

# Distortion of MoS<sub>2</sub> host layers in intercalation compounds with various guest species: correlation with charge transfer

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## Abstract

The MoS<sub>2</sub> host layers in various intercalation compounds freshly prepared from single-layer dispersions are substantially distorted compared to those in parent crystalline 2H-MoS<sub>2</sub>. The coordination number for the Mo–Mo sphere ( $d \sim 3.2 \text{ \AA}$ ) obtained from Mo K-edge EXAFS data can be used as a convenient parameter to estimate qualitatively the degree of distortion, which is shown to correlate fairly with the residual negative charge kept by the host layers. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Molybdenum disulfide; Intercalation compounds; Distortion; EXAFS

## 1. Introduction

Intercalation compounds of layered transition metal dichalcogenides have been attracting significant attention over the last years. Among them, systems based on molybdenum disulfide are of particular interest since they are of great potential importance as catalysts (for oil hydro-treatment processes), electrodes, solid state lubricants, and materials with unusual two-dimensional magnetic properties. For a long time, alkali metal derivatives were the only known class of MoS<sub>2</sub> intercalation compounds. The

situation completely changed in 1986 when Gee et al. [1] found that LiMoS<sub>2</sub> can be exfoliated as single layers upon reaction with water under ultrasonication. The use of single-layer dispersions allowed to extend the nature of the guests, which can be included between the MoS<sub>2</sub> layers. Up to now, a variety of MoS<sub>2</sub>-based intercalated materials including simple organic (trichloroethylene, styrene, phenanthroline, alkylammonium cations, etc.), polymeric, organometallic (metallocenes, ruthenium hydroxoarene complexes, etc.), and inorganic (post-transition metals, metal hydroxides) species have been prepared and characterized (for examples, see Refs. [2–4]).

As it was recently understood, intercalation of lithium into MoS<sub>2</sub> [5–7] leads to a change in the electronic structure of the host layers due to

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a nearly complete one-electron transfer from Li atoms to MoS<sub>2</sub> layers. This transfer is also accompanied by a change of Mo coordination from trigonal prismatic to octahedral one and by a substantial rearrangement of the in-layer organization which results in clustering of Mo atoms due to displacements from their ideal positions in the layer. As it was shown by Py and Haering [5], the transformation is observable at lithium contents higher than 0.1.

In the reaction of LiMoS<sub>2</sub> with water, lithium atoms pass into the solution as hydrated Li<sup>+</sup> ions, and partially negatively charged single-layers of MoS<sub>2</sub> are formed. These layers continuously, but slowly, discharge in the dispersion due to a reaction with water, which produces molecular hydrogen and OH<sup>-</sup> anions. Owing to a residual negative charge on the MoS<sub>2</sub> layers, the structural changes typical for LiMoS<sub>2</sub> are partially retained in MoS<sub>2</sub> single-layer dispersions [8] and in some solid intercalated materials freshly prepared from them [3,9,10].

We report here some recent results on distortions of host layers in MoS<sub>2</sub> intercalation compounds with various guests studied by X-ray absorption spectroscopy. Special attention was paid to correlations between the degree of distortion and the charge transfer from a guest to the host layers.

## 2. Experimental

Details on preparation and characterization (e.g. chemical analysis, X-ray diffraction) of intercalates with different guests can be found in the following references: Ref. [11] (transition metal hydroxides), Ref. [12] (tetraalkylammonium cations), Ref. [13] (ruthenium hydroxoarene complexes), Ref. [14] (phenanthroline/phenanthroline).

Mo K-edge X-ray absorption spectra were collected at the Siberian Synchrotron Radiation Centre (Novosibirsk) in transmission mode using a Si(111) channel-cut monochromator and ion chambers for both  $I_0$  and  $I_t$  detection. The

energy step was  $\sim 1.7$  eV. Energy calibration was done by assigning the value of 20 020 eV to the maximum derivative point in the experimental spectra. Good quality EXAFS spectra were obtained: data up to  $k = 16 \text{ \AA}^{-1}$  could be used for analysis. EXAFS data analysis was performed using the UWXAFS curve-fitting software [15] with FEFF [16] amplitude and phase functions. The esd's of the structural parameters used as variables in the curve-fitting procedure are estimated to be  $\pm 15\%$  for  $N$  (coordination number),  $\pm 0.02 \text{ \AA}$  for  $R$  (interatomic distance), and  $\pm 0.001 \text{ \AA}^2$  for  $\sigma^2$  (Debye–Waller factor). In splitted Mo–Mo coordination spheres, the same  $\sigma^2$  values were fitted for all three components. Scale factor  $S_0^2$  was held constant at 0.83.

