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Preparation and Mössbauer Effect of Tin Intercalates of Layered Transition Metal Dichalcogenides

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Mössbauer data has been obtained on six new, distinct tin intercalates which in addition to three others already reported in the literature comprise three distinct groups of compounds.

The compounds contain tin in a single site in the +2 formal oxidation state. A singlet Mössbauer peak was found for all of the compounds except the 2S-, totally-filled intercalates, which show quadrupole splitting. The criteria for classification of these compounds are discussed.

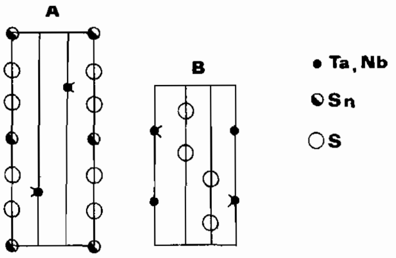

Fig. 1. 110 section of $SnTaS_2$ (A) and 2H-TaS_2 (B).

Introduction

The dichalcogenides of tantalum and niobium have been investigated extensively [1]. These compounds can be visualized as a sandwich three atomic layers thick, MX_2, with the chalcogens of each layer only weakly held to the next layer by van der Waals forces. Because of the weak interlayer bonding, these materials can accept other species between layers forming intercalation complexes [2, 3]. The unit cell in the intercalation compounds usually includes two slabs of MX_2 as in 2H-TaS_2 itself, with the intercalated atoms occupying either tetrahedral, octahedral or trigonal prismatic holes.

The unusual magnetic and superconductive properties of these materials has prompted a considerable amount of work centered around bonding properties.

TABLE I. Preparation and Lattice Constants for Tin Intercalates.

Compound	Mol Sn/MX_2 starting mix	Reaction Conditions days/°C	Lattice Constants (A)	
			a	*c*
2S-$SnTaS_2$[a]	–	–/850	3.28	17.40
2S-$SnNbS_2$[b]	0.66	18/700	3.32	17.36
2S-$SnTaSe_2$	>1.0	6/480	3.42	18.38
2S-$SnNbSe_2$	1.0	19/550	3.46	18.16
1S-$SnNbSe_2$	0.5	14/950	3.42	9.30
2S-$Sn_{1/2}NbSe_2$	1.4	12/520	3.46	14.89
3S-$Sn_{1/3}NbS_2$	1.5	11/520	3.34	20.40
2S-$Sn_{1/3}TaS_2$[a]	0.33	–/900	$3.29\sqrt{3}$	14.35
2S-$Sn_{1/6}TaS_2$	0.50	10/550	$3.30\sqrt{3}$	13.44

[a] See reference [3]. [b] See reference [10].

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TABLE II. Observed X-ray Patterns for the Tin Intercalated Compounds.

