9-17-1979

Electron-Energy-Loss Study of Stage-1 Potassium-Intercalated Graphite

D. M. Hwang

Mark Utlaut
University of Portland, utlaut@up.edu

M. S. Isaacson

S. A. Solin

Electron-Energy-Loss Study of Stage-1 Potassium-Intercalated Graphite

D. M. Hwang,[a] M. Utlaut, M. S. Isaacson,[b] and S. A. Solin[c]
The James Franck Institute, The Enrico Fermi Institute, and The Department of Physics, The University of Chicago, Chicago, Illinois 60637
(Received 5 July 1979)

Electron-energy-loss spectra of stage-1 K-intercalated graphite single crystals were obtained with a scanning transmission electron microscope. The complex dielectric function with electric polarization perpendicular to the c axis was derived by Kramers-Kronig analysis. The energy-loss peak at 2.5 eV is consistent with previous optical measurements, while the splitting of the one at 27 eV can be interpreted by folding the Brillouin zone of pristine graphite. Splittings and shifts of the interband transitions were observed and compared with calculations.

There has been considerable recent interest in the electronic properties of intercalated layer compounds[1] in general and of graphite intercalates[2-4] in particular. This interest is spurred not only by the technological potential for their very anisotropic high conductivity but also by the need for a fundamental understanding of their electronic properties.

While there are many phenomenological studies of various kinds of intercalated layer compounds, theoretical calculations of the electronic band structures have at present been limited to systems with the simplest crystal structures, i.e., stage-1 potassium-intercalated graphite C_8K,[5-7] and stage-1 lithium-intercalated graphite C_6Li.[7-9] Therefore, electronic band structures based on the rigid-band model, which are proposed[10] for high-stage intercalates, have been used to interpret experimental data even for low-stage intercalates. Nevertheless, the band structure of C_8K recently calculated by Inoshita, Nakao, and Kamimura (INK) exhibits measurable deviations from that of pristine graphite. Therefore, it is important to test experimentally the validity of

both the rigid-band approximation and the existing theoretical band-structure calculations.

C_8K has been studied extensively with various experimental techniques including electrical conductivity, Hall effect, magnetoresistance, heat capacity, thermoelectric power, etc.[3,4,11] Although those quantities are directly related to the collective behavior of free carriers on the Fermi surfaces, they provide only qualitative justification[10] of theoretical models due to the complexity of the Fermi surfaces. On the other hand, knowledge about the interband transition energies, which can be quantitatively compared with the calculated results, is crucial for a proper evaluation of the band structure and can be used to establish the validity of different theoretical models. Such knowledge, which can be directly deduced from the dielectric function, is still lacking. Only optical reflectivity data from 0.6 to 2.85 eV have been reported.[11]

The dielectric functions of solids in the energy range of electronic interband transitions can be conveniently obtained[12] from electron-energy-loss spectroscopy. To date, the only reported electron-energy-loss study on intercalated layer compounds was performed by Ritsko and Rice.[13] They chose to study stage-1 $FeCl_3$-intercalated graphite because of its stability in air, vacuum, and a variety of solvents. However, its crystal structure is so complicated that there is no existing electronic-band-structure calculation for that compound and the rigid-band model was used to interpret the experimental results. In this Letter we report electron-energy-loss studies of C_8K and compare our results with both the rigid-band model and theoretical calculations.

Pristine graphite samples with thicknesses of ~ 100 Å were prepared from New York natural graphite single crystals by a method similar to that reported by Price and Venables.[14] Since C_8K is extremely air sensitive, a special vapor-phase intercalation chamber with vacuum transfer mechanism was constructed to permit sample transfer at ~ 10^{-9} Torr. Electron micrographs, diffraction patterns, and energy-loss spectra for both pristine graphite and C_8K were recorded before and after intercalation from the same sample regions (within 1-μm) with use of a scanning transmission electron microscope equipped with an electron energy analyzer.[15] For recording energy-loss spectra, an electron beam size of ~ 500 Å was used and sample regions of uniform thickness and without noticeable defects were probed.[16] The in-plane structure C_8K was confirmed by comparing the diffraction pattern with published data.[17] Data for C_8K were collected within one week after intercalation. After having been kept inside the microscope at room temperature and ~ 3×10^{-10} Torr vacuum for about one month, the intercalated sample apparently degraded as changes in the diffraction patterns and energy-loss spectra were observed.

