Optical absorption spectrum of C_{60} at high pressure

D .W. Snoke, K. Syassen, and A. Mittelbach

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Federal Republic of Germany

(Received 13 October 1992)

We report measurements of the optical absorption spectrum of solid C_{60} in the pressure range from 0 to 40 GPa. At low pressure we find a linear shift of the absorption edge of -0.14 eV/GPa eV. Above 20 GPa, the fullerenes transform irreversibly to amorphous carbon; we find no evidence of transparency greater than that of amorphous carbon produced by other means.

Recent work[1-4] has focused much attention on the behavior of the optical gap of C_{60} at high pressures. High-pressure studies of the optical gap relate to two important questions in regard to the fullerenes. First, what is the proper hydrostatic deformation potential for the highest-occupied molecular-orbital–lowest-unoccupied molecular-orbital gap? The value of the deformation potential yields the electron-phonon coupling constant which is important for theories of superconductivity of doped C_{60}. Second, what is the nature of the high-pressure phase of C_{60}? An irreversible phase transition at about 20 GPa to a new phase of carbon was reported in 1991 on the basis of x-ray,[5] Raman,[6] and electrical data.[7] Moshary *et al.*[2] have called into question the identification of this phase as amorphous carbon by reporting anomalously high transparency.

Values of the shift of the band gap with pressure have varied by more than a factor of 2. Early electrical measurements[8] were interpreted to give a shift of the band gap to 1.2 eV at 10 GPa, or about -0.06 eV/GPa, assuming a band gap of 1.8 eV at zero pressure. A study of the reflectivity of C_{60} reported an average shift of the reflectivity edge of -0.1 eV/GPa for pressures up to 10 GPa.[3] More recently, absorption data reported by Moshary *et al.*[2] have reported a shift half that amount, -0.055 eV/GPa, in contradiction with the theoretical model of Xu, Huang, and Ching[9] which predicts a value

of -0.12 eV/GPa. A study of the photoluminescence up to 5 GPa by Sood *et al.*[4] has given a value closer to this prediction, -0.138 eV/GPa. An absorption study of a mixture of C_{60} and C_{70} by Dolganov *et al.*[10] at four pressures yielded a value of -0.08 eV. Because of the scatter of values, we have undertaken further measurements of the absorption spectrum of C_{60} in the range 0–6 GPa.

Figure 1 shows transmission spectra of highly purified C_{60} at various hydrostatic pressures. For these measurements we used thin layers of C_{60} (Ref. 11) in a diamond-anvil cell with solid CsCl as a pressure medium. Hydrostatic pressure was calibrated via luminescence from ruby powder in the cell.[12] A sharp transition from complete transparency to 90% opacity is seen within an energy range of about 0.05 eV; we see no substantial broadening of the absorption edge with increasing pressure.

In Fig. 2 we plot the shift of the transmission edge, which we define as the energy at which the transmission is 1% of the average value in the transparent region. We use the transmission threshold here instead of the absorption threshold, as used in Ref. 2, simply to extend the range of the data, since already by 2.5 GPa the absorption threshold is beyond the range of our photomultiplier. Because the shape of the transition remains essentially the same as pressure increases, as seen in Fig. 1, we can use any point in the transition as a measure of the *relative* shift of the optical gap; using the absorption threshold as in
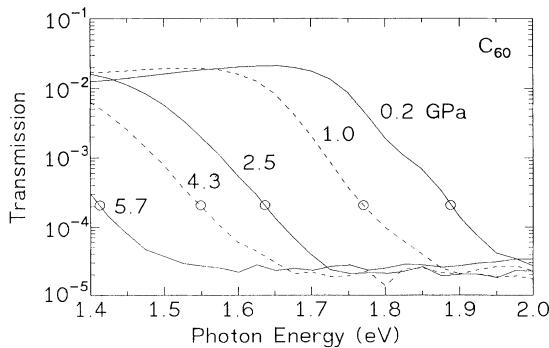

