Stabilization of the Misfit Layer Compound PbS-**¹***:***13TaS2 by Metal Cross Substitution**

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Photoemission microspectroscopy on the layered misfit compound $(PbS)_{1,13}TaS_2$ provides direct evidence for Ta substitution into PbS layers as well as for Pb substitution into $TaS₂$ layers. This metal cross substitution alters the charge balance between alternating layers and can explain the remarkable stability of $(PbS)_{1.13}TaS_2$ and, possibly, of analogous misfit compounds. It is suggested that even formally stoichiometric misfit compounds can be stabilized by this mechanism.

Bonding in layered materials is a challenging problem because it includes various types of interactions ranging from strong local covalent bonds over electrostatic interactions to rather weak nonlocal van der Waals (vdW) forces [[1](#page-3-0)]. Prototype layer compounds are provided by the family of transition-metal dichalcogenides (TMDCs) whose crystal structures consist of hexagonal chalcogen transition metal—chalcogen sandwiches. While strong covalent and ionic bonding prevails within the sandwiches, intersandwich bonding is dominated by weak vdW forces. Consequently, the electronic properties of TMDCs are highly anisotropic which favors, e.g., the occurrence of a plethora of charge-density-wave phases [[2](#page-3-1)] and correlation effects [\[3,](#page-3-2)[4](#page-3-3)]. Moreover, due to the weak vdW interlayer interactions and the relatively large layer-to-layer distances, TMDCs allow for the insertion of foreign atoms or molecules into the vdW gaps. This intercalation is generally accompanied by a charge transfer from the intercalant to the host layers which leads to electrostatic contributions to the interlayer interactions [\[5](#page-3-4)].

If instead of single atoms or molecules crystalline bilayers of cubic monochalcogenides (MCs) are inserted into the TMDC vdW gaps (see Fig. [1\)](#page-0-0), interlayer bonding and stability considerations become more complex and potentially more relevant. Since the resulting crystals are composed of alternating TMDC and MC layers in a very high stacking order, they constitute a simple, well-ordered heterostructure whose interface properties, if properly understood, may help to understand the interfaces of more complex multilayer systems [[6](#page-3-5)].

The MC-TMDC layer compounds can be described by the general formula $(MX)_{1+\delta}(TX_2)_n$, where *M* denotes a metal atom (Sn, Pb, Sb, Bi, or rare earth), *X* a chalcogen atom (S or Se), and *T* a transition metal atom (Ti, V, Cr, Nb, Ta) [[7](#page-3-6)]. The number of TMDC slabs between two MC layers can be $n = 1, 2, 3$. Because of the different crystal symmetries of the subsystems, the lattice constants match only along one crystallographic axis parallel to the surface. Perpendicular to this commensurate direction the lattice constants are in an irrational ratio described by the misfit

DOI: [10.1103/PhysRevLett.100.065502](http://dx.doi.org/10.1103/PhysRevLett.100.065502) PACS numbers: 61.50.Lt, 68.37. -d, 79.60. -i

parameter δ (0.08 $< \delta$ < 0.28). Since the lattice mismatch, the alternation of different layers, and the occurrence of MC bilayers (whereas pristine MC compounds have a three-dimensional rock salt structure) all act against a low total energy, it comes as a surprise that the misfit compounds are more stable than a mixture of phase separated chalcogenides. Yet, despite extensive efforts [\[8](#page-3-7)–[14\]](#page-3-8), the dominant interlayer bonding mechanism as the key to the stability of these compounds has remained elusive.

FIG. 1 (color online). Crystal structure of the misfit layer compound $(PbS)_{1,13}TaS_2$. The large yellow (light gray) spheres represent sulfur atoms of both subsystems, the smaller blue (dark gray) spheres correspond to the lead atoms of the PbS subsystem, and the small gray spheres represent the tantalum atoms of the $TaS₂$ subsystem (left: side view, right: front view, top: top view). Commensurate and incommensurate directions are indicated. Possible interlayer bonding mechanisms (a)–(d) are described in the text.

