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Z.-X. Bao, V.H. Schmidt, N.S. Dalal, C.-S. Tu, N.J. Pinto, C.-X. Liu, Y.-L. Li, and D.-B. Zhu, "Electrical properties, equations of state and phase transition in solid C60 at high pressure," *Chinese Physics* 9, 676-679 (2000).

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ELECTRICAL PROPERTIES, EQUATIONS OF STATE AND PHASE TRANSITION IN SOLID C₆₀ AT HIGH PRESSURE*

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(Received 3 April 2000)

Electrical properties and equations of state in solid C₆₀ at room temperature and high pressure have been studied in a diamond anvil cell using capacitance and resistance measurements and a piston-cylinder type device using P - V measurements, respectively. Experimental results by capacitance and P - V measurements indicate that solid C₆₀ also undergoes a phase transition at room temperature and a lower pressure, about 2GPa. The phase transition may be from a face-centered-cubic to a simple-cubic structure.

Keywords: C₆₀, capacitance, equation of state, phase transition

PACC: 7200, 6400

I. INTRODUCTION

Since solid C₆₀ was discovered,^[1] there has been tremendous interest in its physical and chemical properties, and much work has been done on its properties. The study of the properties of solid C₆₀ has become a new and quite active field in the world. At ambient conditions the C₆₀ molecules are centered on sites of a face-centered-cubic(fcc) Bravais lattice with $a_0=1.42$ nm.^[2] The bonding between molecules in solid C₆₀ is extremely weak, making it a narrow-band semiconductor with an energy gap of 1.5eV.^[3] Doped with alkali metal, solid C₆₀ becomes superconducting at temperature as high as 33K.^[4] The crystal structure^[5] and electrical^[6,7] and optical^[8-12] properties of solid C₆₀ at high pressure have recently been studied, and some new and interesting phenomena were observed. The X-ray diffraction^[4] and electrical resistance^[6,7] measurements show that solid C₆₀ undergoes a phase transition in a pressure range of 15-22 GPa. Recent studies confirmed that solid C₆₀ has a new phase transition from the high-temperature fcc to a low-temperature simple-cubic (sc) structure at 249 K,^[2] and that the order-disorder transition temperature increases with increasing pressure, so that at room temperature solid C₆₀ has a sc phase at pressures

above 0.3-0.45 GPa.^[13-15] The high pressure Raman spectra study^[9] of solid C₆₀ also showed that a solid-solid transition might occur at 1.3 GPa.

In order to confirm if solid C₆₀ also has a phase transition at room temperature and lower pressure, we studied capacitance-pressure(C - P), resistance-pressure (R - P) and pressure-volume (P - V) relationships for solid C₆₀ at high pressure in the present work, and obtained some new and interesting results.

II. EXPERIMENTAL

The original state of the solid C₆₀ samples is polycrystalline powder, with a purity above 99% and density 1650kg/m³.

A. C - P and R - P measurements

The C - P and R - P relationships for the samples have been measured in a diamond anvil cell (DAC) using capacitance and resistance measurements. Details of the experimental techniques were described in our previous work.^[16,17]

In this work, we made some improvement on the experimental techniques in order to raise the measuring precision and to reduce the data acquisition time:

*Project supported by the U.S.-China Grant and National Natural Science Foundation of China (Grant No. 19374070).

(a) The distance between the two Mo electrodes was decreased to 0.03–0.05mm.

(b) A Wayne Kerr Model 6425 Precision Component Analyser, which gives fast and accurate readout of component values and has a GPIB Interface, was used in the measurements.

(c) The data (including capacitance, resistance and pressure, etc.) obtained in the experiments were automatically measured and recorded by a computer, and were also displayed on the computer screen.

Capacitance measurements were made with the 6425 Precision Component Analyser at a frequency of 10kHz. Because the sample resistance was above 10 G Ω , which was over a limiting value of 1G Ω for the Model 6425 Analyser, resistance measurements were carried out with a 621 Electrometer and a General Radio Model 1621 Capacitance Measurement System at 500 Hz.

Samples were kept in a desiccator, and during the measurement dry argon was passed through the DAC. All the samples studied were prepressed to definite pressures before the measurement.

