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Synthesis and Characterization of a Mercury-Intercalated Molybdenum Disulfide

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Elemental mercury cannot be intercalated into crystalline molybdenum disulfide as such, probably for structural reasons, the *a* parameter of the host being too small. On the contrary, we show that a reaction between restacked MoS_2 and liquid mercury allows the synthesis of such an intercalate. X-ray absorption spectroscopy experiments show that such different behavior is due to the appropriate structural configuration of the restacked phase. Intercalated mercury stabilizes the structural and d^3 electronic configuration of molybdenum. © 1999 Academic Press

Key Words: **Molybdenum disulfide; mercury; intercalation; X-ray absorption spectroscopy.**

1. INTRODUCTION

More than 20 years ago, very preliminary results (1–3) showed that mercury could be added to the long list of chemical species (element, ions, organic molecules) that can be intercalated into the van der Waals gap of the lamellar transition metal dichalcogenides (TMDCs). In these experiments tantalum and niobium disulfides and diselenides have been considered host structures. Some years later, the possibility of intercalating mercury into TiS_2 was demonstrated, by a very simple reaction between the sulfide powder and elemental liquid mercury at room temperature (4). These intercalated compounds have been deeply investigated and they evidence a very peculiar behavior among the intercalated compounds. Structure determination (5) shows that the host and intercalated mercury structures are not commensurate in one direction of the layers, in agreement with the nonstoichiometric composition $Hg_{1.24}TiS_2$. Mercury is not intercalated as individual species, but forms chains running inside tunnels made of adjacent trigonal prisms. Hg–Hg interactions inside and between the chains are strong enough to induce a distortion of the TiS_2 structure. Nevertheless, this constraint can be released on heating up to 200°C. At this temperature, the Hg network undergoes a reversible solid–liquid transition (6). The way mercury is intercalated and interatomic distances in the intercalated compound tend to prove that mercury is primarily neutral. Band structure calculations and XPS and XAS experiments have been used to characterize the electronic exchange and possible bonds between mercury and the host (7).

Almost at the same time, the mercury-intercalated tantalum disulfides have been investigated and the study concludes that the behavior of TiS_2 and TaS_2 is very similar (8, 9). More recently we have undertaken a systematic study of mercury intercalation into the TMDCs. The results will be published in detail elsewhere. It appears that only some of the possible hosts may intercalate mercury, namely, the Ti, V, Nb, and Ta disulfides and some mixed selenides. In using mixed systems, we have been able to define a basal plane *a* parameter range suitable for mercury intercalation. This tends to indicate that, due to the above-mentioned structural constraints imposed on the host by mercury arrangement, only some hosts are able to adapt it. Nevertheless, the *a* range is different for sulfides and selenides and we cannot exclude also some electronic reasons, such as Hg–chalcogen interactions, to explain why only some dichalcogenides may be hosts for mercury. The reader notes that molybdenum disulfide MoS_2 is not among the possible hosts, partially because its *a* parameter is too small (3.159 Å), compared with the lower limit of the above-mentioned range (3.22 Å). During the last decade, it was demonstrated that exfoliation of Li_1MoS_2 in water produces MoS_2 single layers extremely capable of forming intercalates (10–13). All the syntheses have been performed with MoS_2 aqueous dispersions. However, MoS_2 freshly reprecipited from the dispersion without intercalation was reported to have a rather disordered and distorted structure, in which, in particular, an increase in the *a* parameter up to 3.27 Å can be detected (11). We have tried to use in the present study this metastable form of MoS_2 to prepare a mercury-intercalated molybdenum disulfide. This paper describes our success in this matter and the investigations we did on this

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compound to explain why crystalline MoS_2 does not intercalate mercury and the restacked phase does.