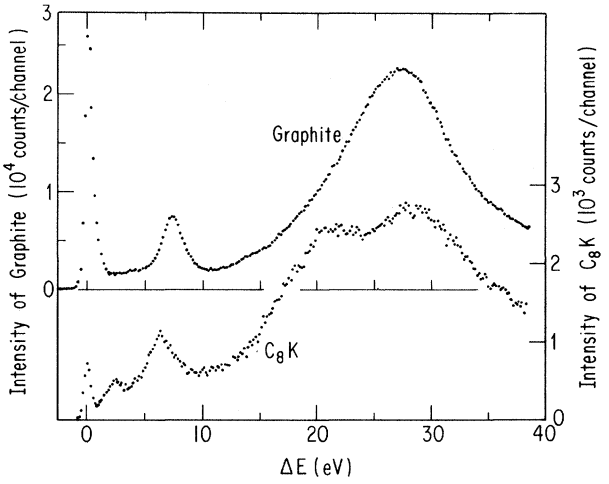

FIG. 1. Raw electron-energy-loss spectra of pristine graphite and stage-1 potassium-intercalated graphite C_8K obtained with identical conditions before and after intercalation. The incident 12-keV electron beam was parallel to the c axis and the scattering angle was 2.3 ± 0.6 mrad. The energy resolution was 0.7 eV as indicated by the full width at half maximum of the zero-loss peak.

A typical electron-energy-loss spectrum of C_8K, recorded with a 12-keV incident electron beam parallel to the c axis and at a scattering angle of 2.3 mrad, is shown in Fig. 1. The half angular widths of both the incident beam and the spectrometer collection aperture were 0.6 mrad. The corresponding momentum transfer perpendicular to the c axis, $q_\perp$, is 0.13 ± 0.03 $Å^{-1}$, while the momentum transfer parallel to the c axis, $q_\parallel$, varies linearly from zero at zero energy loss, to 0.07 $Å^{-1}$ at 30 eV loss. Therefore, the derived dielectric function is essentially $\epsilon_\perp(\omega)$ and contains[12] less than 7% of $\epsilon_\parallel(\omega)$ for energy loss less than 15 eV, and 22% of $\epsilon_\parallel(\omega)$ for energy loss of 30 eV. The momentum transfer of ~ 0.13 $Å^{-1}$ is ~ 1/26 of the Brillouin-zone dimension of graphite and ~ 1/13 of that of C_8K. Transitions with this momentum transfer are generally considered[12] as vertical transitions and the derived dielectric function should therefore be comparable to that obtained from optical measurements.

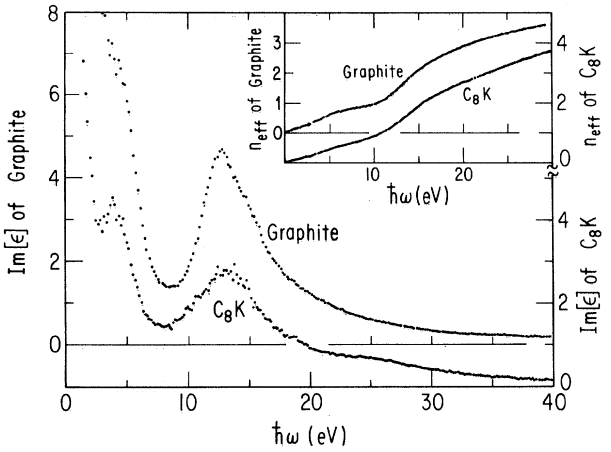

FIG. 2. The imaginary parts of the dielectric functions $\mathrm{Im}[\epsilon(\omega)]$ graphite and C_8K derived from Fig. 1. The inset shows the $n_{\mathrm{eff}}(\omega)$ graphite and C_8K calculated from the corresponding $\mathrm{Im}[\epsilon(\omega)]$.

