

## Low temperature thermal expansion of fullerite $C_{60}$ alloyed with argon and neon

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The linear thermal expansion of compacted fullerite  $C_{60}$  alloyed with argon ( $Ar_xC_{60}$ ) and neon ( $Ne_xC_{60}$ ) are investigated by a dilatometric method. The experimental temperature is 2–12 K. In the same temperature interval the thermal expansion of  $Ar_xC_{60}$  and  $Ne_xC_{60}$  are examined after partial desaturation of the gases from fullerite. It is found that Ar and Ne alloying affects the temperature dependence of the thermal expansion coefficient of  $C_{60}$  quite appreciably. The libration and translation contributions to the thermal expansion of pure  $C_{60}$  are separated. The experimental results on the thermal expansion are used to obtain the Debye temperature of pure  $C_{60}$ . The effects observed are tentatively interpreted.

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Previously [1,2] we detected a negative coefficient of linear thermal expansion of polycrystalline and single-crystal  $C_{60}$  at helium temperatures. The effect was tentatively attributed to tunnelling rotation of the  $C_{60}$  molecules. In the orientational glass, which evolves in fullerite below 90 K, the potential barriers  $U_\phi$  impeding rotation of the molecules can vary within wide limits. The tunneling rotation can be performed only by those molecules for which the  $U_\phi$  barriers are quite low. Such molecules are referred to below as defects. If the  $U_\phi$  barriers grow with a decrease in the crystal volume, the tunneling rotation leads to negative thermal expansion of the crystal [3,4]. The tunneling rotation is also characterized by high absolute values of the Grüneisen coefficient [3]. These are the features that we detected experimentally [1,2].

The factors that might cause the negative thermal expansion of fullerite  $C_{60}$  were analyzed in [5,6]. Since the  $C_{60}$  molecules have fivefold symmetry axes, the molecules cannot be orientationally ordered completely; hence, certain defects are inevitable at low temperatures. The negative thermal expansion was explained qualitatively [6] assuming the coexistence of different orientational domains in the simple cubic lattice of  $C_{60}$ . The

potential relief is much smoother in the interdomain space (domain walls) than inside the domains, and the  $U_\phi$  barriers impeding rotation of the molecules are much lower in the domain walls. As a result, the molecules in the domain walls (unlike those inside the domains) can remain nearly free rotators down to much lower temperatures.

The aim of this study was to test the assumptions used in [1,2]. We investigated the thermal expansion coefficient  $\alpha$  of a compacted  $C_{60}$  alloyed with inert gases at 2–12 K. The alloying gas atoms introduced into the fullerite lattice were expected to change the  $U_\phi$  barriers impeding rotation of the neighboring  $C_{60}$  molecules. They could thus influence the probability of rotational tunneling of these molecules and the tunneling-induced contribution to the thermal expansion. If the  $U_\phi$  barrier height and (or) width increase, the total negative thermal expansion  $\int \alpha dT$  should decrease and shift towards lower temperatures. Let us remember that in the low-temperature phase each  $C_{60}$  molecule is associated with two tetrahedral and one octahedral interstitial cavities whose average linear dimensions are about 2.2 Å and 4.2 Å, respectively [7–9]. According to x-ray and neutron diffraction data [10–13], the Ne and Ar atoms, with gas-kinetic diameters

2.788 Å and 3.405 Å [14], respectively, occupy only the octahedral cavities. The studies were carried out using a high-sensitivity capacitance dilatometer [15]. The experimental procedure was described in [1]. The sample was prepared by compacting high-purity (99.99%)  $C_{60}$  powder under about 1 kbar at room temperature. The method of preparation of a sample excludes appreciable contents of argon and atmospheric gases in fullerite [1]. The grain sizes were 0.1–0.3 mm. The resulting sample was a cylinder 9 mm high and 10 mm in diameter. The preliminary results were published in [16].

### Ar-alloyed fullerite

The linear expansion coefficient of the  $C_{60}$  sample was first measured before alloying at 2–12 K. The sample was then alloyed with argon at room temperature under atmospheric pressure. The alloying lasted for 460 hours. The alloyed sample was slowly cooled in the alloying gas atmosphere to helium temperatures. Since in the process of cooling and measurement the walls of the measuring cell of the dilatometer are colder than the sample, the alloying gas becomes condensed on the cell walls (not on the sample) as the temperature falls. Then the thermal expansion coefficient of the Ar-alloyed  $C_{60}$  was measured at 2–12. Note that on cooling, the phase transitions of  $C_{60}$  occurred in an Ar atmosphere.

