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G. Loupías, J. Chomilier, D. Guérard. Lithium intercalated graphite: experimental Compton profile for stage one. *Journal de Physique Lettres*, 1984, 45 (7), pp.301-306. 10.1051/jphyslet:01984004507030100 . jpa-00232347

HAL Id: jpa-00232347

<https://hal.science/jpa-00232347>

Submitted on 1 Jan 1984

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Classification
Physics Abstracts
78.70

Lithium intercalated graphite : experimental Compton profile for stage one

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(Reçu le 25 novembre 1983, accepté le 14 février 1984)

Résumé. — La distribution d'impulsions électroniques du composé intercalaire du graphite de premier stade LiC_6 est mesurée par diffusion inélastique de photons X et comparée à celle du graphite, grâce au spectromètre à haute résolution de LURE-DCI. La différence des profils Compton est compatible avec un transfert total de l'électron de conduction du lithium vers une bande π comme le prévoit un modèle de bandes rigides. Mais ce modèle est insuffisant pour expliquer tous les aspects du profil différence qui sont en fait l'illustration de la modification électronique due à l'insertion.

Abstract. — Electron momentum distribution of the first stage lithium intercalated graphite (LiC_6) is measured by X-ray inelastic scattering and compared to the graphite one, using the high resolution spectrometer from LURE-DCI synchrotron source. The Compton profile difference is consistent with a total transfer of the lithium conduction electron to a π band as expected in a rigid band model. But this model is clearly insufficient to explain all the measured profile difference features which reflect the total electronic change in intercalation.

1. Introduction.

When diffusing lithium atoms in graphite, the layer structure of the graphite host is conserved : in the first stage lithium intercalated graphite (LiC_6), each lithium layer is between two carbon layers. The stacking sequence of carbon atoms, A-B in graphite, is modified to A-A in LiC_6 . The physical properties of LiC_6 are very different from those of graphite [1] ; for instance the anisotropy of the in-plane to c -axis conductivity is three orders of magnitude smaller, which means that LiC_6 can hardly be considered as a bi-dimensional material, which is generally admitted for graphite. Many experiments have been made to determine the electronic structure modification introduced by the presence of the Li 2s electron [2], and X-ray inelastic scattering is a very suitable tool for studying such delocalized electrons. So we compared the LiC_6 Compton profile to the graphite one under the same experimental conditions.

Recently a self-consistent pseudopotential electronic structure calculation has been carried out for LiC_6 by Holzwarth *et al.* [3] and a charge density has been derived. To estimate the role played in the intercalation compound by the outer Li electron, they make the difference between LiC_6 and C_6 densities (C_6 is actually a graphite with A-A stacking sequence) and establish that the total electron difference density (between LiC_6 and C_6) is a π density distorted in the direction of the Li ions. Within the same method a charge density calculation has been performed on pristine graphite as well [4].

Previous measurements have been performed on pyrolytic graphite using γ -ray inelastic scattering by Reed *et al.* [5] and by Paakari [6], both with a low resolution. They exhibit large discrepancies with pseudopotential and molecular orbital calculations by Reed *et al.* [5]. In principle, similar information can be obtained by angular correlation profiles from positron annihilation but as Berko *et al.* have shown [7], a quantitative information is difficult to extract due to the preferential positron annihilation with the π electrons.

We present here the first Compton profile measurement on LiC_6 and, in the discussion, we will compare the result with the measurement of Cartier *et al.* [8] by positron annihilation.

