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# The influence of air on the structural phase transition in fullerene C<sub>60</sub>

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## Abstract

A dielectric study of the structural phase transition from cubic fcc ( $Fm\bar{3}m$ ) to simple cubic sc ( $Pa\bar{3}$ ) at  $T = 260$  K in a fullerene C<sub>60</sub> monocrystal as well as the influence of absorbed oxygen on  $T_c$  are presented. For the first time the results of dielectric measurements of a C<sub>60</sub> monocrystal without any oxygen trapped inside showed a typical first order structural phase transition. It has been shown that absorbed oxygen affects the mechanism of the structural phase transition at  $T_c = 260$  K in the C<sub>60</sub> single crystal. In the cooling run, the electric permittivity  $\epsilon'$  in the vicinity of phase transition decreases for the oxygen free C<sub>60</sub> monocrystal whereas it increases for the C<sub>60</sub> crystal exposed to oxygen.

## 1. Introduction

The fullerene C<sub>60</sub> and fullerene-based compounds are still very fascinating materials, because they exhibit extraordinary physical properties. Pure C<sub>60</sub> has very interesting properties: it is a model plastic molecular crystal. Solid fullerene C<sub>60</sub> may be regarded as a soft dielectric material, in the sense that its dielectric behavior may depend on its structural characteristics, as well as the concentration of oxygen. Pekker *et al* [1] and Iwasiewicz *et al* [2] recently showed interesting results of rotor–stator molecular crystals of C<sub>60</sub> fullerene doped by cubane molecules C<sub>8</sub>H<sub>8</sub>. At room temperature the C<sub>60</sub> molecules rotate freely at the lattice sites. Cubane molecules C<sub>8</sub>H<sub>8</sub> occupy octahedral voids in the fullerene lattice while they are in an orientationally ordered (static) state. Such a modification of the fullerene lattice leads to a strong reduction in the critical temperature for the structural phase transition, i.e. from 260 K in pure C<sub>60</sub> to 140 K in C<sub>60</sub>·C<sub>8</sub>H<sub>8</sub> [1]. To better understand this phase transition it is necessary to understand all mechanisms leading to the structural phase transition in the pure C<sub>60</sub> crystal.

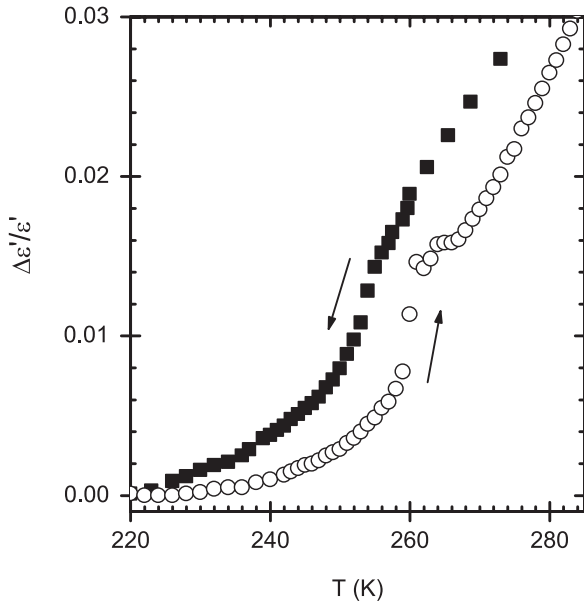
In the high temperature fcc phase ( $Fm\bar{3}m$ ) C<sub>60</sub> molecules undergo free isotropic rotation. At  $T_c = 260$  K the symmetry of the lattice becomes reduced to the simple cubic (sc)  $Pa\bar{3}$ . In the low temperature phase C<sub>60</sub> rotation is restricted to three specific axis [3]. Both x-ray study and high-resolution dilatometry show that at  $T_c$  there is a change in the lattice parameter  $\Delta a = 0.005$  nm from 1.415 to 1.410 nm [4–6] (a

decrease of the lattice parameter  $a$  on cooling). The length of the crystal decreases by  $\Delta l/l = 0.325\%$  [7]; it gives a volume change  $\Delta V/V$  of about 1%.

