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POLARIZATION-DEPENDENT XANES OF POTASSIUM HYDRIDE AND POTASSIUM INTERCALATED GRAPHITE


*Laboratoire de Minéralogie-Cristallographie, U.P.M.C. and Université Paris VII, T 16, 4, place Jussieu, F-75252 Paris Cedex 05, France
**L.U.R.E. (C.N.R.S., C.E.A., M.E.N.), Bâtiment 209 D, F-91405 Orsay Cedex, France
***Laboratoire de Chimie Théorique, Université Nancy I, BP 239, F-54506 Vandoeuvre-lès-Nancy Cedex, France
**Laboratoire de Chimie du Solide Minéral, Université Nancy I, BP 239, F-54506 Vandoeuvre-lès-Nancy Cedex, France

ABSTRACT

XANES of potassium hydride graphite intercalation compounds are recorded and compared to potassium-graphite compounds. This study is a try to link the details of the band structure above the Fermi level to the superconductivity.

INTRODUCTION

Because the interlayer interaction in graphite is relatively weak, it is possible to diffuse foreign atoms or molecules into the space between carbon layers. The binary compounds are constituted by one species of inserted atoms forming a layer in between two carbon layers. The number of carbon layers between two successive layers of intercalated species is called the stage n of the graphite intercalation compound (GIC). Inserted metals are electron donors to carbon layers, i.e. the metal conduction electrons are mainly transferred to the graphite layers.

In the superconducting GIC's reported to date, the intercalate species acts as a donor. The present tendency to increase the transition temperature Tc is to insert two different species in graphite; such compounds are called ternary ones. Promising results are obtained with intercalated amalgam (1), and recent studies (2,4) are performed on first and second stages alkali hydride GIC (KH0.8C4n with n=1 or 2) of the same structure as amalgam GIC (figure 1).

\[
\text{Fig 1: Structure of alkali hydride GIC} \\
\text{KH}_{0.8}C_{4n} \quad \text{KH} \quad \text{C} \quad \text{K} \\
\text{Carbon layers} \\
\text{peak intensity (arb.unit)} \\
\text{sin}0
\]

\[
\text{Fig 2: Dependence of the first peak intensity of KC8 versus } \text{sin}0
\]
In the binary potassium compounds series, the superconductivity is observed in the first stage compound \( \text{KC}_8 \), but cannot be detected in the second stage \( \text{KC}_{12n} \) down to 60mK(3). In the hydrogen second stage potassium ternary GIC, the superconductivity is controversial(2,4), while low concentration of diluted hydrogen in \( \text{KC}_8 \) increases the temperature \( T_c \)(5).

Even if the superconductivity mechanism is not well understood, it depends strongly upon the details of the band structure above the Fermi level. Polarization-dependent X-ray absorption (XANES) is a powerful tool for studying such layered compounds where the two main problems to solve are:

- the charge transfer from metal to carbon and hydrogen
- the symmetry of final states.

COMPOUNDS PREPARATION

The binaries serie \( (\text{KC}_2, \text{KC}_{24}, \text{KC}_{36}, \text{KC}_{84}) \) has been synthetized with the already established methods (6), as well as ternary compounds of stoichiometry \( \text{KH}_8 \text{C}_{24n} \) (7). All samples are prepared from HOPG (Highly Oriented Pyroilitic Graphite). The insertion of KH into graphite to produce the ternary compound occurs in two steps:

-1- Almost exclusive insertion of potassium into graphite
-2- Simultaneous insertion of potassium and hydrogen

Actually, at the end of step 1, the binary compound contains some hydrogen diluted in the potassium layers. This intermediate "binary" compound is then \( \text{KC}_{24}\text{H}_x \), with \( x \) less than 0.1(8); this compound is not a three-layers structure.

The quality of samples is checked with X-rays, and for a good conservation, they are kept in cells with 12 \( \mu \)m-thick kapton windows.

EXPERIMENTAL CONDITIONS

The measurements of the potassium absorption threshold have been performed at LURE-DCI, by transmission through the sample, on the EXAFS 2 station equipped with mirrors for harmonics rejection.

Depending upon the potassium concentration, the sample thickness (homogeneous) varies from 5\( \mu \)m to 50\( \mu \)m to optimize the statistics. In these layered materials the cristallographic \( c \) axis is always perpendicular to the sample.

The 2-D nature of GIC is due to the directionality of the native graphite orbitals. The \( \sigma \) type orbitals lie in the basal plane, so the dipole selection rule leads to an intensity for a pure transition, excited by a polarized light of electric field \( E \), is proportional to \( \sin^2(E,\mathbf{c}) \) and is proportional to \( \cos^2(E,\mathbf{c}) \). As a result, by varying the angle \( \theta \) between the electric field and the \( c \)-axis, the symmetry of the final states can be selected. Because the graphite host is HOPG, no directional information can be obtained in the basal plane.

We have performed measurements for angles \( \theta \) ranging from 90° to 30° by steps of 15°. For each spectrum the energy step is 0.15 eV.

