RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 12 15 SEPTEMBER 1995-II

Brillouin-scattering determination of the elastic constants of epitaxial fcc C_{60} film

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(Received 25 July 1995)

Brillouin-light-scattering measurements have been performed on a (111) fcc film of C_{60} (fullerite) epitaxially grown on Ni(110). The Rayleigh surface wave has been detected for propagation along several directions on the film surface and shows an anisotropic behavior consistent with the (111) texture of the film. Bulk acoustic modes have also been measured. The Brillouin data allow the determination of the three independent elastic constants of fcc C_{60}. The breakdown of the Cauchy condition indicates intermolecular interactions of noncentral character.

The long-wavelength dynamical properties of fcc C_{60} (fullerite) have not been completely studied yet, despite the great interest in this material. Neutron scattering measurements[1] have provided a fairly detailed knowledge of the phonon dispersion curves of fcc and simple cubic (sc) C_{60} over the whole Brillouin zone. However, it is well known that extrapolation of the phonon curves to the small wave-vector region can lead to large errors in the determination of their slopes, i.e., of the elastic constants of solids.

So far the investigation of the elastic moduli of fcc C_{60} single crystal has been limited to measurements of the bulk modulus of small samples under the application of hydrostatic pressure[2–4] or using the piston and cylinder technique.[5] The determination of the whole set of elastic constants of fullerite is obviously out of the reach of these methods. The diamond anvil cell technique has been also applied to polycrystalline samples.[6] The propagation of surface acoustic waves (SAW's) in disordered fullerite films has been investigated by acoustic techniques[7] to measure the dispersion curves of the SAW's below 250 MHz. The density and the elastic constants of the film material have been determined by fitting the data with a suitable model. The longitudinal and transverse sound velocities in compacted polycrystalline bulk samples of fullerite have also been measured.[8] Unfortunately, the results of all these measurements are rather different. For example, the values of the bulk modulus are scattered in the range 6–18 GPa.

A technique that has been used in the last decade for the elastic characterization of opaque and transparent supported films is surface Brillouin scattering (SBS).[9] It has many advantages over the above-mentioned techniques because it does not require the external excitation of acoustic modes and because it probes materials in thermal equilibrium condition. In addition, under favorable circumstances, SBS allows the complete determination of all the elastic constants of crystalline films.[10] A previous attempt to study the elastic properties of C_{60} single crystals by Brillouin scattering[11] has shown that the material undergoes a transformation under laser irradiation in the presence of oxygen, so that the measured acoustic properties were different from those of solid C_{60} and similar to those of slow polymers or high porous materials. On the other hand, no surface Brillouin peak was observed from the C_{60} crystals, even when the specimens were kept in vacuum or in inert atmosphere.

In this paper we show that the SBS technique can actually be used to detect surface and bulk acoustic waves and therefore to measure the three independent elastic constants of a thick supported fcc fullerite film. The ordered C_{60} film was grown on a Ni(110) substrate in an ultrahigh vacuum system with a base pressure of 10^{-10} mbar. The Ni sample was cleaned by cycles of Ne^+ ion sputtering and annealing at 900 K followed by baking to 870 K in O_2 and H_2 at 10^{-8} mbar. Sample cleanliness and surface order were checked by Auger electron spectroscopy and low-energy electron diffraction (LEED). 99% pure C_{60}, obtained by Texas Fullerenes, was sublimated from a Ta crucible at 700 K onto the Ni(110) substrate. The first C_{60} monolayer was dosed with the substrate at 650 K to form a well-ordered quasihexagonal and close-packed phase.[12] The long-range order of the first layer was checked by LEED. The nearest-neighbor distance in the first monolayer differs by less than 2% from that of bulk C_{60}. The other C_{60} layers were sublimated with the substrate kept at 400 K. At this temperature C_{60} grows epitaxially layer by layer along [111] on well-ordered close-packed C_{60} monolayers[13,14] and the LEED shows a well-defined hexagonal pattern with low background. An ellipsometric investigation on the sample gave the following complex dielectric constant at 2.41 eV: $\epsilon=5.23+2.1i$. This value is slightly different from that recently measured for C_{60} single crystal;[15] in particular, the refractive index is lower and the optical absorption is higher than in the single crystal. The film thickness measured from fringes below the absorption edge turned out to be about 1.5 μm.