d(obs)	hkl	Intensity
2S-$SnTaS_2$		
8.689	002	s
4.353	004	s
2.903	006	w
2.867	100	m
2.831	101	m
2.718	102	m^+
2.571	103	m
2.217	105	w^+
2.181	008	s
2.040	106	w
1.881	107	w^+
1.746	00.10	w
1.656	110	m
1.623	112	w
1.603	109	w
1.548	114	w^+
1.491	10.10	w^+
1.455	00.12	m
1.433	116	w^-
1.429	200	w
1.414	202	w
1.391	10.11	w
1.319	118	w^+
1.298	10.12	w
1.285	206	w
1.247	00.14	w^-
1.202	11.10	w
1.189	208	w^+
1.107	20.10	w^-
1.091	11.12	m
1.081	00.16	w
1.075	212	
1.075	10.15	w
1.064	213	w
1.015	216	
1.015	10.16	w
2S-$SnNbS_2$		
8.672	002	w
4.332	004	s
2.889	006	m^+
2.879	100	m
2.730	102	m^+
2.571	103	m^-
2.214	105	w^-
2.168	008	s
2.038	106	m^+
1.740	00.10	w^-
1.734	108	w^-
1.659	110	m
1.551	114	w
1.485	10.10	w
1.447	00.12	w^+
1.417	202	w^-
1.393	203	w^-
1.318	118	w
1.292	10.12	w
1.289	206	w
1.206	10.13	w^-
1.139	10.14	w^-
1.091	11.12	w
1.086	210	w
1.083	00.16	w
1.017	216	w
2S-$SnTaSe_2$		
9.213	002	s
4.634	004	s
2.959	100	m^+
2.921	101	s
2.814	102	m^-
2.679	103	w
2.481	104	m
2.295	008	s
2.295	105	w
2.127	106	m^+
1.831	00.10	m
1.728	110	m^+
1.707	111	m^-
1.657	113	m^+
1.485	116	w^+
1.485	200	w^+
1.459	202	w
1.364	10.12	w
1.364	118	w
1.331	206	w
1.304	00.14	m
1.202	10.14	w
2S-$SnNbSe_2$		
4.529	004	m
3.013	006	s
2.988	100	m^+
2.950	101	s
2.849	102	m^-
2.683	103	m^-
2.309	105	s
2.262	008	m^+
2.122	106	s
1.955	107	m^+
1.810	00.10	w
1.737	110	s
1.695	112	m
1.588	114	m
1.554	10.10	w^+
1.503	00.12	m^+
1.498	116	m^+
1.455	10.11	m^+
1.395	118	m^+
1.344	10.12	m^+
1.274	10.13	m^+
1.251	11.10	w
1.152	20.10	m
1.134	11.12	m
1.117	10.15	w
1S-$SnNbSe_2$		
9.309	001	m^-
4.646	002	w
3.100	003	w
2.964	100	m^+
2.827	101	s
2.501	102	m
2.321	004	s
2.151	103	m
1.859	005	m^-
1.834	104	w
1.713	110	s
1.575	105	m^+
1.549	006	m^-
1.465	201	w^-
1.375	106	w
1.375	114	
1.337	203	m^-
1.262	115	w^-
1.206	107	w^-
1.145	116	w
2S-$Sn_{1/2}NbSe_2$		
7.437	002	s
2.998	100	m
2.940	101	s
2.780	102	m^-
2.567	103	m
2.335	104	s
2.118	105	m^+
1.914	106	m
1.864	008	s
1.734	107	m^+
1.734	110	
1.688	112	m^-
1.637	113	w
1.585	108	w
1.496	00.10	m^-
1.495	115	w
1.495	200	
1.453	109	m
1.441	203	w
1.395	204	m
1.342	10.10	w
1.342	117	
1.342	205	
1.271	118	m^+
1.132	11.10	m
3S-$Sn_{1/3}NbS_2$		
6.810	003	s
3.401	006	m
2.867	101	s
2.780	102	m
2.515	104	m
2.359	105	s
2.051	107	s

TABLE II. *(continued)*

d(obs)	hkl	Intensity	d(obs)	hkl	Intensity	d(obs)	hkl	Intensity
1.914	108	w	1.996	204	m^-	3.357	004	m^-
1.701	00.12	m^-	1.773	116	w	2.862	110	s
1.670	110	s	1.670	008	m	2.784	104	m^+
1.623	113	m^-	1.653	300	w	2.248	006	m^-
1.499	116	w	1.607	108	w^+	2.040	106	m^+
1.445	201	m^-	1.603	302	w	1.996	204	m^-
1.394	204	w	1.492	304	m	1.773	116	w
1.363	00.15	m^-	1.449	118	m^-	1.670	008	m
1.296	207	w	1.432	220	w	1.653	300	w
			1.363	00.10	w	1.607	108	w^+
2S-$Sn_{1/3}TaS_2$			1.331	306	w	1.603	302	w
6.732	002	s	1.293	10.10	w	1.492	304	m
4.979	100	w	1.113	00.12	w	1.449	118	m^-
4.022	102	w	1.091	10.12	w	1.432	220	w
3.357	004	m^-	1.046	30.10	m^-	1.363	00.10	w
2.862	110	s				1.331	306	w
2.784	104	m^+	2S-$Sn_{1/6}TaS_2$			1.293	10.10	w
2.248	006	m^-	6.732	002	s	1.113	00.12	w
2.040	106	m^+	4.979	100	w	1.091	10.12	w
			4.022	102	w	1.046	30.10	m^-

For example tin intercalates have been synthesized [3–5] and extensively characterized by Mössbauer effect, nuclear magnetic resonance and photoelectron spectroscopy [6–9]. A recent structure determination of $Sn_{1.0}$ TaS_2 by Eppinga and Weiger [10] has described a very unusual coordination for the tin: the matrix TaS_2 can be described as a /AbA AcA/ type with the tin atoms linearly coordinated to two sulfur atoms of the TaS_2 slabs (Fig. 1).

In this paper we describe the preparation, X-ray diffraction data, and Mössbauer characterization of six new, distinct tin intercalates.

Experimental

The TaS_2, $TaSe_2$, NbS_2 and $NbSe_2$ matrices used as starting materials for the preparation of the intercalation compounds were prepared by literature methods [2, 11] to yield 2H-type (/AbA CbC/) structures as confirmed by X-ray powder diffraction patterns.

In general the preparation of the intercalated complex proceeded by sealing one to three grams of the MX_2 matrix with the desired ratio of 99.8% pure tin granules in an evacuated Vycor tube. The mixture was raised 50 °C per hour until the appropriate temperature was reached and at the end of the heating period the sample was allowed to cool slowly to room temperature (Table I).