2. EXPERIMENTAL

Purified natural MoS_2 (molybdenite) from Russia was used after being ground to a particle size smaller than 100 μm. The purity of the phase was checked by X-ray powder diffraction. Lithium intercalation was performed by the *n*-butyl lithium technique (14) to obtain the Li_1MoS_2 phase, which was exfoliated in water. The suspension obtained was acidified by HCl to a pH lower than 2 and filtered, and a so-called "restacked" MoS_2 was obtained. The powder was dried under vacuum and immediately placed in contact with liquid mercury at room temperature, as described for mercury intercalation into TiS_2 (4). EDX analysis performed in a scanning electron microscope shows a large inhomogeneity in mercury content. The overall composition of different crystallites in the preparation varies from about $Hg_{0.7}MoS_2$ to $Hg_{1.3}MoS_2$. The stage 1 mercury-intercalated disulfides previously prepared have a composition close to 1.3 Hg per mole. We may then consider that the preparation contains some high-stage intercalated compounds. In the case of mercury-intercalated TiS_2, the simultaneous presence of fully intercalated and pristine disulfide, or high-stage intercalated compounds, has also been observed, depending synthesis parameters such as Hg/TiS_2 ratio and temperature. Due to the low accuracy of the EDX analysis and the resolution of SEM, it is impossible to define a precise composition for the stage 1 mercury-intercalated molybdenum disulfide, which we refer to as $Hg–MoS_2$ in the remainder of this paper.

Powder X-ray diffraction patterns of the various compounds were collected on an INEL CPS diffractometer with monochromatized K-L3 copper radiation in transmission mode, the sample being placed in a 0.1-mm-diameter glass capillary.

X-ray absorption spectroscopy (XAS) data were collected on the molybdenum and sulfur *K* edges at LURE, the French synchrotron facility, on the DCI and Super ACO storage rings, respectively. Data were treated using the series of programs written by Michalowicz (15). XANES spectra were calibrated by using pristine ZnS as a reference and normalized at 80 eV above the edge. For the EXAFS data, the preedge was removed by linear simulation and the atomic contribution after the edge was extracted by a polynomial contribution. Fourier transforms of the resulting EXAFS spectra were calculated after convolution with a Hanning window. For the fitting procedure, experimental amplitude and phase shift of the pristine MoS_2 were used.

3. RESULTS

Due to the poor registry between the adjacent restacked MoS_2 single sheets, the X-ray diffraction pattern is of bad quality and gives essentially information on the *c* parameter, which is the periodicity perpendicular to the slabs. The powder X-ray diffraction pattern of the phase obtained after a 10-min reaction of liquid mercury with restacked MoS_2 is shown in Fig. 1. We may clearly identify sharp peaks corresponding to 001 lines, from which a *c* parameter of 9.12 Å can be deduced. Such a value corresponds to an expansion of 2.98 Å, which compares well with the diameter of the mercury atom in the α modification of the metal (2.99 Å) (16) and the *c* parameter expansion observed for TiS_2 on mercury intercalation (2.94 Å). Despite its bad quality, this pattern is a clear evidence of mercury intercalation into MoS_2. Moreover, the presence of additional peaks, marked by asterisks in Fig. 1, has been attributed to the higher stages already suggested by EDX analysis. The 003 and 006 peaks are much broader than the 001 and 002 peaks. By comparison with rather well-crystallized $Hg–TiS_2$ and $Hg–TaS_2$ systems, this phenomenon can be explained by the occurrence close to these angles of the *h*0*l* and *hhl* lines, and the very poor registry between the subsequent MoS_2 sheets.

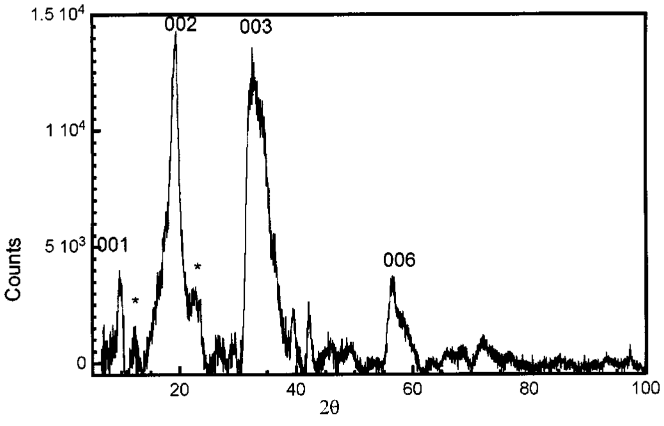

FIG. 1. Powder X-ray diffraction pattern of $Hg–MoS_2$.

As postulated in the Introduction, mercury intercalation into TMDCs requires structural and electronic conditions. It is then interesting to explain why such an intercalate cannot be obtained with the crystalline MoS_2, but can with the restacked phase.