## 3. Results and discussion

Fourier transforms (FTs) of Mo K-edge EXAFS spectra for the studied samples are shown in Fig. 1. Local order structural parameters obtained from EXAFS fits are summarized in Table 1. Experimental curves of normalized EXAFS (solid lines) along with the best-fit model curves (dots) for selected samples are depicted in Fig. 2.

The closest coordination sphere of chemically bonded sulfur atoms does not change significantly in all the samples studied, with Mo–S distances varying in the range 2.39–2.44 Å (see Table 1). Fitted coordination number for the first Mo–S sphere is somewhat diminished (3.9–5.4) probably pointing to a substantial static disorder in highly dispersed intercalated particles (about effect of static disorder on coordination numbers obtained from EXAFS see, for example, Ref. [17]). Freshly prepared intercalates exhibit, however, the above-mentioned strong distortions of the second atomic shell around Mo atoms as compared to the untreated MoS<sub>2</sub> ( $d_{\text{Mo–Mo}} = 3.16 \text{ \AA}$ ). This Mo–Mo sphere is substantially diminished and split, giving rise to three contributions at shorter ( $\sim 2.8 \text{ \AA}$ ),

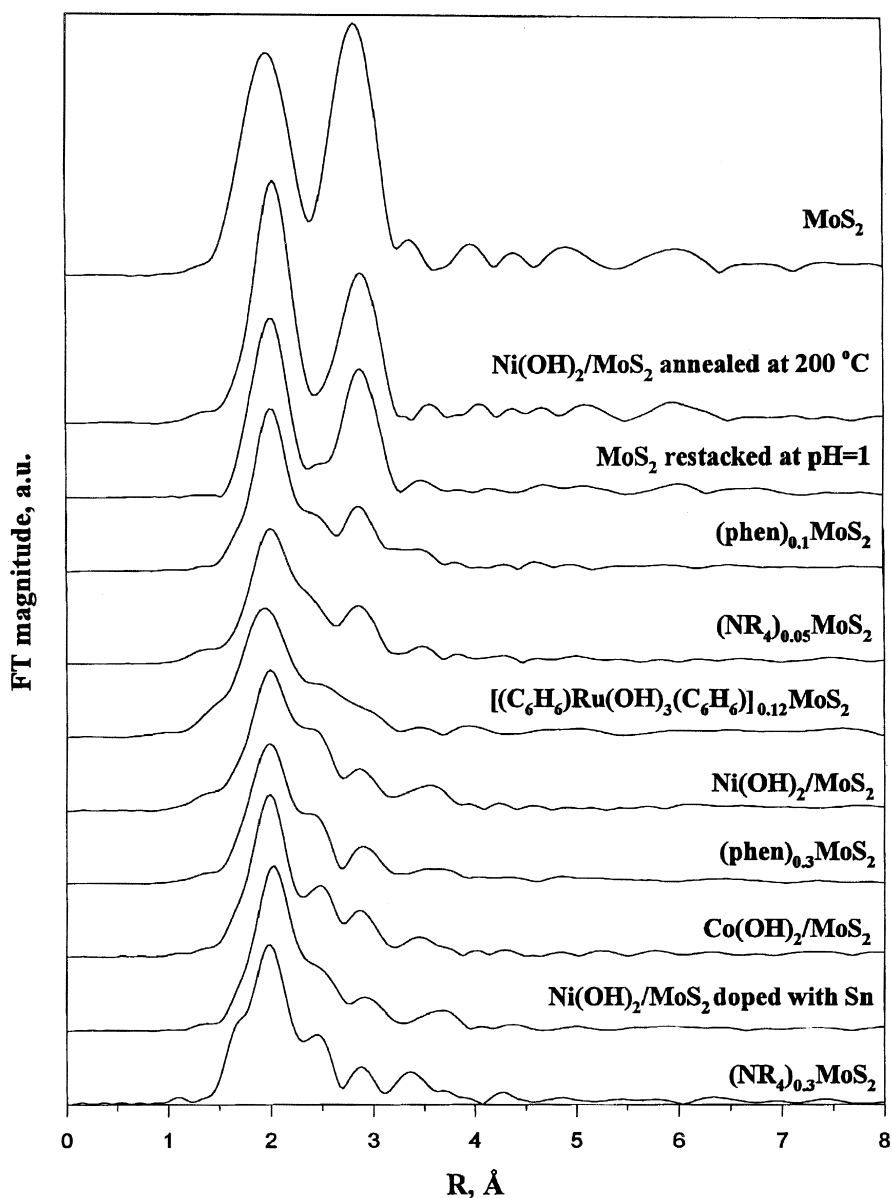


Fig. 1. FT of Mo K-edge EXAFS spectra for the studied intercalates.

nearly unchanged ( $\sim 3.2$  Å), and longer ( $\sim 3.8$  Å) distances, as it may be seen in Fig. 1 and Table 1.