DISCUSSION

1. Charge transfer and electronic structure of the stage 1 potassium GIC.

In \( \text{KC}_8 \) the predicted charge transfer of potassium varies from 0.6(9) to 1(10). A recent review(11) of experimental results does not clearly favor one of the two calculations. Nevertheless, the models(12) used to explain its superconductivity are supported by a no-total charge transfer. The experimental absorption edges for the stages 1 to 3 potassium binary compounds are compared to KH and to the stage 7(\( \text{KC}_{84} \)) edges. The charge transfer is not total for K 4s electron in KH (0.7 according to Pauling's electronegativities), and it corresponds to a measured chemical shift of 1.7 eV (figure 6) compared to the totally ionized potassium in different surroundings (face-centered cubic KCl as well as \( \text{KC}_{24} \) or \( \text{KC}_{84} \) for which the total transfer is universally admitted). All the edges for totally ionized \( K^+ \) in different surroundings have identical positions and are superimposed with the \( \text{KC}_8 \) one.

Then, at the precision of the experiment, the potassium initially 4s electron in \( \text{KC}_8 \) is totally transferred. This confirms the predictions of DiVincenzo and
Rabii(10) who argue for a model with an empty K4s band.

The spectra show (figure 3) dramatic variations in peak intensities as the angle $\theta$ is varied and leads to identify the symmetry bands above the Fermi level. Only two spectra are reported but four are measured. The initial peak has been shown to be a K(ls) to $\sigma$ excitation by the linear dependence of the peak intensity versus $\sin^2 \theta$ (figure 2). A more elaborated comparison with the band structure calculation of Rabii taking into account the hybridization of C and K (s,p and d) orbitals, as well as the explanation of small differences in energy positions of the near-edge structures are in progress(13).

2. Polarization dependent XANES of higher stages potassium GIC.

The spectra for two values of $\theta$ (90° and 45°) are reported for second KC$_{24}$ and third KC$_{34}$ stages on figures 4 and 5. In the energy range of 60 eV above the edge, the photoelectrons have a mean free path large enough to be multiple scattered. The polarization effect is spectacular and increases with the stage. This shape resonance depends upon the cluster geometry related to the dilution of potassium which increases with the stage both along the c-axis and also in the 2-D layers (1 potassium for 8 carbon in the first stage and only 1 for 12 in higher stages). The sensitivity of the 2-D surrounding is confirmed by the similar peak positions and amplitudes for both the stages 2 and 3 spectra measured with $\theta=90^\circ$ compared to the far different spectrum for stage 1 (figure 3) because of a different stoichiometry in the plane.

3. Charge transfer in potassium hydride GIC's.

-Ternary compounds (first and second stages):

The second stage KH$_{0.6}$C$_8$ edge has the same position as all the binary compounds: the experimental charge transfer of the K4s electron is total. For the
The experimental absorption edge is compared to the KH and KC\textsubscript{0.8} \textsuperscript{0.8} \textsubscript{C\textsubscript{4}} on figure 6. It corresponds to a chemical shift equal to 0.6 eV compared to the totally ionized potassium. As a result, the transfer of the K\textsubscript{4s} electron is not total in this compound.

Binary compound with diluted H (second stage KC\textsubscript{24}H with x<0.1)

The edge is reported on the figure 6 and exhibits a chemical shift from KC\textsubscript{24} evaluated to 0.3 eV. This experimental result is surprising because the charge transfer is less than in KC\textsubscript{24} and the only known result concerning the electronic state of hydrogen in such a compound is claimed by Enoki to be an anion H\textsuperscript{+} by positron annihilation measurements\cite{Enoki}.

<table>
<thead>
<tr>
<th>First stage compounds</th>
<th>Second stage compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>binary</td>
<td>diluted H</td>
</tr>
<tr>
<td>KC\textsubscript{8}</td>
<td>KC\textsubscript{8}X</td>
</tr>
<tr>
<td>super conductivity</td>
<td>yes(1)</td>
</tr>
<tr>
<td>measured transfer</td>
<td>total</td>
</tr>
</tbody>
</table>

Table 1: Summary of charge transfer and superconductivity results

*: chemical shift between this compound edge and the totally ionized K\textsuperscript{+} edge.

We can observe (table 1) that a partial charge transfer is not sufficient to predict superconductivity: KC\textsubscript{8} is a superconductor with a quasi-total charge transfer, but if a small amount of the initially K\textsubscript{4s} electron remains in potassium, it participates at a conduction band. On the opposite, in KH\textsubscript{0.8}C\textsubscript{4}, a larger amount of the K initially 4s electron remains on inserted K and moreover it occupies localized electronic states because of the ionic insulator character of potassium hydride KH.

In conclusion, as it is pointed out by Preil and Fisher\cite{Preil} for the amalgam GIC, the symmetry of states at the Fermi level is preponderant to understand the superconductivity mechanism. Elaborated band calculations as well as measurements of electronic density of valence electrons in ground state by Compton scattering\cite{Compton} are needed to interpret the hydrogenated potassium GIC superconductivity.

**BIBLIOGRAPHY**

13. RABII S., private communication.