

Reversible first-order phase transition with a large change in volume in the fullerite C₆₀ under pressure

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An abrupt change in the pressure dependence of the volume of C₆₀ at a temperature of 557 K has been observed. This abrupt change is explained in terms of a reversible first-order phase transition.

The behavior of the fullerite C₆₀ under pressure has been the subject of many studies. The research has focused on two aspects of the problem. The first is a phase transition in C₆₀ at $T_c \approx 250$ K (Refs. 1–8). This transition results from an orientational ordering of the C₆₀ molecules,¹ with the result that the fcc structure of the high-temperature phase ($a_0 = 14.17$ – 14.198 Å; Refs. 1 and 2) gives way to a simple cubic structure (sc; space group *Pa*3; Refs. 1 and 3). At atmospheric pressure the change in volume at the fcc–sc transition is^{4,5} about 1%, and the heat of the transition has been estimated^{1,2,6} to lie in the range 6.7–9.9 J/g. The shift of the transition temperature in a helium atmosphere measured at pressures up to 10–14 kbar is 10.4–11.7 K/kbar, while that in nitrogen or in a mixture of pentane and isopentane reaches ~16 K/kbar (Refs. 2, 7, and 8). This large difference in the slopes dT_c/dP has been explained⁸ on the basis that molecules of the hydrostatic medium penetrate into interstitial positions in the C₆₀ lattice.

Raman, x-ray, and IR spectra have been measured under pressure in diamond anvils. It has been reported that the spherical C₆₀ molecules are stable at hydrostatic pressures up to 200 kbar, but a uniaxial compression distorts the molecules or the crystal structure even below 100 kbar (Ref. 9). The application of a pressure of 150–300 kbar may cause transitions to diamond, graphite, or amorphous carbon, accompanied by the formation of hybridized bonds between molecules (a reversible polymerization) at intermediate stages of the transition.^{10–15}

The experimental data which we are reporting here indicate that yet another phase transition occurs in the fullerite C₆₀ under pressure. These results were obtained by a piezometric method.

To prepare the initial powder of crystalline C₆₀, a fullerene-containing soot was subjected to extraction by toluene in a Soxhlet extractor in an argon atmosphere. Light was excluded. After the extract was evaporated and washed with ether, the mixture of fullerenes was separated chromatographically into components in an effective column

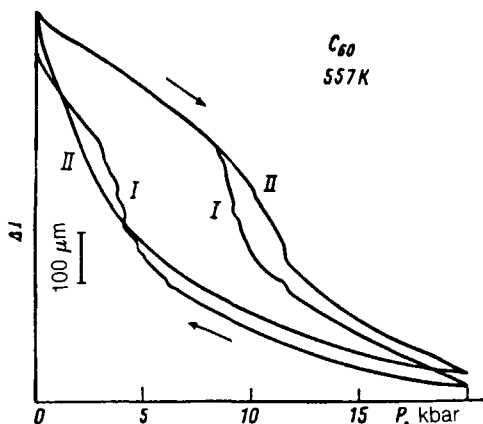


FIG. 1. Change in volume due to the phase transition in C_{60} at a temperature of 557 K on experimental curves recorded at loading-unloading rates ~ 0.1 kbar/min (curve 1) and ~ 1 kbar/min (curve 2). The arrows show the direction in which the pressure is varied.

of neutral aluminum oxide, shielded from light. A 1:4 mixture of toluene and hexane, driven by flowing argon, was used as eluant. The C_{60} fraction was selected; the concentration of impurity C_{70} in it was less than 0.01% by mass, according to high-efficiency liquid chromatography. The C_{60} solution was concentrated by evaporation on a rotating evaporator. Crystals of pentane were precipitated, washed with ether, and recrystallized from the toluene-pentane mixture. Solvent molecules were removed from the resulting crystal solvate by drying in a vacuum of 10^{-5} torr at 540 K for 50 h. Analysis by the method of high-efficiency liquid chromatography showed that there was no C_{70} and that there were no other impurities detectable by this method at the sensitivity level of the chromatograph ($< 0.01\%$). The IR spectrum corresponded to pure C_{60} and contained no C-H vibrations. Differential thermogravimetry also showed that no solvent molecules were present. The x-ray diffraction pattern of the original C_{60} corresponded to the pure product (fcc lattice with $a_0 = 14.19 \text{ \AA}$).

The pressure dependence of the volume at one of several fixed temperatures was measured with a piston-cylinder piezometer made of VK6 alloy; the diameter of the working channel was 6 mm (Ref. 16). A sample with a mass of 0.198 g was compressed into a cylinder 4.8 mm in diameter, placed in an aluminum cell, and installed in the working channel. The relative displacements of the pistons upon a change in the pressure or temperature were measured by a clock-type gauge (with a sensitivity of 0.001 mm) and simultaneously recorded on an x, y chart recorder. The chamber was heated to 650 K with the help of a Nichrome furnace wound around a steel housing, which was pressed onto the hard-alloy cylinder of the piezometer. Because of the large volume of the heated zone, the temperature could be held constant within ± 1 K in the vicinity of the transition.

At the beginning of the measurements, the sample was subjected to repeated cycles of loading up to 30 kbar and unloading at temperatures of 290–435 K. The temperature of the high-pressure cell was then raised to ~ 560 K.

