UC-25
LBL-20794
c.1

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
FEB 18 1986
LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Presented at the Symposium on Intercalated Graphite Compounds, Pittsburgh, PA, November 28-30, 1984; and published in the Proceedings

COMPTON PROFILE OF GRAPHITE AND LITHIUM-INTERCALATED GRAPHITE

M.Y. Chou, M.L. Cohen, and S.G. Louie

November 1984

For Reference
Not to be taken from this room

LBL-20794
c.1

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

COMPTON PROFILE OF GRAPHITE AND LITHIUM-INTERCALATED GRAPHITE

M. Y. Chou*, Marvin L. Cohen*, and Steven G. Louie
Department of Physics, University of California, and
Lawrence Berkeley Laboratory, Berkeley, California 94720

The momentum distribution of the valence electrons in graphite and lithium-intercalated graphite LiC_6 is studied by calculating the Compton profiles. The wave functions are generated from a self-consistent calculation using the pseudopotential method within the local density functional formalism and a mixed basis set consisting of plane waves and linear combinations of atomic orbitals. Compton profiles along the (0001) direction are presented for both graphite and LiC_6. The difference between profiles of LiC_6 and graphite exhibits characteristic features which provide information about the change in the electronic properties resulting from intercalation.

1. Introduction

The first-stage lithium-intercalated graphite (LiC_6) has attracted considerable experimental interest in recent years. It is important to know how intercalation changes the electronic properties of graphite. In particular, the question of how the lithium 2s electron affects the graphite energy levels and adjusts itself in the new system is often asked. The intercalation of lithium atoms results in a 10% expansion in the interlayer distance and the layer stacking pattern is changed from *ABAB* in graphite to $A\alpha\ A\alpha$ in LiC_6. In this work, the Compton profiles of both graphite and LiC_6 are calculated. These are measurable quantities and reveal information about the momentum distribution of the valence electrons. This supplies complementary information on the electronic structure of the systems in addition to optical, photoemission, and transport measurements. Characteristic features are found in the difference between LiC_6 and graphite profiles[1]. These results are different from those obtained using the rigid-band model.

2. Calculations

The wave functions are obtained from self-consistent calculations for graphite and LiC_6 [2] using the pseudopotential method[3] within the local-density-functional scheme[4]. A mixed basis set consisting of plane waves and linear combinations of atomic orbitals is used to represent the wave functions in the crystal. The norm-conserving pseudopotentials[5] and the exchange-correlation energy functional of Hedin and Lundqvist[6] are employed. Except for some nonuniform shifts, the valence bands of LiC_6 are similar to those of graphite folded into the new Brillouin zone. The extra electron from lithium occupies part of the π antibonding orbitals which are almost empty in graphite. It appears as if the Fermi level is raised within rigid bands of graphite, as is proposed by the rigid-band model.

The projected momentum distribution of valence electrons along specific directions (the Compton profile) is calculated within the impulse approximation. We use the tetrahedron linear interpolation method[7] to performing the summation over the k-points in the Brillouin zone with a grid of 45 k-points in the irreducible zone. Because the detailed dispersions ($\sim$0.01 ev) along the *K-H* direction near the Fermi level in graphite are beyond the our calculational accuracy, the valence bands are

