

Argon effect on thermal expansion of fullerite C₆₀ at helium temperatures

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The linear thermal expansion of compacted Ar-doped fullerite C₆₀ (Ar_xC₆₀) is investigated at 2–12 K using dilatometric method. The thermal expansion of Ar_xC₆₀ was also studied after partial desaturation of argon from fullerite. It is revealed that argon doping resulted in the considerable change of the temperature dependence of the thermal expansion of fullerite. An explanation of the observed effects is proposed.

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We have already reported the detection and investigation of a negative linear thermal expansion coefficient α of fullerite C₆₀ at helium temperatures [1,2]. The effect was tentatively attributed to tunneling transitions between energetically equivalent orientations of C₆₀ molecules. To test this assumption, we have studied the thermal expansion of Ar-doped C₆₀ at liquid helium temperatures. The results of these studies are presented in this communication. In a fullerite crystal each C₆₀ molecule is associated with two tetrahedral and one octahedral interstitial cavities [3] whose average linear dimensions are about 2.2 Å and 4.2 Å, respectively [4]. According to x-ray [5] and neutron diffraction [6, 8] data, the Ar atoms with the gas-kinetic diameter 3.405 Å [7] occupy only the octahedral cavities. It should also be noted that at 15 K the lattice parameter of a saturated Ar_xC₆₀ solution is 0.006 Å smaller than that of fullerite [6]. We assumed that the Ar atoms occupying the octahedral interstices would increase the potential barrier impeding rotation of the C₆₀ molecules and thus diminish the probability of rotational tunnel transitions and consequently the tunneling splitting of the ground state of the molecules [2]. If this assumption is correct, the total negative thermal expansion

$\int \alpha dT$ should decrease and the region of negative expansion will shift towards lower temperatures after doping.

An Ar-doped C₆₀ sample was studied at 2–12 K using a high-sensitivity capacitance dilatometer [9] and with the same procedure as was applied to pure C₆₀ earlier [1,2]. The sample was prepared by compacting high-purity (not worse than 99.98% C₆₀) powder under about 1 kbar. The grain sizes were 0.1–0.3 mm. The resulting C₆₀ sample was a cylinder 9 mm high and 10 mm in diameter. The thermal expansion coefficient along the cylinder axis was first measured at 2–12 K before doping. The evacuated sealed measuring cell with the sample has been warmed to room temperature and filled with argon under atmospheric pressure. The doping lasted for 19 days.

When the doping process was completed, the Ar-filled measuring cell with the sample was slowly cooled to helium temperatures. In this case both the phase transitions of C₆₀ (at 260 and 90 K) occurred in an Ar atmosphere. Figure 1 shows the measured coefficients before (curve 1) and after (curve 2) Ar-doping. It is seen that the doping not only leads to the expected decrease in the negative thermal expansion and its shift towards lower temperatures

but that it also reduces strongly the (positive) thermal expansion coefficient above 5.5 K.

It seems natural to assume that the Ar-induced increase in the barrier impeding rotational motion of the C_{60} molecules should also enhance the angular dependence of the non-central forces acting upon the C_{60} molecules. As a result, the frequencies of the orientational oscillations of the molecules should increase and hence the normal (positive) thermal expansion coefficient dependent on these oscillations should decrease. This is what we observed experimentally at $T > 5.5$ K. The experimental results can thus be explained qualitatively proceeding from the assumption that the atomic Ar impurity introduced to the octahedral interstices of C_{60} suppresses the splitting of the ground state of the C_{60} molecules and modifies the orientational oscillation spectrum of the molecules.

It appears that dissolved Ar atoms influence very strongly the thermal expansion even though they are able to move quite freely inside the octahedral lattice interstices. We should also bear in mind that in our experiment the Ar atoms occupy only a part of the octahedral interstices. We did not estimate the quantity of the dissolved Ar. According to Morosin et al. [10], neon occupies only 21% of the octahedral interstices under identical conditions (room temperatures, atmospheric pressure). 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 Ar atoms nearby. However, because the Ar atoms are larger than Ne atoms, this number must be considered an upper limit of occupancy only.

Another important consideration here is that we believe that only a small fraction of the C_{60} molecules (the so-called «defects») for which the rotation-impeding barrier U_{ϕ} is quite low contributes to the negative thermal expansion of fullerite [2]. Correspondingly the doping-induced change in the negative thermal expansion is determined only by the Ar atoms neighboring these «defects». At the same time, the positive thermal expansion is affected by all the dissolved Ar atoms.

To obtain more information, we studied how the thermal expansion coefficient changed when the doping atoms were removed from the sample. For this purpose, the measuring cell with the sample was warmed to room temperature and evacuated to $1 \cdot 10^{-3}$ mm Hg. The gas evacuation at room temperature lasted for 3 days. The thermal expansion was then measured at low temperatures. The results

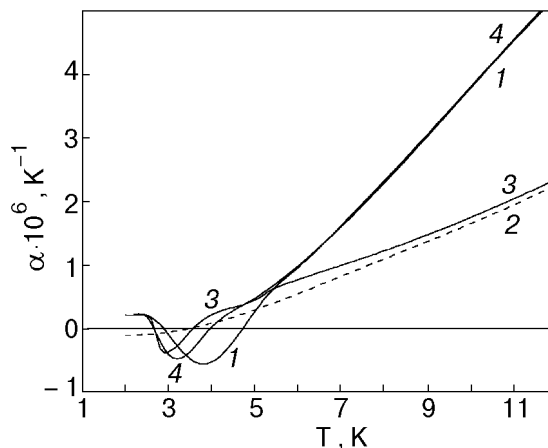


Fig. 1. Temperature dependences of the thermal expansion of compacted fullerite C_{60} : pure fullerite before doping (1); Ar-doped fullerite (2); fullerite after evacuation of Ar for 3 days (3) and for 45 days (4).

are shown in Fig. 1 (curve 3). It is seen that the thermal expansion coefficient changes only slightly above 5 K but below 3.5 K the negative thermal expansion again has the minimum typical for undoped C_{60} . The measuring cell with the sample was warmed again to room temperature and gas evacuation was continued for 42 days. The thermal expansion coefficient was then measured with the results shown in Fig. 1 (curve 4). Note, in particular, that after a total of 45 days evacuation of argon the «high-temperature» part of the thermal expansion coefficient was restored completely. The negative thermal expansion in the range 2.5–5 K, however, still differed from that of the initial pure sample.

This can be accounted for assuming the following. The octahedral voids adjacent to defects, i.e., C_{60} molecules with low U_{ϕ} barriers, form deeper potential wells for the impurity atoms than the regular octahedral interstices do. It is therefore more difficult to remove the impurities from these near-defect regions, and the residual impurities concentrated around defects are precisely those responsible for the negative thermal expansion of fullerite. There is also another fact supporting this assumption. The thermal expansion coefficients α of all our C_{60} samples, both used in Refs. 1, 2 and in this study, agree quite well above 5 K but they differ considerably in the temperature region where α is negative. These samples were prepared under different conditions and vary in quality and in the amount of residual impurities.

The proposed qualitative explanation of the effect observed cannot replace a consistent theoretical

interpretation. Several interesting ideas have been published to date, which are concerned with a tentative mechanism of the negative thermal expansion of molecular crystals [11]. In the case of fullerite, we decide in favor of our explanation since it accounts for the unusually high Gruneisen coefficients, which were observed experimentally.

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