2. Experimental method.

The Compton profile $J(p_z)$ is proportional to the one-dimensional electron momentum density of the scatterer, i.e.

$$J(p_z) = \sum_i \int_{p_x} \int_{p_y} n_i(\mathbf{p}) dp_x dp_y \quad (1)$$

where the sum is over all the electrons, $n_i(\mathbf{p})$ is the momentum density for the electron i

$$n_i(\mathbf{p}) = \chi_i(\mathbf{p}) \chi_i^*(\mathbf{p}) \quad (2)$$

with $\chi_i(\mathbf{p})$ the momentum space wave function and

$$q = p_z = \mathbf{k} \cdot \mathbf{p} / k \quad (3)$$

the projection of the momentum $\mathbf{p}$ on the scattering vector $\mathbf{k}$. Therefore the spectral analysis is an accurate test for wave functions, especially for valence and conduction electrons, since they are well localized in the momentum space. Moreover, this method, insensitive to defects, is particularly suitable for less organized materials. As it appears from equation (1), the electron density is integrated on planes perpendicular to the scattering vector; the experimental set-up is chosen so that $\mathbf{k}$ is parallel or perpendicular to the c -axis.

Compton profiles have been measured with the use of a three axis focusing spectrometer described elsewhere [9, 10]. The synchrotron radiation beam of LURE-DCI is monochromatized to provide 12.858 keV photons in a 15 eV bandwidth. The photons scattered at an angle of 137° are energy analysed through a curved crystal and are collected with a position sensitive detector. The full width at half maximum of the measured resolution is 25 eV i.e. 0.15 atomic unit (a.u.) of momentum; this has to be compared with the 0.46 a.u. resolution in γ -ray experiments.

To keep the same data processing, the same geometry for the apparatus and the samples is conserved. No correction has been made for the resolution function. Because we compare profiles, all the isotropic processes i.e. multiple scattering [11], electron-electron correlations [12], impulse approximation deviation, are not to be taken into account.

3. Samples.

Two Highly Oriented Pyrolytic Graphite (HOPG) samples, with orientational deviations along the c -axis around 0.5° , are used to study the electron density parallel to the c -axis and the average in the basal plane. They are $0.8 \times 1.5 \times 0.5$ cm with the largest surface respectively perpendicular and parallel to the c -axis. A third sample has been intercalated by heating graphite and lithium at 400° in a copper tube according to the method described elsewhere [13]; it allows us to measure the Compton profile with the scattering vector along the c -axis. It was kept in a sealed cell with a beryllium window, under dry argon.

To be sure we did not get a second stage compound, we measured the 001 reflections with a θ - 2θ spectrometer, before and after the experiment. The bright yellow colour was an extra proof of the stage, and the evidence of no presence of lithium at the surface.

4. Experimental results.

A LiC_6 directional Compton profile is shown in figure 1. For a photon energy loss equal to the C atom 1s binding energy (284 eV, i.e. -1.6 a.u.) we observe a clear slope discontinuity corresponding to the core profile departure. The Li edge departure (55 eV) is too small to be evidenced. The Hartree-Fock calculated [14] 1s core electrons profile reported on the same figure starts just after the thresholds.

The graphite anisotropy for positive values of q is reported in figure 2. It is compared with γ -ray results [5, 6] and with the two calculated ones [5]. For the scattering vector parallel to the c -axis, we compare the Compton profiles obtained on LiC_6 and graphite in figure 3. The graphite profile is normalized to the four valence and conduction electrons of C atom while the LiC_6 profile is normalized to 1/6 electron more. In such a way, the difference between the two profiles is the profile of the Li excess electron fraction by C atom.

Fig. 1. — All electron LiC_6 Compton profile. The raw curve is the experimental profile. For large q it fits with the core-electron calculated one. The thermal peak is around -3.0 a.u.

Fig. 2. — Graphite anisotropy. $J(q)$ for $\mathbf{k}$ parallel to the c -axis minus $J(q)$ for $\mathbf{k}$ perpendicular to c . Present experiment (—), γ -ray experiment by Reed *et al.* [5] (— · —), γ -ray experiment by Paakari [6] (— — —), pseudopotential calculation (— · · · —) and molecular orbital calculation (— · — · —) by Reed *et al.* [5].

5. Discussion.

For the graphite anisotropy (Fig. 2), we observe a good general agreement between our experiment and γ -ray ones by Paakari [6] and by Reed *et al.* [5].

