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Physica B 208 & 209 (1995) 307–308

PHYSICA B

XAFS analysis of the low symmetry octahedral molybdenum and tungsten oxides

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Abstract

Comparative XAFS analysis of the main isostructural crystalline phases of $W(Mo)O_3$ oxides and $W(Mo)O_3 \cdot nH_2O$ hydrates has been done at the $W L_3$ and $Mo K$ edges. These compounds have (1) 3D perovskite-type (PT) structure ($m-WO_3$); (2) 2D PT structure ($WO_3 \cdot H_2O$ and $MoO_3 \cdot nH_2O$ ($n = 1, 2$)); (3) 2D hexagonal-type structure ($WO_3 \cdot 1/3H_2O$) and (4) 2D double layered structure ($\alpha-MoO_3$). The detailed analysis of X-ray absorption fine structure (XAFS) in the low-symmetry structures shows that in order to simulate the experimental spectrum, it is sufficient to take into account single-scattering contributions in the range from 1.7 to $\sim 5.0 \text{ \AA}$ and a number of multiple-scattering paths from nearly linear atomic chains in the first and second shells. The results obtained by XAFS are only in partial agreement with known X-ray diffraction data (XRD). The strong deviation of the short-range order, detected by XAFS, from the one, given by XRD, has been found in $W(Mo)O_3 \cdot nH_2O$.

The $W(Mo)$ oxide polymorphs represent a wide class of materials having several types of crystallographic structures obtained by X-ray diffraction (XRD) methods [1, 2]. They are composed of distorted $[W(Mo)O_6]$ octahedral units sharing their corners and/or edges with $W(Mo)$ ions in off-center positions, and can be divided into four groups with regard to the bulk structure topology: (1) 3D perovskite-type (PT) structure as in $m-WO_3$ [3]; (2) 2D PT structure as in $WO_3 \cdot H_2O$ [4] and $MoO_3 \cdot nH_2O$ ($n = 1, 2$) [2]; (3) 2D hexagonal-type structure as in $WO_3 \cdot 1/3H_2O$ [5] and (4) 2D double layered structure ($\alpha-MoO_3$) [5]. Since XRD gives only the average long-range lattice structure, we were interested to compare its results with the ones obtained by X-ray absorption spectroscopy (XAS) which is a local probe method and provides complementary to XRD

information on the short-range lattice distortions. In the present work we compare (1) experimental X-ray absorption fine structure (XAFS) with the result of ab initio theoretical calculations, based on crystallographic data obtained by XRD, and (2) the results of the first shell XAFS best-fit procedure with known XRD data.

The XAFS spectra at the $W L_3$ and $Mo K$ edges were measured in transmission mode at room temperature using a standard setup of the DCI D13 (EXAFS-3) beam line at LURE. The synchrotron radiation was monochromatized using the Si (311) double-crystal monochromator, and its intensity was measured by two ionization chambers filled with argon. The samples were prepared from finely ground polycrystalline powders and had a thickness to give an absorption jump ~ 1.0 .

The MS calculations were performed using the FEFF6 code [6] for a cluster of 6 \AA radius taking into account all MS paths up to the eighth order. Theoretically calculated

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Table 1

Best-fit values of coordination numbers (N), distances (R , Å) and Debye–Waller factors (σ^2 , Å²) for the first coordination shell of W(Mo) obtained by XAFS in comparison with known XRD data. $\Delta = \bar{R}_{\text{XRD}} - \bar{R}_{\text{XFS}}$ is the difference between average distances (in Å)

Compound	XAFS				XRD				
	N	R	σ^2	\bar{R}	N	R	\bar{R}	Δ	
m-WO ₃	1.6	1.76	0.0030	1.92	1	1.74 [3]	1.93	0.01	
	2.1	1.84	0.0034		3	1.87			
	2.3	2.11	0.0054		2	2.11			
WO ₃ ·H ₂ O	4.5	1.76	0.0105	1.82	3	1.78 [4]	1.92	0.10	
	1.1	1.92	0.0012		2	1.93			
	0.4	2.27	0.0005		1	2.34			
WO ₃ ·1/3H ₂ O	1.4	1.75	0.0040	1.83	0.5	1.8 [5]	1.91	0.08	
	4.2	1.84	0.0140		5.0	1.9			
	0.4	2.07	0.0030		0.5	2.1			
α -MoO ₃	2.5	1.68	0.0043	1.94	2	1.70 [2]	1.98	0.04	
	1.7	1.96	0.0017		2	1.95			
	1.0	2.21	0.0020		1	2.25			
MoO ₃ ·H ₂ O	0.8	2.36	0.0021	1.84	1	2.33	1.98	0.14	
	4.2	1.73	0.0066		2	1.69 [2]			
	1.1	1.96	0.0055		2	1.95			
MoO ₃ ·2H ₂ O	0.7	2.34	0.0035	1.89	2	2.31	1.96	0.07	
	2.3	1.71	0.0035		2	1.73 [2]			
	1.4	1.77	0.0019		1	1.80			
	0.7	2.03	0.0033		1	2.05			
	1.7	2.16	0.0077		2	2.22			

backscattering amplitude and phase functions for the W–O and Mo–O pairs were also utilized in the best-fit procedure of the first shell XAFS signals. The obtained results are presented in Table 1 in comparison with known XRD data.

Good agreement between calculated and experimental XAFS spectra was found for all compounds in the outer shells, however, the short-range order parameters obtained by XAS differ in W(Mo)O₃· n H₂O from the ones observed by XRD.

The analysis of the first coordination shell XAFS signals shows (Table 1) that only for m-WO₃ and α -MoO₃ good agreement between XAFS and XRD results can be found both for the average and single Me–O distances. General shortening of the Me–O bonds, compared to the XRD data, is present in W(Mo)O₃· n H₂O, so their average Me–O distances differ significantly by ~ 0.07 – 0.14 Å.

JP and AK are grateful to the LURE laboratory for providing the beam time and partial support.

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