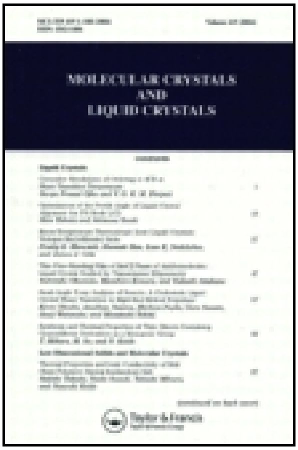

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Localisation of Anionic Species in Lamellar Double Hydroxides by XAFS Study at Low Temperature

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A [Zn-Cr-Br] Lamellar Double Hydroxide is studied by PXRD and XAFS at Zn, Cr and Br K-edges. The local environment around these three probes is discussed.

Keywords: Lamellar Double Hydroxide; Anionic Clay; Hydrotalcite; XAFS; EXAFS

INTRODUCTION

The general formula: $[M^{II}_{x}M^{II}_{1-x}(OH)_2]^{x+}$ $[X^{m-}_{x/m}.nH_2O]^{x-}$ describes Lamellar Double Hydroxides (LDHs). Such phases are based on positively charged brucite-like $M(OH)_2$ main layers (M = metals) separated by charge-balancing interlamellar domains (X = anions) and water molecules. The charge density of the layers is directly proportional to the trivalent metal substitution ratio $x = M^{III} / (M^{II}+M^{III})$; we use the $_x[M^{II}-M^{III}-X]$ short notation. The structure of the main layers is well known from PXRD experiments but the ill-organised interlamellar domains need a more accurate characterisation. In this work, we present an XAFS study of the localisation of interlamellar species in the $_{1/3}$[Zn-Cr-Br] phase.

EXPERIMENTAL

Preparation

The $_{0.33}$[Zn-Cr-Br] phase was obtained by anionic exchange on a $_{0.33}$[Zn-Cr-Cl] precursor prepared by the coprecipitation method[1] at pH=4.9. The exchange reaction is performed in an excess of molar KBr solution under stirring; after a few hours, a fresh KBr solution is used in order to remove the last chloride traces. The precipitate is then washed with CO_2-free water and dried at room-temperature. Chemical analysis confirms that the exchange reaction was completed and the trivalent metal ratio x=1/3 maintained.

Characterisation

PXRD measurements were performed on a SIEMENS D501 diffractometer with Cu K_α radiation filtered by a graphite monochromator located between the sample and the detector.

XAFS measurements at Cr, Zn and Br K-edges were performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université de Paris Sud, on D44 line. All samples were maintained at low temperature (8K) in a Helium cryostat. The EXAFS data was obtained on a 1000 eV range with a 2 eV step and 2 s per step. The samples were prepared as pellets after dispersion in graphite.

RESULTS AND DISCUSSION

X-ray diffraction

The diffractogram of $_{0.33}$[Zn-Cr-Br] is reported on Figure 1a. All the diffraction lines are attributed with an hexagonal cell (a = 3.119 Å and c = 23.58 Å) and rhombohedral symmetry. The studied compound presents the 3R stacking sequence reported for a great number of LDHs.[1] Such phases are described in the $R\bar{3}m$ space group with a random distribution of metallic cations in the brucitic main-layers. The interlamellar species (anions and water molecules) are distributed around the three fold axis[2] on high multiplicity crystallographic sites 18(h) or 18(g) equidistant to the main layers as shown on Figure 1b. In the particular case of $_{0.33}$[Zn-Cr-Br], a remarkable feature is the (003) line, weaker than the (006) one.

This is due to the presence of the heavy bromide anion between the layers diffracting in phase opposition with the metallic cations of main layers for the (003) Bragg-reflection.

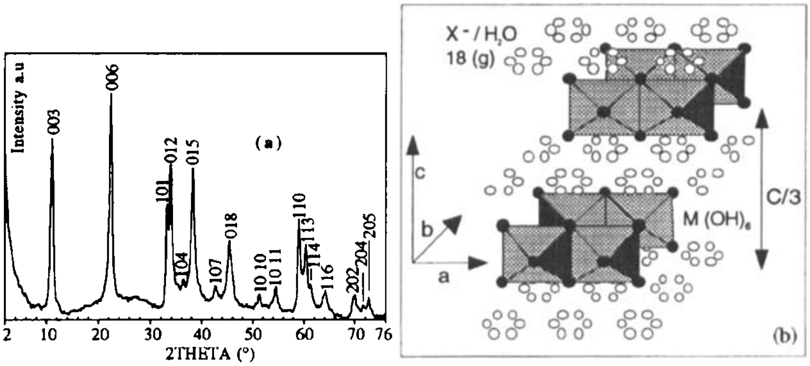

FIGURE 1 [Zn-Cr-Br] diffractogram (a) and wiew of the 3R structure (b).

