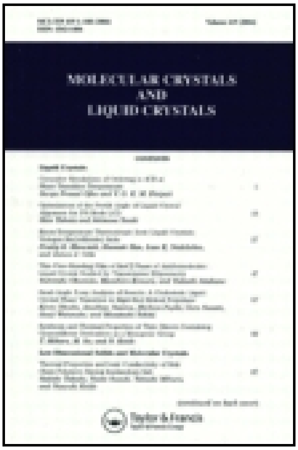

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Theoretical and Experimental Investigation of Electronic Structure of High Pressure Phases of Li Intercalated Graphite

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THEORETICAL AND EXPERIMENTAL INVESTIGATION OF ELECTRONIC STRUCTURE OF HIGH PRESSURE PHASES OF Li INTERCALATED GRAPHITE

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Abstract Electronic structure of a high pressure phase of lithium intercalated graphite has been investigated by theoretical and experimental means. Total energy calculation has shown the existence of a stable phase with LiC_2 composition at c=3.38 Å. A Compton measurement indicates a possible existence of excess Li in the sample.

INTRODUCTION

Graphite-lithium system has been investigated[1] under high pressure, resulting in the synthesis of intercalated graphite compounds with concentrations of alkali atoms well exceeding those possible at atmospheric pressure. The highest concentration achieved corresponds to a stage one compound with composition at or near LiC_2. There has, however, been no theoretical or experimental study of their electronic structures and charge distributions. In this paper we report on the total energy and energy band structure of LiC_2, and the results of Compton profile measurement on a corresponding concentrated, high pressure sample.

THEORY

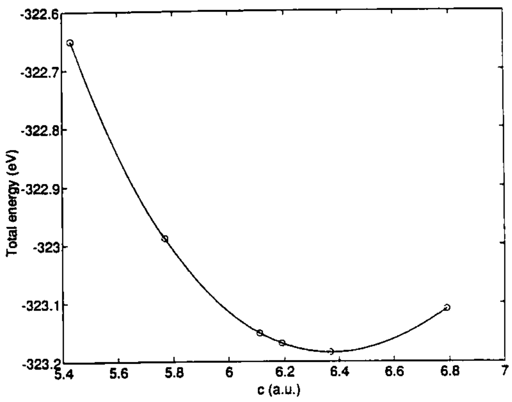

FIGURE 1 Total energy per unit cell for LiC_2 versus c-axis separation.

We have chosen a first stage Li compound with the composition LiC_2 for the theoretical studies. Total energy calculations were carried out as a function of the c-axis repeat distance using the formalism developed by Holtzwarth and Zeng.[2] The calculations were performed within the density - functional - approximation [3, 4] using *ab initio* norm - conserving pseudo - potentials.[5] The exchange-correlation energy was introduced following the analytic representation of Perdew and Wang .[6] The results (Fig. 1) show that there is a sta-

