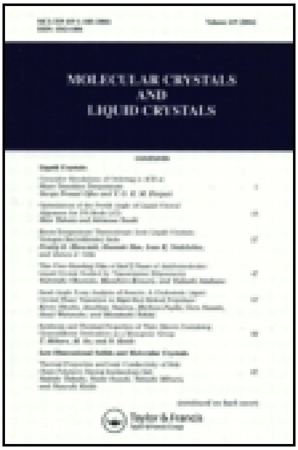

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MERCURY INTERCALATION INTO LAMELLAR TRANSITION METAL DISULFIDES

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Abstract Mercury can be intercalated at room or moderate temperature into lamellar titanium and tantalum disulfides. The structure of intercalated compounds is described by two incommensurate sublattices corresponding to the disulfide host layers and the intercalated mercury,respectively. Depending on the synthetic procedure two different phases are obtained for mercury intercalated tantalum disulfide, which mainly differ in the relative orientation of disulfide and mercury networks. Mercury intercalation of 1T-TaS_2 results in a tantalum coordination change from octahedral to trigonal prismatic. The mercury-to-host charge transfer is very low and more heavily involves the sulfur orbitals than previously observed for lithium intercalated compounds.

INTRODUCTION

Among the various guest species intercalated in the lamellar transition metal dichalcogenides, the post transition elements (groups IIB and IIIB) have been rarely studied. Preliminary studies have been done showing that many elements can be intercalated.[1] However only some of these compounds have been studied in more detail either for their physical properties[2] or structural aspects.[3] More recently, other host structures than 2H-TaS_2 have been studied and it has been shown that mercury can be intercalated into TiS_2 and 1T-TaS_2 as well.[4,5] In this paper we will describe our most recent results for these systems.

SYNTHESES AND STRUCTURES

The TiS_2 case

TiS_2 can be intercalated by mercury up to the composition $Hg_{1.3}TiS_2$ by mixing the lamellar dichalcogenide and liquid mercury at room temperature.[4] Intercalation follows from an interlayer expansion of 2.94 Å. The structure of the fully intercalated phase can be described as incommensurate alternating layers of mercury and dichalcogenide.[4]

Intercalation induces a slight monoclinic distortion for the host-layer unit cell. The parameters of the monoclinic cell describing the host layer structure are a=5.920(4) Å, b=3.409(2) Å, c=8.853(5) Å and β=102.33(7)°. They correspond to an atomic stacking sequence very close to rhombohedral symmetry and evidence a modification in sulfur stacking mode from ABAB to ABCABC or AABBCC. However, this monoclinic cell does not allow the X-ray diffraction pattern to be completely indexed. Despite their poor crystal quality, classical single crystal X-ray diffraction methods (rotating crystal, Weissenberg, Bürger) indicate that the intercalated mercury atoms must be described in a second monoclinic cell (a=4.828(2) Å, b=2.912(1) Å, c=9.247(2)Å and β=110.82(2)°) which is not commensurate with the above monoclinic host layer cell. In the parallel and alternate mercury and TiS_2 sheets, the a and b parameters for both monoclinic cells are incommensurate. Single crystal X-ray experiments show that the ab planes are rotated with respect to each other ≈ 5°. The presence of two incommensurate networks for the host and guest indicates that the mercury atoms do not occupy well defined sites between the TiS_2 layers and must be considered as forming sheets inside the gap.

2. The TaS_2 case

In a preliminary study, Di Salvo et al. intercalated mercury into 2H-TaS_2 at 200°C using a large excess of mercury. Subsequently a thermal gradient was used to remove the free mercury.[1] However, mercury can also be intercalated into 2H-TaS_2 by simply mixing the disulfide with liquid mercury at room temperature.[5] Depending on the synthetic procedure two phases can be obtained. When intercalation is performed with an excess of mercury, compared to the maximum composition of $Hg_{1.3}TaS_2$, a copper colored compound results (phase II). If heated, the compound turns black with a resulting composition close to $Hg_{1.15}TaS_2$ (phase I). Phase II can be reobtained via a reaction with an excess mercury. Phase II is only stable in the presence of excess mercury. In the absence of excess mercury, it changes into phase I, with its rate being temperature dependant. The transition is complete in a few weeks, at ambient temperature. As for Hg intercalated TiS_2, the X-ray powder diffraction patterns can be indexed using two incommensurate cells, corresponding to expanded TaS_2 and mercury networks. For phase II, the intercalated TaS_2 cell can be indexed as an hexagonal cell with a=3.3151(1) Å and c=9.0194(9) Å, corresponding to a c parameter expansion of 2.982 Å. The presence of a weak line which can only be indexed as a (103) reflexion with a doubling of the c parameter, appears to indicate that, as for 2H-TaS_2, the intercalate is best described by a two layer cell. The mercury network is apparently indexable as a hexagonal cell.

