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Crystal structure and band structure calculations of $\text{Pb}_{1/3}\text{TaS}_2$ and $\text{Sn}_{1/3}\text{NbS}_2$

C.M. Fang, G.A. Wiegers*, A. Meetsma, R.A. de Groot, C. Haas

*Laboratory of Chemical Physics, Materials Science Center, University of Groningen,
Nijenborgh 4, NL-9747 AG Groningen, The Netherlands*

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Abstract

The crystal structures of $\text{Pb}_{1/3}\text{TaS}_2$ and $\text{Sn}_{1/3}\text{NbS}_2$ were determined using single-crystal X-ray diffraction. The space group is $P6_322$ and the unit cell dimensions are: $a = 5.759(1)$, $c = 14.813(1)$ Å and $a = 5.778(1)$, $c = 14.394(1)$ Å, for the Pb and Sn compounds, respectively. The post-transition metal atoms occupy one-third of the trigonal-antiprismatic holes between sandwiches NbS_2 and TaS_2 . The Nb and Ta atoms are in trigonal-prismatic coordination by sulfur atoms. The stacking of sandwiches is the same as in 2H disulfides. The arrangement of the post-transition metal atoms is different for the two compounds. A bond valence calculation showed Sn and Pb to be divalent.

Ab initio band structure calculations were performed for $\text{Sn}_{1/3}\text{NbS}_2$ using the localized spherical wave method, and for $\text{Pb}_{1/3}\text{TaS}_2$ with the augmented spherical wave method with spin-orbital interactions included. The calculations show that the rigid band model is approximately valid for the electronic structures; the main difference with those of 2H- NbS_2 and 2H- TaS_2 being the presence of Sn 5s and 5p (Pb 6s and 6p) bands and a larger S 3p/Nb(Ta) 4d (5d) gap in the intercalates (1.0 eV for $\text{Sn}_{1/3}\text{NbS}_2$, 1.3 eV for $\text{Pb}_{1/3}\text{TaS}_2$). The Sn 5s (Pb 6s) bands are at the bottom (bonding) and top (antibonding) of the valence bands which range from about -7 to about 0 eV. The conduction bands are composed of Nb 4d₂ or Ta 5d₂ orbitals hybridized with S 3p. These bands are filled to about 0.3 holes per Nb (Ta), corresponding to a donation of two electrons per Sn (Pb).

1. Introduction

DiSalvo et al. [1] were the first to study the compounds M_xTaS_2 with M a post-transition element (Ga, In, Ge, Sn, Pb); they used X-ray powder methods for characterization. Eppinga and Wiegers [2] synthesized, besides the compounds already found by DiSalvo et al. [1], a number of compounds M_xNbS_2 and M_xTaS_2 with M = In, Sn, Pb and Bi, using also powder X-ray diffraction for characterization. For the $x = \frac{1}{3}$ compounds two structure types are found,

both based on post-transition metal atoms present in one-third of the available trigonal-antiprismatic holes between NbS_2 or TaS_2 sandwiches which have Nb or Ta in trigonal-prismatic coordination by sulfur. The NbS_2 and TaS_2 sublattices are similar to those of the pure dichalcogenides 2H- NbS_2 ($a = 3.324$, $c = 11.95$ Å [3]), and 2H- TaS_2 ($a = 3.314$, $c = 12.097$ Å [4]), the space group being $P6_3/mmc$. Due to the occupation by Sn and Pb of only one-third of the available sites, the a axis is $\sqrt{3}$ times that of Nb and Ta dichalcogenides and the c axes are expanded by about 2.5 Å. The Sn (Pb) atoms in layers $\frac{1}{2}c$ apart are on top of each other for $\text{Pb}_{1/3}\text{TaS}_2$

* Corresponding author.

