

DIELECTRIC STUDY OF PRESSURE INDUCED fcc–sc PHASE TRANSITION IN FULLERENE C₆₀

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(Received November 19, 1999; revised version April 26, 2000;
in final form July 27, 2000)

Phase transition in polycrystalline fullerene C₆₀ from fcc phase to a simple cubic phase sc induced by hydrostatic pressure up to 0.5 GPa was studied by dielectric method. Pressure coefficient $dT_c/dp = 144 \pm 8 \text{ K/GPa}$ was determined. This value is consistent with pressure coefficients obtained with other experimental techniques.

PACS numbers: 74.70.Wz, 77.22.Ch, 62.50.+p, 64.70.-p

1. Introduction

Fullerene C₆₀ undergoes first-order phase transition from fcc to sc phase under ambient pressure [1]. Fullerene molecules rotate isotropically in face centered cubic phase fcc (space group $Fm\bar{3}m$) while in simple cubic phase sc (space group $Pa\bar{3}$) the rotation is restricted to three axes separated by energy barriers [2]. First dielectric studies around the phase transition were published by Alers et al. [3]. There is a change in the lattice constant $\Delta a \approx 0.05 \text{ \AA}$ at T_c giving the volume change $\Delta V/V$ of about 1% [1]. Further dielectric studies [4] showed anomaly of electric permittivity ϵ' at T_c . Temperature of the phase transition increases linearly with pressure. The pressure coefficient dT_c/dp determined by different experimental techniques ranged from 105 K/GPa to 164 K/GPa [5–9]. Electric permittivity measurements have not been applied so far to pressure studies of C₆₀. The purpose of present work was to determine pressure coefficient by studying pressure dependence of electric permittivity ϵ' in polycrystalline C₆₀.

2. Experimental

Silver electrodes were pasted on a pressed pellet of polycrystalline C₆₀. The sample was placed in a steel high-pressure cylinder. The pressures up to 0.5 GPa were applied using the petroleum ether as pressure transmitting medium. The C₆₀ is not soluble in this ether under pressure [9]. Capacity of the sample was measured by RLC 1689M GenRad bridge. The temperature was determined with Cu/constantan thermocouple.

3. Results and discussion

Structural studies [1] found the phase transition at $T_c = 260$ K with a discontinuity of $\Delta a \approx 0.05$ Å in lattice constant. Such change in structure implies the change in the value of induced polarizability α , which for pure C_{60} gives the only contribution to electric permittivity. Any dipolar impurity, e.g. even small amount of C_{70} or oxygen, gives additional contribution to electric permittivity. Hence, the change in ϵ' at the phase transition can be difficult or even impossible to be observed. Because fullerene C_{60} is susceptible to defects and impurities influencing structural phase transition at $T_c = 260$ K, noticeable change in electric permittivity may not be measured. To check if our sample of C_{60} is defected, temperature dependence of ϵ' at zero pressure was studied first. It has been found that upon cooling ϵ' slightly decreases. At $T_c = 260$ K there is a jump-like change in ϵ' characteristic of a first-order phase transition. Hence, the measurements were made at three different temperatures (293, 283, and 270 K) as a function of pressure.

Electric permittivity versus pressure at 293 K is shown in Fig. 1. With increasing pressure electric permittivity monotonically decreases. Distinct reversible jump in ϵ' has been observed for $p_c = 0.23$ GPa evidencing the phase transition from fcc phase to ordered sc phase. There is additional jump in ϵ' at $p \approx 0.34$ GPa in Fig. 1. This is probably related to the onset of orientation freezing of the rotation of C_{60} molecules visible at ambient pressure at $T_0 = 150$ K. The effect of this freezing was observed in bulk C_{60} [10–12] and C_{60} thin films [13, 14]. This freezing leads to the glass-like phase in C_{60} at $T \approx 90$ K. Similar reversible pressure dependencies were measured at 283 K and 270 K with jump-like change

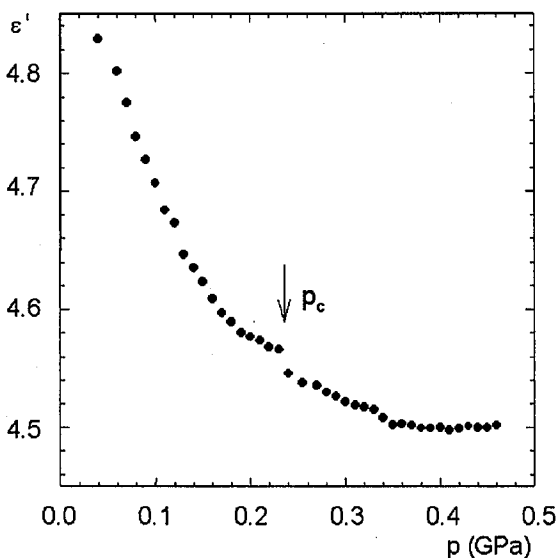


Fig. 1. Pressure dependence of electric permittivity ϵ' of the polycrystalline C_{60} at temperature $T = 293$ K.

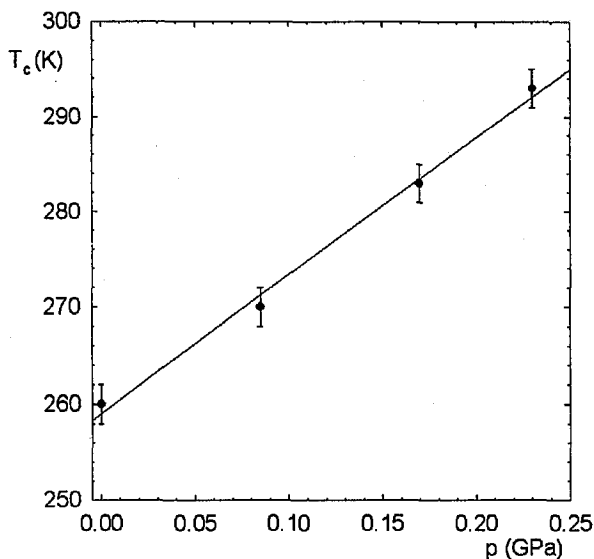


Fig. 2. Phase diagram of C_{60} . The solid circles denote the phase transition points from our experiments.

in ϵ' at 0.17 GPa and 0.085 GPa, respectively. The phase diagram resulting from these measurements is presented in Fig. 2. The pressure coefficient value thus determined equals 144 ± 8 K/GPa. This value is close to those obtained by other experimental techniques [5–9].

Pressure dependence of T_c for the first-order phase transition is described by the Clausius–Clapeyron equation

$$dT_c/dp = \Delta V/\Delta S = T_c \Delta V/Q, \quad (1)$$

where ΔV is the change of the unit cell volume, ΔS — change of entropy and Q represents the latent heat. Using the mean value of the lattice parameter for fcc and sc phases at the phase transition, obtained by Heiney et al. from X-ray and neutron diffraction measurements [1], we calculate the discontinuity of the unit cell volume $\Delta V = 26.4 \pm 2.4 \text{ \AA}^3$. From our value of $dT_c/dp = 144 \pm 8$ K/GPa, we get $\Delta S = 26 \pm 4.2$ J/(K mol) and $Q = 7.2 \pm 1.1$ kJ/mol.

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