For phase I the splitting of some lines indicates a monoclinic distortion of the TaS_2 cell with a=5.7604(5) Å, b=3.3075(3) Å, c=17.812(1) Å and β=89.935(8)°. In addition, broad but intense lines are visible which can only be explained by a two layer cell. The mercury network can be primarily indexed on the basis of a hexagonal cell. Probably due to stacking faults, intercalate single crystals were of poor quality and did not allow a structural determination from their diffraction intensities. Nevertheless a classical study using film diffraction techniques confirmed the existence of two non commensurate networks of TaS_2 and intercalated mercury. For phase II, it appears that the hexagonal cells are oriented in the *ab* plane in such a way that the *a* parameters are rotated by 30° with respect to each other (the large diagonal of one cell is aligned with the *a* axis of the other one). For phase I there is a 5° misalignment between the nearly hexagonal Hg and TaS_2 layers, similar to that observed for $Hg_{1.3}TiS_2$.

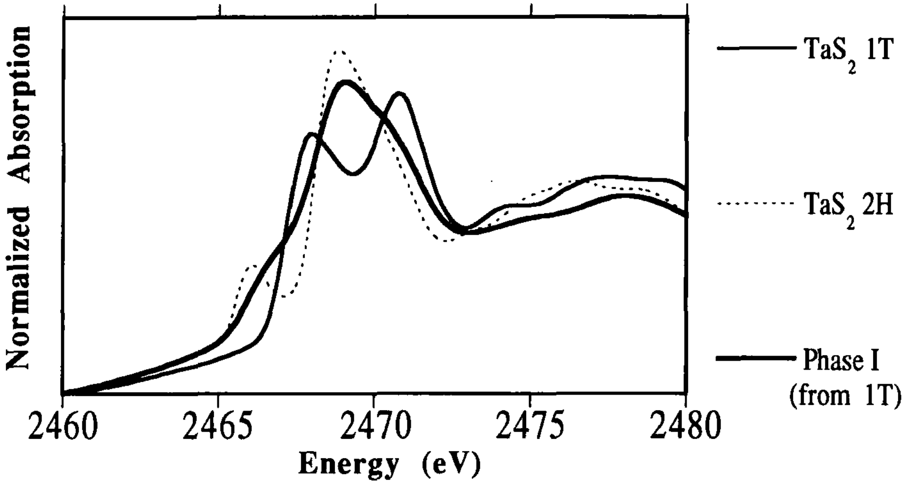

FIGURE 1 X-ray absorption at the sulfur K edge for 1T- and 2H-TaS_2 and mercury intercalated 1T-TaS_2.

Mercury intercalation can also be performed in 1T-TaS_2, where tantalum atoms are octahedrally coordinated. In situ Time Differential Perturbed Angular Correlation (TDPAC) experiments have shown that a minimum temperature of 150°C is required[6], and that mercury intercalation induces a tantalum coordination change from octahedral to trigonal prismatic[7]. The tantalum coordination change has been confirmed by X-ray absorption experiments at the sulfur K edge (XANES) (Figure 1). The edge shape is highly characteristic of the transition metal coordination. It is a doublet for octahedral coordination and a more unique intense peak for trigonal prismatic coordination. It is evident from figure 1 that a tantalum coordination change occurs in mercury intercalated 1T-TaS_2.

It is possible to distinguish two phases for the compounds prepared from the 1T form under the same conditions used for 2H-TaS_2 intercalation. Despite having the same tantalum coordination, the mercury intercalated compounds obtained from the 1T and 2H forms are significantly different. X-ray powder diffraction shows differences in the cell parameters. As an example, a=3.3185 (2) Å and c=8.9786 (7) Å for the hexagonal cell of the TaS_2 part in phase II prepared from 1T-TaS_2. The main difference comes from the fact that no reflections indicating a doubling of the c parameter appear in the pattern. We may consider that the intercalated structure retains the layer repeat of the host unit cell, with a one (1T) or two (2H) layer repeat. Another difference is the amplitude of the monoclinic phase I distortion. This distortion is less pronounced for the compound obtained from the 1T host than for the one derived from the 2H host (line broadening rather than actual splitting). The relative orientations of the TaS_2 and mercury networks are the same regardless of the form of the host TaS_2.

CHARGE TRANSFER

Of the large number of intercalated transition metal dichalcogenides, the mercury intercalated compounds exhibit novel structural characteristics. The super stoichiometric ratio and the non commensurate mercury network indicate that mercury atoms cannot be considered as individual species occupying well defined sites in the van der Waals gap. Intercalated mercury is probably best described as a compact sheet (more or less distorted) of mercury atoms experiencing covalent interactions not very far from what they are in the elemental state. This could also explain the distortions observed for the intercalate's host-layer structure as being necessary to adapt to the intercalated mercury network. This peculiar structural behaviour suggests an unusual charge transfer process.

