

Effect of biatomic gas impurities on thermal expansion of fullerite C₆₀

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Orientational glasses with gas molecules occupying the octahedral interstitial sites in the C₆₀ lattice have been investigated by the dilatometric method in a temperature interval of 2.5–23 K. At temperatures 4–6 K the glasses undergo a first-order phase transition which is evident from the hysteresis of the thermal expansion and the maxima in the temperature dependences of the linear thermal expansion coefficients $\alpha(T)$ and the thermalization times $\tau_1(T)$ of the samples. The effect of the noncentral CO–C₆₀ interaction upon the thermal expansion and the phase transition in these glasses was clarified by comparing the behavior of the properties of the CO–C₆₀ and N₂–C₆₀ solutions.

В интервале температур 2,5–23 К выполнены dilatометрические исследования ориентационных стекол C₆₀ с заполнением молекулами газовых примесей октаэдрических междоузлий решетки фуллерита. В температурном интервале 4–6 К в исследованных стеклах наблюдалось фазовое превращение первого рода, подтверждаемое гистерезисом теплового расширения, присутствием максимумов на температурных зависимостях коэффициента линейного теплового расширения и времени термализации τ_1 образцов. Сопоставление поведения свойств растворов CO–C₆₀ и N₂–C₆₀ позволило установить влияние нецентрального взаимодействия молекул примесей с молекулами C₆₀ на тепловое расширение изученных стекол и фазовое превращение в них.

Below $T = 90$ K, fullerite C₆₀ is transformed into an orientational glass. According to dilatometric and X-ray structural data [1–7], the gases dissolved in C₆₀ effect significantly the glass thermal expansion and cause a first-order phase transition (polyamorphism) therein. It is of interest to study the effects of the gas impurity molecular parameters on the properties of C₆₀. To judge accurately of a certain molecular parameter, we must choose gas impurities that differ mainly in this particular parameter. In the case of biatomic gases, it is convenient to assess the role of the impurity-matrix interaction by comparing the behavior of CO–C₆₀ and N₂–C₆₀ solutions. In contrast to O₂, CO and N₂ molecules do not react chemically with C₆₀ at the tempera-

tures to which C₆₀ has to be heated to desorb the volatile impurities. These molecules are essentially identical in molecular weights ($M(\text{CO}) = 28.0105$, $M(\text{N}_2) = 28.0134$) and close gas-kinetic diameters ($\sigma(\text{CO}) = 3.766 \text{ \AA}$, $\sigma(\text{N}_2) = 3.756 \text{ \AA}$) [8], but they differ significantly in electric quadrupole moments Q ($Q(\text{CO}) = -2.839 \cdot 10^{-26}$ esu, $Q(\text{N}_2) = -1.394 \cdot 10^{-26}$ esu) [9]. It is evident from the discussion below that the quadrupole moments are the main factors determining the effect of these impurities upon the low-temperature thermal expansion and polyamorphism of C₆₀.

The dilatometric data on orientational C₆₀ glasses with molar N₂ concentrations (N₂-to-C₆₀ molecule ratio) of 9.9 % and 100 % were published in [3].

