

## Diamond from fullerenes: Evidence from Raman measurements

M. Núñez Regueiro\*

*Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique,  
Boîte Postale 166 CEDEX 9, 38042 Grenoble, France*

L. Abello and G. Lucazeau

*Laboratoire d'Ionique et d'Electrochimie du Solide de Grenoble, Ecole Nationale Supérieure d'Electrochimie  
et de Electrometallurgie de Grenoble, Boîte Postale 75, 38402 Saint Martin d'Heres CEDEX, France*

J-L. Hodeau

*Laboratoire de Cristallographie, Centre National de la Recherche Scientifique,  
Boîte Postale 166 CEDEX 9, 38042 Grenoble, France*

(Received 13 July 1992)

We present the Raman characterization of transformed fullerene samples obtained by applying high ( $\sim 20$  GPa) nonhydrostatic pressures on  $C_{60}$  or  $C_{60}$ - $C_{70}$  powders. Only two clear features are observed. The first is a peak at  $1330\text{ cm}^{-1}$ , signature of the existence of cubic diamond. The second is a broadband of unknown origin centered at approximately  $1450\text{ cm}^{-1}$ . These results confirm previous crystallographic analysis that showed that our samples consist of polycrystalline diamond embedded in an amorphous matrix.

The behavior of  $C_{60}$  under pressure is rich in new phenomena. The application of a hydrostatic compression<sup>1</sup> conserves the cage structure and the face-centered-cubic structure up to a pressure of 20 GPa. Nonhydrostatic application of pressure induces, however, a series of phase transitions.<sup>1,2</sup> The most interesting result is the report of the obtention of cubic diamond at room temperature. Fullerene soot does indeed transform to a transparent solid solely by application of pressure above 15 GPa under strict nonhydrostatic conditions.<sup>3</sup> Electron diffraction patterns and x-ray spectra showed that these samples consisted of polycrystalline cubic diamond of grain size always smaller than  $1000\text{ \AA}$  embedded in an amorphous material of seemingly  $sp^3$  character. As reported by other groups,<sup>4-6</sup> less stringent conditions cause the formation of a different form of carbon, that is amorphous and can speculatively but attractively be viewed as disorderly interconnected  $C_{60}$  cages. The preferential  $sp^2$  hybridization of the cages together to the  $sp^3$  character of the intermolecular bridges may explain the measured Raman "diamondlike" spectra.<sup>5,6</sup> Preliminary standard macro-Raman measurements performed on one of our samples were incapable of detecting any clearly discernible feature on a high luminescent background.<sup>7</sup> We report here micro-Raman measurements performed on several of our samples. We observe that all of them give the expected diamond Raman peak at  $1330\text{ cm}^{-1}$ , together with a broadband centered at  $1450\text{ cm}^{-1}$  of unknown origin.

The samples were made out of purified  $C_{60}$  kindly furnished by P. Bernier from the University of Montpellier, and C. Fabre and A. Rassat from the Ecole Normale Supérieure de Paris or  $C_{60}$ - $C_{70}$  mixture from Strem Chemicals. The first series of samples ( $A-M$ ) made using the technique described in Ref. 3 weighted around  $100\text{ }\mu\text{g}$ , or

much less if part of the cell was occupied by other bodies (e.g., razor blade chips to produce the pressure gradient). An improvement of this technique within the same apparatus allows now the obtention of bulk samples of up to  $300\text{ }\mu\text{g}$ . We present here Raman data of three different samples. Sample  $A$  (same nomenclature as in Ref. 3) was produced from purified  $C_{60}$  powder in a slanted anvil configuration at  $25\pm 5$  GPa. Sample  $M$ , also from purified  $C_{60}$ , was obtained by compression to  $20\pm 5$  GPa together with a small razor blade chip, while sample  $N$  was made using the improved technique from as-received  $C_{60}$ - $C_{70}$  soot, and transformed at about  $20\pm 5$  GPa.

The Guinier powder pattern obtained with Fe  $K\alpha$  radiation on sample  $N$  is given in Fig. 1. It showed only the (111) and (220) reflections of cubic diamond. Due to the x-ray beam size, by this method we cannot observe and quantify any diffuse scattering of the amorphous part of the sample since its support and glue also yielded diffusion. Electron diffraction patterns show the existence in chips of this sample of either an amorphous phase or polycrystalline cubic diamond with grain sizes ranging from  $50$  to  $500\text{ \AA}$ . The color of the bulk sample is yellowish by transparency.

