



**Experiment title:**  
**Angular dependence of Ca K-edge XANES spectra in intercalated graphite compounds**

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**Report:**

Superconductivity in graphite intercalation compounds (GICs) was subject of intensive studies during the late 80's and early 90's, due to their quasi-2D structure [1]. 40 years ago, some of GICs have been found superconducting, but at very low temperature, like  $\text{KC}_8$  with  $T_c=0.14\text{K}$  [2]. One year ago, superconductivity was discovered in  $\text{YbC}_6$  (with  $T_c=6.5\text{K}$ ) [3]. Then, we have demonstrated the existence of bulk superconductivity in  $\text{CaC}_6$  [4] with a  $T_c=11.5\text{K}$ , and very recently we have succeeded in synthesizing **bulk  $\text{Li}_3\text{Ca}_2\text{C}_6$**  ( $\beta$  phase) [5], with a  $T_c=11.15\text{K}$  [6]. These two last compounds exhibit the highest  $T_c$ , measured for GICs elaborated at ambient pressure, i.e. **almost 2 orders of magnitude larger** than in  $\text{KC}_8$ . Recent *ab initio* calculations indicate the crucial role played by the charge in the intercalated Ca plane [7, 8]. The calculations [7] point at a BCS behaviour with a moderate electron-phonon coupling. The carriers are mostly electrons in Ca Fermi surface coupled with C phonons, perpendicular to graphene planes, leading to **superconductivity of Ca intercalant planes**. The role played by the intercalant non-complete ionization is pointed out by this **new scenario** and even **higher  $T_c$**  seem to be possible.

In order to investigate the full electronic structure of these two superconducting compounds, we have performed recent measurements at ESRF: Ca K-edge XANES spectra of  $\text{CaC}_6$ ,  $\text{Ca}_2\text{Li}_3\text{C}_6$  and  $\text{Ca}_3\text{Li}_{0.5}\text{C}_6$  have been measured on ID12 and  $\text{CaC}_6$  Compton profiles have been measured ID15B, cf. Report HE 2135.

**I. EXPERIMENTAL SETUP**

The samples consist of three plates of intercalated graphites, synthesized by the Nancy's group, from highly oriented pyrolytic graphite (HOPG) [4]. The resulting compound is made of randomly oriented crystallites in the planes perpendicular to the **c**-axis (i.e. in a graphite plane) while they are highly oriented along their **c**-axis, allowing us to define its angle (0 or  $\pi/2$ ) with the polarization vector  $\mathbf{\epsilon}$ . The plates are 3 mm side and

200  $\mu\text{m}$  thick, with the  $c$  axis normal to the surface. Since the samples are reactive to ambient air, they were loaded in individual cell under argon atmosphere, and the cell were closed by kapton windows.

The sample cells were placed and **oriented in the beam line in such a way the angular dependence could have been measured without rotating them.** Therefore the sample surface exposed to the photon beam is the same for the two polarization vectors that have been selected. By so doing differences of self-absorption effects are avoided when recording the angular dependence. Details about the undulator, the energy calibration, etc, are missing in this report. The detection is achieved in fluorescence mode by seven Si photodiodes symmetrically placed around the photon beam.

Between 15 and 30 spectra were recorded for each polarization and each sample.

## II. DETERMINATION OF THE SAMPLE ORIENTATIONS TOWARDS THE POLARIZATION VECTORS

For each sample, the absorption at the Ca K-edge has been measured for two distinct orientations of the polarization vector (called  $\theta_1$  and  $\theta_2$ ). The samples are supposed to be dichroic compounds. For any angle  $\theta$ , being the angle between the high symmetry axis of the sample and the polarization vector  $\mathbf{\epsilon}$ , the absorption cross section is given, as a function of absorption cross-sections, by [9]:

$$\sigma(\theta) = \cos^2 \theta \sigma_{\parallel} + \sin^2 \theta \sigma_{\perp},$$

where  $\sigma_{\parallel}$  is the absorption cross section for  $\mathbf{\epsilon}$  along the symmetry  $c$ -axis.