Possible bonding mechanisms are illustrated in Fig. [1](#page-0-0). While vdW forces between the TMDC and MC layers are certainly present [Fig. $1(a)$], they can probably not account for the remarkable stability of the misfit compounds. Since it is natural to compare with other TMDC intercalation compounds, one may expect the misfit layer compounds to be stabilized by electron transfer from the MC layers to the TMDC layers [Fig. $1(b)$]. However, there has been much controversy over whether this kind of charge transfer really occurs in these compounds [\[8](#page-3-7)[–14\]](#page-3-8). Electron removal from the *MX* layer would imply a formal oxidation state of *M* higher than $+2$, which is normally not found in sulfides with the rock salt structure $[12]$ $[12]$. Furthermore, the pristine *MX* compounds are semiconductors, and the presence of a band gap between occupied and empty bands does not favor electron donation. From the absence of charge transfer in x-ray photoelectron spectroscopy [[9\]](#page-3-10) and from the results of band structure calculations [[11](#page-3-11)] it was thus concluded that the interlayer interactions are of covalent character [Fig. $1(c)$]. Finally, in a study of several misfit layer compounds by means of electron probe microanalysis, Moëlo *et al.* [[12](#page-3-9)] found a systematic depletion of *M* atoms and a corresponding excess of *T* atoms, suggesting that *T* atoms were substituted into the *MX* layers [Fig. $1(d)$]. They pointed out that such a substitution may provide the changes in the charge balance needed to stabilize the misfit layer structure, and suggested that the deviation from the ideal, stoichiometric structure is a necessary condition for the stability of these compounds.

In this Letter we clarify the nature of the interlayer bonding in misfit layer compounds by photoelectron microspectroscopy measurements on the compound $(PbS)_{1.13}TaS_2$. Our results strongly support the idea that Ta atoms are substituted into the PbS layers, in accordance with the suggestions of Moëlo *et al.* [\[12\]](#page-3-9), but we also find strong evidence for Pb substitution into the $TaS₂$ layers. This novel metal cross-substitution mechanism alters the charge balance between the two types of layers in a way that strongly enhances the interlayer bonding. We argue that metal cross substitution is of fundamental importance for the stability of $(PbS)_{1,13}TaS_2$, as well as for analogous misfit layer compounds, and we suggest that even formally stoichiometric compounds may be stabilized by this mechanism.

The $(PbS)_{1,13}TaS_2$ crystals were grown by chemical vapor transport, i.e., by adding stoichiometric ratios of the elements and iodine as a transport agent in an evacuated quartz tube and placing the quartz tube in a temperature gradient of 780–940 \degree C for 25 days. The high quality of the grown crystals was confirmed by x-ray diffraction and transmission electron microscopy [[14](#page-3-8),[15](#page-3-12)]. The crystals were attached to the sample holder by silver-filled epoxy resin and clean (0001) surfaces were obtained by cleavage in ultrahigh vacuum. In order to identify surface species, Cs was deposited *in situ* from carefully outgassed SAES getter sources with a base pressure in the low 10^{-10} mbar range. During Cs deposition the pressure in the preparation chamber increased to approximately 5×10^{-10} mbar. All cleavages, depositions, and measurements were performed with the sample at room temperature. Reproducible photoemission results were obtained from three different samples.

Spatially resolved core level spectra and images were measured at the undulator based beamline 31 (BL31) at the MAX-lab synchrotron radiation facility in Lund, Sweden [\[16\]](#page-3-13). Additional measurements with lower spatial but higher energy resolution were taken at the undulator beamline BW3 at HASYLAB, Germany [\[17\]](#page-3-14). Both beamlines feature a plane-grating monochromator. But while the focusing unit of BW3 consists of a refocusing mirror with a focus size of $\approx 100 \times 300 \ \mu \text{m}^2$, the photoelectron microscope of BL31 employs a Kirkpatrick-Baez objective and a ring-shaped ellipsoidal mirror to focus the light to a \approx 1.5 \times 1.5 μ m² spot on the sample. The photoelectrons are detected after passing through hemispherical energy analyzers in normal emission at BW3 and at an emission angle of 47.5° at BL31. Total energy resolutions are 80 meV (BW3) and 330 meV (BL31), respectively.

Figure [2](#page-2-0) shows a typical surface area map of $(PbS)_{1,13}TaS_2$, as imaged by photoemission from the Pb 5*d* core level as well as from Ta 5*d* valence and Ta 4*f* core states. The Pb and Ta images are complementary, demonstrating that cleavage produces domains terminated either by PbS or TaS_2 layers. After Cs evaporation, significantly higher Cs 4*d* core level intensities are found on the PbS terminated regions [Fig. $2(d)$], indicating that Cs adsorption occurs predominantly on the PbS domains.