(AA type stacking) and in an AB type stacking for $\text{Sn}_{1/3}\text{NbS}_2$. The space group is P6_322 in both cases. Because of the large difference in the scattering factors of Nb(Ta) and Sn(Pb) on the one hand and S on the other hand, the powder method gives the coordinates of sulfur and therefore the Sn(Pb)–S and Nb(Ta)–S bond distances rather inaccurate. A single-crystal structure determination of the title compounds is described in this paper. Band structures have been calculated using the localized spherical wave (LSW) and augmented spherical wave (ASW) methods for the Sn and Pb compounds, respectively. The knowledge of the structures, chemical bonding (charge transfer) and electronic structure would be helpful to understand the stability, chemical bonding and physical properties of the misfit layer compounds containing Pb and Sn, such as $(\text{SnS})_{1.17}\text{NbS}_2$ [5].

2. Structure determination

The compounds were synthesized and crystals were grown by vapor transport as described before [2]. Plate-shaped crystals of approximate dimensions $0.18 \times 0.03 \times 0.008$ and $0.28 \times 0.30 \times 0.007 \text{ mm}^3$, for the Pb and Sn compounds, respectively, were selected and mounted on a fiber glass tip onto a goniometer head. Single-crystal diffraction data were collected on an Enraf-Nonius CAD-4F diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters were determined by using the setting angles of 22 randomly distributed reflections having θ near 20° . The unit cell parameters and the orientation matrix were determined from a least-squares treatment of the SET4 [6] setting angles with the crystal in “flat setting” [7]. The unit cells were checked for the presence of higher lattice symmetry [8]. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements [9, 10].

The intensities of the three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. A $360^\circ \Psi$ -scan for a reflection close to axial for each sample was measured. Intensity data

were corrected for Lorentz and polarization effects, the scale variation and for absorption (Gaussian integration [11]). The variance $\sigma^2(I)$ was calculated on the basis of counting statistics plus the term $(PI)^2$, where P is the instability constant [12] as derived from the excess variance in the reference reflections. Inspection of the data sets showed the Laue symmetry to be $6/\text{mmm}$; the $00l$ reflections with l odd are systematically extinct, which indicates the space group to be P6_322 . Equivalent reflections were averaged and reduced to F_o [13]; they were stated to have been observed if they satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. Crystal data are summarized in Tables 1(a)–(c).

Coordinates for the refinement were from the powder data [2]. The Patterson method [14] confirmed the proposed coordinates. The positional and thermal displacement parameters (anisotropic except for sulfur in $\text{Pb}_{1/3}\text{TaS}_2$) were refined on F_o with full-matrix least-squares procedures (CRYLSQ [15]) minimizing the function $Q = \sum_h [w(|F_o| - k|F_c|)^2]$. Neutral atom scattering factors [16] were used and anomalous dispersion factors [17] were included in F_c . Among the low-angle reflections, no corrections for secondary extinction was necessary. All calculations were performed with the program packages Xtal [18] and PLATON [19] (calculation of geometric data).

Some difficulties remain for the weak reflections with l odd for the Pb compound. The agreement between F_o and F_c is good for $h - k = 3n$ (h and k not equal to $3n$), but for $h - k \neq 3n$, $F_c > F_o$ for large l . Since F_o is only determined by z of Ta(1), it indicates that z ($= -0.002(2)$) from the refinement is somewhat too large. A z coordinate of Ta(1) deviating from zero leads to two slightly different types of Ta(1)–S distances. For reflections with h and k equal to $3n$ and l odd, F_c is calculated as zero, while the F_o 's are slightly above the 2σ limit. Since the $00l$ reflections with l odd are absent, it indicates the presence of some scattering density at positions with x and/or y deviating from $\frac{1}{3}$ and $\frac{2}{3}$. The same was found for the Sn derivative.

Table 2 lists the final fractional atomic coordinates and equivalent isotropic thermal displacement parameters.

