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**POLARIZATION EFFECTS IN XANES OF LAYERED MATERIALS : ALKALI-GRAPHITE INTERCALATION COMPOUNDS STUDY**

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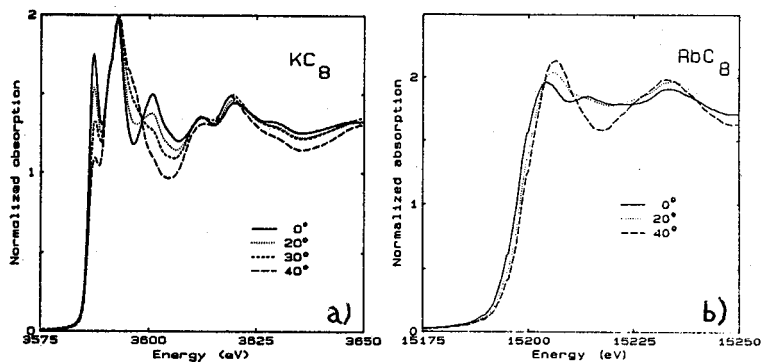
**Résumé :** Les spectres d'absorption des rayons X au voisinage des seuils de composés d'insertion alcalins du graphite sont présentés. Ces matériaux  $MC_8$  et  $MC_{24}$  ( $M = K, Rb, Cs$ ) sont lamellaires et leurs coefficients d'absorption présentent une forte dépendance angulaire. Une analyse par régression linéaire des spectres à chaque énergie pour différents angles d'incidence ( $\theta \leq 40^\circ$ ) a permis d'extrapoler le cas limite  $\theta = 90^\circ$ . Pour les composés du potassium, dont la durée de vie du trou en couche profonde est grande, la comparaison avec des structures de bandes publiées met en évidence les effets des règles de sélection.

**Abstract :** X-ray absorption spectra in the near edge region of alkali graphite intercalation compounds are reported.  $MC_8$  and  $MC_{24}$  ( $M = K, Rb, Cs$ ) compounds are lamellar and their spectra exhibit a high orientation dependence. At each energy, a linear regression analysis of the absorption for different incidence angles ( $\theta \leq 40^\circ$ ) permits to obtain the limiting case spectrum  $\theta = 90^\circ$ . In the case of potassium, where the core hole lifetime is large, implying a small broadening of the spectra, comparison is made with published band structures, showing selection rules effects.

Anisotropic media (like surfaces or lamellar compounds) are extensively studied by a lot of techniques. Graphite intercalation compounds is a class of highly anisotropic metals which exhibit a lot of interesting properties [1] - staging, 2D phase transition, incommensurability... In this communication, we present XANES spectra of alkali first and second stage compounds:  $MC_8$  and  $MC_{24}$  ( $M = K, Rb, Cs$ ) - K-edge for potassium and rubidium and L-edges for cesium. The spectra were taken at several angles  $\theta$  between the photon beam and the normal to the basal planes of the samples, the rotation axis being normal both to the beam and to the polarization vector. An angular analysis of the data is presented and the results are discussed in connection with published band-structures.

Experiments were performed in transmission mode at the X-ray beam line EXAFS II for  $KC_n$  and  $CsC_n$  and EXAFS I for  $RbC_n$  of LURE-DCI. Since the samples are very air-reactive, they were kept under vacuum ( $10^{-1}$  mb) in special containers, which permit their rotation. The crystallographic quality of the samples was checked by X-ray diffraction after the experiments. The angles were determined within a  $\pm 2^\circ$  precision. The beam line EXAFS II was equipped with a harmonics rejection device made of two parallel mirrors [2]. This was particularly important to avoid thickness effects [3]. Polarization of the incident beam is estimated to be about 90% (we verify that its exact value does not affect the conclusions).

Figure 1 presents angular dependence of alkali XANES spectra of first stage K and Rb compounds. After a simple pre-edge background subtraction, the curves are normalized with respect to the thickness of the sample i.e. multiplied by  $\cos \theta$  to take into account the apparent thickness at non-zero angle.



**Fig. 1** : Thickness normalized K-edge XANES spectra for several orientations.

a) :  $KC_8$   
b) :  $RbC_8$

### Discussion

As pointed out in ref.[3], materials with symmetry lower than cubic, and threefold or higher about the normal to the layers, present absorption coefficient  $\mu$  with no dependence with the polarization in the layered planes and which vary as

$$\mu(\theta) = (\mu_{\parallel} - \mu_{\perp}) \cos^2 \theta + \mu_{\perp}$$

This dependence holds at each energy and can be used to determine, via linear regression and extrapolation, the spectrum which could have been measured if the polarization vector was perpendicular to the layers (fig 2). With that kind of materials, it should be impossible to obtain samples thin enough to make possible transmission experiments along the planes. The quality of this treatment may be checked in plotting experimental normalized absorption versus  $\cos^2 \theta$  at several energies or in comparing re-interpolated curves (using angularly weighted  $\mu_{\parallel}$  and  $\mu_{\perp}$ ) and experimental ones.

