Phonons in the Graphite-Potassium Intercalation Compound $C_{36}K$

A. Magerl[a]
National Measurement Laboratory, National Bureau of Standards, Washington, D. C. 20234, and University of Maryland, College Park, Maryland 20742

and

H. Zabel
Loomis Laboratory of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 21 November 1980)

An inelastic-neutron-scattering study of the [001] L phonons in $C_{36}K$ shows, for the first time, zone-folding effects along with frequency gaps between acoustic and optic modes. Phonon dispersion and structure factors can be modeled by a linear chain with two different masses and two force constants: $\varphi_1 = 3450$ dyn/cm for the coupling of graphite and potassium planes, and $\varphi_2 = 2850$ dyn/cm for the coupling between two adjacent graphite planes.

PACS numbers: 63.20.Dj, 61.12.Fy, 61.60.+m

In recent years, graphite intercalation compounds have attracted much research interest because of their unique properties as a test ground for fundamental studies of electronic properties,[1] dynamics,[2] and of phase transitions[3] in quasi-two-dimensional systems. In particular, our understanding of lattice dynamics has benefitted from detailed infrared and Raman spectroscopy studies of graphite-alkali-metal and graphite-molecular compounds[4-7] by Dresselhaus, Solin, and coworkers. However, these studies are restricted to infrared or Raman-active modes and provide information only on $q = 0$ phonons. Except for early work by Ellenson *et al.*,[8] a rigorous study of the phonon dispersion in graphite intercalation compounds by means of inelastic neutron scattering has been unavailable for two reasons: first, the lack of large single crystals (which also restricted the pure graphite study by Nicklow, Wakabayashi, and Smith[9] to some particular modes); and second, the achievement of satisfactory homogeneity of large samples required for inelastic neutron scattering.

In the following we report on a neutron spectroscopic study of the [001] L phonon branches in stage-3 $C_{36}K$. In this compound every third graphite plane is followed by a potassium layer in the ordered sequence along the hexagonal c axis: *A/ABA/ACA/A* (capital letters refer to graphite planes, solidi refer to potassium planes). The [001] L modes are characterized by the vibration of graphite and potassium planes along the [001] direction, while the intraplanar distances of the atoms are not changed. Since these phonons are not sensitive to any stacking along the c axis, stacking will be neglected in the following.

The measurements show, for the first time, zone-folding effects along with the opening of frequency gaps for [001] L phonons at the center and at the boundary of the Brillouin zone (BZ), to be described below.

We used pyrolytic graphite with a c-axis mosaic spread of ~6°. The sample had a volume of about 50 cm^3 and was intercalated with potassium in a two-stage furnace in the usual manner.[10] The stage and the homogeneity of the compound were determined by an elastic neutron (00l) scan, shown in Fig. 1. From the position of the Bragg reflections and the absence of diffuse scattering between the (00l) reflections, we conclude that the bulk sample is a pure stage-3 compound, with a c-axis repeat distance of 12.07 Å, in good agreement with the literature.[10] The (00l) scan was repeated several times during the inelastic-scattering study to ensure stability of the sample composition.

The sample was mounted with its c axis in the scattering plane. A cryostat allowed temperature

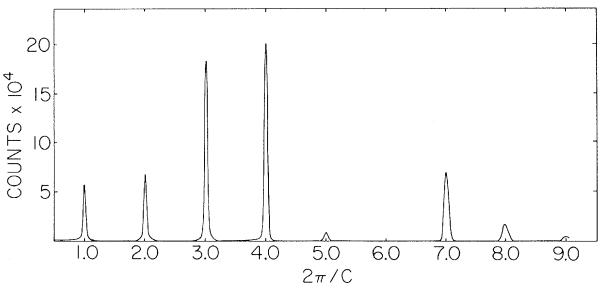

FIG. 1. Elastic (00l) scan, measured at 300 K.