Table 1(a)
Crystal data and details of the structure determination

Chemical formula	Sn _{1/3} NbS ₂	Pb _{1/3} TaS ₂
Formula weight, g mol ⁻¹	196.60	313.14
Crystal system		Hexagonal
Space group, No.		P6 ₃ 22, 182
<i>a</i> , Å	5.778(1)	5.759(1)
<i>c</i> , Å	14.394(1)	14.813(2)
<i>V</i> , Å ³	416.17(11)	425.47(11)
<i>Z</i>		6
<i>D</i> _{calc} , g cm ⁻³	4.707	7.356
<i>F</i> (000), electrons	538	794
μ (Mo K α), cm ⁻¹	84.06	595.57
Approx. crystal dimension, mm	0.27×0.30×0.007	0.18×0.30×0.008

Table 1(b)
Data collection

	Sn _{1/3} NbS ₂	Pb _{1/3} TaS ₂
Radiation		Mo K α
Wavelength, Å		0.71073
Monochromator		Graphite
Temperature, K		295
θ range; min., max., deg	1.42, 35.0	1.38, 36.0
$\omega/2\theta$ scan, deg		$\Delta\omega = 1.10 + 0.34 \tan \theta$
Data set	<i>h</i> : 0 → 9; <i>k</i> : -4 → 9; <i>l</i> : 0 → 22	<i>h</i> : -9 → 8; <i>k</i> : 0 → 9; <i>l</i> : 0 → 24
Crystal-to-receiving-aperture distance, mm		173
Horizontal, vertical aperture, mm		3.2 + $\tan \theta$; 4.0
Reference reflections, r.m.s. dev. in %	$\bar{2}0\bar{2}$, 0.6 $0\bar{2}\bar{2}$, 0.9 $\bar{1}\bar{1}\bar{1}$, 0.4	$\bar{1}1\bar{2}$, 0.8 004, 2.0 $\bar{1}10$, 2.8
Instability constant, <i>P</i>	0.009	0.03
Drift correction	0.994–1.000	0.985–1.000
Min. and max. absorption correction factor	1.38–6.27	1.27–18.01
X-ray exposure time, h	61.8	77
Total data	2037	2554
Unique data	430	470
Observed data (<i>I</i> ≥ 2.5 σ (<i>I</i>))	412	306
<i>R</i> 1 (= $\sum (I - I)/\sum I$)	0.179	0.119
<i>R</i> 2 (= $\sum \sigma/\sum I$)	0.015	0.041
Number of equivalent reflections	2014	2530

Table 1(c)
Refinement

	Sn _{1/3} NbS ₂	Pb _{1/3} TaS ₂
Number of reflections	408	306
Number of refined parameters	17	12
Final agreement factors:		
$R_F = \sum (F_o - F_c) / \sum F_o $	0.038	0.080
$wR = [\sum (w(F_o - F_c)^2) / \sum w F_o ^2]^{1/2}$	0.048	0.085
Weighting scheme	1	
G.O.F.:		
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	2.85	8.3
m = number of observations		
n = number of variables		
Min. and max. residual densities;		
residual electron density in final		
difference Fourier map, $e/\text{\AA}^3$	4.44, 2.20	−6.4, 15.7
Max. (shift/ σ) final cycle	0.2796×10^{-4}	0.5219×10^{-2}
Average (shift/ σ) final cycle	0.6967×10^{-5}	0.2325×10^{-2}

Table 2
Atomic positions and temperature factors for Pb_{1/3}TaS₂ and Sn_{1/3}NbS₂. Estimated standard deviations are given in parentheses; a bar means a coordinate fixed by symmetry

		x	y	z	$U_{eq}(\text{\AA}^2)^a$
Pb(1)	2b	0.(−)	0.(−)	0.25(−)	0.0111(4)
Ta(1)	4f	0.33333(−)	0.66667(−)	−0.002(2)	0.0026(7)
Ta(2)	2a	0.(−)	0.(−)	0.(−)	0.0029(3)
S(1)	12i	0.336(3)	0.337(3)	0.1052(4)	0.0053(4)
Sn(1)	2c	0.33333(−)	0.66667(−)	0.25(−)	0.0102(3)
Nb(1)	4f	0.33333(−)	0.66667(−)	−0.00048(8)	0.0042(2)
Nb(2)	2a	0.(−)	0.(−)	0.(−)	0.0042(3)
S(1)	12i	0.3330(5)	0.3309(5)	0.10837(11)	0.0072(5)

