DIELECTRIC STUDY OF PRESSURE INDUCED fcc—sc PHASE TRANSITION IN FULLERENE C_{60}

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Phase transition in polycrystalline fullerene C_{60} 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 \( dT_c/dp = 144 ± 8 \text{K/GPa} \) was determined. This value is consistent with pressure coefficients obtained with other experimental techniques.

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1. Introduction

Fullerene C_{60} 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 \( Fm\overline{3}m \)) while in simple cubic phase sc (space group \( Pa\overline{3} \)) 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 \( \Delta a \approx 0.05 \text{ Å} \) at \( T_c \) giving the volume change \( \Delta V/V \) of about 1% [1]. Further dielectric studies [4] showed anomaly of electric permittivity \( \varepsilon' \) 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 C_{60}. The purpose of present work was to determine pressure coefficient by studying pressure dependence of electric permittivity \( \varepsilon' \) in polycrystalline C_{60}.

2. Experimental

Silver electrodes were pasted on a pressed pellet of polycrystalline C_{60}. 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 C_{60} 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 \( \alpha \), 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 \( \varepsilon' \) 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 \( \varepsilon' \) at zero pressure was studied first. It has been found that upon cooling \( \varepsilon' \) slightly decreases. At \( T_c = 260 \) K there is a jump-like change in \( \varepsilon' \) 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 \( \varepsilon' \) 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 \( \varepsilon' \) 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 \( \varepsilon' \) of the polycrystalline \( C_{60} \) at temperature \( T = 293 \) K.](image-url)
Fig. 2. Phase diagram of C_{60}. The solid circles denote the phase transition points from our experiments.

in $\varepsilon'$ 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 $144 \pm 8$ 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

$$\frac{dT_c}{dp} = \frac{\Delta V}{\Delta S} = \frac{T_c \Delta V}{Q},$$

where $\Delta V$ is the change of the unit cell volume, $\Delta S$ — 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 $\Delta V = 26.4 \pm 2.4 \text{ Å}^3$. 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.

References