The sample has been taken out of the vacuum chamber and kept in atmosphere for subsequent measurements, without observing any appreciable modification. The overall crystalline quality of the film has been tested by x-ray measurements. Coupled $\omega-2\theta$ scans allowed us to identify the crystallographic structure of the sample as that of a fcc crystal grown with the [111] direction normal to the surface of the substrate. The measured lattice parameter was 14.16 ± 0.02 Å, corresponding to a density $\rho=1694\pm7$ kg/m^3. Rocking curves for the (111) and (333) reflections exhibited a full width at half maximum of about 2°, compatible with a single crystal with a small amount of residual stresses, defects, and/or mosaic spread of the same order of magnitude.

Brillouin spectra were taken at room temperature, using a p-polarized light beam from an Ar^+ laser, operating on a single mode of the 514.5-nm line. The incident light was focused onto the surface of the specimen and the backscattered light collected by means of a lens with f number 2 and focal length 50 mm. The frequency analysis was performed using a Sandercock-type, 3+3 pass, tandem Fabry-Pérot interferometer,[9] characterized by a finesse of about 100 and a contrast ratio higher than 5×10^{10}. To avoid the photoinduced reaction effects in the presence of oxygen,[11] the specimen was maintained in vacuum for one week to allow the desorption of oxygen from the film surface and kept in inert atmosphere (pure argon) during measurements. In addition, the incident power was limited to about 4 mW, corresponding to a laser flux of about 4000 W/cm^2. For SBS, such incident power is quite low, so that sampling times per spectrum were very long, typically 20 h. In air and without oxygen desorption the measurements were not feasible, because the laser beam caused macroscopic surface modification [deep etching, as observed by scanning electron microscopy (SEM)]. Instead, in the experimental conditions previously described, SEM images did not show any modification after laser irradiation, not even cracks as in small single crystals.[16]

An important question arises about the actual chemical and physical condition of the material during Brillouin measurements. It is known that laser irradiation[17–19] and temperature variations[20,21] may change the electronic configuration and the structure of fcc C_{60}. It has been suggested[18] that intense light exposure produces photopolymerization of fullerite, which results in appreciable changes in the Raman spectra. A fingerprint of the phototransformation is the appearance of a new line at 1458 cm^{-1} together with the bleaching of the A_g pentagonal pinch mode at 1469 cm^{-1}.[17] In general, however, the question is controversial, because of the strong dependence of these effects on the nature and history of the sample.[21] In particular, our Ni supported film dissipates heat much more than the small crystals that have been extensively studied. For all these reasons, our film has been directly studied by Raman spectroscopy[22] in conditions (vacuum followed by He atmosphere) very similar to those used for the Brillouin measurements. It has been found that at intermediate laser fluxes (500–1000 W/cm^2) the 1458-cm^{-1} line of polymerized C_{60} becomes a relevant spectral feature, but it disappears at high laser flux (more than 3000 W/cm^2). In the Brillouin experimental conditions (4000 W/cm^2) the 1469-cm^{-1} line is well present in the spectra, together with a satellite located at about 1465 cm^{-1}, whose origin is presently not clear. It could be related to the presence of an excited phase due to heating.[19]

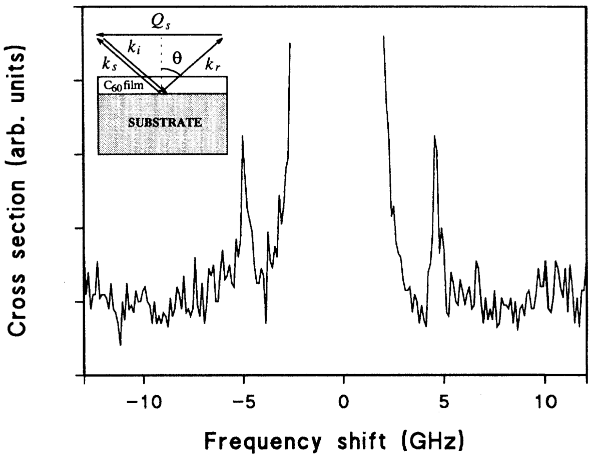

FIG. 1. SBS spectrum showing Stokes and anti-Stokes peaks assigned to the RW of C_{60}. The incidence angle is $\theta=45°$ and the surface wave vector is at an angle of 9° with respect to the $[11\bar{2}]$ direction.