Figure 1 shows the measured coefficients before (curve 1) and after (curve 2) Ar-alloyed. It is seen that the alloying has strongly affected the thermal expansion of  $C_{60}$ : the introduction of the alloying gas reduced considerably the positive coefficients and strongly suppressed the negative thermal expansion effect and shifted it towards lower temperatures. To explain the effects observed, it seems natural to assume that the atoms of Ar impurity impede rotation of the  $C_{60}$  molecules and thus enhance the noncentral forces acting upon the  $C_{60}$  molecules. With the noncentral forces enhanced, the libration frequencies  $\omega_i$  of the  $C_{60}$  molecules should increase, and at  $T < \hbar\omega_i/k$  the contribution of librations to the heat capacity and thermal expansion of the crystal should decrease. At 5–12 K the tunneling effects are no longer important. In this temperature range the translational lattice vibrations and the molecular librations are responsible for the thermal expansion. In [17,18] the libration contribution to the heat capacity of  $C_{60}$  was described using two libration frequencies, 30 K and 58 K. Thus the above inequality holds for the temperature interval 5–12 K and the assumed decrease in the libration contribution into the thermal ex-

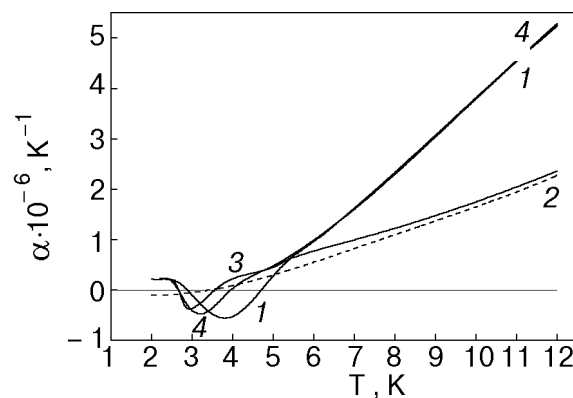


Fig. 1. Temperature dependences of the thermal expansion of compacted fullerite  $C_{60}$ : pure fullerite before alloying with Ar (1); Ar-alloyed fullerite (2); fullerite after evacuation of Ar for 3 days (3) and for 45 days (4).

pansion at these temperatures seems to be reasonable. As the noncentral forces increase, the  $U_\phi$  barriers impeding rotation of the molecules also become higher. This diminishes the probability of rotational  $C_{60}$  tunneling and the tunneling splitting of the energy levels. As a result, the negative thermal expansion decreases and the region of tunneling effects shifts towards lower temperatures.

We should remember that the libration contribution is made by all  $C_{60}$  molecules, while the negative contribution is made only by the molecules which we call «defects».

When the measurement of the thermal expansion coefficient of the alloyed  $C_{60}$  sample at low temperature was completed, the sealed measuring cell with the sample was warmed to room temperature and evacuated to  $1 \cdot 10^{-3}$  mm Hg. The gas was evacuated at room temperature for 3 days. The thermal expansion of the sample was then investigated again at low temperatures. The results obtained are shown in Fig. 1 (curve 3). It is seen that the thermal expansion coefficient changes only slightly above 5 K. Below 3.5 K the change is more appreciable: there appears a region of negative thermal expansion with a nonmonotonic temperature dependence  $\alpha(T)$ . Qualitatively, the dependence is similar to that for the sample before alloying, but the minimum in curve 3 is smaller and shifted towards lower temperatures. Since the temperature dependence of the thermal expansion coefficient of pure  $C_{60}$  was not restored after the 3-day gas evacuation, the measuring cell with the sample was warmed again to room temperature and evacuated for 45 day. We then repeated the measurement of the thermal expansion coefficient at low temperatures. The results obtained are shown in Fig. 1 (curve 4). In contrast to the short-evacuation re-

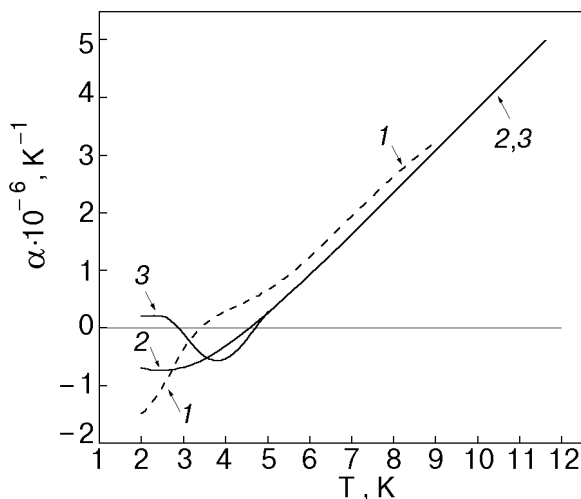


Fig. 2. Temperature dependences of the thermal expansion of pure fullerite  $C_{60}$ : polycrystalline samples [1] (1); single crystal [2] (2); polycrystalline samples (3) (in this study).

sults, the prolonged evacuation changes the «high temperature» part ( $T > 5$  K) of the dependence  $\alpha(T)$  more significantly. After a 48-day evacuation, the coefficients  $\alpha$  of the pure and alloyed  $C_{60}$  samples practically coincide at  $T > 5$  K, whereas their dependences  $\alpha(T)$  at  $T < 5$  K still differ considerably.