B. P - V measurements

The piston-cylinder type measurement device^[18] for the P - V relationship was used in the present work. The deformation of the sample and the external force on it under high pressure were changed into electrical signals by a displacement sensor and a pressure sensor, and then measured by a digital displacement meter and a digital measuring force meter,^[19] respectively. The calibration method for the pressure and the data precessing of the relative volume compression values were the same as those in Ref.[18] The samples measured were formed cylinders at a certain pressure.

III. RESULTS AND DISCUSSION

The C - P relationships for 14 solid C_{60} samples were measured at room temperature at pressures up to 16 GPa. Figures 1 and 2 show the experimental results of these samples. Figure 1 shows the C - P relationships for four of these samples. The four samples were prepressed to 1–3 GPa before measurement. It can be seen from Fig.1 that the capacitance gradually increases up to about 1.6 GPa, and suddenly decreases above about 1.6 GPa. Figure 2 shows the C - P relationships for the other 10 samples. These samples were prepressed to 0.8–2.8 GPa before measurement. We also see a sudden change in capacitance at about

2.3 GPa in Fig.2.

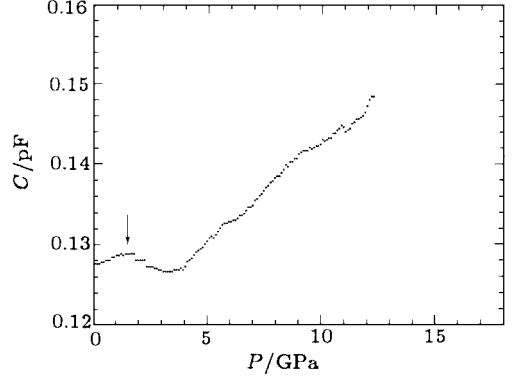


Fig.1. C - P relationship for four of solid C_{60} samples.

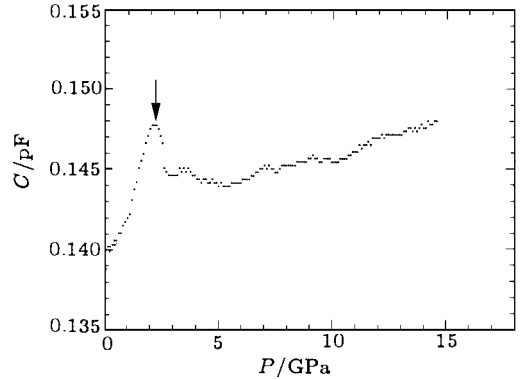


Fig.2. C - P relationship for ten of solid C_{60} samples.

We think that all the anomalous changes in capacitance with pressure are due to a phase transition, which occurs in a pressure range of 1.6–2.3 GPa. It may be a disorder-order transition from fcc to sc structure, as indicated by the differential thermal analysis (DTA)^[13,14] at high pressure. We have known from X-ray diffraction^[5] and resistance^[6,7] measurements that the phase transition in solid C_{60} at higher pressure also occurs in a larger pressure range of 15–22 GPa, however it does not occur at a definite pressure. We think that it is related to the non-homogeneity of pressure. In general, the transition pressure measured under non-hydrostatic conditions are lower than those under hydrostatic conditions because of the shear stress effect.

However, the phase transition was not observed in our resistance measurements for another four samples. In addition, the phase transition has also not been observed in high pressure X-ray diffraction^[5] and electrical resistance^[6,7] measurements.

In this work, the P - V relationships for two solid C_{60} samples at room temperature were measured. The P - V relationship for one of the samples is shown in Fig.3. It is shown from the experimental results that the porosity in the samples measured could be eliminated through twice of compression to 4.5 GPa. The P - V data given in this work were those of the samples which were densely compacted.

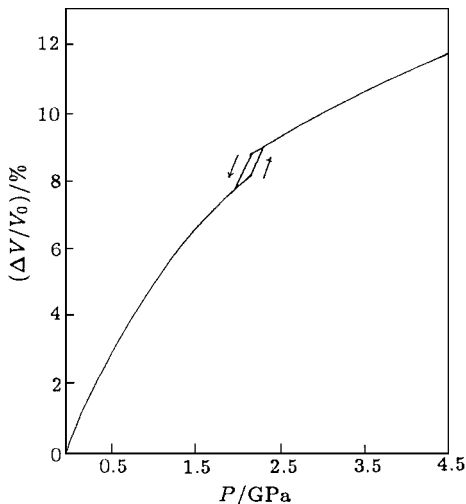


Fig.3. P - V relationship for solid C_{60} up to 4.5 GPa.