The dielectric permittivity should be affected by symmetry lowering and a change in the lattice parameter. A similar phase transition has been observed, for instance, in the ionic crystal Ni(NH<sub>3</sub>)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>. There, at  $T_c = 244$  K (on cooling) there is a discontinuous change in the lattice parameter during  $Fm\bar{3}m \rightarrow Pa\bar{3}$  symmetry reduction [8]. Additionally, a hysteresis typical of a structural phase transition of the first order of  $\Delta T = 6$  K, is observed.

Dielectric studies on fullerene C<sub>60</sub> reported so far [9–15] exhibited an increase in  $\epsilon'$  at  $T_c$  on a cooling run. However, the increase at  $T_c$  in  $\epsilon'$  for the pure C<sub>60</sub> is anomalous. The reduced lattice parameter in the fcc–sc structural phase transition should have decreased the crystal polarizability  $\alpha$  and decreased the electric permittivity. Studies on C<sub>60</sub> single crystals have shown that solid C<sub>60</sub> dielectric constant increases [9–15], because of a change in the rotational dynamics of C<sub>60</sub> molecules, which is accompanied with a fcc–sc structural transition. These dipolar moments have been attributed to orientational disorder among oriented C<sub>60</sub> molecules [10], and charge transfer between oxygen and C<sub>60</sub> molecules [12]. If the behavior of the dielectric response is dominated by oxygen molecules residing in the more readily filled regions, these molecules would thus reflect the influence of the structure of the host solid C<sub>60</sub> medium.

In this paper we present new experimental results of dielectric measurements of C<sub>60</sub> crystal. For the first time



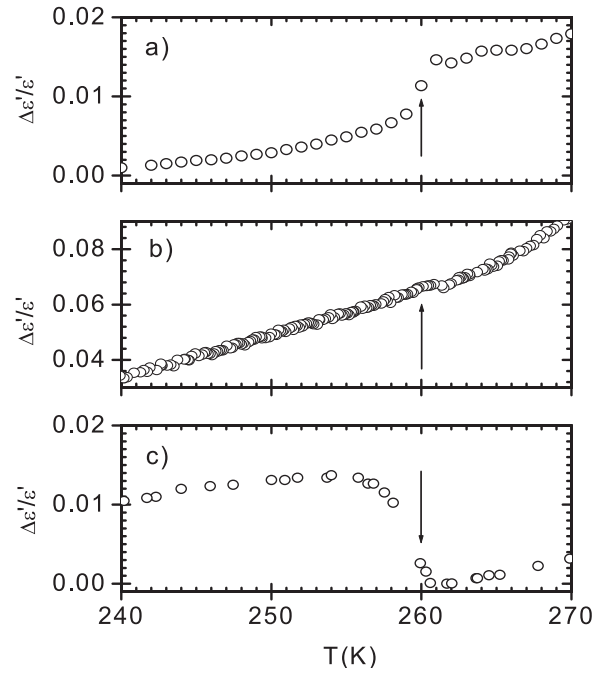
**Figure 1.** Temperature dependence of relative electric permittivity  $\Delta\varepsilon'/\varepsilon'(T)$  of the oxygen free  $C_{60}$  crystal; full squares—on cooling, open circles—on heating. The hysteretic behavior is clearly visible.

the results of dielectric measurements of a  $C_{60}$  monocrystal without any oxygen trapped inside and a typical first order structural phase transition are presented. Next, it will be shown that  $O_2$  molecules, present in the  $C_{60}$  crystal structure in octahedral interstices [16–18], couple to the lattice vibrational modes [19] affecting the change in the lattice parameter at  $T_c$ . In addition, via the  $O_2$ – $C_{60}$  interaction, additional dipole moments arise, giving as a result an increase in  $\varepsilon'$  at  $T_c$ .

## 2. Experimental details

Electric permittivity studies were performed on a HP 4275A LRC bridge operating from 10 kHz to 1 MHz. The measurements were performed in a helium flow cryostat enabling the temperature to be decreased from 300 K down to 4 K. The temperature was controlled with  $\pm 0.1$  K accuracy by an Oxford Instruments ITC-503 unit.