A qualitative estimate of the degree of layer-distortions may be based on the coordination number ( $N_0$ ) for the Mo–Mo sphere at  $\sim 3.20$  Å, since the value  $N_0 \sim 6$  evidently corresponds

to the undistorted structure and, unlike the two other Mo–Mo contacts, the sphere at  $R \sim 3.20$  Å should not be affected by overlapping with Mo–S ( $\sim 2.4$  Å) and Mo–S ( $\sim 4.0$  Å, not accounted for in the current fitting procedure) contributions. Using this criterion, all intercalates can be arranged according to the degree of

Table 1  
Parameters of local atomic order around Mo atoms in various intercalates according to Mo K-edge EXAFS data

Compound	$R_f$	$\Delta E$ , eV	Mo–S			Mo–Mo		
			$N$	$R$ , Å	$\sigma^2$ , Å <sup>2</sup>	$N^a$	$R$ , Å	$\sigma^2$ , Å <sup>2</sup>
MoS <sub>2</sub>	0.016	0.79	5.6	2.39	0.0028	<b>6.4</b>	3.15	0.0032
Ni(OH) <sub>2</sub> /MoS <sub>2</sub> annealed at 200°C	0.014	4.85	5.7	2.43	0.0033	0.3 <b>3.8</b> 0.3	2.87 3.20 3.78	0.0042
MoS <sub>2</sub> restacked at pH = 1	0.021	0.67	4.5	2.43	0.0036	0.3 <b>2.8</b> 0.3	2.83 3.20 3.74	0.0055
(phen) <sub>0.1</sub> MoS <sub>2</sub>	0.030	2.96	4.1	2.42	0.0041	0.9 <b>1.5</b> 0.7	2.80 3.19 3.79	0.0040
(NR <sub>4</sub> ) <sub>0.05</sub> MoS <sub>2</sub>	0.023	4.67	3.9	2.41	0.0047	0.9 <b>1.3</b> 0.5	2.78 3.16 3.76	0.0039
[(C <sub>6</sub> H <sub>6</sub> )Ru(OH) <sub>3</sub> (C <sub>6</sub> H <sub>6</sub> )] <sub>0.12</sub> MoS <sub>2</sub>	0.009	0.04	4.1	2.41	0.0043	1.2 <b>1.2</b> 0.4	2.75 3.14 3.76	0.0043
Ni(OH) <sub>2</sub> /MoS <sub>2</sub>	0.019	−2.09	5.4	2.44	0.0062	1.3 <b>1.1</b> 1.1	2.81 3.20 3.83	0.0041
Co(OH) <sub>2</sub> /MoS <sub>2</sub>	0.020	−3.52	4.0	2.41	0.0036	1.0 <b>0.9</b> 0.6	2.78 3.16 3.77	0.0029
(phen) <sub>0.3</sub> MoS <sub>2</sub>	0.020	−2.53	4.0	2.41	0.0044	1.0 <b>0.9</b> 0.5	2.78 3.18 3.79	0.0033
Ni(OH) <sub>2</sub> /MoS <sub>2</sub> <sup>b</sup>	0.016	4.58	4.8	2.44	0.0048	1.0 <b>0.8</b> 0.8	2.81 3.20 3.83	0.0038
(NR <sub>4</sub> ) <sub>0.3</sub> MoS <sub>2</sub>	0.025	−8.93	4.4	2.40	0.0039	1.0 <b>0.7</b> 0.9	2.77 3.15 3.76	0.0030

<sup>a</sup>Values of  $N_0$  (see text) are marked with bold.

<sup>b</sup>Tin-doped sample with atomic ratio Sn/Mo = 0.015.