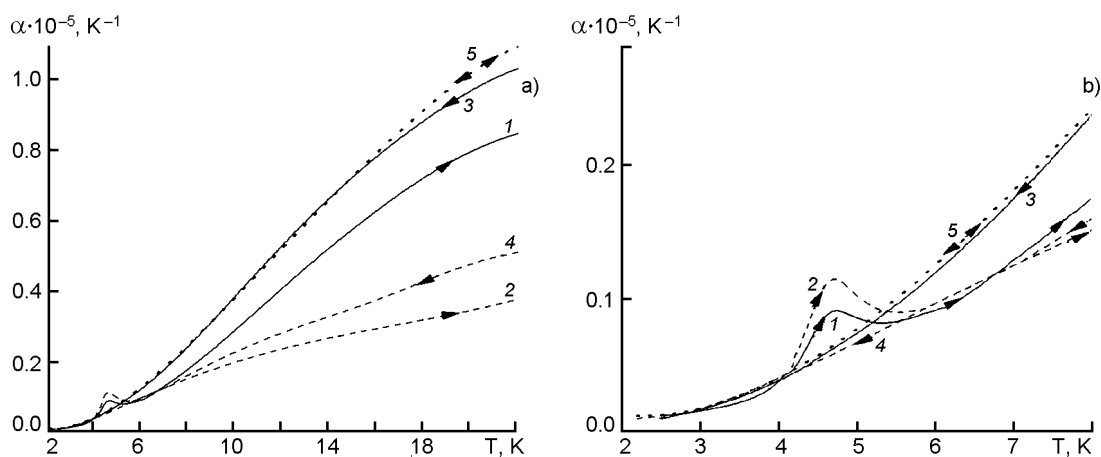


Fig. 1. Temperature dependences of the linear thermal expansion coefficient for CO-C₆₀ solutions in temperature intervals 2.5–23 K (a), and 2.5–8 K (b). Curves 1 and 2 correspond to heating of 26 mol. % and 90 mol. % CO-C₆₀ samples, respectively; curves 3 and 4, to cooling of 26 mol. % and 90 mol. % CO-C₆₀ samples, respectively. The dotted line (5) is for pure C₆₀ for either heating or cooling the sample.

The impurity (N₂, CO) molecules occupy the octahedral interstitial cavities in the C₆₀ lattice, which has one octahedral cavity per C₆₀ molecule. In the experiments, the molar CO and N₂ concentrations were equal to the N₂ and CO occupancies of the octahedral sites in the C₆₀ lattice.

The C₆₀ sample with 26 mol. % CO was prepared as follows. Prior to saturation with CO, the sample (a 9 mm high cylinder of 10 mm in diameter; the preparation procedure is described in [2]) was kept for 72 h under dynamic evacuation at $P = 1 \cdot 10^{-3}$ Torr and $T = 400^\circ\text{C}$. The outgassed cell with the sample was filled with CO gas at room temperature to the 760 Torr pressure and sealed. The sample was kept in these conditions for 105 days. As a result, about 26 % of the octahedral cavities in the C₆₀ lattice were occupied by CO. After measuring the thermal expansion of the sample, the gas impurity composition was determined qualitatively and quantitatively using a vacuum desorption gas analyzer [12]. The preparation and analysis techniques for the C₆₀ sample with 90 mol. % CO are described in [13].

Thermal expansion of the CO-C₆₀ solutions was studied using a low temperature capacitance dilatometer. The instrument design and the measurement technique are detailed in [14]. Immediately before dilatometric measurement, the measuring cell filled with CO was cooled slowly to 65 K and then the CO that remained unabsorbed by the sample was removed. The further cooling of the sample and the subsequent dilatometric

investigations were performed in vacuum at least $1 \cdot 10^{-5}$ Torr. The thermal expansion of the CO-C₆₀ sample was measured after its four-hour exposure at $T = 4.2$ K.

The temperature dependences of the linear thermal expansion coefficient (LTEC) α of pure C₆₀ and the C₆₀ samples with different contents of the CO impurity are shown in Fig. 1. The α values are averaged over several measurement series. Due to the cubic symmetry of the lattice, the thermal expansion of the samples can be described using a single LTEC.

The thermal expansion of the investigated samples exhibited a number of specific features. On heating (curves 1, 2) and subsequent cooling (curves 3, 4), the thermal expansion coefficient has a hysteresis that indicates a first-order phase transition in the orientational CO-C₆₀ glasses. No hysteresis is observed for pure C₆₀ (curve 5). As the impurity concentration rises, the hysteresis onset shifts towards higher temperatures — from 3 K at 26 mol. % CO to 4 K at 90 mol. % CO. Below these temperatures, the $\alpha(T)$ values are practically identical on heating and cooling. Moreover, the LTECs of both the CO-C₆₀ samples (26 and 90 mol. % CO) and pure C₆₀ coincide within the measurement error. On heating in the 4 to 6 K interval, there is a region of instability with higher experimental errors and local LTEC maxima (Fig. 1), the errors being appreciably lower than the maxima heights. It is assumed [3–5] to include the temperatures of the first-