An electron-energy-loss spectrum of pristine graphite taken before intercalation is also shown in Fig. 1. It is similar to previous results[12,18] and shows two plasma peaks at 7.5 and 27 eV. The spectrum of C_8K is quite distinct from that of pristine graphite with the following features: (1) There is an additional energy-loss peak at 2.5 eV; (2) the 27-eV peak of graphite splits into two broad peaks centered at 22 and 28 eV; (3) the 7.5-eV peak of graphite is broadened and shifts to 6.3 eV. Spectra have been recorded for electron energy losses up to 150 eV and no additional features have been observed.

The complex dielectric functions $\epsilon(\omega)$ of graphite and C_8K were derived from the energy-loss spectra by Kramers-Kronig analysis as described by Venghaus.[18] The imaginary parts of the derived dielectric functions $\mathrm{Im}[\epsilon(\omega)]$ of graphite and C_8K are shown in Fig. 2. Our result for graphite is in agreement with that reported by Venghaus[18] and shows two interband transitions at 4.5 and 13 eV. Upon intercalation to C_8K, the 4.5-eV peak of graphite becomes more pronounced and shifts down to 3.8 eV, while the 13-eV peak becomes broader without significant shift. There is an additional broad weak bump centered at ~25 eV. The overall absolute height decreases and many reproducible structural features appear.

All calculations of the electronic band structure of graphite[19-22] indicate that the 4.5- and 13-eV peaks in $\mathrm{Im}[\epsilon(\omega)]$ are due to transitions between π electron bands at critical points M_3^+ and M_4^-, and between σ electron bands at critical points M_3^- and M_1^+, respectively (notations of Ref. 22 are used).

Theoretical calculation of the electronic band structure of C_8K is not yet complete. INK[6] calculated only the π electron bands by a semiempirical tight-binding scheme. DiVincenzo *et al.*[7] used a modified Korringa-Kohn-Rostoker method with non-muffin-tin corrections, but only preliminary results have been reported. However, the general behavior of the electron-energy-loss data of C_8K can be interpreted with the help of the rigid-band zone-folding scheme.[6] The observed energy shifts of interband transitions are then compared with the results of theoretical calculations.[6,7]

Consider the two-dimensional rigid-band approximation. Then because the unit cell of C_8K in the x-y plane is four times larger in area than that of pristine graphite, the electronic band structure of C_8K should be similar to that of graphite but with the graphite Brillouin zone appropriately folded so that the M (or Q) points map back to the Γ point. Therefore, some nonvertical transitions in graphite will become vertical transitions in C_8K. The splitting of the 22- and 28-eV peaks in the energy-loss spectrum of C_8K is due to the weak interband transition at ~25 eV as shown in Fig. 2. Such a transition is not observable in pristine graphite with the same momentum transfer of 0.13 Å^{-1}. However, a similar but slightly upshifted double-peak feature was found[23] in the energy-loss spectrum of graphite with a large momentum transfer of 0.85 Å^{-1}. [The distance between Γ and K (or P) points in the Brillouin zone of graphite is 1.7 Å^{-1}.] The splitting is associated with an unassigned weak interband transition at ~29 eV.[23] Although the origins of those transitions are not known, it appears that the 25-eV transition in C_8K originates from the same bands that are responsible for the 29-eV nonvertical transition in graphite which becomes an allowed vertical transition as a result of zone folding. The splitting of this plasmon peak cannot be explained as the result of Bragg scattering[24] since it is observed with a momentum transfer much less than the Brillouin-zone dimension.