SBS measurements were performed in the backscattering geometry, as illustrated in the inset of Fig. 1. The relationship between the frequency shift f of the Brillouin peaks and the phase velocity v of the surface acoustic modes is given by[9]

$$v=\pi f/k_i\sin\theta, \tag{1}$$

where k_i is the wave vector of the incident light and θ the angle of incidence. In the case of bulk phonons (inset of Fig. 3) the phase velocity is given by

$$v=\pi f/nk_i, \tag{2}$$

with n the refractive index of the medium. Since the film thickness of our sample is much higher than the phonon wavelength, the influence of the Ni substrate on the phase velocity of the SAW is negligible, so that the film can be considered as a semi-infinite medium. In Fig. 1 we show a spectrum taken with the surface wave vector at an angle of 9° with respect to the $[11\bar{2}]$ direction and an incidence angle $\theta=45°$. The peaks of this spectrum are due the surface Rayleigh wave (RW) of the semiopaque film of fullerite, detected through the so-called ripple effect.[9] Measurements performed for different directions of the phonon wave vector on the surface plane enabled us to study the behavior of the

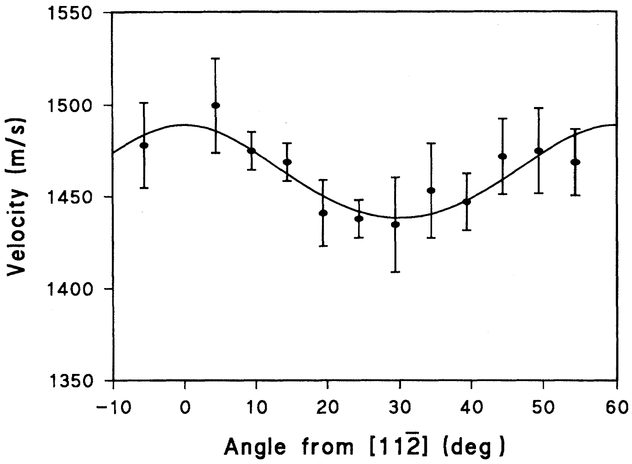

FIG. 2. Measured phase velocity of the RW propagating on the (111) surface of C_{60} at certain angles from the [11$\bar{2}$] direction. Error bars are individual standard deviations. The solid line represents the best fit to the experimental data.

RW phase velocity on the (111) plane. As expected, we have observed an oscillatory behavior with a period of 60°, as shown in Fig. 2. This result proves that our C_{60} film maintains azimuthal orientational epitaxy on a length scale of at least 11 μm, i.e., the diameter of the laser spot; in addition, it confirms that in our experimental conditions the sample keeps the typical azimuthal behavior of a cubic anisotropic (111) film, while a photopolymerized solid should become isotropic. The data points of Fig. 2, derived through the use of Eq. (1), yield essentially two pieces of information: the average value of the RW phase velocity on the (111) plane of C_{60} (about 1460 m/s) and the amplitude of the oscillation (about 50 m/s). However, these two data are not sufficient to determine the three independent elastic constants of fcc C_{60}. The third independent piece of information was obtained by detection of the peak corresponding to a longitudinal acoustic (LA) phonon, whose phase velocity can be obtained by using Eq. (2). A spectrum that clearly exhibits the LA peak is reported in Fig. 3. It is fortunate that the RW and the LA bulk velocities depend on different combinations of elastic constants, so that surface and bulk scattering gives independent information, allowing a meaningful fitting procedure.

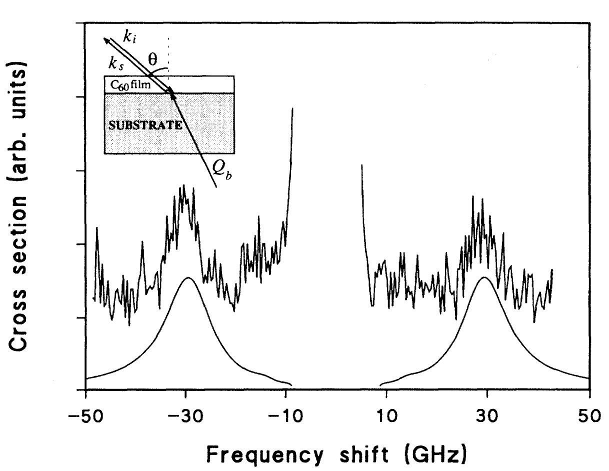

FIG. 3. Experimental Brillouin spectrum of C_{60} showing LA bulk peaks. The solid line is the cross section calculated in the frequency range of the bulk resonance (Ref. 9).