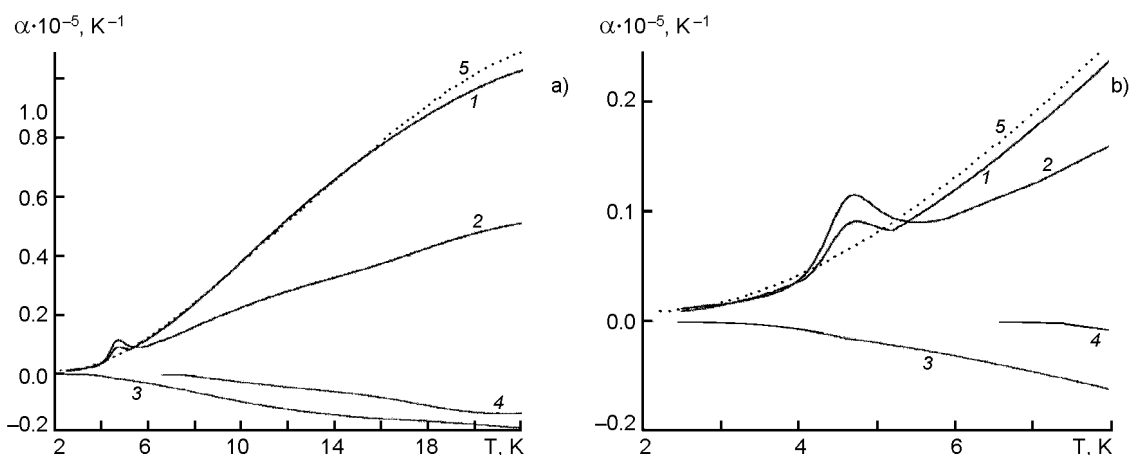


Fig. 2. Temperature dependences of the positive and negative components of the thermal expansion coefficient of CO-C₆₀ solutions in the intervals 2.5–23 K (a), and 2.5–8 K (b). The positive contributions are characterized by curves 1 (26 mol. % CO), and 2 (90 mol. % CO); the negative contributions, by curves: 3 (26 mol. % CO), and 4 (90 mol. % CO). Pure C₆₀ which exhibits a positive contribution only is shown by dotted line (5).

order phase transitions in orientational glasses doped with impurities.

Previous investigations [1–5] show that the thermal expansion of gas-doped C₆₀ contains positive and negative components with different characteristic relaxation times (τ_1 and τ_2 , respectively). The positive component is attributed [1–5] to the process of temperature equalization over the sample volume (thermalization); the negative one accounts for reorientation of the C₆₀ molecules. Since the C₆₀ crystal is perceived as consisting of domains with different orientational orders of the C₆₀ molecules and interlayers between the domains, it is concluded theoretically [15–17] that at low temperatures, the C₆₀ reorientation responsible for the orientational component of the thermal expansion occurs in the domain interlayers.

The thermal expansion of C₆₀ samples doped with CO also has two components. Those were separated using technique described in [1]. The temperature dependences of the positive and negative components for samples with different CO concentration are illustrated in Fig. 2. It is seen that the LTECs measured on heating both the CO-C₆₀ samples above 5.5 K and on cooling the 90 mol. % CO-C₆₀ sample are significantly lower than the LTEC of pure C₆₀ (Fig. 1). The effect increases with the CO concentration and persists even if only a positive component is accounted for (Fig. 2). In N₂-C₆₀ solutions, the effect exists only at high N₂ concentrations and is much weaker [3]. This feature is explained as follows. At the

temperatures of the experiment, the thermal expansion of pure C₆₀ is determined by translational lattice vibrations, C₆₀ librations and by the contributions from the two-level systems and soft modes that are typical for glasses, including the orientational ones. The admixed gas molecules can affect the above contributions and make their own contribution to the thermal expansion of the solid CO-C₆₀ solution.