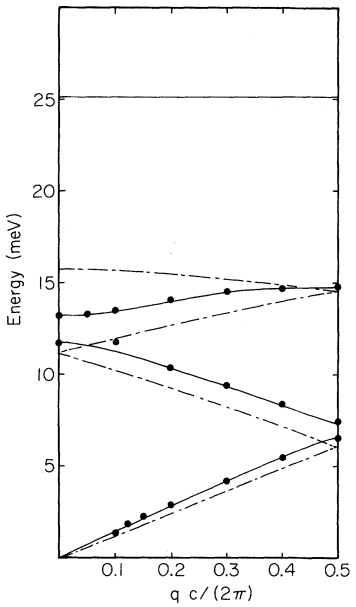

FIG. 2. Dots represent measured phonon energies for [001] L modes in $C_{36}K$ at 300 K. The phonon dispersion as calculated by a linear chain is given by full lines. The dash-dotted lines show the phonon energies in pure graphite (Refs. 9 and 12). For details, see text.

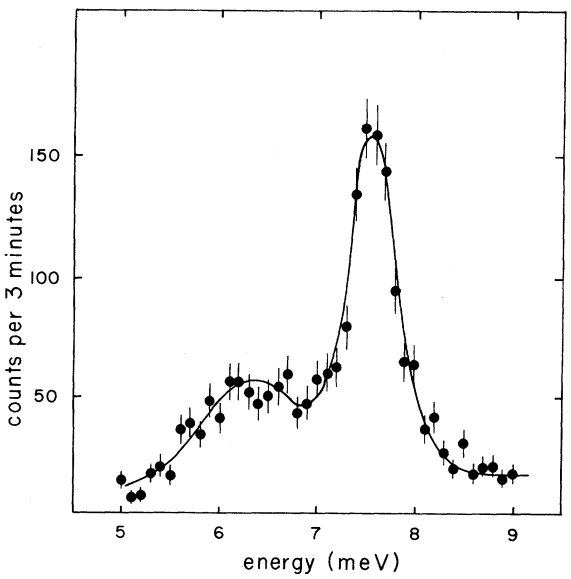

FIG. 3. Zone-boundary phonons, measured at $Q = (0, 0, 4.5)$. Incident energy for this scan was 14.7 meV. The collimations from reactor to detector were 30′-12′-24′-40′.

scans between 78 and 300 K, although the majority of the spectra were taken at room temperature. Constant-Q scans[11] were performed with use of triple-axis spectrometers at the National Bureau of Standards reactor with fixed incident energies between 14 and 15 meV. The measured phonon energies are shown in Fig. 2 in the BZ of $C_{36}K$ (dots). For comparison, the corresponding phonon dispersion of pure graphite[9,12] is also given by dash-dotted lines. Here, we assume—in analogy to $C_{36}K$—a repeat distance of four (identical) graphite planes. The artificial extension of the graphite c-axis lattice constant causes a backfolding of the [001] L phonon dispersion with four branches in its smaller BZ. Note that three of them have vanishing structure factors.

The salient features of Fig. 2 are as follows: (1) Phonon spectra for the acoustical and two optical branches could be observed—it was not possible to measure an inelastic signal for the third optical branch; (2) a mode splitting at the center and boundary of the BZ could be measured directly—in Fig. 3 a neutron group showing the energy splitting at the zone boundary is reproduced; (3) for the three branches observed in $C_{36}K$, the phonons have up to 20% higher energies than the corresponding energies in pure graphite[9,12]; and (4) an examination of the temperature dependence showed that the lower part of the acoustical branch decreases by about 10% between 300 and 78 K.

A linear chain as shown in Fig. 4 provides an adequate description for the [001] L phonons. Two different masses represent the graphite and alkali metal planes: $M_1 = 3.25$ amu for potassium and $M_2 = 12$ amu for carbon accounts for the correct areal mass densities in the planes. In the model, we assumed only nearest-neighbor harmonic interaction with force constants, φ_1 and φ_2 for the C-K and C-C bonds, respectively, representing the interplanar coupling constants.

Using only the two measured phonon energies at $q = 0$, we calculated $\varphi_1 = 3450 \pm 80$ dyn/cm and $\varphi_2 = 2850 \pm 80$ dyn/cm. Within the error bars, φ_2 is the same as measured for pure graphite,[9,12] demonstrating only minor influence of the inter-

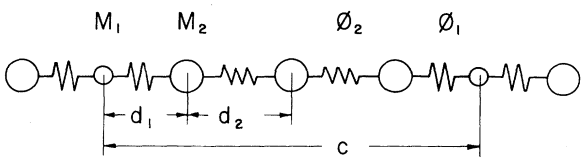

FIG. 4. Linear chain model for (001) L phonons in $C_{36}K$. $a_1 = 2.68$ Å and $a_2 = 3.35$ Å are the distances between C-K planes and C-C planes, respectively. $c = 12.07$ Å is the repeat distance in $C_{36}K$, disregarding any stacking.

calated layer beyond the direct neighbor planes. φ_1 is about 20% larger than φ_2. This agrees well with a change for φ_2 of 19% with respect to φ_1 from compressibility measurements[13] on stage-1 C_8K (corrected for the same number of atoms in the planes as in stage 3).