TABLE I. Measured elastic properties of fcc fullerite (elastic constants, bulk modulus, and Young's modulus in GPa). Errors are given in parentheses.

c_{11}	c_{12}	c_{44}	B	Y
16.24 (±0.76)	8.86 (±0.70)	5.28 (±0.29)	11.32 (±0.53)	9.99 (±1.25)

Since the RW and LA velocities depend nonlinearly on the parameters of the calculation, we used a fitting procedure based on the Levenberg-Marquardt method[23] in order to calculate the best-fit elastic constants. The data considered in the fit are the 12 RW velocities presented in Fig. 2 and the LA bulk velocity extracted from the measurements of Fig. 3 through Eq. (2). The accuracy of the determination of the elastic constants is better than 8%, and is shown in Table I for each constant; it takes into account both the experimental error and the statistical error related to the fitting procedure. The derived quantities B (bulk modulus) and Y (Young's modulus along [100]) are also shown in Table I. The angular dependence of the phase velocity of the RW on the (111) plane, calculated with the best-fit elastic constants, shows an excellent agreement with the experimental data, as seen in Fig. 2.

The only elastic experimental data available in the literature for single crystal fcc C_{60} concern the bulk modulus. References 2 and 3 reported $B=14.4$ and 18.1 GPa, respectively. However, these results involve high pressures and transformation to the sc phase. Ludwig *et al.*[6] showed that a correct analysis of C_{60} under pressure requires a modified equation of state and measured a bulk modulus $B=13.4$ GPa for the fcc phase at room temperature. Lundin and Sundqvist[5] instead reported a value as small as 6.8 GPa. Also, the acoustic measurements in disordered films[7,8] gave low values of the bulk modulus (6.4 and 8.4 GPa, respectively). In the latter cases, the comparison with the value measured here seems to prove that the disordered films are more compressible than our fcc film, perhaps because of the porosity of the disordered material.[8] Very recently, the compressibility and bulk modulus of C_{60} have been measured using neutrons and rare gases as pressure media.[4] This low-pressure technique allowed the authors of Ref. 4 to clearly distinguish fcc and sc phases. The fcc result of these authors ($B=12$ GPa) is in good agreement with our value (11.32 GPa).

The determination of the elastic constants of fullerite allows us to get an insight into the nature of the intermolecular interaction in this crystal. In particular, the magnitude of $c_{12}-c_{44}$ is a measure of the deviation from a central intermolecular potential. In fact, the Cauchy relation $c_{12}=c_{44}$ holds when the force constants between molecules are purely radial. Our measurements indicate a large deviation from the Cauchy relation, with $c_{12}>c_{44}$, which is typical of metals and of rare-gas solids. The latter crystals, in some respects similar to fullerite, exhibit smaller deviations from the Cauchy condition than C_{60}. It is interesting to compare our results with the dynamical models used to fit the phonons of fullerite. Pintschovius *et al.*[1] found that the fit of the dispersion curves required either relatively large second-nearest-neighbors (NN's) radial force constants or first-NN tensor forces. Our outcome proves the validity of the latter model, because tangential forces are needed to reproduce the large value of $c_{12}-c_{44}$. On the other hand, the best-fit phonon curves of Ref. 1 seem to be inaccurate in the long-wavelength limit, because they imply the Cauchy condition and overestimate the sound velocities of about 15–30 % with respect to our measured values.

In summary, we have shown that SBS can be successfully used to determine all the elastic moduli of an anisotropic crystalline film of fcc C_{60}. The values we have determined allow a better understanding of the long-wavelength dynamical properties of fullerite. We have found elastic constants in general larger than those of polycrystalline films and strong deviations from the Cauchy relation, implying intermolecular interactions of noncentral character.

We thank C. Petrillo and F. Sacchetti for x-ray measurements, D. Palmeri for SEM, M. Manfredini, P. Milani, and C. E. Bottani for Raman measurements, G. Guizzetti and M. Patrini for ellipsometric characterization, and C. Byloos for useful discussions. This work has been partially supported by Ministero Università e Ricerca Scientifica e Tecnologica. L.G. acknowledges financial support from Alenia.

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[1] L. Pintschovious, B. Renker, F. Gompf, R. Heid, S. L. Chapot, M. Haluska, and H. Kuzmany, Phys. Rev. Lett. **69**, 2662 (1992).

[2] J. E. Fisher, P. A. Heinley, A. R. McGhie, W. J. Romanow, A. J. Denenstein, J. P. McCauley, Jr., and A. B. Smith III, Science **252**, 1288 (1991).

[3] S. J. Duclos, K. Brister, R. C. Haddon, A. R. Korton, and F. A. Theil, Nature (London) **351**, 380 (1991).

[4] J. E. Shirber, G. H. Kwei, J. D. Jorgensen, R. L. Hitterman, and B. Morosin, Phys. Rev. B **51**, 12 014 (1995).

[5] A. Lundin and B. Sundqvist, Europhys. Lett. **27**, 463 (1994).

[6] H. A. Ludwig, W. H. Fietz, F. W. Hornung, K. Grube, B. Wagner, and G. J. Burkhart, Z. Phys. B **96**, 179 (1994).

