

Cobaltocene Intercalation into Misfit Layer Chalcogenides

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A novel intercalation complex is obtained by reaction of cobaltocene solutions in acetonitrile with (PbSe)_{1.12}(NbSe₂)₂ misfit layer compound.

Since the early observation by Dines¹ that metallocenes could be intercalated into layered metal dichalcogenides, cobaltocene intercalation has been extensively investigated.²⁻⁴ Misfit layered chalcogenides⁵⁻⁸ have been recently reported as host materials for intercalation reactions with electropositive metals⁴⁻¹³ and Lewis bases.¹⁴⁻¹⁷ Here we report the preliminary results on the reactivity of (PhSe)_{1.12}(NbSe₂)₂ and (PbS)_{1.12}(NbS₂)₂ towards cobaltocene intercalation. In these solids the trigonal-prismatic coordination of Nb and the presence of a true van der Waals gap between consecutive NbX₂ (X = S, Se) slabs allow a direct comparison with the intercalation properties of 2H-niobium dichalcogenides.

The misfit layer chalcogenides were prepared as described elsewhere.^{7,8} About 100 mg of each powdered sample of sulfide and selenide were dispersed in 3 ml of a 0.05 mol dm⁻³ solution of cobaltocene (provided by Strem) in dry acetonitrile and sealed in glass tubes under vacuum. The reactions were followed at room temp. and 90 °C during different time periods. The resulting solids were extensively washed with acetonitrile inside a dry-box. A change in colour from dark grey to black and a significant swelling of the selenide particles was observed after treatment for 7 d at 90 °C or 14 d at room temp. By contrast, little morphological changes were observed in the sulfide particles after treatment at either temperature. Energy dispersive X-ray microanalysis and atomic absorption spectroscopy analyses indicated absence of intercalation in the sulfide samples, while a stoichiometry [Co(η⁵-C₅H₅)]_{0.31}(PbSe)_{1.12}(NbSe₂)₂ was confirmed by elemental analysis after reaction of the host selenide with cobaltocene. [Found (Calc.); C, 4.50 (4.22); Co, 2.00 (2.07)]. This composition is similar to that found in [Co(η⁵-C₅H₅)]_{0.31}NbSe₂,¹ as only one van der Waals layer per two consecutive NbSe₂ slabs are found in the misfit layer structure. The material is thermally stable under nitrogen up to 500 °C.

X-Ray powder diffraction patterns of misfit layer chalcogenides usually show an intense set of (00*l*) lines and few extra lines, as a consequence of the misfit between sublattices and preferred orientation phenomena. For (PbSe)_{1.12}(NbSe₂)₂, the spacings of the (00*l*) lines indicates a periodic length of 18.75 Å, which implies the following stacking unit of selenide slabs: -NbSe₂-PbSe-NbSe₂.⁸ For cobaltocene intercalated (PbSe)_{1.12}(NbSe₂)₂, the experimental X-ray diffraction pattern shows a different set of lines consistent with a periodic length of 24.33 Å (Table 1). The magnitude of the interplanar expansion (5.58 Å) is similar to the size of the cobaltocene molecule and to the expansions found in other intercalates of transition-metal dichalcogenides,¹ suggesting that the intercalate is located in all NbSe₂-NbSe₂ interlayers leaving empty PbSe-NbSe₂ interlayers, *i.e.* with a NbSe₂-PbSe-NbSe₂-Co(η⁵-C₅H₅)₂- stacking unit. In addition the observed expansions are consistent with cobaltocene molecules oriented with the C₅ axis parallel to the van der Waals layers. The Patterson analysis obtained by using 17 (00*l*) reflection intensities of both pristine and intercalated (PbSe)_{1.12}(NbSe₂)₂ (Fig. 1) reveal that the interatomic distances between Se, Pb and Nb atoms remain basically unaltered in each -NbSe₂-PbSe-NbSe₂-block and that the intercalate dimensions are responsible for the observed expansion almost exclusively. From these results, the model shown in Fig. 2 can be proposed.

Electron diffraction patterns recorded with the incident beam parallel to [00*l*] were coincident for the pristine and

intercalated selenide as a consequence of the topotactic nature of the process. The misfit between sublattices remains unaffected by cobaltocene intercalation as evidenced by the constancy in $a_{\text{PbSe}}/a_{\text{NbSe}_2}$ ratio. The observation of a single relative orientation of both sublattices can be considered as an indirect proof that intercalation takes place between consecutive NbSe₂ slabs. In fact, it was shown that alkali-metal

Table 1 Powder X-ray diffraction data for [Co(η⁵-C₅H₅)]_{0.31}(PbSe)_{1.12}(NbSe₂)₂