Raman spectra were obtained with the multichannel XY DILOR model spectrometer equipped with a microscope. They were excited by the  $\text{Ar}^+$  laser line at  $488\text{ nm}$ . The laser power was kept at  $30\text{ mW}$  and the laser spot was of about  $1\text{ }\mu\text{m}$ . The instrumental linewidth was of  $7.55\text{ cm}^{-1}$ .

We show in Fig. 2 Raman spectra corresponding to different samples. They represent typical data, when the luminescent background permits measurement. Spectra (a) and (b) correspond to sample  $A$ . Spectrum (b) was taken on the surface of the sample, that was in direct contact with the diamond anvils. We observe only a feature-

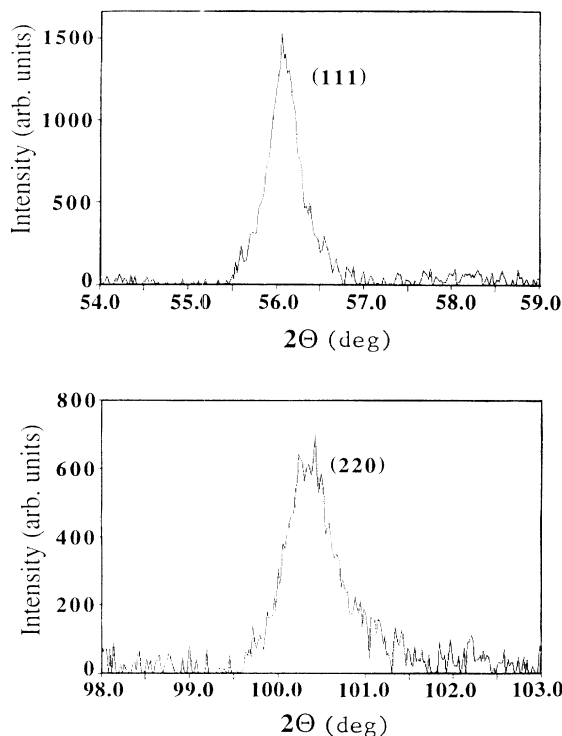


FIG. 1. X-ray spectra of sample *N*, showing the expected diamond reflections.

less variation. However if the beam is focused into the cracks of the sample or on torn-off pieces, we obtain spectra such as (a). It is clear that a strong diamond peak located at  $1330\text{ cm}^{-1}$  is well present in this spectrum, confirming the existence of cubic diamond crystals in the sample.

Curves (c) and (d) of Fig. 2 correspond to samples *M* and *N*, respectively. A small but clearly visible peak is seen at  $1330\text{ cm}^{-1}$ , showing that cubic diamond crystals are also present in these samples. Furthermore, a broadband centered at about  $1450\text{ cm}^{-1}$  is very neatly defined, particularly in sample *N*. In fact, a detailed observation of the data of sample *A* shows that the same band is also visible there. These two features are present in all the samples that we have characterized.

From our results we can conclude that Raman evidence for the existence of cubic diamond in our samples can be obtained using a micro-Raman probe. It is, however, important to scan into the sample, as at the surface the diamond peak is extremely weak. This was expected from the crystallographic analysis, which showed the existence of a preponderant amorphous phase surrounding the diamond crystals. The fact that at the surface in contact with the diamond anvils, the  $1330\text{-cm}^{-1}$  feature is always weak or nonexistent, and that the diamond crystals are detected inside the sample, suggests that the diamond anvils do not aid in the formation of the crystals. The pressure gradient seems to be more important. As macro-Raman techniques give an averaged spectrum, largely obscured by the thin absorbing layer at the surface, it is normal that they could not detect the diamond line originated from small crystals inside the sample, and

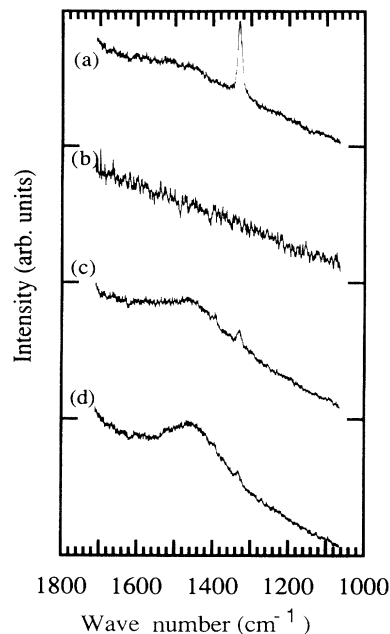


FIG. 2. Raman spectra of transformed fullerene samples. (a) Sample *A* (inside); (b) sample *A* (surface); (c) sample *M* and (d), sample *N*. Note that in all three samples the diamond peak is visible at  $1330\text{ cm}^{-1}$ , together with a broad feature at  $\sim 1450\text{ cm}^{-1}$ . This band may probably be the signature of the highly  $sp^3$  amorphous phase present in our samples.

which can be reached by focusing the laser beam into the cracks.