Using the above values for φ_1 and φ_2, we calculated the phonon dispersion and the neutron inelastic structure factors. The Debye-Waller factor was not taken into account. The scattering lengths used were 0.37×10^{-12} cm for potassium and 0.66×10^{-12} cm for carbon.

The calculated phonon dispersion, as shown by full lines in Fig. 2, agrees very well with the measured phonon energies and reproduces the energy gap at the BZ boundary very well. The model also predicts a third, almost dispersion-free optical branch at 25 meV separated from the second optical branch by an energy gap of about 10 meV. The displacement pattern associated with this branch is characterized by a large and predominate amplitude of the light potassium planes. Nevertheless, their structure factor is very weak, mainly because of the smaller in-plane concentration and lower coherent scattering length of potassium as compared with carbon. Even for a favorable wave-vector transfer, the structure factor of the third optical branch is reduced by a factor of 40, compared to the structure factor for the lower-energy peak in Fig. 3 and, therefore, could not be measured.

We wish to point out that the observed intensity variation of equivalent phonon groups measured around different reciprocal-lattice points always followed the calculated structure factors. Within the model the intensity ratio of the two phonons in Fig. 3 can also be explained. Fitting the spectrum with two Gaussians and taking into account the instrumental resolution, we find an intensity ratio of 2.5:1, compared to a ratio of 2.8:1, predicted by our model.

In conclusion, we have measured the [001] L phonon energies in $C_{36}K$. A linear-chain model with two different masses and only harmonic nearest-neighbor interactions reproduces the observed acoustical and optical branches, including the energy gaps at the BZ center and boundary, as well as the structure factors for the phonon groups.

We acknowledge valuable discussion with J. M. Rowe, J. J. Rush, S. C. Moss, and S. A. Solin. This work was supported in part by the U. S. Department of Energy under Contract No. DE-AC02-76ER01198. One author (A.M.) acknowledges support from the Deutsche Forschungsgemeinschaft.

[a]Present address: Institute Laue-Langevin, 156X, F-38042 Grenoble, France.

[1]J. E. Fischer, Physica (Utrecht) 99B, 383 (1980).

[2]C. Horie, M. Maeda, and Y. Kuramoto, Physica (Utrecht) 99B, 430 (1980).

[3]See, i.e., contributions from H. Zabel, in *Proceedings of the International Conference on Ordering in Two Dimensions, Lake Geneva, Wisconsin, 1980*, edited by S. K. Sinha (North-Holland, New York, 1980), and references therein; R. Clarke, *ibid.*, and references therein.

[4]M. S. Dresselhaus and G. Dresselhaus, in *Intercalated Layered Materials*, edited by F. Levy (Reidel, Higham, Mass., 1979).

[5]P. C. Eklund, G. Dresselhaus, M. S. Dresselhaus, and J. E. Fischer, Phys. Rev. B 21, 4705 (1980).

[6]S. A. Solin, Physica 99B, 443 (1980).

[7]N. Caswell and S. A. Solin, Phys. Rev. B 20, 2551 (1979).

[8]W. D. Ellenson, D. Semmingsen, D. Guérard, D. G. Onn, and J. E. Fischer, Mater. Sci. Eng. 31, 137 (1977).

[9]R. Nicklow, N. Wakabayashi, and H. G. Smith, Phys. Rev. B 5, 4951 (1972).

[10]D. E. Nixon and G. S. Parry, J. Phys. D 1, 291 (1968).

[11]B. N. Brockhouse, *Instrumentation for Neutron Inelastic Scattering Research* (International Atomic Energy Agency, Vienna, 1961), p. 113.

[12]G. Dolling and B. N. Brockhouse, Phys. Rev. 128, 1120 (1962).

[13]N. Wada, R. Clarke, and S. A. Solin, Solid State Commun. 35, 675 (1980).