The  $C_{60}$  monocrystals were grown, using a source material of the  $C_{60}$  powder of purity 99.5%, by a sublimation method from the vapor phase by the double temperature gradient technique [20], in vacuum, into a closed glass tube at 863 K. High-performance liquid chromatography measurements on  $C_{60}$  monocrystals show no signs of impurity. The tube containing the grown crystals was kept in a black box. To minimize the contamination and oxidation effects, the tube was opened in a glove box with a pure gas helium atmosphere just before beginning the experiments. Silver electrodes were pasted to the first  $C_{60}$  crystal of size 1.5 mm  $\times$  0.65 mm  $\times$  0.12 mm (sample #1) in a glove box. During the experiment contact of the  $C_{60}$  monocrystal with the atmosphere was avoided. Two other samples of  $C_{60}$  monocrystals of the size: 1.5 mm  $\times$  0.8 mm  $\times$  0.2 mm, and 1.4 mm  $\times$  0.7 mm  $\times$  0.25 mm, for the study of the influence of oxygen on the phase transition, were first exposed to atmospheric oxygen for



**Figure 2.** Comparison of temperature dependencies of relative electric permittivity  $\Delta\varepsilon'/\varepsilon'(T)$  (on heating) of: (a) oxygen free  $C_{60}$  crystal (as in figure 1, open circles), (b) air (oxygen) exposed  $C_{60}$  crystal for 10 min, (c) air (oxygen) exposed  $C_{60}$  crystal for 1400 h.

10 min (sample #2) and 1400 h (sample #3), after which the silver electrodes were pasted. After oxygen exposure to air, the samples were coated in epoxy resin to protect from further oxygen absorption.

## 3. Results

The temperature dependence of electric permittivity  $\varepsilon'(T)$  of the virgin oxygen free  $C_{60}$  monocrystal (sample #1) is presented in figure 1. The results are presented as  $\Delta\varepsilon'/\varepsilon'(T)$ ; i.e. as the change in  $\varepsilon'$  with temperature relative to the value of  $\varepsilon'$  at 4.2 K. The electric permittivity behavior is typical of a structural phase transition of the first order with a hysteresis of  $\Delta T = 6$  K. On cooling, at  $T = 254$  K, there is a change in crystal structure accompanied by a jump-like change in lattice constant. This results in a decrease in polarizability  $\alpha$ . Below  $T_c$ , the electric permittivity  $\varepsilon'$  still monotonically decreases as an effect of the thermal compression of the crystal lattice. The change of the relative electric permittivity  $\Delta\varepsilon'/\varepsilon'$  at the phase transition amounts to about 1%.

The temperature dependencies (on heating run) of the relative electric permittivity  $\Delta\varepsilon'/\varepsilon'$  in the phase transition region for  $C_{60}$  samples exposed to oxygen (figures 2(b), (c)) show essentially different behavior from the oxygen free virgin  $C_{60}$  sample (figure 2(a)), depending on the time exposure to air. Figure 2(b) presents  $\Delta\varepsilon'/\varepsilon'(T)$  for the sample #2 exposed to oxygen for 10 min. At  $T_c$ , there is no discontinuous change in  $\varepsilon'$  as for the oxygen free  $C_{60}$  (sample #1), only the change in the slope of  $\varepsilon'(T)$ . From room temperature to 4.2 K the total change of the electric permittivity  $\varepsilon'$  amounts to 20%.

For the C<sub>60</sub> sample #3, exposed to oxygen for much longer (1400 h) as compared to the sample #2, the phase transition also shows a jump (figure 2(c)), but in the opposite direction from the oxygen free C<sub>60</sub> sample. The change of the relative electric permittivity  $\Delta\varepsilon'/\varepsilon'$  in the phase transition region for the C<sub>60</sub> sample exposed to air (sample #3) amounts to 1.4%.

#### 4. Discussion

Dielectric studies of C<sub>60</sub>, presented in this paper, show that there is a substantial influence of oxygen exposure on the phase transition at  $T_c = 260$  K. The monocrystal of the virgin, oxygen free C<sub>60</sub> (no O<sub>2</sub> content) exhibits a discontinuous change in  $\varepsilon'$  at the phase transition temperature (figures 1 and 2(a)). The symmetry is lowered from fcc to sc and the lattice parameter changed discontinuously by  $\Delta a = 0.005$  nm; this implies changes in the polarizability of the C<sub>60</sub> lattice.