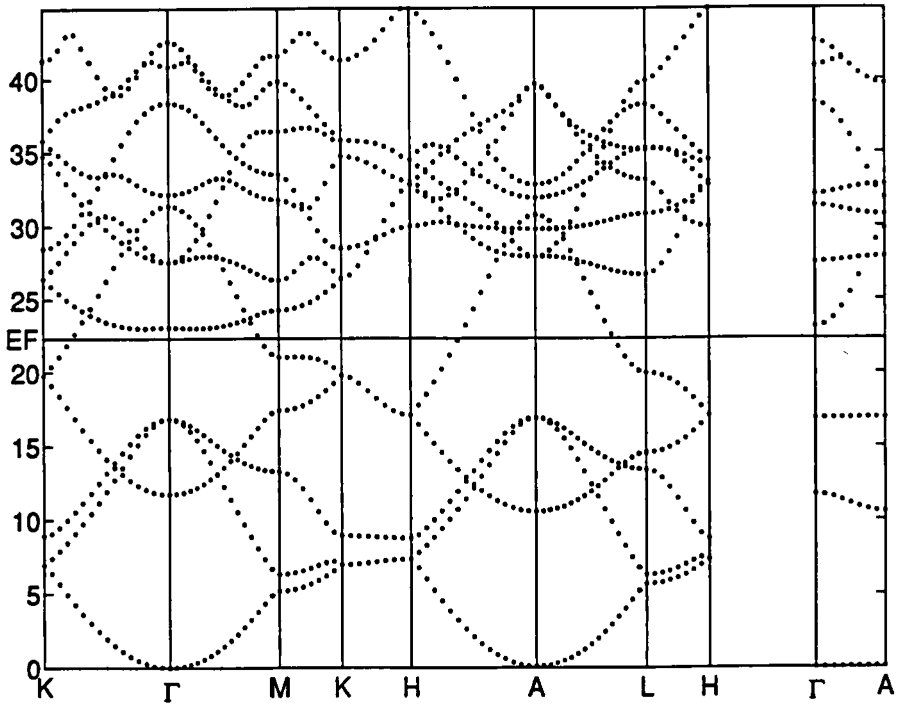

FIGURE 2 Energy band structure of LiC_2

ble phase with this composition at the c-axis separation of 3.38 Å. This is 8.4% smaller than the experimental value reported by Belash *et al* [7]. The energy band structure was calculated at the theoretically determined c-axis repeat distance and is shown in Figure 2. The charge transfer between the alkali and carbon sheets is complete and the transferred electrons occupy the antibonding π bands. The Fermi surface is a cylindrical pocket around the entire vertical sides of the hexagonal Brillouin zone (BZ), with the cross-section slightly increasing as one approaches the upper surface of the BZ (k=π/c). The distortion of the folded graphite bands due to the intercalant appears to be less than the case of LiC_6 [8]. Figure 3 shows the valence charge

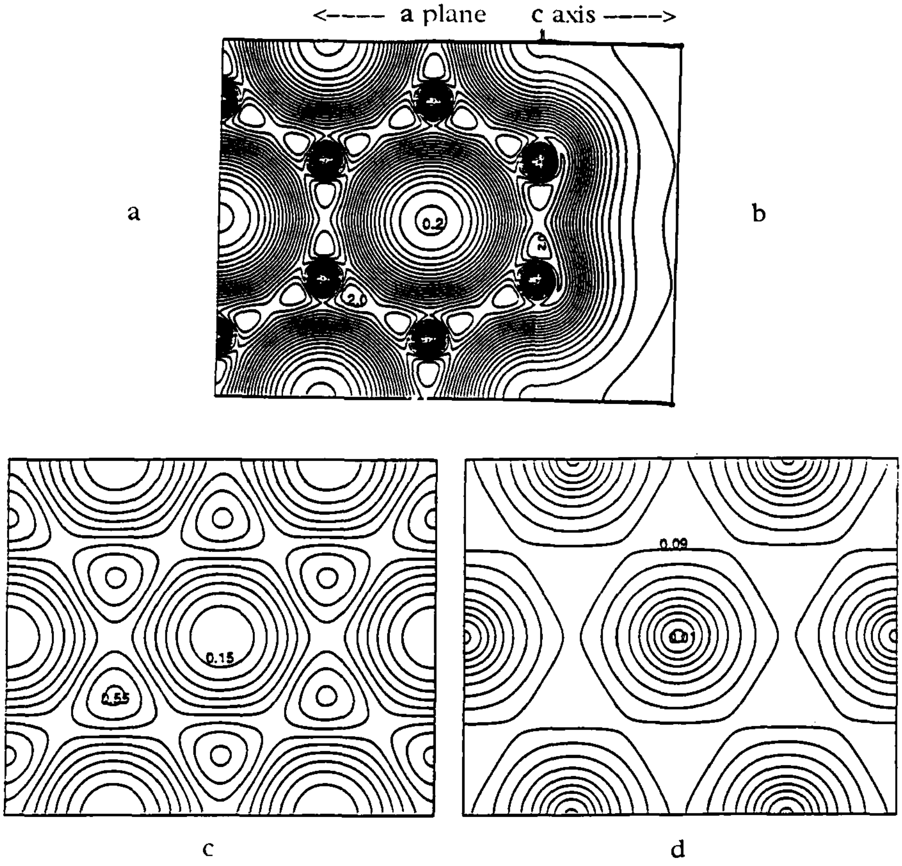

FIGURE 3 Charge density contours for LiC2
3a. Carbon plane; 3b. Perpendicular to carbon plane and containing a C-C bond; 3c. Half distance between C and Li planes; 3d. Li plane. Contours are given in units of 0.9 e /$Å^3$

density contours in 3 planes parallel to the carbon layers and one perpendicular to them and containing a C-C bond. There is very little charge in the Li plane, with the lowest concentration occurring at the Li site.