Near the Fermi momentum, all curves present a minimum but the comparison is difficult because the authors used a different graphite (pyrolytic). There is a large discrepancy with the available calculations in particular near $q = 0.5$ a.u. and 1 a.u. As pointed out by Reed *et al.*, they are respectively the lattice parameter and the interlayer distance in the momentum space and these authors conclude to the « inaccurate treatment of interplane bonding ». In the molecular orbital calculation, this bonding is not even taken into account. So the discrepancy with both models points to the huge effect of the interlayer interaction (i.e. of the stacking geometry). The Compton profile obtained from the self consistent pseudopotential [15] is the best theoretical fit obtained so far.

The electron momentum difference between LiC_6 and graphite exhibits a maximum out of zero momentum; as calculated by Berko [7] the graphite π Compton profile for $\mathbf{k}$ parallel to the c -axis shows a maximum out of zero momentum and is null at zero (Fig. 3). In contrast, a metal-like electron profile has a maximum at zero and collapses rapidly. So our experimental results cannot be totally explained by any of these opposite models. In particular, in the rigid band model, which is a good first approximation, the bands of graphite are folded in the Brillouin zone of LiC_6 with an increase of the Fermi energy so that the excess electron is totally transferred to a graphite π band: hence the density difference in this model is a graphite π profile. The measured difference actually results from the total variation of outer (both valence and conduction) electron

Fig. 3. — Compton profile difference for k parallel to c , $J(\text{LiC}_6)$ minus $J(\text{graphite})$. Our experiment (—) is compared to a graphite Compton profile [7] (---) and to a metal-like profile (— · —). All curves are normalized to 1/6 electron.

density. Two facts are to be taken into account :

- (i) introduction of an excess outer electron ;
- (ii) modification of the graphite charge distribution, due to the presence of the partially or totally ionized lithium, that can be illustrated in particular by the stacking change. Hence, the carbon valence electrons have to be described by different wave functions in LiC_6 and graphite, taking into account both the charge distortion and the change in the adjacent layers interaction.

The theoretical maps of valence and conduction density difference between LiC_6 and C_6 show that the band distortion due to the Li ion only appears for the valence part [3]. In our difference profile (Fig. 3), the non zero momentum maximum is typical of a π profile. The contribution at zero momentum can be attributed to a 2s Li participation that is hybridized with the initial graphite orbital in the LiC_6 valence orbitals. The peak centre is shifted towards low momentum in comparison with the π graphite, which means that the valence and conduction electrons are more delocalized than with the rigid band model. This is consistent with the larger extension of the LiC_6 π density compared to the undistorted graphite π one (Fig. 5 of Ref. [3]) and with the particular sensitivity of the profile near $q = 1.0$ a.u. to interlayer bonding. The Compton profile [15] derived from this model [3] presents the same general features as our measured one.

The positron annihilation of Cartier *et al.* [8] does not exhibit for LiC_6 a narrow component like in a heavy alkali metal (KC_8) « which strongly supports the existence of an alkali-like electron

gas ». Nevertheless they notice that the angular correlation profile, for q parallel to c -axis, is higher than the HOPG one at zero. Both the absence of a narrow component and the enhancement of the profile at zero momentum show a qualitatively good agreement between the results of the two methods.

In conclusion, the zero contribution in the measured difference profile shows that the rigid band model is not accurate enough, thus it is necessary to consider both the charge transfer and the modification of the valence bands.

Acknowledgments.

We wish to thank Drs M. Y. Chou, S. G. Louie, M. L. Cohen and N. A. W. Holzwarth for permission to cite their work prior to publication and for fruitful discussions. We are grateful to Dr. Y. Petroff for his constant interest to the subject. We are indebted to Dr. A. W. Moore from Union Carbide who gave us the HOPG sample. We also wish to acknowledge the Laboratoire de l'Accélérateur Linéaire in Orsay and Drs P. Marin and M. P. Level for providing the synchrotron beam.

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