*Materials and Molecular Division of the Lawrence Berkeley Laboratory

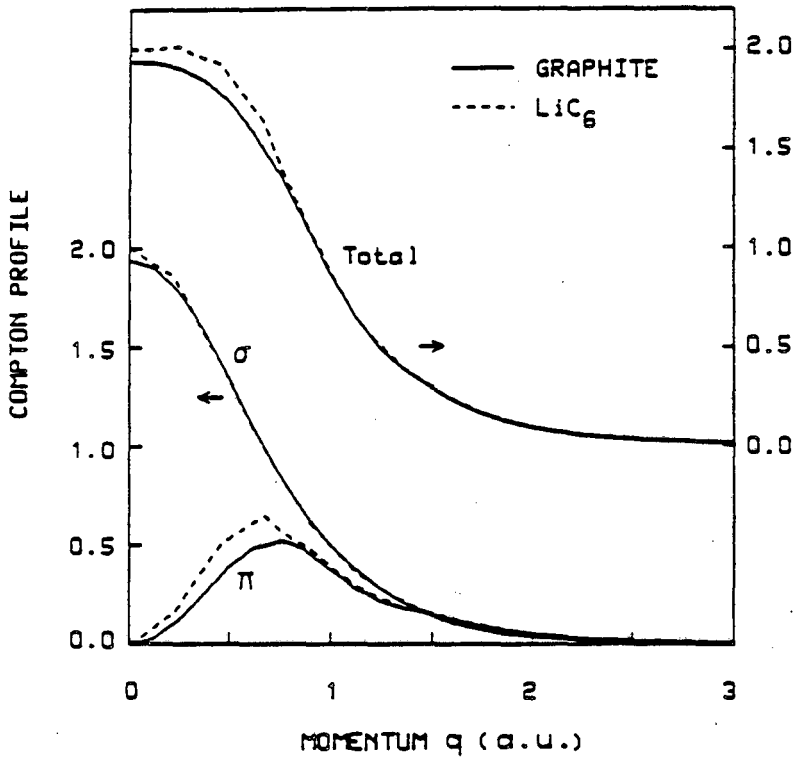

Fig. 1 Comparison of the calculated total Compton profiles of graphite (solid line) and LiC_6 (dashed line) along the c axis when appropriately normalized (see text).