Magnetic susceptibility has been measured at room temperature on a sample of global composition Hg_1TiS_2. The obtained value of $\chi=28.9\times10^{-6}$ emu/mole is not the sum of those measured for pristine TiS_2 (in good agreement with the value of reference 8) and elemental mercury (11.95×10^{-6} and -30.4×10^{-6} emu/mole, respectively), suggesting charge transfer takes place during intercalation. By comparison with the variation of the room temperature magnetic susceptibility for Li_xTiS_2[8], a charge transfer of about 0.2 electron per mercury atom is suggested. This is in good agreement with the value deduced from TDPAC experiments on mercury intercalated TaS_2, i.e. 0.3 electron per tantalum atom for a composition $Hg_{1.3}TaS_2$.[6]

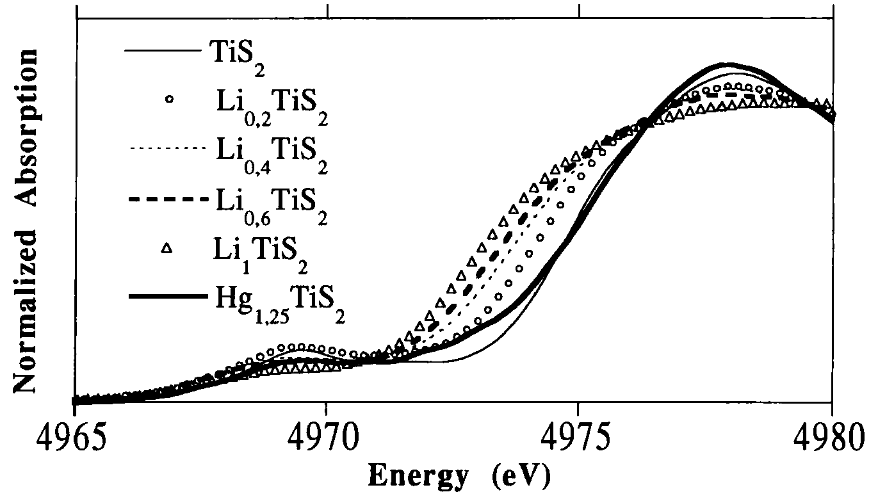

FIGURE 2 X-ray absorption titanium K edge in the Li_xTiS_2 system and $Hg_{1.25}TiS_2$.

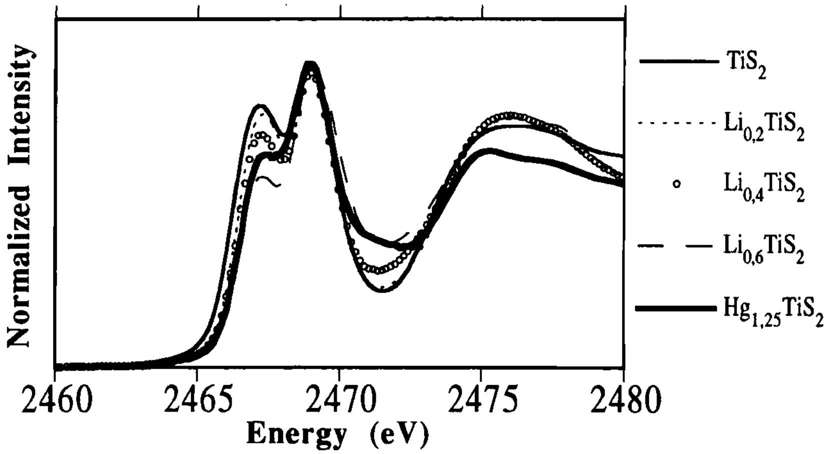

FIGURE 3 X-ray absorption sulfur K edge in the Li_xTiS_2 system and $Hg_{1.25}TiS_2$.

In order to better characterize the actual nature of charge transfer in mercury intercalated TiS_2 phases, an X-ray absorption study at the titanium and sulfur K edges has been undertaken, with the Li_xTiS_2 system used as a reference. Figure 2 shows the titanium K edge for some phases in the Li_xTiS_2 system and pristine and mercury intercalated TiS_2. A pre-edge peak attributed to the $1s^2 3d^0 \rightarrow 1s^1 3d^1$ transition is observed around 4969 eV. Its intensity is very sensitive to the d orbital population along with the site distortion. It decreases regularly with increasing lithium content associated with titanium reduction. A pronounced effect is also observed for the mercury intercalated compound. Nevertheless, the edge position indicates different behaviour for lithium and mercury intercalated phases. A shift towards lower energy values can be seen for the lithium intercalated compounds, associated with titanium reduction. However, for the mercurated compound the edge jump is exactly in the same position as for pristine TiS_2. As mentioned above, the sulfur K edge shown in figure 3 is made of a doublet, characteristic of titanium octahedral coordination. In a first approximation, we may consider that the first peak is mainly of p_z character, the second one corresponding to p_x and p_y sulfur orbitals. The intensity of the first peak decreases regularly upon lithiation, and the effect observed for the mercurated compound is more pronounced than expected for a charge transfer of only 0.25 electron. From these results it is difficult to describe precisely the nature of the charge transfer between mercury and TiS_2. Nevertheless, there is no doubt that the process is substantially different from that encountered for the lithium intercalated phases. It is generally considered that in this last case the intercalated species are fully ionized with a corresponding reduction of titanium. For mercury intercalated compounds, sulfur atoms are more involved in the charge transfer process, with possible covalent interactions between mercury and sulfur atoms, which could explain the observed structural distortion. This general problem of charge transfer in mercurated lamellar compounds is currently being studying by combining different mercury intercalated hosts and techniques such as XPS, XAS and EELS.

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