Landau's mean-field approximation [21, 22] was used to describe the temperature dependence of  $\varepsilon'$  of the oxygen free C<sub>60</sub> monocrystal (figures 1 and 2(a)). The free-energy expansion in the form:

$$F = F_0 + \frac{1}{2}\alpha(T - T_c)\eta^2 + \frac{1}{4}\beta\eta^4 + \frac{1}{6}\gamma\eta^6 - \frac{1}{2}a\eta^2 E^2 - \frac{1}{2}\varepsilon' E^2 \quad (1)$$

has been used for describing the transition at  $T_c$ , where  $F_0$  denotes the free energy of the high temperature (disordered) phase,  $a$  is a constant describing the density of effective charge and  $E$  is the electric field. The temperature dependence of the order parameter resulting from equation (1) is:

$$\eta^2 = -\frac{\beta}{2\gamma} \left[ 1 + \sqrt{1 - 4\frac{\alpha\gamma}{\beta^2}(T - T_c)} \right]. \quad (2)$$

Using equations (1) and (2) we get:

$$\varepsilon' = 4\pi a\eta^2 + \varepsilon'_0. \quad (3)$$

For  $a < 0$  an increase of order parameter  $\eta$  gives a decrease of crystal polarizability  $\alpha$  and a decrease of electric permittivity. At  $T_c$  and below  $T_c$  the electric permittivity  $\varepsilon'$  is given by:

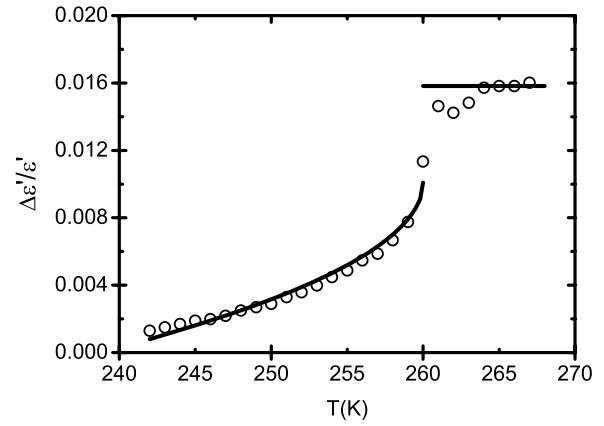
$$\varepsilon' = \varepsilon'_0 \quad \text{for the right side of } T_c, \quad (4a)$$

$$\varepsilon' = \varepsilon'_0 - \frac{2\pi a\beta}{\gamma} \quad \text{for the left side of } T_c, \quad (4b)$$

$$\varepsilon' = \varepsilon'_0 - \frac{2\pi a\beta}{\gamma} \left[ 1 + \sqrt{1 - 4\frac{\alpha\gamma}{\beta^2}(T - T_c)} \right] \quad \text{for } T < T_c. \quad (4c)$$

Figure 3 shows the behavior of the relative electric permittivity  $\Delta\varepsilon'/\varepsilon'$  of the oxygen free C<sub>60</sub> crystal as a function of increasing temperature in the vicinity of the phase transition. The solid line in figure 3 is a fit to the data from figure 1. This fit was obtained using equations (4a)–(4c).

The oxygen exposed C<sub>60</sub> samples show different electric permittivity behavior in the phase transition region in  $\varepsilon'(T)$ —figures 2(b)–(c). A short oxygen exposure (10 min) gives only a change in the slope of the  $\Delta\varepsilon'/\varepsilon'$  temperature dependence. A much longer oxygen exposure (1400 h) caused a distinct increase in the electric permittivity  $\varepsilon'$  at  $T_c$  (figure 2(c)),



**Figure 3.** Temperature dependence of the relative electric permittivity  $\Delta\varepsilon'/\varepsilon'(T)$  of the oxygen free C<sub>60</sub> crystal. The solid line is a fit obtained using equations (4a)–(4c).

described by equation (2) from the paper of Fartash [13]. This shows that oxygen present in the crystal lattice of C<sub>60</sub> is responsible for the character of the discussed transformation.