As noted above, the thermal expansion coefficients of pure C₆₀ and the CO-C₆₀ solutions coincide at the lowest temperatures of the experiment. This means that at these temperatures, the CO impurity has a little effect on the dominant contributors to the thermal expansion — translational lattice vibrations, two-level systems and soft modes [18]. The weak effect of the impurity on the C₆₀ lattice translational vibrations is quite natural because CO adds little to the effective molecular weight of the CO-C₆₀ solutions, changing the lattice constant of C₆₀ at most by 0.15 % [19]. As the temperature rises, the contributions from the C₆₀ librations and CO vibrations increase significantly. But the latter can only result in higher LTEC values. Therefore, the lower LTECs of the CO-C₆₀ solutions in comparison with those of pure C₆₀ may be attributed to a lower contribution from the C₆₀ librations. The reason is as follows. At $T \leq 77$ K, the CO molecules are oriented in a certain way in the octahedral interstitial sites of C₆₀ [11, 20, 21]. Thus, the non-central interaction between the impurity and the surrounding C₆₀ molecules is not nulli-

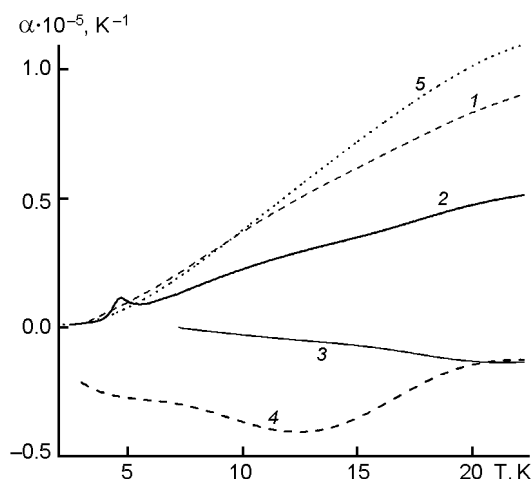


Fig. 3. Temperature dependences of the positive and negative components of the linear thermal expansion coefficient for CO-C₆₀ (solid lines) and N₂-C₆₀ (dashed lines) [3] solutions. The positive components characterized by curves: 1 (90 mol. % CO), and 2 (100 mol. % N₂), the negative components, by curves 3 (90 mol. % CO), and 4 (100 mol. % N₂). Pure C₆₀ which has a positive contribution only is shown by dotted line (5).

fied due to the rotation of CO molecules. The CO molecule has a dipole and a quadrupole electrical moments. The dipole moment is rather weak [22], and the non-central CO-C₆₀ interaction is mainly determined by the quadrupole moment of the CO molecule. This interaction enhances the non-central forces acting on the C₆₀ molecules and increases the librations frequency thereof. As a result, the contribution from the C₆₀ librations to the thermal expansion positive component decreases at these temperatures and its interval shifts towards higher temperatures. This effect is weaker in the N₂-C₆₀ solutions, since the quadrupole moment of N₂ molecules is much lower (see Fig. 3). In this Figure, compared are the positive and negative components of the thermal expansion for samples with 90 mol. % CO and 100 mol. % N₂, because the effects of impurities on the thermal expansion of doped fullerenes are most evident at high impurity concentrations.

