of Pb and Ta antisite atoms as well as representative DOS curves for Pb and Ta atoms in their original layers. The Pb antisite DOS shows a very localized peak around −8 eV (Pb *s*), but more importantly, a "metallic *s* DOS" which completely fills the gap present in PbS. Its shape around E_F is very similar to the 5*d* DOS of Ta in TaS_2 and, in particular, when the Ta atom is close to the Pb antisite atom their peaks match. The integrated charge in the Pb atom in the TaS_2 domain (Table VI) is significantly larger than in the PbS domain. This increase could be due to the tails of the sulfur atoms, which are much closer to the Pb atom in the TaS_2 than in the PbS layer.

On the other hand the Pb-DOS in the PbS layer has shifted back to lower energies (almost as in bulk PbS) and the charge transfer that was present in ideal $(PbS)_{1.14}TaS_2$ changed back due to the Ta antisite atoms in the PbS layer. These antisite Ta atoms have a completely different DOS than Ta in TaS_2 and we see almost exclusively Ta *d* states with (approximate) e_g symmetry (Ta *d* orbitals pointing toward the S neighbors) in the valence band, separated by a gap from the localized t_{2g} peak at 1.7 eV above E_F. Thus, the Ta antisite atoms are formally 3+ ions and some of its *d* charge has been backdonated to the Pb atoms in the PbS layer. This is consistent with the slightly smaller Ta antisite charge (Table VI) but the increased sulfur charge when it has a Ta neighbor.

These latter effects explain why nonstoichimetry, i.e., Ta impurities in the PbS layer improve the stability of this compound. These antisite atoms restore the original "insulating PbS" DOS due to some charge transfer but in addition only bonding Ta *d* states (with the S atoms) are occupied while the nonbonding Ta *d* states are shifted above E_F. On the other hand, Pb antisite atoms are very compressed, have a metallic DOS at E_F and thus bring no stabilizing effect.

The metal cross-substitution model was based on an analysis of Pb 5*d* and Ta 4*f* x-ray photoemission spectroscopy (XPS) core-level shifts.[7] In order to interpret their data these authors found that for both atoms at least two different atomic sites were necessary. They could assign the observed peaks to the corresponding regions (PbS or TaS_2 layers) from where they originate. The Ta 4*f* core states of the Ta antisite atoms had an energy shift of about 2.15 eV toward higher binding energies with respect to the Ta 4*f* states in TaS_2 while the Pb 5*d* states of the antisite atoms were shifted by about 0.55 eV toward lower binding energy.

If we just analyze the core eigenvalues of our calculations of the metal cross-substitution model, the corresponding core-level shifts give a higher binding energy of about 0.8 eV for Ta 4*f* antisite states, but more or less no shift for Pb 5*d* states of antisite atoms. In any case, the effects are much smaller than in experiment. It is clear that DFT ground-state eigenvalues do not give a perfect estimate of XPS excitation energies. Our binding energies calculated from the fully relativistic eigenvalues for the Ta $4f_{5/2}$ and Pb $5f_{3/2}$ states are 20.9 eV and 18.2 eV, respectively, which can be compared to the experimental values of 24.6 and 21.8 eV. The spin-orbit splitting of 2.0 and 2.6 eV for these two states matches experiment very well. Still, one could expect that relative shifts are more reliable provided they originate mainly from a static charge-transfer effect. However, in the present case this condition does not hold at all, because the Ta (Pb) antisite atoms have an insulating (metallic) DOS while the Ta (Pb) atoms in the TaS_2 (PbS) layer are metallic (insulating) and thus the final state screening effects are very different for them. In order to better account for those effects, we have done a number of supercell calculations using Slater's transition state method,[23,24] where half an electron has been removed from one atom. The resulting core eigenvalues are much closer to the experimental binding energies (25.1 eV and 21.1 eV, respectively) and contain both, the effects of charge transfer and (static) screening. Such calculations result in energy shifts of about 0.9–1.5 eV toward higher binding energies for the substituted Ta atoms and of about 0.2–0.5 eV toward lower binding energy for the substituted Pb atoms in qualitative agreement with experiment. We do find the correct sign of the corresponding energy shifts but the magnitude (in particular, for Ta 4f shifts) is still too small.