The origin of the  $1450\text{-cm}^{-1}$  broad feature is intriguing, as it is not present in the usual phases of carbon. We must consider, though, that there is a sharp band<sup>8</sup> at  $1469\text{ cm}^{-1}$  in pure  $C_{60}$ . A broader band,  $\sim 50\text{ cm}^{-1}$  of full width at half maximum (FWHM), has also been observed at  $1450\text{ cm}^{-1}$  in a carbonaceous compound obtained by laser irradiation of highly oriented pyrolytic graphite.<sup>9</sup> This band was interpreted in terms of disordered  $C_{60}$ -like material. Similarly, the Raman component at  $1470\text{ cm}^{-1}$  observed in the spectrum of a  $12\text{-\AA}$  layer obtained by laser ablation of graphite was also associated with a possible five member ring as in  $C_{60}$  clusters.<sup>10</sup> However, such a feature is not seen in transformed  $C_{60}$  samples obtained by other methods.<sup>4-6</sup> Though a more detailed study must still be made, it seems that the intensity of this band and the diamond line are interrelated. If this is indeed confirmed, it is tempting to attribute this band to the amorphous phase observed by crystallographic methods in our samples. Recent x-ray measurements taken with synchrotron radiation at LURE show that the spectrum for the amorphous material is similar to that of amorphous silicon, in agreement with a major  $sp^3$  configuration.<sup>11</sup> It is theoretically expected<sup>12</sup> that 100% tetrahedrally coordinated amorphous carbon would give a broad band at  $1200\text{ cm}^{-1}$ . Following the same calculation we would expect slightly more than 50% of  $sp^3$  carbon atoms in our amorphous material. However, the calculation does not take into account the probable existence of dangling bonds. We can therefore

speculate that the  $1450\text{-cm}^{-1}$  band, because of its FWHM, is the Raman signature of a highly  $sp^3$  amorphous carbon. Quantitative measurements are under way to confirm this.

In conclusion, careful micro-Raman measurements on transparent samples obtained by crushing  $C_{60}$  or  $C_{60}\text{-}C_{70}$

mixtures show the existence of the diamond  $1330\text{-cm}^{-1}$  characteristic line, in agreement with previous crystallographic measurements. In addition, an unidentified broad band observed at  $1450\text{ cm}^{-1}$  may correspond to a preponderantly tetrahedrally coordinated, carbon amorphous phase.

---

\*On leave from Comision Nacional de Energía Atómica and Consejo Nacional de Investigaciones Científicas y Técnicas, Centro Atómico Bariloche, 8400 Bariloche, Argentina.

<sup>1</sup>S. J. Duclos, K. Brister, R. C. Haddon, A. R. Kortan, and F. A. Thiel, *Nature* **351**, 380 (1991).

<sup>2</sup>M. Núñez-Regueiro, P. Monceau, A. Rassat, P. Bernier, and A. Zahab, *Nature* **354**, 289 (1991).

<sup>3</sup>M. Núñez-Regueiro, P. Monceau, and J-L. Hodeau, *Nature* **355**, 237 (1992).

<sup>4</sup>F. Moshary, N. H. Chen, I. F. Silvera, C. A. Brown, H. C. Dorn, M. S. de Vries, and D. S. Bethune (unpublished).

<sup>5</sup>C. S. Yoo and W. J. Nellis (unpublished).

<sup>6</sup>D. W. Snoke, Y. S. Raptis, and K. Syassen, *Phys. Rev. B* **45**,

14419 (1992).

<sup>7</sup>G. Martinez (private communication).

<sup>8</sup>D. S. Bethune, G. Meijer, W. C. Tang, and H. J. Rosen, *Chem. Phys. Lett.* **174**, 219 (1991).

<sup>9</sup>L. Abello, N. Rosman, F. Genet, and G. Lucazeau, *J. Phys. C* **7**, 497 (1991).

<sup>10</sup>J. Díaz, J. A. Martín Gago, S. Ferrer, F. Comin, L. Abello, and G. Lucazeau, *Diamond Relat. Mater.* **1**, 824 (1992).

<sup>11</sup>J-L. Hodeau, J. M. Tonnerre, B. Bouchez-Favre, and M. Núñez-Regueiro (unpublished).

<sup>12</sup>D. Beeman, J. Silverman, R. Lynds, and M. R. Anderson, *Phys. Rev. B* **30**, 870 (1984).