Inelastic Neutron Scattering Study of the External Vibrations in Single Crystal C_{60}

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(Received 4 August 1992)

The external vibrations in solid C_{60} were studied by means of inelastic neutron scattering. The translational spectrum extends to 6 meV at room temperature and hardens by 5% on cooling below T_s. Narrow librational excitations were observed up to temperatures very close to T_s at energies around 2.4, 3.6, and 4.6 meV. Calculations based on a van der Waals potential give about the correct frequency range for the translations, but frequencies considerably too low for the librations. Bond-charge models give better results only for an unrealistic choice of parameters.

PACS numbers: 63.20.Dj, 61.12.Ex

Over the past year several inelastic neutron scattering studies of C_{60} have contributed significantly to the understanding of the intramolecular vibrational modes [1-5] as well as of the rotational dynamics above and below the transition to the low-temperature ordered phase [6-8]. In addition, two groups [3,5] reported the observation of lattice modes at surprisingly high frequencies, i.e., between 10 and 18 meV. However, this observation is highly questionable in view of an analysis of specific-heat data [9] which indicate a much lower frequency of the external modes. Our inelastic neutron scattering data on a polycrystalline sample [8] gave a range of up to 6 meV for the external modes, but it was difficult to decompose the total spectrum into the translational and the librational part. After we succeeded in growing C_{60} single crystals of a few mm^3, we have been able to measure the dispersion of several phonon branches as well of some librational ones and thus to get very detailed information on the intermolecular forces. In particular, we have found that the librational spectrum does not consist only of the well-known band around 2.4 meV, but contains two further bands around 3.6 and 4.6 meV.

The single crystals were grown by a sublimation technique [10]. The specimens used for the measurements had volumes of 2 and 3 mm^3, respectively. They had shiny faces, indicating a high degree of crystal perfection. The mosaic distribution was found to be less than 0.3°. However, both crystals showed some degree of twinning: The additional domains differ from the bulk of the sample by a 60° rotation around a 111 axis. From investigations on a four-circle diffractometer [11] we conclude that the total volume of the misoriented domains was about 10%. A part of the measurements was done on the 3-mm^3 crystal and the remainder on a composite sample using both crystals.

The single-crystal measurements were carried out on the 2T triple-axis spectrometer located at the ORPHEE reactor at Saclay. Horizontally and vertically focusing pyrolitic graphite crystals were used as monochromator and analyzer to maximize the intensity. In contrast to what is often expected, the gain in intensity by horizontal focusing is not accompanied by an appreciable loss in q resolution, as is evidenced from the narrow width of a constant-E scan through a transverse acoustic branch [Fig. 1(a)]. Figure 1 further shows that counting times were not exceedingly long in spite of the small size of the sample.

The phonon density of states was measured on a time-of-flight spectrometer located at the SILOE reactor at Grenoble. The sample mass was about 1 g. Special care was taken to avoid contamination of the sample with hydrogen. The spectra were corrected for background and multiphonon contributions.

At room temperature, C_{60} crystallizes in an fcc lattice. The fact that C_{60} is a molecular solid with sixty atoms in the unit cell is reflected in a strong Q dependence of the elastic or inelastic structure factors. For the elastic case, this Q dependence can be very well described by that of a hollow sphere [12]. We found that this description holds equally well for the inelastic case. The Q dependence of

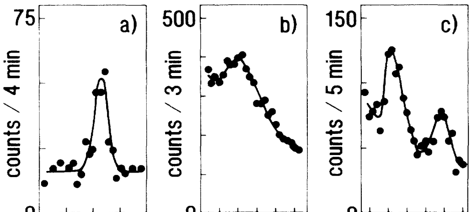

FIG. 1. Examples of inelastic neutron scattering peaks: (a) Constant-E scan through a transverse acoustic branch; sample volume $V_s = 2$ mm, final energy $E_f = 11.4$ meV, $T = 295$ K. (b) Constant-Q scan at $\mathbf{Q} = (13,0,0)$ showing a librational peak; $V_s = 5$ mm^3, $E_f = 22$ meV, $T = 200$ K. (c) Constant-Q scan at $\mathbf{Q} = (5,4,4)$ showing two librational peaks; $V_s = 3$ mm^3, $E_f = 13.4$ meV, $T = 200$ K.

the structure factor shows a series of maxima with deep minima in between which reduces the number of Brillouin zones to be used for the measurements. Furthermore, as the height of the maxima decreases sharply with increasing Q, measurements have to be restricted to small Q, which, however, is unfavorable because of the factor Q^2 in the inelastic neutron scattering cross section. Consequently, intensities are inevitably low for the translational modes, which can be easily understood by the fact that they make up only 3 out of 180 degrees of freedom.

