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X-RAY ABSORPTION IN LAMELLAR COMPOUNDS

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Résumé: Etant donné le caractère bidimensionnel des matériaux lamellaires, les spectres d'absorption des rayons X sont très sensibles aux effets de polarisation qui révèlent l'anisotropie des propriétés électroniques et structurales. Plusieurs exemples sont donnés pour le graphite, les dichalcogénures, ainsi que leurs composés d'insertion. En XANES, on obtient la symétrie des états finals et la densité partielle des états vides. L'EXAFS permet de déterminer les angles de liaisons et la dépendance en température des facteurs de Debye-Waller.

Abstract: Some classes of lamellar compounds are discussed as well as their corresponding intercalated forms. Because of the high anisotropy of these materials, X-ray spectra are very sensitive to the polarization effects which reveal the anisotropy of the electronic and structural properties. Several examples are given for dichalcogenide and graphite intercalation compounds. From XANES, it is possible to obtain the symmetry of the final states and to describe the partial density of the empty states. EXAFS spectra permit the determination of the bond angles and the thermal dependence of the Debye-Waller factors.

The first definition which can be given for a lamellar compound is: Every material with a symmetry less than cubic. In that case there is always an anisotropy of the physical properties. For example Fe₂O₃ corresponds to this definition, nevertheless it is not usually considered as a lamellar compound, so the definition must be improved. It is necessary to say that the bond strengths are largely anisotropic. Then, a lamellar compound is constituted of a stacking of layers in which the atoms are strongly bonded. The binding energy between the layers is very weak, it corresponds generally to Van der Waals interaction.

A lot of layered compounds can be intercalated with atoms or molecules which are weakly bonded through the host layers, they correspond to other lamellar compounds. The swelling of the lamellar compound depends on the intercalate and varies in a large range. So it is possible to vary the physical properties by the intercalation and particularly to modify the anisotropy of the material. Nevertheless, the intercalation is not always possible. Some charge transfer can occur between the intercalate and the host, in that case there is a change in the electrical and thermal properties of the material.
Materials can be classified in several classes, the most usual are:
- graphite and related intercalation compounds
- dichalcogenides and related intercalation compounds
- III-V layered compounds
- FeOCl, MPS₃, Ta₂S₂C, UO₂F₂
- Some organic and biological compounds (for example: ferrocene and heme in myoglobin

**Graphite and its intercalation compounds**

The graphite is highly anisotropic, the plane consists of carbon atoms covalently bonded by sp² hybridization in a hexagonal arrangement with a carbon-carbon distance of 1.42 Å. Perpendicularly, the 3.35 Å spacing between the graphitic planes is determined by the interactions between pₓ orbitals of carbon atoms from adjacent layers. The layers are arranged in alternating stacking sequence (ABAB...). For a given intercalant, several in plane stoichiometric compositions can be obtained. The stage of a compound is the number of carbon layers between nearest intercalant layers. For example, MC₈ (M= K, Rb, Cs) which is a stage 1 has the structure given in the figure 1, MC₂₄ is a stage 2.

**Dichalcogenides and intercalation compounds**

A layer of a dichalcogenide is constituted by a stacking of sheets [XTX], the central T sheet corresponds to a compact hexagonal network of transition ions between the two X sheets of chalcogenides atoms (S, Se, Te), also with a hexagonal arrangement. Bonding in the layer is intermediate between ionic and covalent, and the stacking is due to Van der Waals interactions. Different stacking can exist (polytypism) giving rise to different physical properties, they are related to the relative positions of the hexagonal networks of the sheets. The local structure depends on the polytypism as it is shown figure 2. In contrast with the graphite, intercalation gives always stage 1 compounds with a variable filling of the intercalant layer. An example is given figure 2 for the intercalated 2H-polytype Cu₀.₅ Nb S₂.

**XANES**

Several investigations have been done by angular studies or by modifying the intercalated species. Heald and Stern [3] have shown that for a lamellar compound the K-edge spectrum recorded with the polarization in the plane corresponds to a pₓ or pᵧ-like final state, and to a pₓ-like state if it is perpendicular. The intensity of the spectrum depends on the local partial density of states. For a K-edge, it means for states with a p-like character for which the density is considered at the point of the excited atom.

This fact is clearly demonstrated in the polarization dependence of the K-edge of carbon atoms in graphite (Rosenberg et al.[4]) for which dramatic changes in the intensity of the first peak is observed. This peak disappears for polarization in the plane and corresponds to a transition toward a maximum of the density of states of the first empty π-band (pₓ-like band) (figure 4). Several π and σ band peaks agree well with the band structure of graphite.
Alkali graphite intercalation compounds are investigated by Fréigny et al. [5]. In the case of potassium in KC₈, the first peak has a Pₓᵧ-like behavior in contrast with graphite, showing the effect of the alkali atom orbitals. In that later case, the number of states increases by comparison to the graphite, because of the additional alkali atom orbitals and the folding of the Brillouin zone. Spectra for heavier alkali atoms are very broadened because of shorter lifetimes of their core holes.

Fig. 1: Structure of the stage 1 MC₈ (M = K, Rb, Cs) (from [1]).

Fig. 2: Perspective structures of TS₂ (T = Ti, Nb, Mo) compounds (from [2]).

Fig. 3: Structure of the intercalated 2H-polytype Cu₀.₅NbS₂ (from [11]).