The orientations of the single crystal towards the two  $\mathbf{\epsilon}_1$  and  $\mathbf{\epsilon}_2$  polarization vectors, called  $\theta_1$  and  $\theta_2$  respectively, were estimated using the following method. We used an oriented single crystal of calcite,  $\text{CaCO}_3$ . Calcite crystallizes in the trigonal system, with  $-3m$  point group. It is then also a dichroic compound [2]. For calcite, we recorded the Ca K-edge absorption signal for four distinct angles:  $\theta_1$ ,  $\theta_2$ ,  $\theta = 0^\circ$  and  $\theta = 90^\circ$ . These two latter correspond to  $\sigma_{\parallel}$  and  $\sigma_{\perp}$ , respectively. The spectra are shown in figure 1. The  $\theta$  angles ( $i = 1, 2$ ) were then determined by a fit procedure. The fitting function is given by:

$$\sigma_i \equiv \sigma(\theta_i) = \alpha_i \sigma_{\parallel} + (1 - \alpha_i) \sigma_{\perp},$$

where  $\alpha_i = \cos^2 \theta_i$ , are the fitting parameters. In the above equation, the coefficients  $\alpha_i$  were varied until the resulting spectrum coincide with experimental data  $\sigma(\theta_1)$  and  $\sigma(\theta_2)$ , shown in fig.1. The results of the fitting procedure are shown in Table I and in figures 2 and 3.

$$\begin{aligned} \alpha_1 = 0.695 &\Rightarrow \theta_1 = 33.5^\circ \\ \alpha_2 = 0.29 &\Rightarrow \theta_2 = 57.5^\circ \end{aligned}$$

TABLE I: Results of the fitting procedure: orientation of the two polarizations vectors.

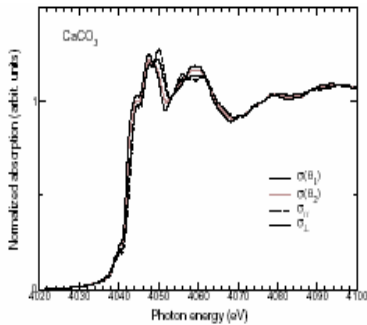


FIG. 1: Ca K-edge angular-dependent XANES spectra in an oriented single crystal of calcite.

Fitting procedure results are shown in Table I and figs 2 and 3.

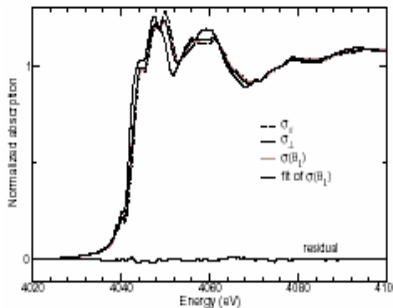


FIG. 2: Result of the fitting procedure of  $\sigma(\theta_1)$

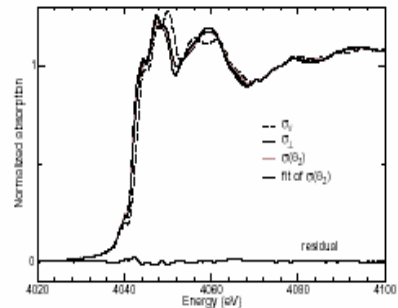


FIG. 3: Result of the fitting procedure of  $\sigma(\theta_2)$

## II. RESULTS AND DISCUSSION

For  $\text{CaC}_6$ , 32 scans were recorded for each  $\theta_1$  and  $\theta_2$  orientations. Each scan comprises the seven signals recorded by the seven working photodiodes. We have looked carefully at the  $7 \times 32 \times 2$  spectra. We have selected 19 scans for each polarization, a scan being the average of the seven signals. For  $\text{Ca}_2\text{Li}_3\text{C}_6$ , 17 scans were recorded for each  $\theta_1$  and  $\theta_2$  orientations. The resulting spectra are obtained by averaging 10 scans for each polarization. For  $\text{Ca}_3\text{Li}_{0.5}\text{C}_6$ , the non-superconducting  $\alpha$  phase, 13 scans were recorded for each  $\theta_1$  and  $\theta_2$  orientations. The resulting spectra are obtained by averaging 5 scans for each polarization.

One can say the spectral shape of  $\text{CaC}_6$  is rather different of the Li-bearing compounds, that are more similar. The spectra of  $\text{CaC}_6$  do not exhibit the thin exciton peak around 4040 eV very well defined on the  $\text{Ca}_2\text{Li}_3\text{C}_6$  spectrum. Instead the  $\text{CaC}_6$  spectra present two distincts features. In addition, the **angular dependence of the Ca K-edge is found to be much more important in the superconducting materials.**

Using the evaluation of  $\theta_1$  and  $\theta_2$  from the  $\text{CaCO}_3$  data, we are reconstructing absorption cross-sections for the three compounds.

Our preliminary calculations on CaC<sub>6</sub>, using *ab initio* calculations [7], present a **good overall agreement** in terms of sign and shape of dichroic signal but not concerning the intensities of measured structures. Calculations are still in progress, taking into account, in particular, a better description of core-hole effects.

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