In the context of the above consideration, the negative component of the thermal expansion is defined by the reorientation probability of the C₆₀ molecules in the domain interlayers. The negative LTEC component of the CO-C₆₀ solution decreases considerably as the CO concentration increases from 26 % to 90 % (Fig. 2). The

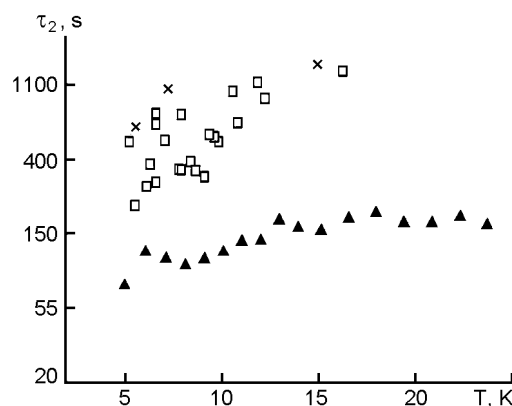


Fig. 4. Characteristic time (τ_2) for C₆₀ reorientation derived from the negative components of thermal expansion: CO-C₆₀ with 90 mol. % CO (x), and 26 mol. % CO (□); and N₂-C₆₀ with 100 mol. % N₂ (▲).

absence of the negative component in the thermal expansion of pure C₆₀ prompts a conclusion that on dissolution of CO in C₆₀, the probability of C₆₀ reorientation in the domain interlayers increases first and then starts to decrease as the CO concentration rises. By contrast, in the N₂-C₆₀ solutions, where the non-central interaction between the N₂ and C₆₀ molecules is weaker, the negative contribution to the thermal expansion is much greater at high N₂ concentrations than at low ones. Note that a change from low to high impurity concentrations reduces the temperature interval of the negative contribution for the CO-C₆₀ solution and increases it for the N₂-C₆₀ one [3].

In our opinion, this behavior suggests a competition of two mechanisms. On the one hand, the CO and N₂ impurities introduced into the interstitial sites of C₆₀ push the neighboring C₆₀ molecules farther apart, thus suppressing the non-central interaction between the C₆₀ molecules and promoting their reorientation. This increases the negative contribution to the thermal expansion. On the other hand, the non-central interaction between the impurity and the neighboring C₆₀ molecules reduces the probability of C₆₀ reorientation and decreases the negative contribution to the thermal expansion. The first mechanism dominates in the N₂-C₆₀ solutions, while the other prevails in the CO-C₆₀ solutions with high CO concentrations.

The noncentral interaction between the impurity and C₆₀ matrix is expected to affect the characteristic times τ_2 of C₆₀ reorientation. As seen in Fig. 4, the τ_2 values

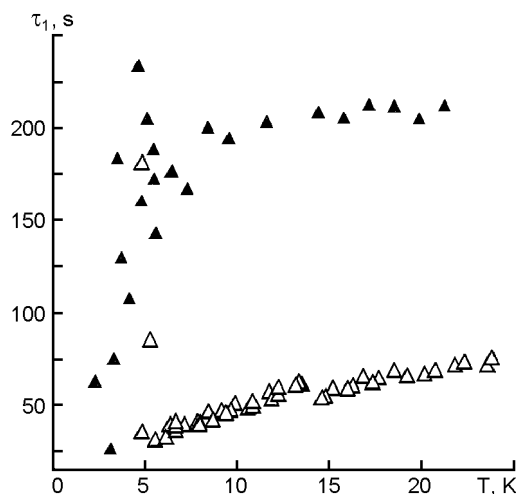


Fig. 5. Characteristic times τ_1 of the positive components of thermal expansion for 90 mol. % CO-C₆₀ (▲) and 26 mol. % CO-C₆₀ (△).

are much higher for the CO-C₆₀ solution than for the N₂-C₆₀ one, thus indicating that the CO molecules having a larger quadrupole moment reduce considerably the probability of C₆₀ reorientation.

The local maxima in the temperature dependences of the positive components of the LTECs $\tau_1(T)$ for the CO-C₆₀ samples may indicate that the interval 4–5.5 K includes the temperatures of phase transformations in the orientational CO-C₆₀ glasses. The assumption is supported by the analysis of the $\tau_1(T)$ dependences for the CO-C₆₀ solution. The sample thermalization time τ_1 increases sharply in the temperature interval of the local LTEC maxima (see Fig. 5), because the heat supplied to the sample during heating is partly consumed in the phase transformation of the orientational glass.