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{cal}	(<i>hkl</i>) _{obs}
0	0	<i>n</i>	24.69	24.33	100
0	0	2 <i>n</i>	12.19	12.16	62
0	0	3 <i>n</i>	8.146	8.110	18
0	0	4 <i>n</i>	6.094	6.082	46
0	0	5 <i>n</i>	4.874	4.866	18
0	0	6 <i>n</i>	4.058	4.055	10
0	0	7 <i>n</i>	3.477	3.476	47
0	0	8 <i>n</i>	3.042	3.041	52
0	0	9 <i>n</i>	2.703	2.703	18
0	0	10 <i>n</i>	2.434	2.433	14
0	0	11 <i>n</i>	—	2.212	—
0	0	12 <i>n</i>	—	2.027	11
0	0	13 <i>n</i>	—	1.871	—
0	0	14 <i>n</i>	1.7383	1.7378	7
0	0	15 <i>n</i>	1.6226	1.6220	12
0	0	16 <i>n</i>	1.5213	1.5206	16
0	0	17 <i>n</i>	—	1.431	—

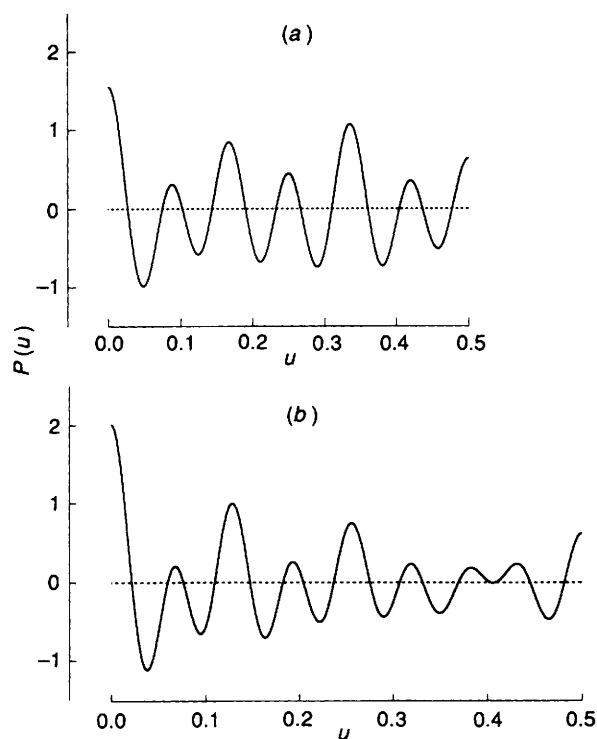


Fig. 1 Scaled one-dimensional Patterson diagrams for the half-cells of (PbSe)_{1.12}(NbSe₂)₂ (a) and [Co(η⁵-C₅H₅)]_{0.31}(PbSe)_{1.12}(NbSe₂)₂ (b)

intercalation into $(MS)_{1+y}(\text{NbS}_2)_2$ ($M = \text{Sn}, \text{Pb}$) between MS and NbS_2 slabs leads to orientation anomalies between both sublattices.^{10,11}

Preliminary XPS results show a single $\text{Co } 2\text{P}_{3/2}$ photoline from $[\text{Co}(\eta^5\text{C}_5\text{H}_5)]_{0.31}(\text{PbSe})_{1.12}(\text{NbSe}_2)_2$ with the peak located at 782 eV, which was assigned to Co^{3+} , indicative of a complete electron transfer from the guest to the misfit layer selenide host. This result contrasts with the low but non-zero Co^{2+} content found in other cobaltocene intercalates.⁴ However, recent infrared spectroscopic studies are consistent with the presence of only the cationic form of the cobaltocene within the SnS_2 host.³

The poor cobaltocene intercalation properties of the sulfide sample as compared with $(\text{PbSe})_{1.12}(\text{NbSe}_2)_2$ were also evident by X-ray and electron diffraction data and agree with previous results obtained for 2H-NbS_2 and 2H-NbSe_2 . While

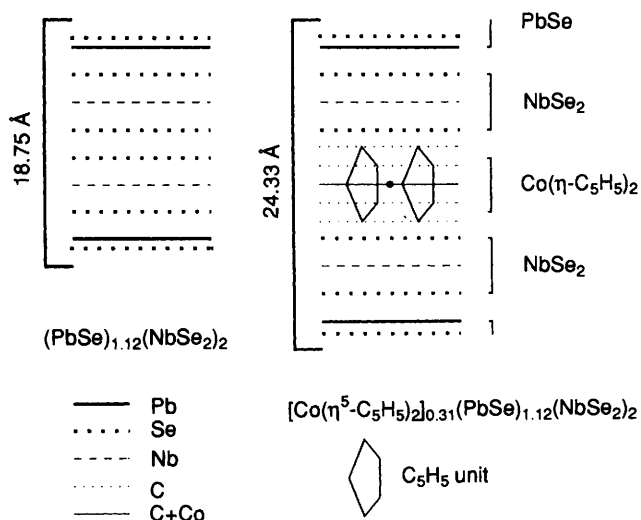


Fig. 2 Schematic projection of atom layers along c for $(\text{PbSe})_{1.12}(\text{NbSe}_2)_2$ and $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)]_{0.31}(\text{PbSe})_{1.12}(\text{NbSe}_2)_2$

cobaltocene intercalation into 2H-NbSe_2 was reported by Dines,¹ Clement *et al.*² were unable to obtain intercalation products by direct reaction of different metallocenes with 2H-NbS_2 .

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