V. SUMMARY

In the present work we have performed *ab initio* electronic-structure calculations of the $(PbS)_{1.14}TaS_2$ misfit layer compound. In order to understand a mechanism of its stabilization the two experimentally predicted models of stabilization, namely, metal cross substitution and/or nonstoichiometry, were studied using large supercells. It was found that the metal (Pb,Ta) cross substitution cannot stabilize the $(PbS)_{1.14}TaS_2$ compound according to the calculated formation energies. On the contrary the nonstoichiometric model, where Ta atoms substitute Pb in the PbS layer, has a strong stabilizing effect and thus must be the stabilizing mechanism in these misfit layer compounds. We find a minimum in the formation energy for an impurity concentration around $n_{\mathrm{Ta}_{imp}}=0.15$ in very good agreement with experimental estimates. Of course, due to high-temperature and nonequilibrium conditions during the growth of these materials, also Pb impurities in the TaS_2 layer are possible.

We found large distortions of the flexible PbS layers when Ta atoms are incorporated but only a "breathing" when Pb substitutes Ta in TaS_2. The stabilizing effect can be explained by analyzing the DOS and the related charge transfer. The calculated XPS core-level shifts are in fairly good agreement with experiments.

ACKNOWLEDGMENTS

This work was supported by the Austrian Science Fund (FWF) within the Science College CMS under Grant No. W004. We also acknowledge fruitful discussions with H. I. Starnberg.

---

[1] G. A. Wiegers, Prog. Solid State Chem. **24**, 1 (1996).
[2] C. M. Fang, S. van Smaalen, G. A. Wiegers, C. Haas, and R. A. de Groot, J. Phys.: Condens. Matter **8**, 5367 (1996).
[3] Y. Moëlo, A. Meerschaut, J. Rouxel, and C. Auriel, Chem. Mater. **7**, 1759 (1995).
[4] Q. Lin, C. Heideman, N. Nguyen, P. Zschack, C. Chiritescu, D. Cahill, and D. Johnson, Eur. J. Inorg. Chem. **2008**, 2382.
[5] Y. M. Yarmoshenko, V. A. Trofimova, S. Shamin, I. V. Solovyev, E. Kurmaev, A. R. H. F. Ettema, and C. Haas, J. Phys.: Condens. Matter **6**, 3993 (1994).
[6] C. M. Fang, A. R. H. F. Ettema, C. Haas, G. A. Wiegers, H. van Leuken, and R. A. de Groot, Phys. Rev. B **52**, 2336 (1995).
[7] M. Kalläne, K. Rossnagel, M. Marczynski-Bühlow, L. Kipp, H. I. Starnberg, and S. E. Stoltz, Phys. Rev. Lett. **100**, 065502 (2008).
[8] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K: An Augmented Plane Wave and Local Orbitals Program for Calculating Crystal Properties* (Vienna University of Technology, Austria, 2001).
[9] D. J. Singh and L. Nordström, *Planewaves, Pseudopotentials, and the LAPW Method*, 2nd ed. (Springer, New York, 2006).
[10] G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, Phys. Rev. B **64**, 195134 (2001).
[11] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[12] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[13] Z. Wu and R. E. Cohen, Phys. Rev. B **73**, 235116 (2006); Y. Zhao and D. G. Truhlar, *ibid.* **78**, 197101 (2008); Z. Wu and R. E. Cohen, *ibid.* **78**, 197102 (2008).
[14] F. Tran, R. Laskowski, P. Blaha, and K. Schwarz, Phys. Rev. B **75**, 115131 (2007).
[15] J. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).
[16] D. Koelling and B. Harmon, J. Phys. C **10**, 3107 (1977).
[17] J. Wulff, A. Meetsma, S. Van Smaalen, J. L. De Boer, and G. A. Wiegers, J. Solid State Chem. **84**, 118 (1990).
[18] Y. Noda, K. Matsumoto, S. Ohba, S. Saito, K. Toriumi, Y. Iwata, and I. Shibuya, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **43**, 1443 (1987).
[19] V. S. Pervov, Z. V. Dobrokhotova, E. V. Makhonina, V. V. Volkov, and V. M. Novotorsev, Inorg. Mater. **38**, 274 (2002).
[20] A. Meetsma, G. Wiegers, R. Haange, and J. De Boer, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **46**, 1598 (1990).
[21] P. Blaha, J. Phys.: Condens. Matter **3**, 9381 (1991).
[22] K. Suzuki, T. Enoki, and H. Tajima, Phys. Rev. B **52**, 16400 (1995).
[23] J. C. Slater, Adv. Quantum Chem. **6**, 1 (1972).
[24] S. Lizzit *et al.*, Phys. Rev. B **63**, 205419 (2001).