In addition to zone folding, the electronic bands in graphite would shift and split in C_8K because of the change of the symmetry and the crystal forces along c axis. Thus, the spectra of C_8K become broader and contain more allowed interband transitions. Exact band-structure calculations are required to predict the amounts of band splitting and shifting.

The calculation of INK[6] shows that the most significant interband optical transition in C_8K oc-

curs at the zone center Γ with a transition energy of 3.2 eV. This transition is derived from the 4.5-eV $M_3^+ \rightarrow M_4^- \pi$ electron transition in graphite with an energy shift of 1.3 eV. We observed the corresponding transition at 3.8 eV. The observed energy shift of 0.7 eV is only half of that calculated by INK[6]. The preliminary but more rigorous calculation of DiVencenzo *et al.*[7] indicates that the 4.5-eV transition in graphite will be split and lowered in energy to about 4 eV in C_8K which agrees well with our observed data. In a previous optical transmission measurement[25] (from 0.55 to 6 eV) on C_8Cs the absorption maximum in C_8Cs was found to be ~0.5 eV downshifted from the corresponding peak of graphite at ~4.7 eV. Since C_8Cs and C_8K have the same in-plane structure and identical reflectivity spectra[3,11] (from 0.5 to 2.85 eV), their electronic band structures should be similar. The above facts indicate that INK[6] did not predict the correct interband transition energy, and therefore their calculated Fermi surfaces are somewhat doubtful.

The 2.5-eV peak in the loss function of C_8K can be interpreted mainly as a collective oscillation due to the free carriers donated by the potassium atoms. The position of this plasmon peak is consistent with the optical reflectivity measurement[3,11] (from 0.6 to 2.85 eV) which shows a reflectivity minimum at 2.6 eV. The optical transmission[25] of C_8Cs also shows an absorption minimum at 2.7 eV.

Finally, we note that the difference of the overall intensities of $\mathrm{Im}[\epsilon(\omega)]$ of graphite and C_8K in Fig. 2 is mainly due to the difference of carbon densities in graphite and C_8K. We have calculated $n_{\mathrm{eff}}(\omega)$, the effective number of electrons per carbon atom (or per $CK_{1/8}$ unit) participating in transitions up to $\hbar\omega$,[12] for both graphite and C_8K from the corresponding $\mathrm{Im}[\epsilon(\omega)]$, and have plotted the results in the inset of Fig. 2. The result for graphite is consistent with the published data.[12] The $n_{\mathrm{eff}}(\omega)$ of C_8K is comparable to that of graphite within the experimental error. (The absolute intensity of dielectric functions derived from electron-energy-loss spectra is reliable to 15%.[12]) The intercalated potassium atoms are expected to contribute 0.125 to the $n_{\mathrm{eff}}(\omega)$ of C_8K for $\hbar\omega$ exceeding a few eV.[26] Otherwise, both $n_{\mathrm{eff}}(\omega)$ should be similar.

We conclude that the two-dimensional rigid-band model together with the zone-folding scheme can qualitatively describe the band structures of C_8K in considering the interband transitions. The shifts and splittings of the interband transition energies are of the order of 10%. We find that the band-structure calculation of DiVencenzo *et al.*[7] yields a value for the $M_3^+ \rightarrow M_4^-$ interband transition energy which is in agreement with our observation.

We would like to thank Mr. L. Mlinarski for designing the intercalation chamber and Professor A. V. Crewe for the use of the laboratory. This work was supported by the National Science Foundation Materials Research Laboratory of the University of Chicago.

---

[a] On leave from the Department of Physics, Tsing-Hua University, Hsinchu, Taiwan, Republic of China.
[b] Present address: School of Applied and Engineering Physics, Cornell University, Ithaca, N. Y. 14853.
[c] Present address: Department of Physics, Michigan State University, East Lansing, Mich. 48824.