Below T_s, the C_{60} lattice is simple cubic $Pa3$ with four molecules in the unit cell. However, there is strong evidence that there is rotational disorder also well below T_s. Different models were used to calculate inelastic structure factors for the low-temperature phase. The most sophisticated one was based on the structure proposed by David *et al.* [13], i.e., assuming two inequivalent orientations for each molecule with an occupation probability of 65% and 35% at $T=200$ K. For small Q, the calculated structure factors were similar to those of the disordered fcc phase. For large Q, no systematic Q dependence was found for the translations, whereas the sum of the structure factors for the librational bands follows closely that of free rotations. We found that no model could reliably predict inelastic structure factors for individual modes, so that we had to rely on general trends and on results depending on the symmetry only. As a consequence, assignments were not unambiguous in some cases where librational and translational frequencies were close to each other. In these cases, the assignment may be further complicated by some mixing between librational and translational degrees of freedom.

The experimental results for the translational modes are depicted in Fig. 2. Apparently, the dispersion does not change very much upon cooling below T_s, apart from a general hardening by about 5%. Lines are the result of a fit based on a two-parameter force-constant model with only longitudinal force constants for the first and second nearest neighbors (NNs). A fit of similar quality can be obtained by assuming tensor forces between first NNs only, which, however, requires three fit parameters. For the calculations we assumed an fcc structure also for the low-temperature phase, thereby ignoring the lifting of degeneracies produced by the loss of symmetry. The good agreement between model and experiment indicates that this assumption is reasonable for the translational vibrations.

The general shape of the dispersion curves is similar to that found for the solid noble gases [14], which is not astonishing in view of the spherical shape of the C_{60} molecule and a similar type of bonding, i.e., mainly of the van der Waals (vdW) type. However, a closer look reveals that the force field in C_{60} is not quite so simple: The fit requires either a relatively large second NN force constant (9% or 13% of the value of the first NN force constant at 295 and 200 K, respectively) or first NN tensor forces which indicate a relatively strong deviation from axial symmetry for the intermolecular interactions. This can be traced back to a ratio of the frequencies of the transverse acoustic modes at (1,0,0) and (0.5,0.5,0.5), which is only 1.2 for C_{60} at 200 K, whereas a model with longitudinal first NN forces only gives a value of $\sqrt{2}$.

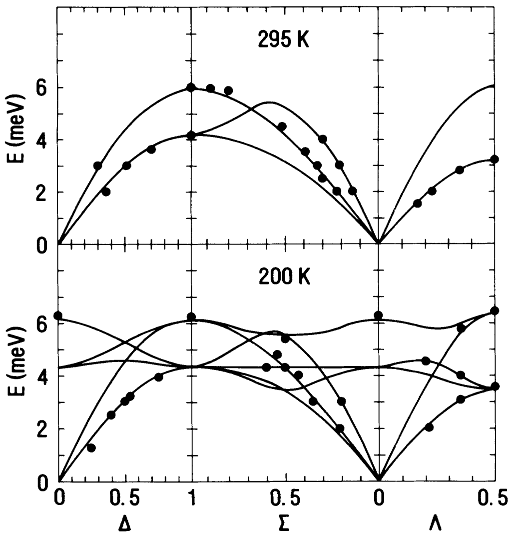

FIG. 2. Dispersion of translational modes above and below T_s. Lines are the result of a fit with a two-parameter force-constant model. The results for 200 K are shown in an extended zone scheme corresponding to an fcc lattice.

From powder measurements it was known that there are librations in a narrow frequency band around 2.4 meV [7,8]. From the intensity of this peak relative to the total spectrum we conjectured that this band contains only 1 degree of freedom. Therefore we made a systematic search for librations at higher energies and found further excitations around 3.6 and 4.6 meV. From model calculations we learned that the twelve librational branches cannot necessarily be grouped in just three bands, except for the high-symmetry points (0.5,0.5,0) and (0.5,0.5,0.5), where all modes are fourfold degenerate. Thus we focused our effort on the determination of all three librational frequencies at (0.5,0.5,0) and (0.5,0.5,0.5) to get a basis for outlining the librational spectrum. The experimental results are summarized in Fig. 3.