X-ray absorption spectroscopy (XAS) is very well known to provide valuable information about the atomic structural environment, whatever the crystalline state of the material, in the so-called EXAFS part, and about the electronic state of an element in probing the empty electronic levels in the XANES part. Moreover, previous XANES experiments at the sulfur *K* edge on the two modifications of TaS_2, 1T and 2H, which correspond to octahedral and trigonal prismatic sulfur environments of tantalum, respectively, have proved to be very powerful in giving a clear signature of the symmetry type (17). In the first paper on lithium intercalation into MoS_2, Py and Haering (18) claimed a simple

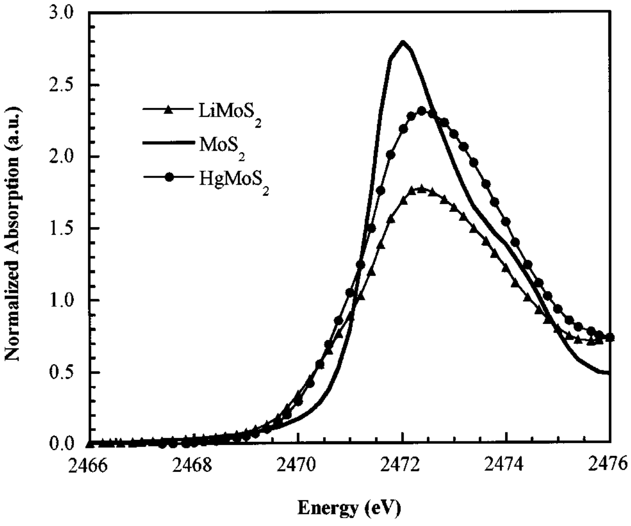

FIG. 2. Comparison of the XANES part of the X-ray absorption spectra at the sulfur K edge for pristine MoS_2, $LiMoS_2$, and Hg–MoS_2.

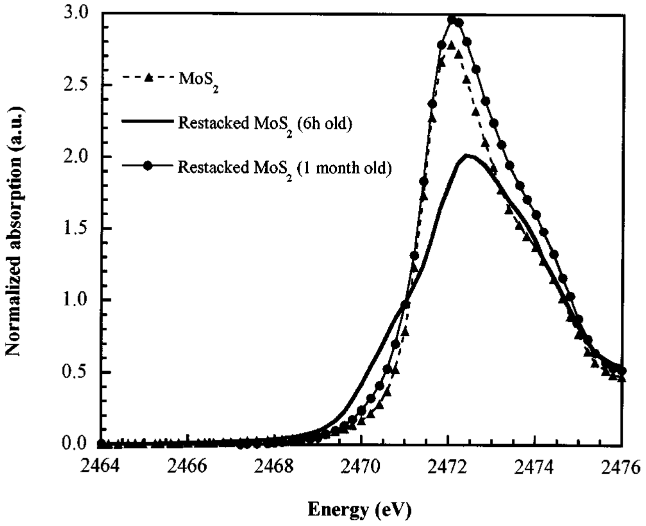

FIG. 3. Comparison of the XANES part of the X-ray absorption spectra at the sulfur K edge for pristine MoS_2, 6-h-old restacked MoS_2, and 1-month-old restacked MoS_2.

coordination change of molybdenum from trigonal prismatic to octahedral on lithium intercalation into molybdenum disulfide. We have recently shown that the sulfur K-edge shape in only slightly changed by lithium intercalation, and EXAFS experiments at the molybdenum K edge indicate a large shortening of Mo–Mo distance (19). Similar studies have been undertaken on the mercury-intercalated compound. Figure 2 compares the sulfur K edges for pristine MoS_2, Li_1MoS_2, and mercury-intercalated MoS_2. Edges of intercalated phases are very comparable. They differ from those of pristine MoS_2 mainly in the occurrence of a shoulder at low energy. In any case we do not observe a well-defined doublet which is the signature of the classic splitting of the electronic d levels in "*t2g*" and "*eg*" groups in the octahedral coordination, as shown by experiments on 1T TiS_2 and TaS_2 (17). Moreover, it is remarkable that the edge shape of the mercury-intercalated phase does not change on aging, even for months. On the contrary, the restacked MoS_2 powder is largely metastable. In fact, after 1 month, the edge shape of the restacked compound returns to that of the pristine compound (Fig. 3).