EXAFS study

The $k^3\chi(k)$ weighed radial distributions around metallic cations of the main layers are reported on Figures 2a at Zn K-edge and 2b at Cr K-edge. Their similar shapes are related to the presence of both metallic cations in the same crystallographic sites of the main layers. The first peak corresponds to the six hydroxyl groups and the second to the six nearest metallic cations in the layer.

The fits performed on the first peaks (Figures 2c and 2d) show that two slightly different distances are necessary to describe the first coordination shell for both metals. For the second peaks (Figures 2e and 2f), two different distances are also used at zinc K-edge but only one distance at chromium K-edge. When two different distances are used for the same peak, the corresponding number of neighbours is fixed at its theoretical value. These results are reported in Table I.

For the second peak, the observed mean values of distances are very close to the lattice parameter a = 3.119 Å. This confirms the structure of the layers of the studied phase and most of the peaks observed at higher distances can be attributed to atoms of the same layer. The low intensity features observed in the 3.7 — 4.7 Å range seem to be related to distances from interlamellar species; the profiles of radial density curves are here different at Zn an Cr K-edges but the attribution of these peaks is uncertain.

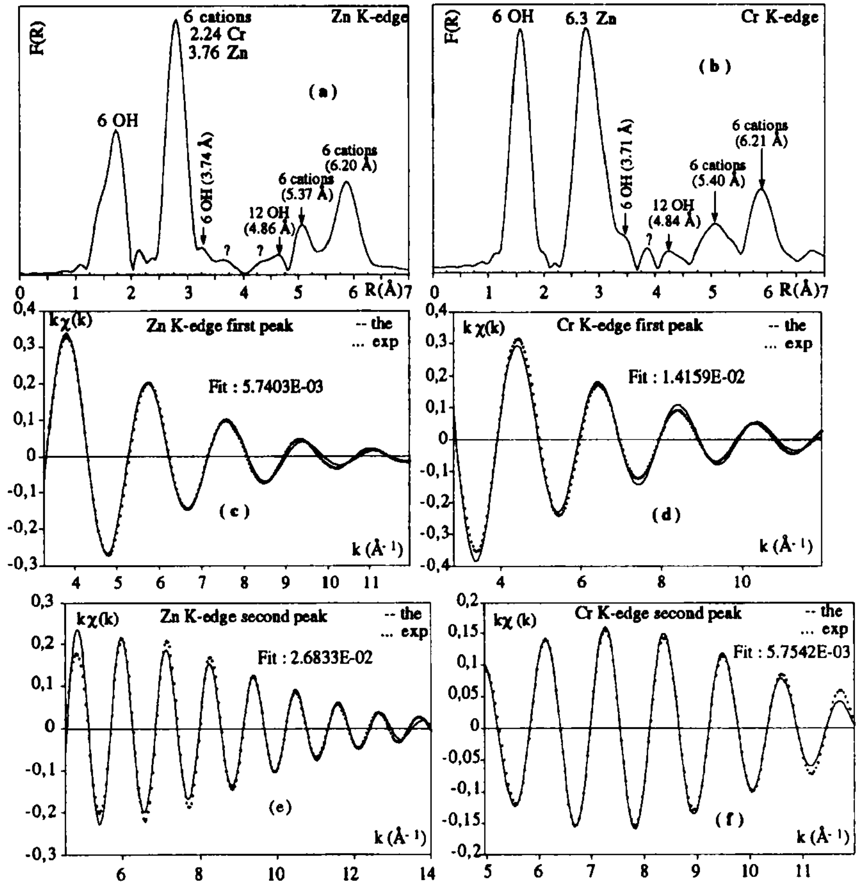

FIGURE 2 Radial density curves at Zn and Cr K-edges and corresponding fits

TABLE I Environment of Zn, Cr, and Br atoms in [Zn-Cr-Br] LDH

	Zn K-edge	Cr K-edge	Br K-edge
first peak	1.92 O (2.03 Å)	3.99 O (1.99 Å)	1.07 O (2.80 Å)
	4.08 O (2.16 Å)	2.01 O (2.11 Å)	3.10 O (2.87 Å)
second peak	2.24 Cr (3.05 Å)	6.30 Zn (3.12 Å)	1.02 Cr (3.01 Å)
	3.76 Zn (3.13 Å)	-	-