The changes in  $\alpha(T)$  after removal of argon from the sample may be explained as follows. The molecules that we call «defects» are inevitably displaced with respect to the lattice sites. As a result, the octahedral voids surrounding such molecules are not identical, and the potential wells that they form for the impurity are different—deeper or shallower than the octahedral potential wells adjacent to most of the  $C_{60}$  molecules. At the initial stage of evacuation, the Ar atoms first leave the shallow potential wells near the defects, which causes faster changes in the negative part of  $\alpha(T)$ . The removal of the Ar atoms from the deeper wells is slower than from most of the crystal volume. That is why at the completing stage, the positive part of  $\alpha(T)$  is restored faster at  $T > 5$  K.

Note another interesting fact. Figure 2 shows the linear thermal expansion coefficients for a single crystal [2] (curve 2) and two polycrystalline samples investigated in this study (curve 3) and in [1] (curve 1). At  $T > 5$  K the  $\alpha$  values of all the samples are close to each other. However, considerable distinctions are observed in the temperature region where the thermal expansion becomes negative. We attribute this to different amounts of the «residual» impurity whose particles are still present in the deep potential wells near the defects. The

negative thermal expansion should therefore be particularly sensitive to the pre-history of the sample.

### Ne-alloyed fullerite

To speed up saturation (desaturation) of  $C_{60}$ , we needed a gas with smaller particles. Our choice was neon. It is known from the literature [10,19] that saturation of  $C_{60}$  with Ne proceeds much faster than in the case of Ar: at room temperature it takes no more than 24 hours. To estimate the saturation time of our sample from these data, we need to know the grain sizes in [10,19]. In [20] (the same laboratory as in [19]), the average grain size was  $l \sim 0.08$  mm. Since the characteristic time of saturation is  $\tau \sim l^2$ , it should be  $\tau \sim 10^2$  hours in our case. The choice of Ne as an alloying gas is also based on the fact that Ne (and Ar) atoms become localized in the octahedral interstices. At room temperature and under atmospheric pressure they occupy 21% of these interstices [10]. Taking into account that in a simple cubic lattice each of  $C_{60}$  molecules is surrounded by six octahedral interstices, the 21% occupancy implies that with randomly distributed impurity atoms, about 75% of the  $C_{60}$  molecules have Ne atoms nearby.

$C_{60}$  was alloyed with Ne at room temperature under atmospheric pressure for 340 hours by the same procedure as was applied for Ar-alloying. The sample was then cooled in a Ne atmosphere to the temperature of the experiment, and the linear thermal expansion coefficients were measured.

The results obtained are shown in Fig. 3 (dashed curve 2). For comparison, the same figure shows the thermal expansion coefficient of Ar-alloyed  $C_{60}$  (curve 4). It is seen that above 6 K the curves practically coincide; below 6 K neon influences the

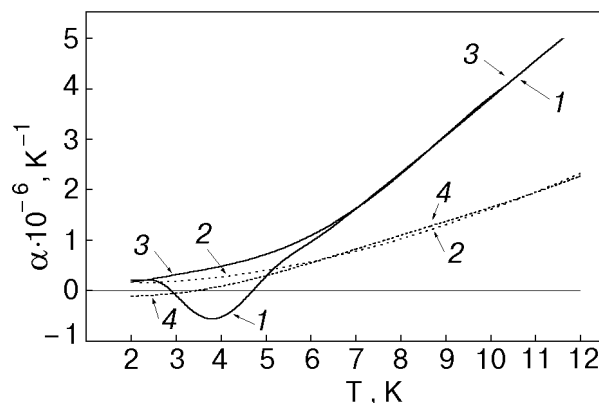


Fig. 3. Linear thermal expansion coefficients of fullerite  $C_{60}$  alloying with Ne: pure compacted fullerite before alloying (1); compacted fullerite alloyed with Ne (2); compacted fullerite after evacuation of Ne (1 day) (3); compacted fullerite alloyed with Ar (4).

thermal expansion coefficient more strongly than Ar does. The behavior of the low-temperature part of curve 2 (see Fig. 3) can be accounted for by a larger amount of Ne in the sample, since Ne dissolves much faster than Ar.

We then removed some quantity of Ne from the sample (24 hours at room temperature) and measured the thermal expansion coefficient again (Fig. 2, curve 3). It is seen that above 7 K the coefficient came back to its prior-to-alloying values. Below 7 K the distinctions between the coefficients measured before and after alloying even increased.