FIG. 1. The transmission spectra of samples of C_{60} approximately 10 μm thick, at various pressures. The open circles indicate the points taken as the transmission edge for the pressure shift plotted in Fig. 2.
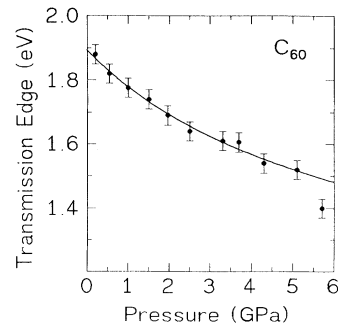
FIG. 2. Solid circles: the transmission edge (the energy at which transmission is 1% of the value in the region of transparency) as a function of pressure. Solid lines: a fit to the simple nonlinear function described in the text.

Ref. 2 would simply shift the curve of Fig. 2 to lower energy.

As seen in Fig. 2, at low pressures the shift is roughly linear with pressure, while it slows at higher pressures. The solid curve shows a fit of these values to a simple nonlinear model, $d(\ln E_G)/dP = [d(\ln E_G)/dP]_{P=0} + \alpha P$. The fit yields the slope of the shift at $P = 0$ of $dE_G/dP = -0.14$ eV/GPa; the nonlinear parameter α is equal to -0.073 GPa^{-2}.

Figure 3 shows the shift of the low-energy edge of the reflectivity spectrum, from the reflectivity data of Ref. 3. As in the absorption data, the gap initially shifts down approximately linearly with pressure and then slows. The dashed line in Fig. 3 corresponds to a slope of -0.11 eV/GPa. Since these data depend primarily on states near the joint-density-of-states peak at 2.5 eV, while the absorption data depend on the band edge, these data indicate that the bottom of the band shifts almost rigidly.

Given the agreement of the value of dE_G/dP in the absorption, reflectivity,[3] and luminescence[4] measurements, as well as theory,[9] we feel that the shift of the band gap may be taken as -0.14 ± 0.02 eV. Some optical studies may have yielded a lower value because inhomogeneities in sample thickness broadened the optical transition. Using the reported value of the bulk modulus of C_{60} of 18.1 GPa from x-ray studies,[5] our measurement of the shift of the gap implies a value for the hydrostatic volume deformation potential of 2.5 eV, or average linear deformation potential, as defined by Sood et al.,[4] of 7.5 eV. A more recent study using a cylinder and piston method at low pressures[13] has yielded a bulk modulus of 8.4 GPa; using this value gives a volume deformation potential of 1.2 eV.

If we define the optical gap energy as the absorption edge, i.e., the point of 1% absorption, these measurements yield a value of the optical gap at zero pressure of 1.74 ± 0.02 eV. Values for the lowest allowed optical gap of C_{60} have also suffered a degree of scatter. Our value is in basic agreement with previous

absorption,[14] luminescence,[4] and ellipsometry[15] studies, all of which put the optical gap at 1.7–1.9 eV, in agreement with recent orthogonalized linear-combination-of-atomic-orbitals theoretical calculations;[16] according to these theoretical calculations the peak at 2.5 eV seen in resonance Raman[17] and reflectivity[3] measurements is due to a sharp peak in the density of states at that energy. We do not see any structure at the absorption edge characteristic of a dominant exciton state, which Lof et al.[18] have proposed.

The second regime of interest in absorption studies is the high-pressure regime above 20 GPa. Early x-ray studies[5] showed that C_{60} transforms to a new phase with no discernible order at around 20 GPa; electrical studies[7] showed that this phase is insulating. A Raman study[6] of a mixture of C_{60} and C_{70} with solvent showed a transition to hydrogenated amorphous carbon (a-C:H) with the distinct two-peaked Raman spectrum associated with graphitic regions;[19,20] later Raman work with purified C_{60} (Ref. 2 and 3) yielded a Raman spectrum characteristic of the pure amorphous "diamondlike" carbon state (a-C).[21] The reflectivity spectrum[3] of this high-pressure phase showed that it is not the same as the high-pressure phase of graphite.