Figure 4 shows a comparison of the phonon density of states (PDOS) calculated from the single-crystal data to that directly determined on a powder sample. In default of a reliable model for the librations we assumed these modes to lie in a narrow band around 2.4 meV and two broad bands around 3.6 and 4.6 meV. The widths chosen reflect the range of observed librational frequencies. The calculated and the experimental DOS agree very well in respect to peak positions and to the cutoff. The main disagreement lies in the fact that the experimental spectrum does not show a real gap between the cutoff at 6

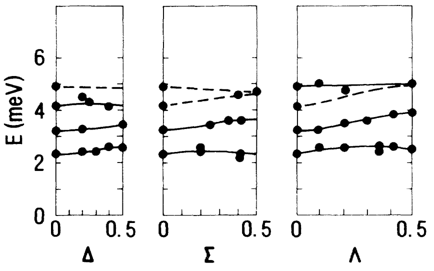

FIG. 3. Dispersion of librational modes observed at $T = 200$ K. Lines are only a guide to the eye.

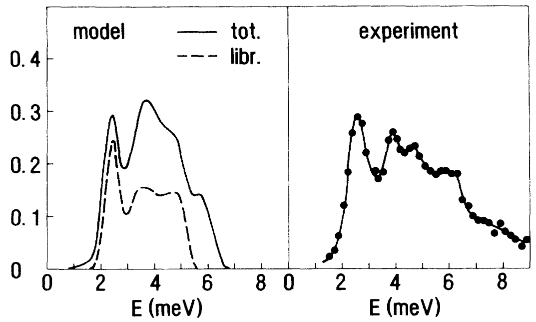

FIG. 4. Comparison of the calculated and experimental PDOS for $T = 200$ K. The experimental PDOS has been normalized for $0 \leq E \leq 6.5$ meV. The calculated PDOS was folded with the experimental resolution.

meV and the internal modes at $E \gtrsim 30$ meV. We suspect that this is due to impurities. This point will be discussed in detail in a separate publication.

We calculated the low-temperature specific heat from our spectrum and compared it to the data of Beyermann *et al.* [9]. There is good agreement, as could be expected from the similarity of the spectra proposed by Beyermann *et al.* [9] to that shown in Fig. 4. Minor deviations may be due to sample imperfections as the calculated specific heat is in nearly perfect agreement up to 20 K with recent data taken by Ahrens *et al.* [15].

Neumann *et al.* [7] reported that the librations show a strong broadening on approaching the phase transition: They give a width of 1.5 meV at 200 K and even 2.3 meV at 240 K. Our measurements do not confirm this broadening: As can be seen from Fig. 5, the width of the librational peak observed at (5,4,4) was found to be resolution limited up to $T = 230$ K. Even at 245 K the broadening is moderate with an intrinsic width of no more than 0.4 meV (FWHM). Powder data may be misleading as the librations do *not* fall in one single narrow band.

The observation of sharp librations close to T_s allows us to draw two conclusions: (i) As the pronounced rotational disorder already present below T_s does not lead to a significant line broadening, the bonding must be very similar for the different orientations of the molecule, and (ii) the rotational ordering transition seems to be strongly first order.

Lattice dynamical calculations of the phonon dispersion relations may be carried out in the rigid molecule approximation since the lowest internal vibration energy of 30 meV is well above that of the external ones. A model based on vdW interactions between atoms of neighboring molecules may be expected to be reasonable since the closest intermolecular carbon-carbon separation of 3 Å is large compared to the usual covalent-bond separation of 1.4 Å. Indeed, vdW models based on the various available values [16,17] of the potential parameters give translational phonon frequencies which are close to those observed and reproduce the experimental lattice constant within 1%. However, these models yield forces which correspond to just a longitudinal first NN spring constant, whereas experiment showed the need for a second NN spring constant or tensor forces. What is more, the vdW models produce librational frequencies which are only about 40% of those found in experiment. Attempts have been made to improve the vdW models by considering the nonspherical character of the charge distribution around the carbon atoms. Sprik, Cheng, and Klein [18] have put a negative charge on the double carbon-carbon bond and the compensating positive charge on the atom itself, whereas Lu, Li, and Martin [19] have put the compensating charge on the single bond. In addition, Sprik, Chen, and Klein [18] postulate a vdW interaction between bond centers. While such models produce an absolute potential minimum for the observed structure and predict higher librational frequencies than simple vdW models, these are still too low by 30% or more. We tried bond-charge models with various charge distributions and