[1] A. D. Yoffe, Chem. Soc. Rev. 5, 51 (1976).
[2] L. B. Ebert, Annu. Rev. Mater. Sci. 6, 181 (1976).
[3] J. E. Fischer and T. E. Thompson, Mater. Sci. Eng. 31, 211 (1977).
[4] J. E. Fischer and T. E. Thompson, Phys. Today 31, No. 7, 36 (1978), and references therein.
[5] R. Swanson, Ph.D. thesis, Stanford University, 1969 (unpublished).
[6] T. Inoshita, K. Nakao, and H. Kamimura, J. Phys. Soc. Jpn. 43, 1237 (1977), and 45, 689 (1978).
[7] D. DiVincenzo, N. A. W. Holzwarth, S. Rabii, and P. Seven, Bull. Am. Phys. Soc. 24, 409 (1979), and private communications.
[8] N. A. W. Holzwarth and S. Rabii, Mater. Sci. Eng. 31, 195 (1977); L. A. Girifalco and N. A. W. Holzwarth, Mater. Sci. Eng. 31, 201 (1977).
[9] N. A. W. Holtzwarth, S. Rabii, and L. A. Girifalco, Phys. Rev. B 18, 5190 (1978); N. A. W. Holtzwarth, L. A. Girifalco, and S. Rabii, Phys. Rev. B 18, 5206 (1978).
[10] M. S. Dresselhaus, G. Dresselhaus, and J. E. Fischer, Phys. Rev. B 15, 3180 (1977).
[11] D. Guerard, G. M. T. Foley, M. Zanini, and J. E. Fischer, Nuovo Cimento 38B, 410 (1977), and references therein.
[12] J. Daniels, C. V. Festenberg, H. Raether, and K. Zeppenfeld, in *Springer Tracts in Modern Physics*, edited by G. Höhler (Springer, Berlin, 1970), Vol. 54, p. 77.
[13] J. J. Ritsko and M. J. Rice, Phys. Rev. Lett. 42, 666 (1979), and Bull. Am. Phys. Soc. 24, 409 (1979).
[14] G. L. Price and J. A. Venables, Surf. Sci. 49, 264 (1979).
[15] A. V. Crewe, M. Isaacson, and D. E. Johnson, Rev. Sci. Instrum. 40, 241 (1971).
[16] In the electron micrographs of the graphite single-crystal samples, many defect structures were observed. Upon intercalation, those structures become more pronounced, presumably as a result of the accumulation of

potassium atoms in the defects.

[17]D. D. L. Chung, G. Dresselhaus, and M. S. Dresselhaus, Mater. Sci. Eng. 31, 107 (1977).

[18]H. Venghaus, Phys. Status Solidi (b) 71, 609 (1975).

[19]F. Bassani and G. P. Parravicini, Nuovo Cimento 50B, 95 (1967).

[20]G. S. Painter and D. E. Ellis, Phys. Rev. B 1, 4747 (1970).

[21]M. Tsukada, K. Nakao, Y. Uemura, and S. Nagai, J. Phys. Soc. Jpn. 32, 54 (1972).

[22]H. Nagayoshi, M. Tsukada, K. Nakao, and Y. Uemura, J. Phys. Soc. Jpn. 35, 396 (1973).

[23]K. Zeppenfeld, Z. Phys. 243, 229 (1971).

[24]R. Girlanda, M. Parrinello, and E. Tosatti, Phys. Rev. Lett. 36, 1386 (1976).

[25]G. R. Hennig, J. Chem. Phys. 43, 1201 (1965).

[26]There is a substantial body of evidence indicating that the charge transfer in C_8K is about 50%. However, all the potassium 4*s* electrons, no matter whether they are transferred to the carbon layers or remain in the potassium layers, are free electrons and contribute to $n_{\mathrm{eff}}(\omega)$.