Figure 1 shows a recording of two loading-unloading cycles on the chart recorder. The loading and unloading were carried out at rates of ~ 0.1 and ~ 1 kbar/min (curves 1 and 2, respectively). These curves reflect the pressure-induced change in the

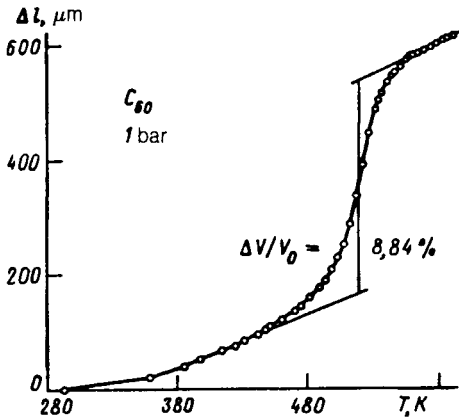


FIG. 2. Change in volume due to the phase transition in C_{60} from the high-pressure phase to the original phase during heating at atmospheric pressure (the piezometer is completely unloaded). Also shown here are approximations in intervals of a linear thermal expansion and the change in volume.

total length (l) of the hard-alloy shafts and the cell holding the C_{60} sample. The initial region of the loading demonstrates the ordinary compressibility of the original C_{60} phase and the various parts of the apparatus. In the interval of applied pressures 8.4–10.6 kbar, there is an abrupt decrease in volume on loading curve l . This decrease is due to a phase transition in the C_{60} . The following region of curve l reflects the compressibility of the high-pressure phase of C_{60} and of parts of the apparatus. During unloading, the inverse transition occurs at applied pressures between 5 and 3 kbar.

Comparison of curves l and 2 shows that when the rate of loading and unloading is increased by a factor of 10, we see that the kinetics of the transition has an effect on the shape of the curves: The intervals of the forward and inverse transitions stretch out, and the hysteresis becomes more pronounced.

We note that curves l and 2 in Fig. 1 do not coincide after the forward transition in C_{60} . We also note that the curve of the slow cycle does not return all the way to the initial point at zero pressure, while the distance by which the reading of the clock gauge indicator falls short of its original position is only $18 \mu\text{m}$. This is an instrumental effect, which we explain in terms of a displacement of the zero of the induction displacement sensor as a result of a change in the temperature profile in the measurement shaft upon a change in the geometry of the apparatus under pressure. The return to the original values occurred along with a restoration of thermal equilibrium in less than 30 min.

The parameters of the transition were determined from $l(P)$ curves, recorded by the clock gauge in a slow cycle. A polynomial approximation of parts of the $l(P)$ curve outside the transition intervals yielded an estimate of the change in volume: $\Delta V = (2.83 \pm 0.14) \times 10^{-2} \text{ cm}^3/\text{g}$. Correcting this figure to the specific volume calculated from x-ray data on the fcc phase under standard conditions, we find $\Delta V/V_0 = 4.73 \pm 0.23\%$. The friction in the chamber, which we assumed to be half the distance along the P axis between the branches of the $l(P)$ plot outside the transition intervals, was 1.85 ± 0.2 kbar. Taking this friction into account, we find that the transition during loading occurs in the interval 6.75–8.95 kbar, while the inverse

transition occurs in the interval 6.65–4.65 kbar. The temperature at which the transitions were observed was 557 ± 1 K.

Loading–unloading cycles carried out at other temperatures showed that a temperature rise ~ 70 K erases the hysteresis in the transition, while a cooling ~ 70 K results in a freezing of the inverse transition. If the high-pressure phase of C_{60} ($P=20$ kbar) is cooled to 290 K, it remains stable down to $P=1$ bar. The inverse transition begins only after the test sample is heated to ~ 480 K (Fig. 2). This result confirms that the transition observed here does not correspond to the known orientational transition. We are continuing our experiments in order to experimentally plot part of the T – P diagram and to determine the nature of the observed transition.

- ¹P. A. Heiney *et al.*, Phys. Rev. Lett. **66**, 2911 (1991).
- ²G. Kriza *et al.*, J. Phys. (Paris) I **1**, 1361 (1991).
- ³R. Sachidanandam and A. B. Harris, Phys. Rev. Lett. **67**, 1467 (1991).
- ⁴W. I. F. David *et al.*, Europhys. Lett. **18**, 219 (1992).
- ⁵P. A. Heiney *et al.*, Phys. Rev. B **45**, 4544 (1992).
- ⁶T. Atake *et al.*, Physica C **185–189**, 427 (1991).
- ⁷G. A. Samuara *et al.*, Phys. Rev. Lett. **67**, 3136 (1991).
- ⁸G. A. Samara *et al.*, Phys. Rev. B **47**, 4756 (1993).
- ⁹S. J. Duclos *et al.*, Nature **351**, 380 (1991).
- ¹⁰M. Núñez-Regueiro *et al.*, Nature **355**, 237 (1992).
- ¹¹M. Núñez-Regueiro *et al.*, Phys. Rev. B **46**, 9903 (1992).
- ¹²C. S. Yoo and W. J. Nellis, Science **254**, 1489 (1991).
- ¹³D. W. Snoke *et al.*, Phys. Rev. B **45**, 14419 (1992).
- ¹⁴C. S. Yoo and W. J. Nellis, Chem. Phys. Lett. **198**, 379 (1992).
- ¹⁵H. Yamawaki *et al.*, J. Phys. Chem. **97**, 11161 (1993).
- ¹⁶I. L. Aptekar' *et al.*, Fiz. Tverd. Tela. (Leningrad) **19**, 3180 (1977) [Sov. Phys. Solid State **19**, 1860 (1977)].

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