EXAFS results confirm the previous observations. The molybdenum radial distribution functions (RDFs) extracted from the data collected on lithium- and mercury-intercalated compounds are very similar, and very different from those for pristine MoS_2 (Fig. 4). This is very clear for the second coordination shell, which is largely reduced in intensity and shifted toward lower distances. As stated in Ref. (19), this is a clear signature of a molybdenum clusterization. It is interesting to note that the same phenomenon has been observed in the exfoliated MoS_2 suspension (12) and in MoS_2 intercalated with nickel hydroxide-like species (20). The EXAFS spectrum of the mercury-intercalated MoS_2 is identical after a long period of aging. On the contrary, as previously mentioned for the XANES part, the RDF of a restacked MoS_2 powder is rapidly changed (Fig. 5). After only 12 h, the shape is similar to that of pristine MoS_2, but not the intensities. These intensities progressively recover, and after 1 month we may consider that the material has returned to its pristine state.

4. DISCUSSION

X-ray diffraction and absorption experiments prove that a mercury-intercalated molybdenum disulfide can be prepared and stabilized over a long period, even if it is not

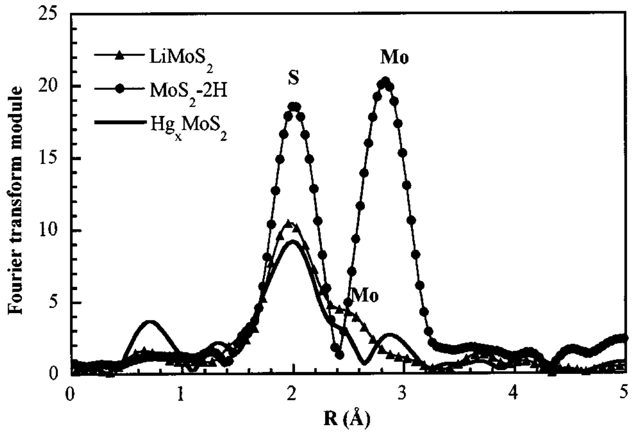

FIG. 4. Comparison of the molybdenum radial distribution functions for pristine MoS_2, $LiMoS_2$, and Hg–MoS_2. Distances have not been corrected for phase shifts.

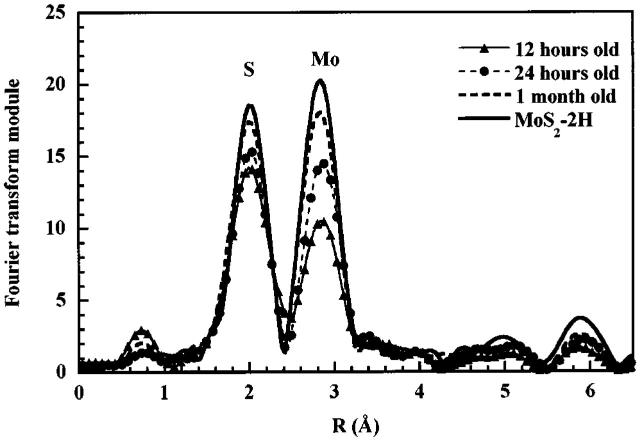

FIG. 5. Comparison of the molybdenum radial distribution functions for pristine MoS_2 and restacked MoS_2 after different periods of aging. Distances have not been corrected for phase shifts.

possible to perform direct mercury intercalation into MoS_2. Such behavior provides information on both the general mercury intercalation process and the MoS_2 transformations on lithium intercalation and the subsequent stability of the restacked MoS_2.

The intercalation process has been generally considered from a structural and charge transfer point of view to define the nature of the driving force for such a spontaneous reaction. This is especially true for mercury intercalation which appears so easy, being completed in only few minutes at room temperature with a gentle mixture of chalcogenide powder and elemental mercury. At the same time, mercury has very peculiar behavior among the intercalated species, with a very low charge transfer and the structural constraints it imposes on the host structure, giving rise to the only basal hexagonal cell distortion ever encountered in the intercalated TMDCs. We have to find the explanation of such a behavior in an energy stabilization of the intercalated mercury network itself, compared with the liquid one, and theoretical total energy calculations are in progress to check this hypothesis.