[7] H. Coufal, K. Meyer, R. K. Grygier, M. de Vries, D. Jenrich, and P. Hess, Appl. Phys. A **59**, 83 (1994).

[8] N. P. Kobelev, A. P. Moravskii, Ya. M. Soifer, I. O. Bashkin, and O. G. Rybchenko, Fiz. Tverd. Tela (Leningrad) **36**, 2732 (1994) [Phys. Solid State **36**, 1491 (1994)].

[9] F. Nizzoli and J. R. Sandercock, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1990), Vol. 6, p. 281.

[10] F. Nizzoli, B. Hillebrands, S. Lee, G. I. Stegeman, G. Duda, G. Wegner, and W. Knoll, Phys. Rev. B **40**, 3323 (1989).

[11] M. Manfredini, C. E. Bottani, and P. Milani, Chem. Phys. Lett. **226**, 600 (1994).

[12] M. R. C. Hunt, S. Modesti, P. Rudolf, and R. E. Palmer, Phys. Rev. B **51**, 10 039 (1995).

[13] J. K. Gimzewski, S. Modesti, and R. R. Schlittler, Phys. Rev. Lett. **72**, 1036 (1994).

[14] J. H. Weaver and D. M. Poirier, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, New York, 1994), Vol. 48, p. 1, and references therein.

[15] P. Milani, M. Manfredini, G. Guizzetti, F. Marabelli, and M. Patrini, Solid State Commun. **90**, 639 (1994).

[16] M. Haluska, H. Kuzmany, M. Vybornov, P. Rogl, and P. Fejdi, Appl. Phys. A **57**, 161 (1993).

[17] P. Zhou, A. M. Rao, K. Wang, J. D. Robertson, C. Eloi, M. S. Meier, S. L. Ren, X. Bi, P. C. Eklund, and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2871 (1992).

[18] A. M. Rao, P. Zhou, K. Wang, G. T. Hager, J. M. Holden, Y. Wang, W. T. Lee, X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, Science **259**, 955 (1993).

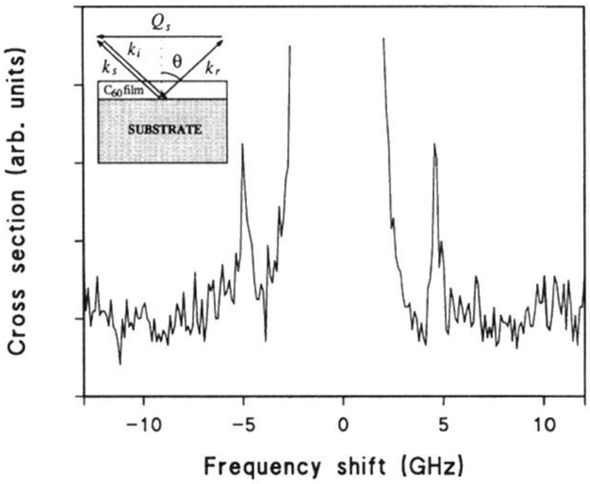
[19] H. J. Byrne, L. Akselrod, C. Thomsen, A. Mittelbach, and S. Roth, Appl. Phys. A **57**, 299 (1993).

[20] Y. Hamanaka, S. Nakashima, M. Hangyo, H. Shinohara, and Y. Saito, Phys. Rev. B **48**, 8510 (1993).

[21] M. Matus and H. Kuzmany, Appl. Phys. A **56**, 241 (1993).

[22] M. Manfredini, P. Milani, and C. E. Bottani (private communication); (unpublished).

[23] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986).



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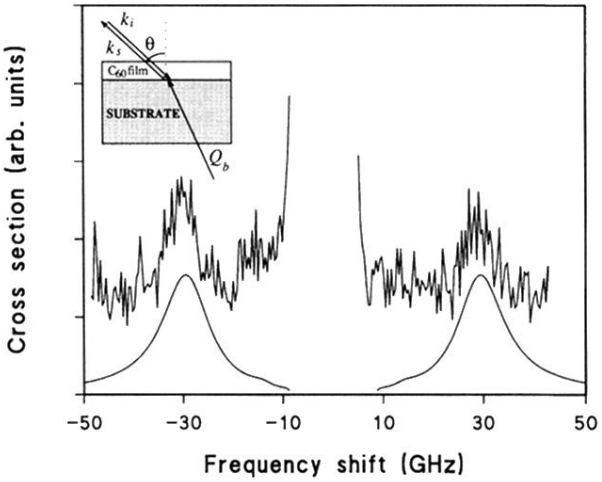

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