The dielectric constant  $\varepsilon'$  of the monocrystal of C<sub>60</sub> increases [9–15], because of a change in the rotational dynamics of C<sub>60</sub> molecules, which accompanies the fcc–sc structural transition. These dipolar moments have been attributed to orientational disorder among oriented C<sub>60</sub> molecules [10] and charge transfer between oxygen and C<sub>60</sub> molecules [12]. Belahmer *et al* [23] have shown, by NMR experiments performed on crystalline C<sub>60</sub> powders, that oxygen molecules hinder the rotations of C<sub>60</sub> molecules surrounded by these molecules.

The experimental result presented in figure 2(b) shows a slight increase in  $\varepsilon'$  in the samples exposed to the oxygen. Long O<sub>2</sub> exposure gives a much stronger effect—figure 2(c). Such an increase can be caused by an increase in the C<sub>60</sub> polarizability  $\alpha$  or by additional permanent dipole moments as a result of the presence of O<sub>2</sub> in a C<sub>60</sub> lattice. The first mechanism of  $\varepsilon'$  increase is ruled out, as it has been shown that lowering the temperature diminishes the polarizability of C<sub>60</sub>. The partial charge transfer from O<sub>2</sub> and C<sub>60</sub> is acceptable, however, the charge transfer from oxygen to C<sub>60</sub> was assumed [12]. Such a process generates permanent dipole moments. The estimated charge transfer was only  $0.04e$ , where  $e$ —charge of the electron. This means that there is a slight shift of electron distribution between C<sub>60</sub> and O<sub>2</sub>. Contrary to [12] we postulate that the charge transfer is reversed: from the C<sub>60</sub> to the O<sub>2</sub>, thus C<sub>60</sub> molecules are slightly positively charged. The electric resistance study of C<sub>60</sub> doped with O<sub>2</sub> has already suggested the charge transfer from C<sub>60</sub> to O<sub>2</sub> [24]. The presence of oxygen caused a  $10^4$  increase in resistivity. This effect was explained as the result of acceptor traps for free carriers.

Analogous to our interpretation one can find presented in [25] measurements of the magnetization of a large single C<sub>60</sub> crystal which has never been exposed to air. Luo *et al* [25] have found, at 260 K, a ‘jump-like’ discontinuity in magnetic susceptibility  $\chi$  with the relative change  $\Delta\chi/\chi$  equal to 1.2%. This value is in good agreement with our results: for the

$C_{60}$  monocrystal  $\Delta\varepsilon'/\varepsilon'$  amounts to about 1%. A similar value (1%) was shown in x-ray measurements for the volume change  $\Delta V/V$  [4–6]. In the previous papers on magnetic properties in  $C_{60}$  close to fcc–sc phase transition there was no evidence of ‘jump-like’ changes in magnetic susceptibility and Curie behavior appearing in the low temperature region due to oxygen presence in the system [24, 25].

Additional support is given by our electron paramagnetic resonance (EPR) study [26–29]. The  $C_{60}$  monocrystal with no oxygen contact is EPR silent. Air/oxygen exposure generates an EPR signal. The intensity of this line increases with the length of exposure [27]. The oxygen molecules execute almost ‘free’ diffusion in the crystal structure. If oxygen is removed from the  $C_{60}$  lattice by connecting the EPR tube to the vacuum line, so that  $O_2$  exposed again, the EPR signal amplitude is restored in a very short time. Nitrogen gave no EPR effect. The reduced pressure is not sufficient to remove the oxygen from the fcc fullerene structure.

## 5. Conclusions

In this paper we presented the investigation of a dielectric study of the structural phase transition from cubic fcc ( $Fm\bar{3}m$ ) to simple cubic sc ( $Pa\bar{3}$ ) at  $T_c = 260$  K in a fullerene  $C_{60}$  monocrystal as well as the influence of absorbed oxygen on  $T_c$ . We conclude that

- (1) The oxygen absorbed affects the mechanism of the structural phase transition at  $T_c = 260$  K in the monocrystal of  $C_{60}$ . The experimental evidence is the dramatic change in the temperature dependence of the electric permittivity  $\varepsilon'$  in the vicinity of phase transition.
- (2) The electric permittivity  $\varepsilon'$  in the vicinity of phase transition decreases (in the cooling run) for the oxygen free  $C_{60}$  monocrystal, whereas it increases for the  $C_{60}$  crystal exposed to oxygen.
- (3) Short oxygen exposure gives only a change in the slope of the temperature dependence of electric permittivity  $\varepsilon'$ .

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