Intercalation products were purified by a previously described densitometric technique [5]. Densities were obtained by displacement of CCl_4 in a liquid pycnometer and stoichiometries calculated as reported elsewhere [5, 11].

Powder diffraction patterns were obtained on a North American Philips powder diffractometer and a scintillation counter coupled to a Minneapolis Honeywell chart recorder using CuK_α radiation with 2θ ranging from 5° to 90°.

The Mössbauer data were collected on a Hewlett Packard, 1024 channel, multi channel analyzer (Model HP - 5421 - A) and Ortec electronics (Models 451 and 406 A) with a Harshaw NaI scintillation detector and an Elscint Function Generator (Model MFG-2) in a constant accelerator mode. The source was a 5.5 millicurie $BaSnO_3$ (New England Nuclear, Model NER 077). The data were analyzed by a conventional least-squares fit to individual Lorentzian shaped absorption peaks on an IBM 360-168 computer. The maximum error calculated for the position of any one absorption peak was ±0.02 mm/s.

Results and Conclusions

Table II lists the observed X-ray patterns of several of the compounds along with the Miller indices (hkl) and visually estimated intensities. All compounds reported can be indexed on a hexagonal unit cell with all of the observed peaks indexable. This indicates that the samples are of high purity and that any conclusions drawn from the Mössbauer characterization in this case are indicative of valid structural and bonding parameters.

TABLE III. Mössbauer Spectral Data for Tin Intercalates.[a]

	Isomer Shift[b]	Δ (mm/s)	Eff. 5S Elec. Den.	Eff. Sn Oxid State
Group I				
2S-SnTaS$_2$[c]	1.14	1.24	1.20	+0.40
2S-SnNbS$_2$	1.12	0.96	1.20	+0.40
2S-SnNbSe$_2$	0.86	1.15	1.15	+0.31
Group II				
1S-SnNbSe$_2$	1.79	0.0	1.32	+0.64
2S-Sn$_{1/2}$NbSe$_2$	1.76	0.0	1.31	+0.63
3S-Sn$_{1/3}$NbS$_2$	1.78	0.0	1.32	+0.64
Group III				
2S-Sn$_{1/3}$TaS$_2$[c]	1.94	0.0	1.35	+0.69
2S-Sn$_{1/6}$TaS$_2$	2.08	0.0	1.37	+0.74

[a] Mössbauer data was unavailable for 2S-SnTaSe$_2$. [b] Peak positions are referred to α-tin (all values are ±0.02 mm/s). [c] Data also obtained by Herber and Davis [8].

An examination of the Mössbauer data given in Table III shows that the compounds may be divided into three distinct groups.

Group I is characterized by the presence of a Mössbauer doublet with an effective tin oxidation state of approximately 0.4. This group of intercalates contain all of the 2S compounds which are completely filled in all the van der Waals layers and have an approximate increase in the *c* axis of 5.5 Å. Eppinga and Weiger [10] have recently shown that SnNbS$_2$ and SnTaS$_2$ are isostructural and contain linearly coordinated tin. SnNbSe$_2$ shows a Mössbauer doublet similar to these two compounds and can be placed in the same group. It could very well be that the Mössbauer doublet in tin intercalation complexes may be indicative of linearly coordinated tin.

Group II intercalates have Mössbauer singlets indicating cubic symmetry for the tin sites with an effective tin oxidation state of approximately 0.6. These complexes have a regular *c* axis and a Sn/Nb mol ratio which varies in a reciprocal relationship to the slab number (*e.g.* 1/3 for 3S; 1/2 for 2S; 1/1 for 1S). It is therefore not surprising that in this redox reaction the effective oxidation state of the tin remains constant because it is acting as the limiting reagent.

Group III contains those intercalates which form superlattice structures and have a Mössbauer singlet and an effective tin oxidation state of approximately 0.7. Judging from this data it would appear that the superlattice complexes have the tin in a single, identical symmetry site.

One can summarize the results of the Mössbauer data as follows:

(1) In each compound studied, there is but a single tin site present.

(2) All the tin is present in the +2 formal oxidation state.

(3) The effective oxidation state of the intercalated tin remains fairly constant within the group, but increases in the higher groups (I < II < III).

(4) Quadrupole splitting of the spectrum occurs only in Group I, 2S-regular lattice compounds, and may well be diagnostic of linear coordination of tin in this class.

Judging from the Mössbauer data it seems reasonable to suppose that elucidating the structure of one of the compounds in the group should be extremely pertinent and useful in obtaining the structure for the other compounds. Uncompleted structural refinement on 2S-SnNbSe$_2$ seems to support a structure in which the tin is in a single site tetrahedrally surrounded by selenium. If refinement supports this initial conclusion, other compounds of group II should also contain tetrahedrally coordinated tin.

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