Moshary et al.[2] have reported that samples of pure C_{60} showed transparency in the visible region in the pressure range 20–40 GPa, sometimes increasing on a time scale of days. This transparency was reported as comparable to the transparency of the untransformed C_{60} below the gap at low pressure, which implies an absorption coefficient orders of magnitude less than measured for a-C created by normal means.[22] We have therefore attempted to observe this transparency in the high-pressure regime. In order to prevent stray light from passing around the sample in the case of an inhomogeneous distribution of sample and pressure medium and/or ruby powder, which could give a spurious observation of transparency, we loaded the gasket hole of the diamond-anvil cell with nothing but pure C_{60} and ruby plates. We performed absorption measurements on pure C_{60} at 100 μm thickness in the range 20–40 GPa, and at 50 and 20 μm thickness in the range 20–30 GPa. In order to achieve a 20-μm-thick sample of C_{60} at these pressures without a pressure medium, we stacked two 20-μm-thick plates of ruby in a gasket of thickness 60 μm and filled the remainder of the gasket hole with the fullerenes. In this case, the absorption spectrum in the range 0–6 GPa could be measured, reproducing the results of Figs. 1 and 2. In each case the sample was allowed to remain at maximum pressure for 4 days.

We have found no evidence of transparency of the high-pressure phase of pure C_{60} in any of these experiments. From our measurements we can put a lower bound on the optical density of the high-pressure phase. For a 20-μm sample, the measured transmission of less than one part in 10^6 over the spectral region from 1.4 to 3 eV implies a minimum absorption coefficient of 10^4 cm^{-1} over the entire range, in agreement with the data of Hauser[22] for amorphous a-C. We therefore see no reason to believe that the high-pressure phase of C_{60} is not normal a-C; we have no explanation for what conditions may have
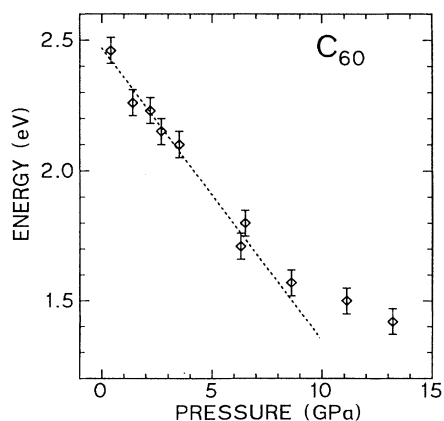

FIG. 3.   Open circles: the position of the reflection edge in the reflection spectrum of C_{60} as a function of pressure, from the data of Ref. 3. Dashed line: a fit of the low-presure data to a straight line with slope -0.11 eV/GPa.

led to the low absorption seen by Moshary *et al.* Slight differences exist in the Raman signal reported in Refs. 3 and 2; this may indicate that Moshary *et al.* observed a different phase, but the experimental conditions leading to such a new phase remain unknown.

Nunez-Regueiro and co-workers have reported[1,23] the appearance of polycrystalline diamond in the same pressure range, based on visual observation[1] and Raman[23] measurements. This result apparently relies on the highly nonhydrostatic pressure conditions used in that work; the sintered diamond used in those experiments may also have contributed diamond granules to the sample under these extreme conditions. In our hydrostatic measurements, we see no evidence for the appearance of cubic diamond in either Raman scattering or in the appearance of small regions of transparency.

In conclusion, we find that the zero-pressure value of dE_G/dP for C_{60} is -0.14 ± 0.02 eV/GPa; the shift of the band gap lessens at higher pressures. This implies a hydrostatic deformation potential of 2.5 eV, using the originally reported value for the bulk modulus. At pressures above 20 GPa, both the Raman data and the absorption data indicate that the C_{60} structure transforms irreversibly to normal amorphous a-C carbon, with no anomalous transparency.

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