^a $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

3. Discussion of the structures

Both compounds have NbS₂ or TaS₂ sandwiches with Nb and Ta in trigonal prisms of S, and Sn and Pb in a trigonally distorted octahedron of S. The structures are shown in Fig. 1. The Nb–S distances are 2.493(2) (3x) Å and 2.470(2) (3x) Å for Nb(1) and 2.472(2) Å (6x) for Nb(2). These distances are close to those for the intercalates Ag_{0.6}NbS₂ (2.479(1) Å) [20] and M_{1/3}NbS₂ with M = Fe, Mn, etc. [21–23]. Note that the Nb–S distances in 2H–NbS₂ are not known accurately because the deviation from $\frac{1}{4}$ for the z coordinate of S is

not known. For Pb_{1/3}TaS₂, the Ta(1)–S distances, 2.45(2) Å (3x) and 2.48(2) Å (3x), and Ta(2)–S distances, 2.487(13) Å (6x), are within the standard deviations equal to those (2.468(2) Å) in 2H–TaS₂ [4], and intercalates such as In_{2/3}TaS₂ (2.471(2) Å) [24], Fe_{1/3}TaS₂ (2.49 Å) and Mn_{1/3}TaS₂ (2.48 Å) [21–23]. The Nb–Nb distances (3.336 Å) and the Ta–Ta distances (3.325 Å) are about 0.01 Å larger than those in 2H–NbS₂ and 2H–TaS₂. The stacking of the sandwiches is similar to those in 2H–NbS₂ and 2H–TaS₂. The conclusion is that the NbS₂ and TaS₂ sublattices deviate only slightly from those in the pure dichalcogenides.

Fig. 1. Projection along [001] of (a) $\text{Pb}_{1/3}\text{TaS}_2$ and (b) $\text{Sn}_{1/3}\text{NbS}_2$. Large circles are S atoms; those at $z \cong 0.10$ and 0.90 are open, those at $z \cong 0.40$ and 0.60 are hatched. Nb and Ta atoms (at $z \cong 0.0$ and $\frac{1}{2}$) are small filled circles. The Pb (square (a)) and Sn (triangles (b)) are at $z = \frac{1}{4}$ and $\frac{3}{4}$.

The Sn (Pb) atoms occupy one-third of the trigonal–antiprismatic sites between the sulfur layers of neighboring NbS_2 (TaS_2) sandwiches; the coordination of Sn and Pb by S is an octahedron which is strongly elongated along the trigonal axis; the angles S–M–S are about 73° and 107° for the Sn compound and 71° and 109° for the Pb compound, compared to 90° for the octahedron. The c/a ratio of the distorted octahedron of six S atoms is 2.58 for Pb and 2.44 for Sn; the value of c/a for an undistorted octahedron is 1.633. The Sn–S and Pb–S distances are $2.814(2) (6x) \text{ \AA}$ and $2.891(12) (6x) \text{ \AA}$, respectively. The stacking of layers Sn and Pb is different. For $\text{Pb}_{1/3}\text{TaS}_2$, the Pb atoms in layers $\frac{1}{2}c$ apart are on top of each other (AA type stacking) while the Sn atoms in layers $\frac{1}{2}c$ apart of $\text{Sn}_{1/3}\text{NbS}_2$ are in an AB type stacking. Such an AB stacking, which is more favorable from an electrostatic point of view compared to the AA stacking, is also found in the $\text{M}_{1/3}\text{NbS}_2$ and $\text{M}_{1/3}\text{TaS}_2$ compounds ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) [20–23], and in $\text{Ag}_{1/3}\text{TiS}_2$ (Ti in trigonal–antiprismatic coordination) [25]. The Sn atoms are between two Nb(1) atoms

so that tri-atom Nb–Sn–Nb complexes are formed. The Sn–Nb(1) distance amounts to $3.605 \text{ \AA}$. The Nb(2) atoms have no direct Sn neighbor. In $\text{Pb}_{1/3}\text{TaS}_2$ there are linear chains Pb–Ta(2)–Pb with Pb–Ta distances of $3.703 \text{ \AA}$. The Ta(1) atoms have no direct Pb neighbor.