At the concluding stage of the experiment the removal of Ne from the sample was continued for 45 days at room temperature, and the thermal expansion coefficient was then measured. The results obtained before and after alloying coincided in the whole temperature interval (Fig. 3, curve 1). We can thus conclude that the  $C_{60}$  sample was completely free of neon. Desaturation for the same length of time was not sufficient to remove all argon from the sample.

Of interest are two features exhibited by the linear thermal expansion coefficient of Ne alloyed  $C_{60}$ . First of all, at 6–12 K the  $\alpha(T)$  values practically coincide for Ar- and Ne-saturated samples. Let us assume that Ar- and Ne-alloying increases the libration frequencies of the  $C_{60}$  molecules to such extent that the contribution of librations to the thermal expansion is negligible up to 12 K. Besides, it is natural to expect that the Ar and Ne impurities have negligible effect on the translational vibration of the lattice and their contribution to the thermal expansion. If this is correct, the thermal expansions of the Ne- $C_{60}$  and Ar- $C_{60}$  solutions and the contribution of the translational vibrations to the thermal expansion of pure  $C_{60}$  should all coincide in the 6–12 K region, where the contributions of librations and tunneling to  $\alpha(T)$  are not observable. We tried to describe this contribution as

$$\Delta\alpha_{\text{trans}} = \gamma C(T/\Theta_D)/BV$$

where  $\gamma$  is the Grüneisen coefficient;  $V$  is the molar volume of  $C_{60}$ ;  $B$  is the bulk modulus of  $C_{60}$ ;  $C(T/\Theta_D)$  is the Debye heat capacity, and  $\Theta_D$  is the Debye temperature. The calculation was made using  $V = 416.7 \text{ cm}^3/\text{mol}$  [21] and  $B = 10.3 \text{ GPa}$  [22].  $\gamma$  and  $\Theta_D$  were fitting parameters. The above expression could describe the experimental  $\Delta\alpha_{\text{trans}}$  values quite well taking  $\gamma = 2.68$  and  $\Theta_D = 54 \text{ K}$ .  $\gamma$  is close to the corresponding values for rare-gas solids [23]. In the literature the  $\Theta_D$  data for  $C_{60}$  vary widely. As follows from the analysis of the temperature dependence of heat capacity,  $\Theta_D = 37 \text{ K}$  [18],

50 K [24,25], 60 K [26], 80 K [27] and 188 K [28]. Studies of the elastic properties of single crystal  $C_{60}$  give  $\Theta_D = 100 \text{ K}$  [29]. Even if we disregard the very high values  $\Theta_0 = 188 \text{ K}$  [28] and  $\Theta_D = 100 \text{ K}$ , where the error is high [29], the scatter of the  $\Theta_D$  values is still wide. The Debye temperatures obtained by the calorimetric method are highly sensitive to the impurities present in the fullerite and the technique employed to separate the contributions to the heat capacity. The  $\Theta_D$  values obtained from ultrasound velocities are more reliable, since they are mainly determined by the translational vibrations of the lattice and are not very sensitive to impurities. According to the ultrasound data for single-crystal  $C_{60}$  at  $T = 300 \text{ K}$ ,  $\Theta_D = 66 \text{ K}$  [30]. In [21] the data in the literature on ultrasound velocities of polycrystalline  $C_{60}$  were analyzed and extrapolated to low temperatures. The Debye temperature thus calculated at  $T > 0$  is 55.4 K. This value of  $\Theta_0$  is very close to ours. We should, however, remember that in our case  $\Theta_D$  is closer to its high-temperature limit  $\Theta_\infty$ . For rare-gas solids the difference between  $\Theta_0$  and  $\Theta_\infty$  amounts to 10–12% [23].

The above consideration suggests that our  $\gamma$  and  $\Theta_D$  are quite realistic and thus support the assumption that curves 2 and 4 in Fig. 3 describes the contribution of translational vibrations to the thermal expansion coefficient of pure  $C_{60}$ . Proceeding from this assumption, we can expect that the difference between curve 1 and curves 2 and 3 (Fig. 3) at 6–12 K represents the contribution of librations  $\Delta\alpha_{\text{lib}}$  to the thermal expansion coefficient of pure  $C_{60}$ .  $\Delta\alpha_{\text{lib}}$  is well described by the Einstein term with the characteristic Einstein temperature  $\Theta_E = 39 \text{ K}$ . This value does not come into conflict with the above results [18].

Another feature of the thermal expansion coefficient of the Ne- $C_{60}$  mixture is the increase (instead of the expected decrease) in  $\alpha(T)$  at 2–5 K after a 24-hour evacuation of Ne. The effect may be caused by a nonmonotonic dependence of the changes in  $\alpha(T)$  upon the impurity concentration. Further quantitative studies of the concentration dependence of  $\alpha(T)$  are called for to obtain more-certain information.

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