Figs. [3\(a\)](#page-2-2) and [3\(g\)](#page-2-2) show combined Ta 4*f* and Pb 5*d* core level spectra taken from PbS and $TaS₂$ domains, respectively. Consistent with inelastic mean free path considerations, the spectrum from each domain contains both Ta 4*f* and Pb 5*d* emissions. Comparing first the Ta 4*f* core level spectra from the two domains, an additional peak (A_3) is found in the spectrum from the PbS domain, with higher binding energy as compared to the main Ta 4*f* peaks (*A*¹ and A_2). Upon Cs deposition, this extra peak shifts towards higher binding energies and it becomes clear that it is the high-energy part of a peak doublet $(A_3 \text{ and } A_4)$ [Fig. [3\(h\)\]](#page-2-2). Since the separation between the two additional peaks amounts exactly to the Ta 4*f* spin-orbit splitting and since the extra peaks are only present in the spectra from the PbS domain, we attribute them to Ta atoms located in the PbS layer. The energy shift of about 2.15 eV towards higher binding energies for the substituted Ta is then probably largely due to less efficient final-state screening in the semiconducting PbS layer. By contrast, the Cs induced Pb 5*d* splitting in the PbS surface domain [Fig. [3\(h\)](#page-2-2)] is presumably caused by two inequivalent Pb sites: the one adjacent to the vacuum, where Cs adsorption takes place, and the one adjacent to the $TaS₂$ layer below.

Comparing now the Pb 5*d* core level spectra from the two domains [Figs. $3(a)$ and $3(g)$], the Pb 5*d* peaks measured from the $TaS₂$ terminated region are broader and their centers of gravity are slightly shifted towards lower binding energies. On closer inspection, it appears that the

FIG. 2. Surface area of $(PbS)_{1.13}TaS_2$, as imaged by photoemission microscopy from (a) the Pb $5d_{5/2}$ core level ($h\nu$ = 73.1 eV), (b) the Ta 5*d* valence band $(E - E_F \approx 0.5 \text{ eV}, h\nu =$ 43.9 eV), (c) the Ta $4f_{5/2}$ core level ($hv = 116.5$ eV), and (d) the Cs $4d_{5/2}$ core level after 3 min. of Cs deposition ($h\nu$ = 116*:*5 eV).

Pb $5d_{3/2}$ and Pb $5d_{5/2}$ lines each have two components (B_1 , B_3 and B_2 , B_4 , respectively). This is further corroborated by measurements with higher energy resolution on a different sample whose cleavage produced two very large domains. Upon crossing the boundary from the PbS to the $TaS₂$ domain, the spatially integrated photoemission spectra clearly reveal the emergence of a Pb 5*d* double peak structure [Figs. $3(b)-3(f)$ $3(b)-3(f)$ $3(b)-3(f)$]: one component with the same binding energy as the corresponding peak obtained from the PbS domain [Fig. $3(a)$], and the other component with somewhat lower binding energy. In analogy with the extra Ta 4*f* peaks in the PbS domain, we attribute the additional Pb $5d$ components seen in the TaS_2 domain to Pb atoms substituted into the TaS_2 layers: the two extra peaks are separated by a value matching the Pb 5*d* spin-orbit splitting and they only show up in the spectra from the TaS_2 domain. In this case, the shift of about 0.55 eV towards lower binding energy is probably largely due to the more efficient final-state screening in the metallic $TaS₂$ layer.

A more detailed quantitative analysis of the observed binding energy shifts is not attempted here. The important point is that from the mere existence of shifted core level components in both surface domains we may conclude that substitution of Pb atoms into TaS_2 layers as well as substitution of Ta atoms into PbS layers occurs in $(PbS)_{1.13}TaS_2$. This Pb-Ta cross substitution can be described by the modified chemical formula $(Pb_{1-x}Ta_xS)_{1.13}(Ta_{1-y}Pb_yS_2)$. In order to determine the concentrations *x* and *y*, we have further analyzed the Pb 5*d* and Ta 4*f* spectra from the two

FIG. 3 (color online). Pb 5*d* and Ta 4*f* core level spectra of $(PbS)_{1.13}TaS_2$, taken at BL31/MAX-lab with high spatial and moderate energy resolution from (a) a PbS domain $(h\nu =$ 116.5 eV) and (g) a TaS_2 domain ($hv = 73.2$ eV). Experimental data (dots) and fit results (solid lines) are plotted. The decomposition of the spectra into different components is indicated. Components originating from cross-substituted atoms are highlighted in red (dark gray). A Shirley background has been subtracted. (b)–(f) Corresponding spectra taken at BW3/ HASYLAB with higher energy and moderate spatial resolution from the transition region between PbS and $TaS₂$ domains of a different sample $(h\nu = 116.5 \text{ eV})$. (h) Core level spectrum measured from the same PbS domain as in (a) after 3 min. of Cs deposition ($h\nu = 116.5$ eV).