The Sn–S and Pb–S distances point to divalent Sn and Pb, as can be seen by using the concept of bond valence [26]. The bond valence V_i is calculated from the relation $V_i = \exp[(d_0 - d_i)/b]$ where d_i is the distance between the atoms of bond i , and d_0 and b are empirical constants: $d_0 = 2.45 \text{ \AA}$ for Sn–S, $d_0 = 2.55 \text{ \AA}$ for Pb–S and $b = 0.37 \text{ \AA}$ [27]. The bond valence or oxidation state V is calculated by summing over all neighboring atoms, $V = \sum V_i$. For $V(\text{Sn})$ and $V(\text{Pb})$ one finds 2.09 and 2.40 v.u. (valence units) respectively; Sn and Pb are therefore divalent.

An interesting point concerns the anisotropy of the thermal motion of the atoms. The thermal displacement parameters of Nb, Sn and Ta do not show an anisotropy; U_{11} , U_{22} and U_{33} of Sn are 2–3 times larger than those for Nb. For Pb, U_{33} is about the same as for Ta, but U_{11} and U_{22} are 3–4 times larger than U_{11} and U_{22} of Ta. It means a shallow potential in the layers for Sn and Pb, and a steeper rise along c for Pb. The shallow in-plane potential is as expected because the intralayer Sn and Pb distances are as large as 5.759 and $5.778 \text{ \AA}$, respectively.

4. Band structure calculations

4.1. Calculation methods

Ab initio band structure calculations were performed for $\text{Sn}_{1/3}\text{NbS}_2$ with the LSW [28] method, and the ASW method [29] with spin–orbital interaction included for $\text{Pb}_{1/3}\text{TaS}_2$. A scalar relativistic Hamiltonian was used in both calculations. We used local-density exchange–correlation potentials [32] inside space-filling, and therefore overlapping spheres around the atomic constituents. The self-consistent calculations were carried out including all core electrons.

Iterations were performed with k -points distributed uniformly in the irreducible part of the first Brillouin zone (BZ), corresponding to a volume per k -point

Fig. 2. Brillouin zone and high-symmetry points of $\text{Sn}_{1/3}\text{NbS}_2$ and $\text{Pb}_{1/3}\text{TaS}_2$.

of the order of $1 \times 10^{-5} \text{ \AA}^{-3}$. Self-consistency was assumed when the changes in the local partial charges in each atomic sphere decreased to the order of 10^{-5} .

The spherical waves were augmented by the solution of the scalar relativistic radial equations indicated by the atomic-like symbols 6s, 6p and 6d for Pb, etc. (Table 3) corresponding to the valence levels of the parent elements Pb, Sn, Nb and S. The internal l summation used to augment the Hankel functions at surrounding atoms was extended to $l = 3$, resulting in the use of 5f orbitals for Pb and Ta, 4f for Sn and Nb. When the crystal is not very densely packed, it is necessary to include some empty spheres in the calculation. The functions 1s and 2p, and 3d as an extension, were used for the empty spheres. The input for the calculations (atomic positions, Wigner–Seitz radii and starting electronic configurations) are given in Table 3. The hexagonal Brillouin zone with high-symmetry points is shown in Fig. 2.

4.2. Electronic structure of $\text{Sn}_{1/3}\text{NbS}_2$ and $\text{Pb}_{1/3}\text{TaS}_2$

The results of the calculations (electronic configuration, charges) are given in Table 4. We remark that not too much significance should be attributed to differences in charge and orbital configurations, as these numbers are dependent on the Wigner–Seitz radii, and the presence of empty spheres. The total and partial densities of states (DOSs) are shown in Figs. 3 and 5, the energy bands along high-symmetry directions in the hexagonal Brillouin zone in Figs. 4 and 6. Results will be compared with calculations of 2H-NbS_2

Fig. 3. Partial and total DOS of $\text{Sn}_{1/3}\text{NbS}_2$.