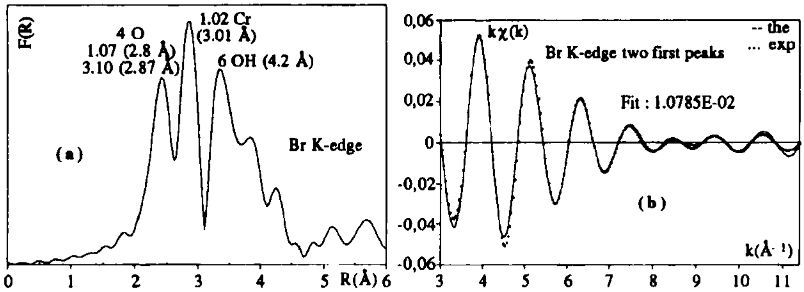

FIGURE 3 Radial distribution at Br K-edge and fit on the two first peaks.

The $k^3\chi(k)$ radial distribution around bromide anions of the interlamellar domains (Br K-edge) display only a very broad band centered at about 3Å when performed at room temperature. At low temperature (8K), this broad band is resolved in several peaks as reported on Figure 3a. The observed shape seeming surprisingly sharp, the measurements were repeated with another sample and a new setting of the experiment. The same shape was observed anew with stable positions for the peaks.

The localisation of the bromide anion at the same distance of two main layers is inconsistent with these EXAFS results. We therefore developped an hypothesis where the bromide cation is off-centered in the interlamellar domain. A fit performed simultaneously on the two first peaks is shown on Figure 3b. The first one was attributed to oxygen atoms: approximatively three atoms at the same distance, belonging to hydroxyl groups of a main layer, and one atom at a shorter distance belonging to an interlamellar water molecule (see Table I). The second peak is consistent with a chromium atom lying beyond the three hydroxyl groups; the proposed disposition is shown on Figure 4.

CONCLUSIONS

The results obtained by EXAFS with three different local probes (Cr, Zn, Br) for the same compound are consistent with the structures of related LDH obtained by X-ray diffraction if one consider that these last determinations give only mean structures.

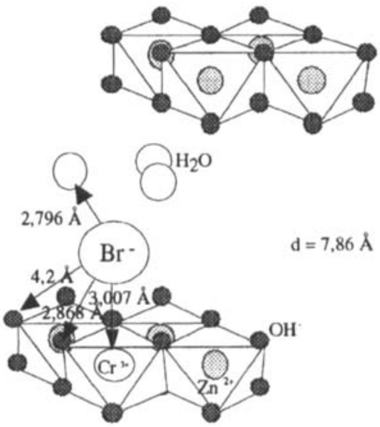

FIGURE 4 Structural hypothesis about the location of bromide in [Zn-Cr-Br]

Even at room temperature, a slight deformation of the D_{3d} octahedral surrounding of the metallic cations is observed. The chromium atoms are surrounded, as second neighbours, only by zinc atoms at the same distances and the zinc atoms by both chromium and zinc atoms at different distances evidencing a local distorsion of the main hexagonal framework of the layers.

A strong dynamic disorder of the interlamellar bromide anions is shown by EXAFS (Br K-edge) at room temperature, while a regular 3R stacking sequence is observed by PXRD. At low temperature, this disorder is "frozen" and the bromide anions are off-centered of about 0.92 Å in the interlamellar domain approaching chromium atoms of the main layers at about 3.01 Å. Such a Zn/Cr ordering with, in addition, Br ions coming relatively close to chromium, could give rise to a supercell with $a=a_0\sqrt{3}$, leading to superstructure lines on PXRD diagrams. Such features are however not observed on diffractograms performed at room temperature; the ordered domains are therefore probably too small.

The $R\overline{3}m$ space group, commonly used to describe the structure of these materials is a good simplification. In fact, in order to describe more precisely the structure, a lower symmetry space group (for example R3m) with partial occupancy of the sites would be used. In practice, this last space group is not used as it leads to a too large number of structural parameters for the relatively poor diffraction pattern. Nevertheless, this description allows the off-centering of the bromide ion which results from the difference in electrostatic interactions between both sides of the interslab space. The bromine ion is in an oxygen trigonal prism which shares one face with one octahedra of one slab and one face with one tetrahedra of the other slab. Therefore, the attraction between the Br anion and the metallic cation leads to the Br off-centering; moreover in order to ensure a local charge neutrality the Br ions tend to be in the vicinity of trivalent Cr ions.

Acknowlegements

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References

[1.] A. de Roy, C. Forano, K. El Malki and J.P. Besse, in Expanded Clays and Other Microporous Solids, edited by M.L. Occelli & H.E. Robson (Van Nostrand Reinhold, New York 1992), vol. II, Chap. 7 pp. 108-169.

[2.] R. Allmann, N. Jb. Miner. Mh., 552 (1969).