COMPTON EXPERIMENT

Method

When a photon is inelastically scattered by an electron, the momentum and energy conservation laws lead to a relation between the photon energy loss and the projection of initial electron momentum **p** on the scattering vector **K**. The energy loss of these photons is composed of two terms : the first is the Compton shift, due to scattering by an electron at rest, and the second is a Doppler broadening around the Compton shift. This last term is named Compton profile and accounts for the motion of the electron in the sample.[9] Its amplitude is equal to the density of the electrons whose momenta have a projection along **K** equal to q, with $q = \mathbf{p}.\mathbf{K}/K$:

$$J(q) = \Sigma_i \iint n_i(\mathbf{p})\, dp_x dp_y$$

where $n_i(\mathbf{p})$ is the density of electron i, in the momentum space. Compton measurement is a check of momentum wavefunctions, according to the relation $n_i(\mathbf{p}) = \chi_i(\mathbf{p})\, \chi_i^*(\mathbf{p})$, where $\chi_i(\mathbf{p})$ is the electronic wavefunction in the momentum space. Since valence electrons in solids have a large extent in real space their resulting localization in momentum space makes Compton scattering a powerful tool for investigation of their electronic density.

Sample

The synthesis of highly saturated compounds was done under high pressure at the Moscow State University[1]. The 5mm-thick sample studied here is a first stage compound of the highest concentration obtained. Since lithium GIC are very reactive, it was kept in a sealed cell filled with dry argon. In addition, the cell was cooled at the liquid nitrogen temperature during the experiment to assure the stability of the sample under the beam.

Experimental details

The experiments are carried out using a monochromatic beam provided by the synchrotron facility and the focusing high resolution spectrometer[10] of LURE-DCI. The energy loss spectrum of the photons is analyzed, by means of a Cauchois type curved crystal. The photons of same energy, emitted at various points of the sample, are Bragg reflected, when going through the analyzer and focused at a single point of the Rowland circle. Each position of the circle is then related to certain energy and a position-sensitive detector is used to record the entire Compton spectrum. The incident energy of is 16378 eV and the scattering angle is 137°, resulting in a Compton shift of 878 eV. The measurement has been performed for the scattering vector **K** along the c axis. The resolution is measured by the full width at half-maximum of thermal line and is equal to 0.16 a.u. of momentum.

Data processing

The raw data are corrected for all energy dependent terms, such as absorption (in sample and analyzer), detector efficiency and analyzer reflectivity. The energy loss scale is then converted into a momentum scale. Because of the flatness of the core profile in momentum space, its contribution is easy to subtract from the experimental profile in order to obtain the contribution of the valence-electrons only, using the quasi-self-consistent-field method of calculation described elsewhere[11] and valid beyond the impulse approximation. The valence profile is normalized to 4.5, the number of valence electrons per carbon ion. Figure 4 shows the Compton profiles for LiC_2 and graphite with the scattering vector parallel to c axis.

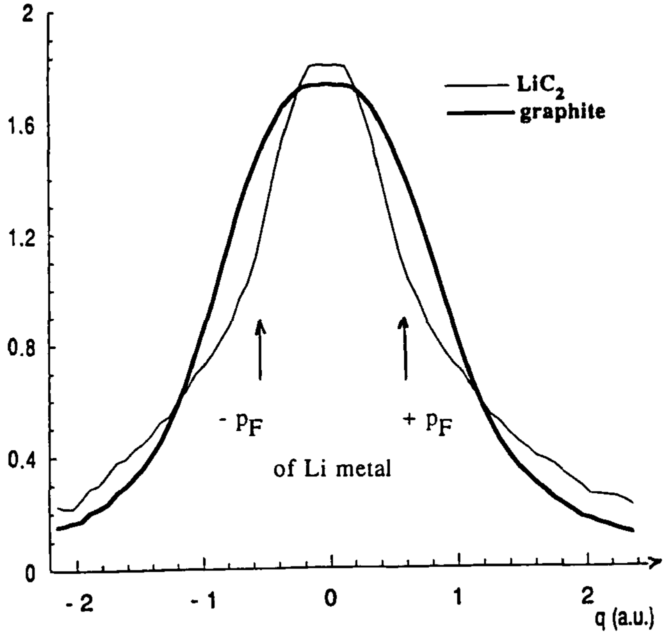

FIGURE 4
Compton profiles for LiC_2 and graphite with K//c axis

The momentum density measured by Compton scattering is much narrower than in LiC_6 near q=0, and a break in the slope can be identified at a q corresponding at Fermi momentum of lithium metal. This points out to possible existence of free Li on the sample, making definitive identification of stochiometry difficult.

CONCLUSION

The total energy calculations predict a stable phase with LiC_2 composition, at a c axis lattice constant of 8.4% less than the experimentally reported high pressure phase. The calculated energy band structure and charge densities for this phase indicate a total charge transfer between the intercalant and the graphite sheets. The Fermi surface has a nearly two dimensional shape. Mea-sured Compton profile is narrower than the case of both graphite and LiC_6.

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