Fig. 4. Dispersion of the energy bands in $\text{Sn}_{1/3}\text{NbS}_2$.

[5] and 2H-TaS_2 [30] using the same methods as for the Sn and Pb intercalates; a review of band structure calculations of 2H-NbS_2 and 2H-TaS_2 was given by Doni and Girlanda [31].

In 2H-NbS_2 the S 3s bands range from -13.8 to -11.8 eV, well separated from other bands by an energy gap of about 6.5 eV. The bands, ranging from -5.2 to $+1.0$ eV, consist of S 3p and Nb 4d states. Near the Fermi level the bands consist mainly of Nb $4d_{z^2}$ orbitals. The Nb $4d_{z^2}$ conduction band ranges from -0.5 to $+0.70$ eV and is half-filled. There is overlap between the S 3p and Nb $4d_{z^2}$ bands.

Table 3

Input parameters for the band structure calculations of $\text{Sn}_{1/3}\text{NbS}_2$ (upper half) and $\text{Pb}_{1/3}\text{TaS}_2$ (lower half). WP is the Wyckoff position. The empty spheres are indicated by Va, the radii of the Wigner–Seitz spheres of Sn, Pb, Nb, Ta and S by R_{WS} (Å)

Atom	WP	Coordinates	R_{WS} (Å)	Starting electr. config.
Sn	2c	(1/3, 2/3, 1/4)	1.5479	[Kr]5s ² 5p ² 5d ⁰ 4f ⁰
Nb(1)	4f	(1/3, 2/3, −0.00048)	1.1753	[Kr]4d ⁴ 5s ¹ 5p ⁰ 4f ⁰
Nb(2)	2a	(0.0, 0.0, 0.0)	1.1753	[Kr]4d ⁴ 5s ¹ 5p ⁰ 4f ⁰
S	12i	(0.333, 0.331, 0.1084)	1.7772	[Ne]3s ² 3p ⁴ 3d ⁰ 4f ⁰
Va(1)	2d	(2/3, 1/3, 0.25)	1.5479	1s ⁰ 2p ⁰ 3d ⁰
Va(2)	2b	(0.0, 0.0, 3/4)	1.5479	1s ⁰ 2p ⁰ 3d ⁰
Pb	2b	(0.0, 0.0, 1/4)	1.7551	([Xe]4f ¹⁴ 5d ¹⁰)6s ² 6p ² 6d ⁰ 5f ⁰
Ta(1)	4f	(1/3, 2/3, −0.002)	1.2957	([Xe]4f ¹⁴)5d ⁴ 6s ¹ 6p ⁰ 5f ⁰
Ta(2)	2a	(0.0, 0.0, 0.0)	1.3221	([Xe]4f ¹⁴)5d ⁴ 6s ¹ 6p ⁰ 5f ⁰
S	12i	(0.336, 0.337, 0.1052)	1.6688	[Ne]3s ² 3p ⁴ 3d ⁰ 4f ⁰
Va(1)	2d	(2/3, 1/3, 0.25)	1.5479	1s ⁰ 2p ⁰ 3d ⁰
Va(2)	2c	(1/3, 2/3, 0.50)	1.5479	1s ⁰ 2p ⁰ 3d ⁰

Fig. 5. Partial and total DOS of $\text{Pb}_{1/3}\text{TaS}_2$.

In $\text{Sn}_{1/3}\text{NbS}_2$ the lowest bands, ranging from −14.70 to −12.70 eV, consist mainly of sulfur 3s orbitals. The next bands, ranging from −7.2 to −1.9 eV, consist mainly of the S 3p and Sn 5s, 5p states. It is remarkable that the Sn 5s states form two parts, one at the bottom of the S 3p bands with a very small dispersion (about 1.0 eV), and the other beginning at −1.5 eV and ending at +0.4 eV above the

Fig. 6. Dispersion of the energy bands in $\text{Pb}_{1/3}\text{TaS}_2$.