Angular effects in XANES may be used to determine symmetry of the empty states [4], in the limit of long elastic mean free path for the photoelectron. The space group of the first stage compounds is Fddd [5]. A simpler group, Fmmm, was

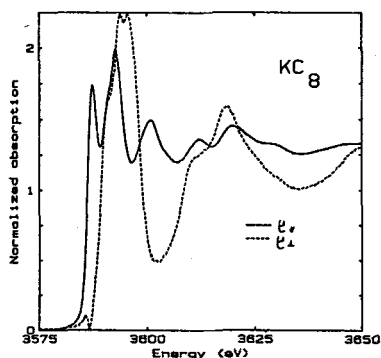
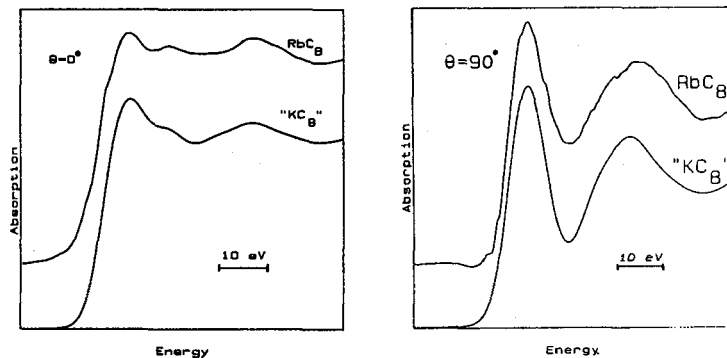


Fig. 2: absorption  $\mu_{||}$  and  $\mu_{\perp}$  obtained after linear extrapolation of the data of fig. 1 a).

chosen [6] to describe the electronics properties. X ray absorption selection rules for transition from  $s$  initial states are simple. The direct product of the symmetry representations of the initial and final wave functions with the dipole moment operator should yield the totally symmetric representation of the group. As the representation associated with the initial state is totally symmetric, final state and dipolar operator should realize the same representation.

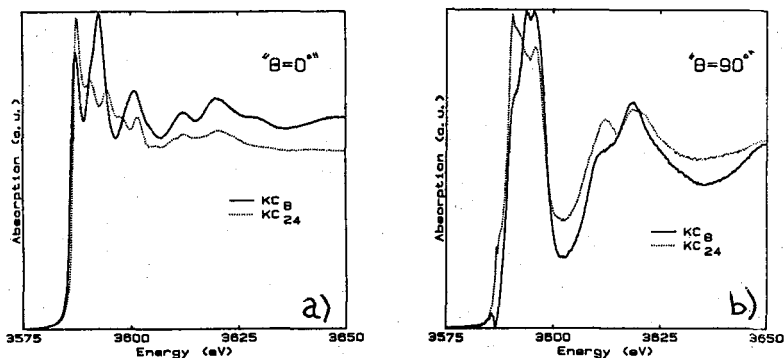
It is interesting to notice that, in pure graphite, the first peak in C-XANES is a  $p_z$ -like [4], due to empty  $\pi$  high density of states. This is not the case in our experiments on intercalation compounds. In a rigid band model, this can be explained since the absorbing atom is not carbon, so the  $p_z$  character is not relevant. Moreover intercalation involves band-folding and modification of the symmetries. It is possible to deduce authorized final bands for complementary polarizations from theoretical band-structures [5,6] using group theory, but the great number of bands makes difficult the location of maxima of density of states. A better comparison should be done with partial density of states localized around the alkali atoms - the absorption process is very localized because of the small extend of the alkali  $s$  initial state.

For a given stage, the three studied compounds are expected to exhibit similar electronic and structural properties [1]. In the spectra shown here, this similarity is not clear. The principal difference is due to the apparent resolution. In each case, the experimental resolution is estimated to be about 1 eV. The cesium and rubidium spectra appear to be very smooth. On the opposite, the potassium ones exhibit many structures. This is due to the lifetime effect. The core hole lifetime broadening is about 0.6 eV for potassium and is above 3 or 4 eV for heavier alkali atoms [7]. A convolution of the potassium spectra leads to results similar to the rubidium K-edge (fig 3) and cesium  $L_1$ -edge near the threshold. The smooth peaks behind this region do not exactly appear at the same energy. These structures, due to multiple scattering, are not directly related to one another because the crystallographic structure neighboring the alkali atoms is not simply homothetic from a compound to another.



**Fig. 3** : Comparison between Rb and K K-edges in  $RbC_8$  and  $KC_8$ . The potassium experimental spectra are smoothed to take into account the core hole life time effect.

Figure 4 presents XANES spectra of first ( $KC_8$ ) and second stage ( $KC_{24}$ ) potassium compounds for both complementary polarizations. There are more peaks in the second stage than in the first one for parallel orientation. This can easily be understood in considering that in-plane stoichiometry is lower in the former case, so band folding is shorter and high density of states regions are multiplied.



**Fig. 4** : Comparison of the absorbance of stage 1 ( $KC_8$ ) and stage 2 ( $KC_{24}$ )  
a) : 0 degree  
b) : 90 degrees

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