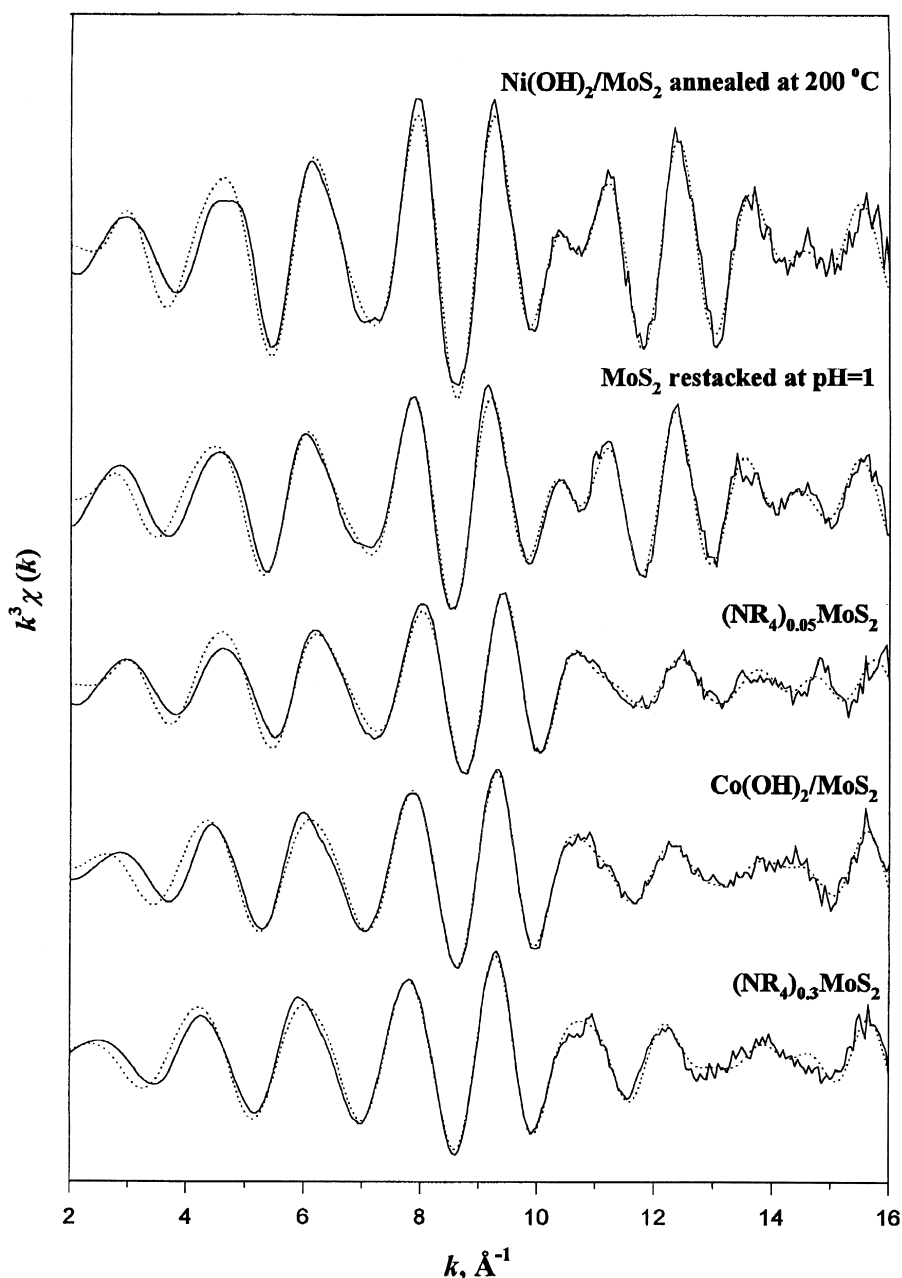


Fig. 2. Normalized EXAFS curves  $k^3\chi(k)$  for selected samples: experiment (solid lines) and best-fit model (dots).

distortion of the  $\text{MoS}_2$  layers: the higher the value of  $N_0$ , the smaller the degree of distortion of the host layers.

The degree of distortion of the host layers in the studied intercalates evidently depends upon the partial negative charge kept by the  $\text{MoS}_2$

layers and balanced by a positive charge of the guest. Actually, for three studied intercalates, viz.  $(\text{R}_4\text{N})_{0.3}\text{MoS}_2$ ,  $[(\text{C}_6\text{H}_6)\text{Ru}(\text{OH})_3\text{Ru}(\text{C}_6\text{H}_6)]_{0.12}\text{MoS}_2$ , and  $(\text{R}_4\text{N})_{0.05}\text{MoS}_2$ , in which the negative charge of  $\text{MoS}_2$  layers can be quite accurately determined basing on stoichiometry