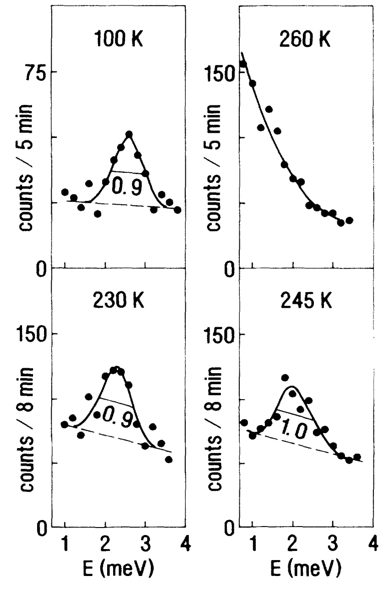

FIG. 5. Results of constant-Q scans at $\mathbf{Q} = (5,4,4)$ taken at different temperatures. The instrumental resolution is about 0.8 meV.

found the best agreement with experiment for a model similar to that proposed by Lu, Li, and Martin [19], but with much larger charges, that is, about $-1e$ on the double bond and $+0.5e$ on the single bond. However, we think that such a model is highly unplausible. A realistic model should have negative, albeit different, charges on all the bonds with the compensating positive charge on the atom itself. Such models produce contributions to the total potential which are much too small even for large values of the bond charges, i.e., $-1e$ and $-2e$ for the single and the double bond, respectively. Therefore, we do not think that the models so far considered can explain the high librational frequencies observed in experiment. Probably, chemical bonding based on hopping [20] is essential to understand the intermolecular forces.

In summary, we have presented the first detailed inelastic neutron scattering data for the external vibrations in solid C_{60}. At $T=200$ K, well-defined librational modes were found up to $E=5$ meV. Neither the translational nor the librational modes can be satisfactorily described by current models of the intermolecular potential. Attempts to improve the agreement with experiment led to unphysical values of the parameters.

S.L.C. thanks the Alexander von Humboldt Foundation for the award of a research fellowship. M.H. and H.K. thank the BfWF, A, for financial support under Project No. 45212.

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[1] R. L. Capelletti *et al.*, Phys. Rev. Lett. **66**, 3261 (1991).
[2] D. S. Bethune *et al.*, Chem. Phys. Lett. **179**, 181 (1991).
[3] C. Coulombeau *et al.*, J. Phys. Chem. **96**, 22 (1992).
[4] K. Prassides *et al.*, Nature (London) **354**, 462 (1991).
[5] K. Prassides *et al.*, Chem. Phys. Lett. **187**, 455 (1991).
[6] D. A. Neumann *et al.*, Phys. Rev. Lett. **67**, 3808 (1991).
[7] D. A. Neumann *et al.*, J. Chem. Phys. **96**, 8631 (1992).
[8] B. Renker, F. Gompf, and A. Heiming, Verh. Dtsch. Phys. Ges. **27**, 970 (1992).
[9] W. P. Beyermann *et al.*, Phys. Rev. Lett. **68**, 2046 (1992).
[10] M. Haluska, P. Rogl, and H. Kuzmany (to be published).
[11] W. Paulus and G. Roth (private communication).
[12] P. A. Heiney *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).
[13] W. I. F. David *et al.*, Europhys. Lett. **18**, 219 (1992).
[14] For a review, see H. Bilz and W. Kress, in *Phonon Dispersion Relations in Insulators*, Solid State Sciences Vol. 10 edited by M. Cardona, P. Fulde, and H. J. Queisser (Springer, Berlin, 1979).
[15] R. Ahrens (private communication).
[16] A. Cheng and M. C. Klein, Phys. Rev. B **45**, 1889 (1992).
[17] A. I. Kitaigorodski, J. Chem. Phys. **63**, 9 (1966).
[18] M. Sprik, A. Cheng, and M. C. Klein, J. Phys. Chem. **96**, 2027 (1992).
[19] J. P. Lu, X. P. Li, and R. M. Martin, Phys. Rev. Lett. **68**, 1551 (1992).
[20] O. Gunnarsson *et al.*, Phys. Rev. Lett. **67**, 3002 (1991).