Fermi level. They correspond, respectively, to mainly the bonding and antibonding Sn 5s states (the “inert” lone pair 5s² electrons). Above the Sn 5s antibonding band is the Nb 4d_{z²} band, which is well separated from the other Nb 4d states. The Nb 4d_{z²} states are filled to about 0.3 holes per Nb. There is also a small amount of unoccupied Sn 5s orbitals at the Fermi surface centered around the Γ point. The Nb 4d_{z²}–S 3p gap is about 1 eV, much larger than that for 2H–NbS₂.

The band structure of 2H–TaS₂ is similar to that of 2H–NbS₂ [30]; however, the Ta 5d_{z²}–S 3p gap is about zero, while it is negative in 2H–NbS₂. In the electronic structure of $\text{Pb}_{1/3}\text{TaS}_2$ the S 3s bands range

Table 4

Valence and atomic configuration of the atoms and empty spheres, obtained from the band structure calculations for $\text{Sn}_{1/3}\text{NbS}_2$ (upper half) and $\text{Pb}_{1/3}\text{TaS}_2$ (lower half)

Atom	Valence	Electronic configuration
Sn	+1.79	$[\text{Kr}]5s^{1.40}5p^{0.57}5d^{0.18}4f^{0.06}$
Nb(1)	+2.14	$[\text{Kr}]4d^{2.42}5s^{0.10}5p^{0.14}4f^{0.20}$
Nb(2)	+2.20	$[\text{Kr}]4d^{2.34}5s^{0.10}5p^{0.14}4f^{0.02}$
S	−1.43	$[\text{Ne}]3s^{1.92}3p^{4.75}3d^{0.49}4f^{0.17}$
Va(1)	−0.40	$1s^{0.10}2p^{0.16}3d^{0.14}$
Va(2)	−0.42	$1s^{0.10}2p^{0.17}3d^{0.15}$
Pb	+1.32	$([\text{Xe}]4f^{1.4}5d^{1.0})6s^{1.72}6p^{0.60}6d^{0.25}5f^{0.12}$
Ta(1)	+1.86	$([\text{Kr}]4f^{1.4})5d^{2.50}6s^{0.26}6p^{0.26}5f^{0.12}$
Ta(2)	+1.64	$([\text{Kr}]4f^{1.4})5d^{2.63}5s^{0.30}5p^{0.30}5f^{0.13}$
S	−0.91	$[\text{Ne}]3s^{1.87}3p^{4.51}3d^{0.41}4f^{0.13}$
Va(1)	−0.60	$1s^{0.12}2p^{0.23}3d^{0.23}$
Va(2)	−0.60	$1s^{0.12}2p^{0.23}3d^{0.23}$

from −14.70 to −12.70 eV. The next bands, ranging from −7.2 to −1.9 eV, consist mainly of the S 3p and Pb 6s, 6p states. The Pb 6s bands, with a small mixing with S 3p states, exist at the bottom and the top of the S 3p bands which form the “inert” lone $6s^2$ pair. The Pb 6s bands are all occupied and therefore do not contribute to the chemical bonding. The conduction bands are mainly composed of Ta $5d_{z^2}$ states, which are well separated from the S 3p bands (the gap is about 1.3 eV) and the other Ta 5d states. The Fermi level is in the Ta $5d_{z^2}$ band. The Ta $5d_{z^2}$ bands are filled to about 0.3 holes per Ta.