(0.3, 0.12, and 0.05  $e^-$  per molybdenum atom) since the guest species are cationic, the respective values of  $N_0$  are 0.7, 1.2, and 1.3. This allowed us to roughly estimate the charge in intercalates for which it cannot be unambiguously derived from the composition. In particular, for intercalates with transition metal hydroxides (cobalt, nickel, and tin-doped nickel samples), this procedure gave the value of 0.15–0.20  $e^-$ . The partial positive charge of the hydroxide layers can be due to partial replacement of  $\text{OH}^-$  anions by water molecules. Similar charge value can be derived for the  $(\text{phen})_{0.3}\text{MoS}_2$  intercalate with phenanthroline which can mean that approximately a half of the phenanthroline species in the interlayer space of  $\text{MoS}_2$  are in the protonated form (phenanthrolium). Consistently, in  $(\text{phen})_{0.1}\text{MoS}_2$  intercalate, the degree of distortion is close to that in  $(\text{R}_4\text{N})_{0.05}\text{MoS}_2$ , indicating that the charge of the host layers therein is of the order of 0.05  $e^-$  or less. It should be noted that  $\text{MoS}_2$  restacked at  $\text{pH} = 1$  without any potential guest in the reaction medium manifests only rather slightly disordered  $2H\text{-MoS}_2$  structure. Similar result was obtained for annealed  $\text{Ni}(\text{OH})_2/\text{MoS}_2$  intercalate, indicating that the distortion of the host layers becomes unstable upon gently heating the samples.

#### 4. Conclusions

Freshly prepared from single-layer dispersions,  $\text{MoS}_2$  intercalates with various guests exhibit substantial changes of the Mo atom cationic surrounding, as compared to the parent  $2H\text{-MoS}_2$ .

The degree of distortion depends upon the value of the negative charge kept by the host layers. As a measure of the degree of structural distortion, the coordination number for Mo–Mo sphere at distance  $d \sim 3.20 \text{ \AA}$  (close to that in undistorted  $\text{MoS}_2$ ) obtained from Mo K-edge EXAFS data was used which allowed to esti-

mate the charge transferred to the host layers in compounds for which the cationic charge of the guest layers is not known.

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#### References

- [1] M.A. Gee, R.F. Frindt, P. Joensen, S.R. Morrison, Mater. Res. Bull. 21 (1986) 543.
- [2] D. Guay, W.M.R. Divigalpitiya, D. Bèlanger, X.H. Feng, Chem. Mater. 6 (1994) 614.
- [3] Ya.V. Zubavichus, A.S. Golub, Yu.L. Slovokhotov, P.J. Schilling, R.C. Tittsworth, J. Phys. IV France 7 (1997) C2–1057.
- [4] A. Golub, G. Protzenko, I. Shumilova, Y. Zubavichus, C. Payen, Yu. Novikov, M. Danot, Mol. Cryst. Liq. Cryst. 311 (1998) 377.
- [5] M.A. Py, R.R. Haering, Can. J. Phys. 61 (1983) 76.
- [6] K. Chrissafis, M. Zamani, K. Kambas, J. Stoemenos, N.A. Economou, Mater. Sci. Eng., B 3 (1989) 145.
- [7] S. Lemaux, PhD Thesis, Nantes, 1998.
- [8] P. Joensen, E.D. Crozier, N. Alberding, R.F. Frindt, J. Phys. C 20 (1987) 4043.
- [9] K.E. Dungey, M.D. Curtis, J.E. Penner-Hahn, J. Catal. 175 (1998) 129.
- [10] Yu.V. Zubavichus, Yu.L. Slovokhotov, P.J. Schilling, R.C. Tittsworth, A.S. Golub, G.A. Protzenko, Inorg. Chim. Acta 280 (1998) 211.
- [11] A.S. Golub, G.A. Protzenko, I.M. Yanovskaya, O.L. Lependina, Yu.N. Novikov, Mendeleev Commun. (1993) 199.
- [12] A.S. Golub, G.A. Protzenko, L.V. Gumileva, A.G. Buyanovskaya, Yu.N. Novikov, Izv. Akad. Nauk, Ser. Khim. 4 (1993) 672.
- [13] A.S. Golub, I.B. Shumilova, Yu.V. Zubavichus, M. Jahncke, G. Süß-Fink, M. Danot, Yu.N. Novikov, J. Mater. Chem. 7 (1) (1997) 163.
- [14] A.S. Golub, I.B. Shumilova, Yu.N. Novikov, J.L. Mansot, M. Danot, Solid State Ionics 91 (3–4) (1996) 307.
- [15] M. Newville, B. Ravel, D. Haskel, J.J. Rehr, E.A. Stern, Y. Yakoby, Physica B 208–209 (1995) 154.
- [16] J.J. Rehr, S.I. Zabinsky, R.S. Albers, Phys. Rev. Lett. 69 (1992) 3397.
- [17] E. Prouzet, A. Michalowitz, N. Allali, J. Phys. France 7 (1997) C2–C261.