Layered transition-metal dichalcogenides TX₂ are composed with metals belonging to the groups IVA, Va and VIA. Octahedral coordination is adopted by group IV compounds (Ti, Zr, Hf) and some group V compounds (V), and the trigonal prismatic coordination by group VI (Mo) and the other group V (Nb) compounds. Ohno et al. [6-8] and by Davies and Brown [9] suggested that the rigid band model is valid for compounds with the same coordination. The host material band structures are discussed in [6-7], they correspond to the band diagrams of the figure 5. Then, as
group V compounds exhibit metallic properties and most of group IV and VI compounds are semiconductors, the authors expect that the addition of an extra electron from an intercalated atom to group IV (V) compounds leads to the same electronic structure as that of group V (VI) compounds, resulting in the semiconductor-metal (metal-semiconductor) transition.

Structure group and representative material:

Structure diagrams of layer transition-metal disulfides: (a) for the group-IV TiS\(_2\) compounds (b) for the group-V TiS\(_3\) compounds, (c) for the group-V 2H(TiS\(_2\)) compounds, and (d) for the group-VI MoS\(_2\) compounds.

Spectra agree well with these expectations. Figure 6a represents S K-edges of group IV host TiS\(_2\) and intercalated TiS\(_3\) and group V VS\(_2\) and some intercalated species, all in octahedral coordination. It is clear that the edges have the same shape. A similarity is obtained for L\(_{III}\)-edge of Nb in group V NbS\(_2\) and L\(_{III}\)-edge of Mo in MoS\(_2\) (figure 6b). Moreover, Ohno et al. [8] show that the intercalation effects on X-ray absorption spectra do not depend so much on the host material studied, as on the intercalated species. It means that the transfer of electron from the intercalated atom to the conduction band of the host layers does not change the two-dimensional behavior of the material and confirms that the rigid band model can be used in the first approximation.

Fig. 6: a) S K-edges of 1T of pure and intercalated dichalcogenides.

b) Nb and Mo L\(_{III}\)-edges of dichalcogenides.
EXAFS

Structures of graphite and dichalcogenides are well known so these materials are used in EXAFS to check features of the spectra [3,9]. By contrast, the interest is evident in the case of intercalation of these compounds, because EXAFS permits to examine the location of the intercalated atom and the bond lengths in the host layer. For example, Bourdillon et al. [10] studied the intercalation compound Rb$_{0.28}$NbSe$_2$ and Thulke et al. [11] Cu$_{0.5}$NbS$_2$. Spectra were compared respectively to NbSe$_2$ and NbS$_2$. Essentially no change in the Nb-Se (Nb-S) near neighbor distance was found, while the Nb-Nb distance was observed to increase by 0.03 Å upon intercalation. The strongest bonding in the crystal is between Nb and Se (S) atoms. The corresponding σ-band, referenced BD2 in the figure 5, lies well below the Fermi level. That band remains unaffected by the charge transfer which fills the BD3 band. This BD3 band has a considerable metal d-character, this explains the repulsion between neighboring Nb atoms.

Heald and Stern [3] gave a general formulation of the orientation dependence of the EXAFS both at K and L-edges. They observed the anisotropy of 2H-WSe$_2$ both on Se K-edge and on W L$_{III}$-edge, taking into account two directions of the electric field with respect to the c-axis, they measured on the Fourier transform the variations of amplitudes of the peaks. The amplitude ratios of these peaks agree well with the known structure of the 2H-WSe$_2$. Moreover, these results confirm that the p-s transitions are small and the p-d transitions dominate.

Several investigations of intercalated graphite have been performed on Br$_2$, alkali atoms and ternary compounds with alkali and tetrahydrofuran. Br K-edge was investigated both in graphite and Grafoil [12-14]. It was demonstrated that Br is present as Br$_2$ molecule in all the cases. Nevertheless, several species were found to present different stretching of the Br-Br distance which have different angular dependence spectra. In the intercalated form, the stretching is about 0.03 Å (2.31 Å instead of 2.28 for Br$_2$ molecule) and the orientation of the molecule is found to be about 20° with respect to the plane owing three angle measurements 0°, 45° and 90° using graphite fibers. The same kind of investigation was done for Rb-graphite with tetrahydrofuran [15], for which three structural models have been proposed. As each one leads to different angular variation spectra, the angular study permits to choose one, which is consistent with the Rb-C distance measured. The most striking behavior is obtained for the binary compounds alkali-graphite. A previous study of Caswell et al.[16] have shown that a stage one KC$_8$ have not the same spectrum than a stage 2 KC$_{24}$. Spectra of RbC$_{24}$ were recorded above and below the temperature of the commensurate-incommensurate transition [17]. At low temperature - commensurate phase - only one Rb-Rb in plane distance was observed. Above the transition two distances appear, one smaller and the other one larger than the low temperature distance.
Spectra of an oriented sample of RbC₈ [18] were recorded for a set of angles from 0° up to 40°. For each peak in the Fourier transform, the amplitude ratio permits to calculate the angle of the corresponding K* vector with respect to the plane. Moreover, that analysis does not need the knowledge of the nature of the neighbor. The obtained results agree well with the known structure of the first stage. The thermal study from 300 K down to 35 K shows a high anisotropy of the Debye-Waller factor, the amplitude of the vibration being larger in the plane. The second stage RbC₂₄ shows a higher static disorder than the first stage RbC₈ and comparison with simulations are shown, they permit to propose a probable model of the disordered intercalant layer.

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