The dependences $\alpha(T)$ and $\tau_1(T)$ for the N₂-C₆₀ solution have no distinct maxima. The glasses coexisting in gas-fullerites solutions differ in orientational orders of C₆₀ molecules [2, 15 – 17]. Since the non-central interaction of the impurity and matrix molecules is stronger in the CO-C₆₀ solution, we can assume that the phase transformation latent heat (a change in the orientational order) is larger for this solution, which is manifested as $\alpha(T)$ and $\tau_1(T)$ maxima.

Gas impurities in high concentrations can often cause microcracking and even fracture of C₆₀ samples [2, 3, 5, 23]. The higher τ_1 values for the sample with the high CO concentration can be attributed to

the microcracks in the sample, which increase its thermal resistance and hence the characteristic thermalization time τ_1 .

To conclude, a first order phase transition was observed in the orientational C₆₀ glass at liquid helium temperatures during dilatometric investigations on two CO-C₆₀ solutions with 26 mol. % CO and 90 mol. % CO. The phase transformation is confirmed by hysteresis of the thermal expansion, local maxima in the temperature dependence of linear thermal expansion coefficients and a maximum in the temperature dependence of the thermalization time τ_1 of the investigated systems. The phase transitions in the orientational glasses of the CO-C₆₀ solutions occurred in the 4–6 K interval. The thermal expansion of the CO-C₆₀ solutions is a total of positive and negative components with the characteristic relaxation times τ_1 and τ_2 , respectively. τ_1 is the time of temperature equalization over the sample (thermalization) and τ_2 specifies the time of C₆₀ reorientation in the interdomain space of the CO-C₆₀ sample. We have compared the thermal expansion of CO-C₆₀ and N₂-C₆₀ solutions where the impurity molecules have close gas kinetic diameters and molecular weights, but N₂ has a much smaller quadrupole moment.

Because of a stronger non-central interaction of the CO and neighboring C₆₀ molecules, the CO-C₆₀ solution has some specific features that distinguish it from the N₂-C₆₀ solution. (i). The linear thermal expansion coefficients are lower in the "high-temperature" phase in comparison with the LTECs of pure C₆₀. This is because the frequencies of C₆₀ librations increase and their contribution to the LTECs shifts to temperatures above the T-interval of the experiment. (ii). The $\alpha(T)$ and $\tau_1(T)$ dependences have maxima in the temperature interval of phase transformation. No maxima are detected in the N₂-C₆₀ solutions. (iii). The C₆₀ molecules have much longer reorientation times τ_2 , which is an obvious consequence of the enhancement of the noncentral interaction between the impurity and matrix molecules. (iv). There is a change in the concentration dependence of the negative contribution to the LTEC. Two effects are responsible for the negative contribution. On the one hand, the impurities increase the spacings between the C₆₀ molecules which depresses their non-central interaction and increases the probability of their reorientation. On the other hand, the noncentral interaction be-

tween the impurity and matrix molecules decreases the probability of C_{60} reorientation. The first mechanism is dominant in the N_2-C_{60} solutions, which the other predominates in the $CO-C_{60}$ solutions which high CO concentration.

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Вплив домішок двоатомних газів на теплове розширення фулериту C_{60}

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В інтервалі температур 2,5–23 К виконано дилатометричні дослідження орієнтаційних стекол C_{60} з заповненням молекулами газових домішок октаедричних порожнин ґратки фулериту. У стеклах, що досліджувалися спостерігалось у температурному інтервалі 4–6 К фазове перетворення першого роду, яке підтверджується гістерезисом теплового розширення, присутністю максимумів на температурних залежностях коефіцієнта лінійного теплового розширення та часу термалізації τ_1 зразків. Зіставлення поведінки властивостей розчинів $CO-C_{60}$ та N_2-C_{60} дозволило встановити вплив нецентральної взаємодії молекул домішок з молекулами C_{60} на теплове розширення стекол, що досліджувалися та фазове перетворення в них.