We can see from Fig.3 that during loading the change of $\Delta V/V_0$ values with pressure suddenly increases at about 2.16 GPa and continues to about 2.30 GPa, while during unloading it suddenly increases at about 2.2 GPa and continues to about 2.08 GPa. The phenomena can all be observed several times in measurements for each sample, indicating that the solid C_{60} sample undergoes a phase transition from fcc to sc structure^[13,14] at about 2.2 GPa, and it is reversible. The result is consistent with that obtained

using capacitance measurement in the DAC in the present work, with only a small difference in the transition pressure. We think that the homogeneity of pressure in the piston-cylinder type measurement device used in the work is better than that in the DAC, so the phase transition in solid C_{60} occurs at a certain pressure, about 2.2 GPa. It is shown again from the P - V relationship measurements that solid C_{60} also has a phase transition at room temperature and lower pressure.

The experimental $(\Delta V/V_0)$ - P data before the phase transition have been fitted by Bridgman equation

$$-\Delta V/V_0 = ap + bp^2 + cp^3,$$

and coefficients a , b and c have been determined by using the least squares method. The calculated results are given in Table 1. Its Grüneisen parameter γ_0 , bulk modulus B_0 and the first-order pressure derivative B'_0 of B_0 have also been calculated using coefficients a and b according to the following relationships:

$$\gamma_0 = -b/a^2 - 2/3,$$

$$B_0 = 1/a,$$

$$B'_0 = -2b/a^2 - 1.$$

Their results are shown in Table 2.

The experimental $(\Delta V/V_0)$ - P data after the phase transition have also been fitted by a polynomial equation,

$$-\Delta V/V_0 = a_0 + ap + bp^2 + cp^3,$$

where a_0 , a , b and c have been determined by using the least squares method. The results are shown in Table 3.

Table 1. Coefficients a , b and c for solid C_{60} in Bridgman equation before the phase transition.

$a/10^{-6}(\text{MPa})^{-1}$	$-b/10^{-10}(\text{MPa})^{-2}$	$c/10^{-13}(\text{MPa})^{-3}$	Pressure range/GPa
64.792	166.56	21.555	0-2.16

Table 2. γ_0 , B_0 and B'_0 of solid C_{60} .

γ_0	B_0/GPa	B'_0
3.30	15.434	6.9352

Table 3. Coefficients a_0 , a , b and c for solid C_{60} in polynomial equation after phase transition.

$a_0/10^{-2}$	$a/10^{-6}(\text{MPa})^{-1}$	$-b/10^{-10}(\text{MPa})^{-2}$	$c/10^{-13}(\text{MPa})^{-3}$	Pressure range/GPa
2.6178	40.066	65.374	4.9636	2.22-4.50

In addition, the phase transition has also been observed by DTA^[13,14] and neutron diffraction^[15] measurements at pressures above 0.3–0.45GPa. However, in these measurements, gases (He, Ne, Ar and N₂) were used as pressure media, and the gases easily permeated into the C₆₀ lattice. In our measurements, solids (the sample itself and indium) were used as pressure media. Using different materials as pressure media, one can expect that the transition pressure could be different. We think that there might be larger pressures in the C₆₀ lattice due to interpenetration of the gases into the lattice of C₆₀, thus the transition pressures of C₆₀ were smaller with gases as pressure media than with solids.

IV. CONCLUSIONS

It has been confirmed from *C-P* and *P-V* mea-

surements that solid C₆₀ also has a phase transition at room temperature and a lower pressure.

The experimental results obtained in this work again show that the capacitance measurement method in the DAC established by us is reliable and useful, and this method can detect phase transitions at high pressure which cannot be observed by high pressure resistance or X-ray diffraction measurement, etc.

ACKNOWLEDGMENTS

The authors express sincere thanks to Profs. J. C. Hermanson, R. J. Swenson, G. F. Tuthill, F. L. Howell, M. Lu, and to N. Williams, E. Andersen, for their support and help. We also thank the University of North Dakota Energy and Mineral Research Center for the loan of the Capacitance Measurement System employed in this work.

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