domains by line shape fitting. To model the spectra, we have used Voigt profiles for the various emissions, except for the Ta $4f$ peaks of the TaS₂ layers. These emissions have a characteristic asymmetric line shape, which is caused by valence electron screening [[18](#page-3-15)]. For them we have used a joint density of states based model similar to the one that was developed to fit the asymmetric Ta 4*f* lines in $2H$ -TaS₂ and intercalated compounds [\[18\]](#page-3-15). In our model we have calculated the joint density of states from a tight binding fit to angle-resolved photoemission spectroscopy (ARPES) data of the Ta 5*d*-derived valence band [[19\]](#page-3-16). Convolution of the resulting line shape with a Voigt profile then reproduces the measured spin-orbit split Ta 4*f* spectra very well [see Figs. [3\(a\)](#page-2-2) and [3\(g\)\]](#page-2-2). By contrast, the Ta 4*f* emissions originating from the semiconducting PbS domains do not show the asymmetric line shape. They are broader, which may be due to the presence of two inequivalent metal sites in the topmost PbS layer, and are well enough reproduced by Voigt profiles.

As illustrated in Figs. $3(a)$ and $3(g)$, the overall fitted line shapes are in excellent agreement with the observed complete spectra. Figures $3(a)$ and $3(g)$ also show the resulting decomposition of the Ta 4*f* emissions from the PbS domain and of the Pb $5d$ emissions from the TaS₂ domain (filled curves). Each of these emissions has a component originating from the buried layer as well as a component originating from the substituted atoms (at lower binding energy for substituted Pb and at higher binding energy for substituted Ta). Taking the ratio of the relevant peak areas and considering the different photoionization cross sec-tions [\[20\]](#page-3-17), we obtain concentrations of $x = 0.18 \pm 0.05$ for Ta substituted into the PbS layer and $y = 0.08 \pm 0.05$ for Pb substituted into the TaS_2 layer.

This Pb-Ta cross substitution will alter the charge balance of the system. In a simple ionic picture, a partial substitution of Ta³⁺ ions for *x* Pb²⁺ ions in the PbS layer can be assumed, which implies a PbS layer that remains semiconducting and a transfer of 1*:*13*x* electrons to the adjacent TaS₂ layer. If, on the other hand, y Ta⁴⁺ ions are substituted by Pb^{4+} ions in the TaS₂ layer [\[21\]](#page-3-18), the Ta 5*d* valence band will contain $1 - y$ electrons per unit cell without charge transfer and $1 - y + 1.13x$ electrons per unit cell with the charge transfer from the $Pb_{1-x}Ta_{x}S$ layer. Using the above values for *x* and *y*, we obtain an increase in the Ta 5*d* band filling of 0.12 ± 0.1 electrons per $Ta_{1-y}Pb_vS_2$ unit, which is in fairly good agreement with Hall effect [\[23\]](#page-3-19) and ARPES [\[19\]](#page-3-16) measurements.

So why are $(PbS)_{1,13}TaS_2$ and analogous misfit layer compounds stable? In accordance with Moëlo *et al.* [\[12\]](#page-3-9), we argue that Ta atoms substituted into the PbS layers induce an electron transfer to the TaS_2 layers so that the alternating PbS and TaS_2 layers become charged and bound together by electrostatic forces. In contrast to Moëlo *et al.* [\[12\]](#page-3-9), who pointed out that nonstoichiometry is a necessary condition for the stability, we emphasize that the cross-substitution mechanism may work even for formally stoichiometric misfit layer compounds. The balance between the two types of substitutions may vary, depending on the crystal growth conditions, but in all cases stabilizing metal substitutions will occur.

In conclusion, by measurements of core level spectra from differently terminated domains on cleaved surfaces of the layered misfit compound $(PbS)_{1,13}TaS_2$ we have found direct spectroscopic evidence for Ta substitution into PbS layers as well as Pb substitution into TaS_2 layers. The concentrations of the substituted atoms are of the order of 5–20%, which leads to an effective charge transfer of \approx 0.1 electrons per TaS₂ unit from the PbS to the TaS₂ layers. We suggest that such metal cross substitution is of fundamental importance for the stability of $(PbS)_{1.13}TaS_2$ and similar misfit layer compounds and that nonstoichiometry may not be a necessary condition for their stability. Further theoretical scrutiny of binding energy shifts and total energy changes in substituted misfit layer compounds is clearly desirable.

This work was supported by the Swedish Natural Science Research Council and the Deutsche Forschungsgemeinschaft via Forschergruppe FOR 353. We gratefully acknowledge the skillful assistance of the MAX-lab and HASYLAB staff.

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