With respect to intercalation into molybdenum disulfide, Py and Haering (18) have claimed that, in the case of lithium, the process is biphasic between a low-rate intercalation compound, $Li_{0.1}MoS_2$, and the complete one, Li_1MoS_2. Despite the loss of crystallinity, the X-ray powder pattern of Li_1MoS_2 has been analyzed as a 1T form very similar to the Li_1TiS_2 form, in which lithium and molybdenum have a sulfur octahedral coordination, even if the molybdenum environment is distorted. A similar distortion has been deduced from studies on the metastable 1T-MoS_2 modification prepared from potassium thiomolybdate (21). In this compound, STM studies conclude that there is a correlative displacement of Mo atoms from the centers of the octahedra to form trimers (22). From a simple electronic structure model, the molybdenum coordination change from trigonal prismatic to octahedral has been explained by an energy stabilization. In fact, the crystal field splitting of the *d* levels in trigonal prismatic coordination stabilizes the *a*1 orbital very well suited for the two *d* electrons of molybdenum at oxidation state IV in MoS_2. This configuration would be more stable than the classic *t2g* and *eg* obtained for octahedral crystal field splitting. On the contrary, on lithium intercalation, molybdenum is reduced to oxidation state III, in a d^3 configuration. The explanation of the structural change is that the added electron would be put into a rather high-energy orbital in the trigonal prismatic configuration compared with the simple addition of one electron to a partially filled *t2g* group. On the exfoliation reaction of Li_1MoS_2 in water, it is considered that the new octahedral molybdenum configuration is kept, the electronic stabilization being ensured by the charges borne by adjacent ions contained in the solution. After the subsequent encapsulation of various chemical species between the MoS_2 single sheets, Mo would retain this configuration. If these sheets are simply restacked without anything inbetween, molybdenum returns to its pristine trigonal prismatic environment, as demonstrated by the above-described XAS experiments.

Our recent XAS studies on Li_1MoS_2 have demonstrated that this picture of the d^3 molybdenum stabilization is too simplistic. EXAFS results show a large shortening of Mo–Mo distances in a probable diamond-shaped Mo_4 unit structural arrangement. This is supported by the theoretical study of Kertesz and Hoffmann (23) on TMDCs in which the transition metal has a d^3 electronic configuration. Moreover, such diamond-shaped clusters are found in rhenium and technetium lamellar dichalcogenides (24) and in the ternary chalcogenide $Co_{0.5}MoS_2$ (25).

The similarity between the XANES and EXAFS data obtained for Li_1MoS_2, Hg–MoS_2, and the freshly restacked MoS_2 proves that molybdenum has, in these phases, the same structural and electronic configurations, i.e., a d^3 in a diamond-shaped cluster arrangement. From a structural point of view such a configuration explains why it is possible to stabilize the mercury network in the restacked phase. In fact, the *a* parameter of this phase is supposed to be very close to those observed in Li_1MoS_2 (3.36 Å) and the single sheets (3.27 Å) and these two values are included in the *a* parameter window which seems to be one essential condition for mercury intercalation into TMDCs. Similar *a* parameters are also found in 1T-MoS_2 (3.23 Å) (21) and $K_{0.7}MoS_2$ (3.3 Å) (22).

The second condition for intercalation is the possibility of a guest–host charge transfer, even if it has not been proved that this is a necessary condition for mercury intercalation for which this charge transfer is estimated to be very low. In this matter, the case of mercury intercalation into crystalline MoS_2 is not very clear. We may consider that the charge transfer is so low that there is no need for an accepting electronic level and that, from this point of view, the mercury intercalation would be possible without changing Mo coordination. On the contrary, even if it is low, any charge transfer would require drastic structural changes in MoS_2 and the electronic benefit would be too low in the case of mercury to allow such a transformation.

What appears unique in the case of mercury-intercalated molybdenum disulfide is that, despite the low charge transfer, the intercalated mercury network is able to stabilize, over a very long period, a molybdenum structural arrangement that is characteristic of a d^3 configuration. Once more, this proves that the essential condition for mercury intercalation or stabilization of such an intercalate is the ability of the dichalcogenide structure to adapt a suitable mercury network in terms of basal plane parameters. The present case of Hg–MoS_2 is extra proof that the arrangement of mercury in a well-ordered chain network provides a large energy benefit, because it is able to stabilize a host network in a structural arrangement normally expected for a different transition metal electronic configuration.

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