5. Discussion and comparison with experimental results

The calculated electronic structures of $\text{Sn}_{1/3}\text{NbS}_2$ and $\text{Pb}_{1/3}\text{TaS}_2$ can be understood by using the rigid band model as a starting point. The partial DOS of the Nb and S (Ta and S) indeed shows a strong resemblance to that of 2H-NbS_2 (2H-TaS_2). Electron transfer from Sn (Pb) to the host NbS_2 (TaS_2) leads to an increased filling of the Nb $4d_{z^2}$ (Ta $5d_{z^2}$) band to about 0.3 holes per Nb (Ta), which means that Sn (Pb) are divalent. The most striking difference in the NbS_2 (TaS_2) part of the electronic structure is the increase of the Nb $4d_{z^2}$ (Ta $5d_{z^2}$)–S 3p gap as compared to the host compounds. For 2H-NbS_2 the Nb $4d_{z^2}$ bands overlap with S 3p, while in $\text{Sn}_{1/3}\text{NbS}_2$ there is a gap

of about 1.0 eV between them. The Ta $5d_{z^2}$ /S 3p gap is about 1.3 eV, while in 2H-TaS_2 the gap is about zero. Increase in the Ta $5d_{z^2}$ /S 3p gap is also found in the band structure calculations by Dijkstra et al. [30] for $\text{Mn}_{1/3}\text{TaS}_2$ (1.61 eV) and $\text{Fe}_{1/3}\text{TaS}_2$ (1.53 eV); these compounds are isostructural to $\text{Sn}_{1/3}\text{NbS}_2$. The calculations showed also a decrease in the bandwidth of the S 3p and Ta $5d_{z^2}$ bands.

The Sn 5s (Pb 6s) bands mixed with S 3p contribute at the bottom (bonding) and top (antibonding) of the S 3p bands; for $\text{Sn}_{1/3}\text{NbS}_2$ there is a small pocket of unoccupied Sn 5s states at the Γ point. There is only a slight difference in the partial density of states between Nb(1) and Nb(2), and between Ta(1) and Ta(2), which means that the interaction between Sn and Nb(1), and Pb and Ta(2) is very small.

Electrical transport measurements by Eppinga et al. [32] showed that the compounds are p-type metals, with about $\frac{1}{3}$ hole per Nb or Ta. This was interpreted as being from a conduction in a d_{z^2} band ($4d_{z^2}$ and $5d_{z^2}$ for Nb and Ta, respectively), similar to the pure dichalcogenides in which this band is half-filled. The increase in the band filling is from a donation of the two valence electrons of Sn and Pb to the d_{z^2} band of NbS_2 and TaS_2 . The divalency of Sn and Pb was confirmed by core level photoelectron spectroscopy performed by Eppinga et al. [32]. The valence band spectra [32] are in good agreement with the band structure calculations.

The Fermi surfaces are quite simple: both compounds have six cylinders along Γ –A with unoccupied Nb $4d_{z^2}$ (Ta $5d_{z^2}$) states, or one cylinder per Nb (Ta) atom; $\text{Sn}_{1/3}\text{NbS}_2$ had also an ellipsoidal pocket with unoccupied Sn 5s states centered at Γ .

6. Conclusions

Single-crystal X-ray diffraction of the intercalates $\text{Sn}_{1/3}\text{NbS}_2$ and $\text{Pb}_{1/3}\text{TaS}_2$ confirmed the structures proposed from powder data, but with much greater precision. The post-transition metal atoms occupy $\frac{1}{3}$ of the trigonal–antiprismatic holes between the sandwiches NbS_2 and TaS_2 . Nb and Ta atoms are in trigonal–prismatic coordination by sulfur atoms. The stacking of sandwiches is the same as in 2H disulfides. The arrangement of the post-transition metal

atoms is different for the two compounds; Pb atoms in layers $\frac{1}{2}c$ apart are on top of each other (2b position of space group $P6_322$), while the two Sn atoms are in AB arrangement (2c position of $P6_322$).

Band structure calculations show that the rigid band model is roughly valid for the electronic structure of the intercalates. Sn (Pb) atoms are divalent. The Sn 5s and Pb 6s states are at the bottom and the top of the sulfur 3p band. There is a charge transfer of about 0.67 electrons per Nb (Ta) from Sn (Pb) to the NbS_2 (TaS_2) sandwiches. The Nb $4d_{z^2}$ ($Ta 5d_{z^2}$) band is filled to about 0.3 holes per Nb (Ta), which in good agreement with the X-ray photoemission spectra for the valence band and the electrical transport measurements.

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