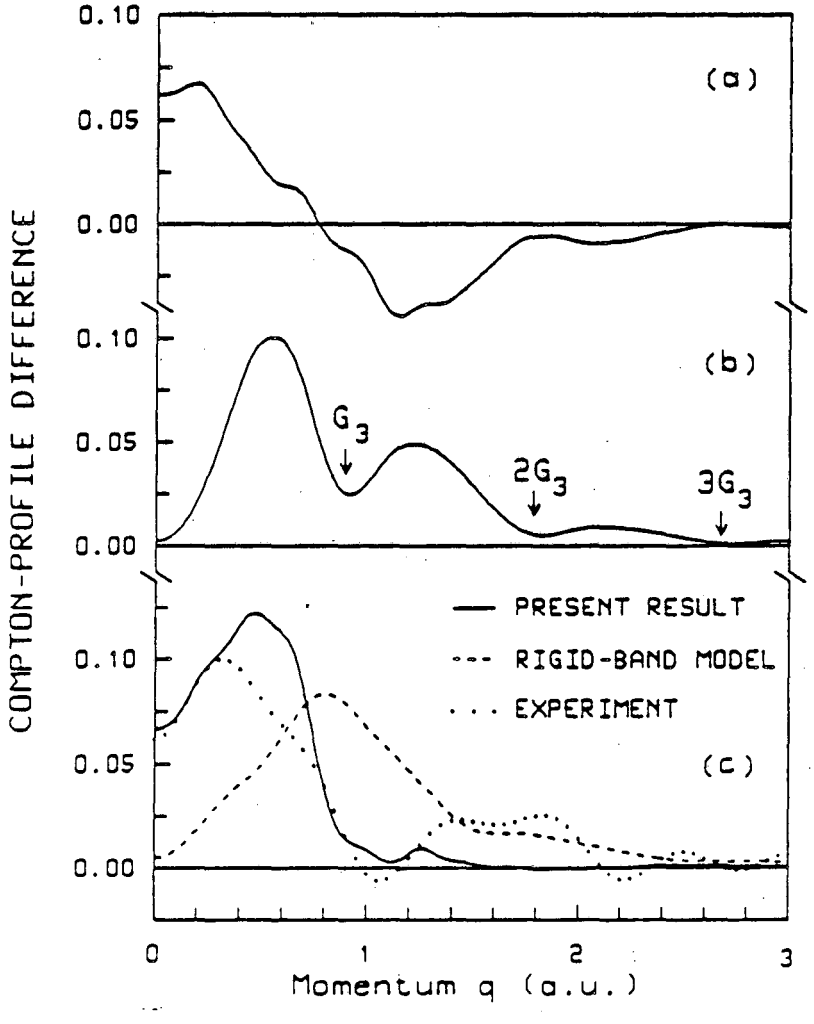

Fig. 2 (a) Difference in the valence-band profiles between LiC_6 and graphite along the c axis. (b) The conduction electron contribution from occupied π antibonding states to the Compton profiles of LiC_6 along the c axis. The curves in (a) and (b) have been convoluted using a Gaussian function with the full width of half maximum being 0.15 a.u. (c) Total difference between the Compton profiles of LiC_6 and graphite: present self-consistent calculation (solid line), the prediction by the rigid-band model (dashed line), and the experimental data[8] (dotted line). All the calculated results are convoluted using the experimental resolution function.

assumed to be filled in the calculation.

3. Results

The calculated valence electron profiles along the c axis are shown in Fig. 1, for both graphite and LiC_6. The normalization is chosen such that the integral from $-\infty$ to ∞ gives 4 (electrons per carbon atom) in graphite and $4\frac{1}{6}$ in LiC_6. Separate contributions from the σ and π bands are also plotted. The larger π contribution in LiC_6 results from the additional filling of the antibonding π orbitals. Because of the antisymmetric nature of π orbitals, a zero amplitude at q = 0 is expected.

In Fig. 2(c), the difference between the profiles of LiC_6 and graphite is plotted. This difference comes from two contributions. One is the difference in the profiles of valence bands, shown in Fig. 2(a), which is positive for low momenta and negative for high momenta. This indicates an intercalant polarization effect, because the electrons in LiC_6 are more spread out in the interlayer region (pulled toward the lithium atoms) than in graphite. The other is the conduction band contribution from the additional partially filled antibonding π states in LiC_6, shown in Fig. 2(b). Some significant oscillatory behavior is found with valleys near *0, G_3, $2G_3$, etc.*, where G_3 is the shortest reciprocal lattice vector along the c axis with length 0.90 a.u. This results from the band dispersions from *M* ($k_z = \frac{1}{2}G_3$, *occupied)* to *L* ($k_z = 0$, *not occupied)* found in the self-consistent calculation. Fig. 2(c) shows the sum of Fig. (a) and (b). The results from the rigid-band model (contribution from the conduction bands of graphite) are shown in a dashed line, and the experimental data[8] are also plotted. The large differences between the results of the rigid-band model and the self-consistent calculation or the experimental curve indicate that the rigid-band model is not reliable for determining the electron momentum distribution. The polarization effects and the dispersions normal to the basal plane for the conduction bands are obtained only when the intercalant interaction is treated properly.

Acknowledgement We would like to thank Dr. G. Loupias and Dr. J. Chomilier for discussions and for sending us the experimental results. This work was supported by National Science Foundation Grant No. DMR8319024 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. One of us (SGL) would also like to acknowledge support by a program development fund from the Director of the Lawrence Berkeley Laboratory.

[1] M. Y. Chou, S. G. Louie, M. L. Cohen, and N. A. W. Holzwarth, Phys. Rev. B **30** , 1062 (1984).
[2] N. A. W. Holzwarth, S. G. Louie, and S. Rabii, Phys. Rev. B **26** , 5382 (1982); *ibid.* **28** , 1013 (1983).
[3] M. L. Cohen, Physica Scripta **T1** , 5 (1982).
[4] P. Hohenberg and W. Kohn, Phys. Rev. **136** , B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140** , A1133 (1965).
[5] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43** , 1494 (1979).
[6] L. Hedin and B. I. Lundqvist, J. Phys. C **4** , 2064 (1971).
[7] G. Lehmann and M. Taut, Phys. Status Solidi B **54** , 469 (1972).
[8] G. Loupias, J. Chomilier, and D. Guérard, J. Physique Lett. **45** , L301 (1984).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720