Thermal expansion and polyamorphism of N_2–C_{60} solutions

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The linear coefficients $\alpha(T)$ of N_2–C_{60} solutions with 9.9% and 100% of the C_{60} lattice interstitials filled with N_2 have been investigated in the interval 2.2–24 K. The dependence $\alpha(T)$ has a hysteresis suggesting co-existence of two types of orientational glasses in these solutions. The features of the glasses are compared. The characteristic times of phase transformations in the solutions and reorientation of C_{60} molecules have been estimated.

Introduction

At room temperature fullerite C_{60} has a FCC lattice. The molecules of the lattice are orientationally disordered and perform a weakly hindered rotation. When the temperature decreases, the rotation slows down gradually and at 260 K there occurs a transition into a partially orientationally ordered phase. The phase has a lattice in which the molecules rotate about the three axes directed along the main cube diagonals. Below 90 K the molecular orientations are frozen completely and an orientational glass appears. The crystal lattice of C_{60} has quite large interstitial cavities which can be occupied by molecules of other substances if they have dimensions permitting them to penetrate inside the cavities. In the C_{60} lattice each molecule has one octahedral and two tetrahedral cavities.

Dilatometric investigations [1–3] on single and polycrystal samples of high-purity (99.99 wt. %) C_{60} revealed a negative thermal expansion coefficient whose magnitude was very high. Arguments were advanced that attribute this unexpected effect to the tunnel rotation of the C_{60} molecules. A theoretical model was proposed [4,5], which explains qualita-

tively the possibility of tunnel rotation of C_{60} molecules.

The influence of admixtures upon the thermal expansion of C_{60} was investigated in the interval 2–20 K in [3,6–8]. The admixtures added to C_{60} were gases consisting of spherically symmetrical atoms (He, Ne, Ar, Kr, Xe) and molecules H_2 and D_2. The thermal expansion of these solutions was described as a sum of positive and negative contributions. The positive contribution was made by the low-frequency excitations of the C_{60} lattice (phonons and librons); the negative contribution came from the tunnel reorientation of the C_{60} molecules. The characteristic times of the contributions and their temperature dependences were estimated. The magnitudes, temperature dependences and the characteristic times of negative contributions exhibited a strong dependence on the type of the dissolved gas. In all experiments the characteristic times of the negative contributions were appreciably larger than those of the positive contributions, i.e., the process of reorientation of C_{60} molecules slower than the thermalization of the phonon and libron subsystems of the C_{60} lattice.

In contrast to particles of other gases, He atoms and H_2, D_2 molecules were found to occupy not only the octahedral cavities of the C_{60} lattice, but the smaller tetrahedral ones as well. The presence of He atoms in the tetrahedral cavities of C_{60} was clearly demonstrated in [9,10].

It is found that some gases dissolved in C_{60} can cause a first-order phase transition in the orientational glass [3,8]. This phenomenon, named polyamorphism [11,12], occurs when the diameters of the atoms (molecules) introduced into C_{60} exceed the effective dimensions of the interstitial cavities of C_{60}. An x-ray investigation [13] of the phase transformation in the orientational glass of the $Xe-C_{60}$ solution covered the whole interval of temperatures where the orientational glass exists. The thermodynamic aspects of polyamorphous transformations in C_{60} saturated with gases were considered in [8].

To continue the above studies [3,6–8], it was expedient to investigate C_{60} solutions with gases having nonspherical molecules. This paper describes the thermal expansion of the N_2-C_{60} solution in the interval 2.2–24 K at high and low concentrations of the dissolved gas. The use of updated experimental equipment has enabled measurements that were impossible in the previous experiments [3,6–8]. In particular, it is now possible to measure quite accurately the amount of absorbed gas at low concentrations in C_{60} and the temperature dependence of the characteristic time of phase transformations in the orientational glass.

Experimental technique and results

The experiment at low N_2 concentrations was made on the C_{60} sample that had been used in [8] to investigate the thermal expansion of the H_2-C_{60} and D_2-C_{60} systems. Before saturating it with N_2, the sample had to be cleaned from the gas impurities, which was done by keeping it at 300–400° C for ten days under the condition of dynamic evacuation ($1 \cdot 10^{-3}$ Hg mm). Then, the linear thermal expansion coefficient was measured on the cleaned sample. The coefficient obtained in this control measurement was positive in the whole interval of temperatures 2.2–24 K (Fig. 1, curve *3*). Curve *3* coincides within the experimental error with the results for pure C_{60} (sample IV in [3]). The temperature dependence of the thermal expansion coefficient of the impurity-free C_{60} sample exhibited no hysteresis either on heating or on cooling. The negative contribution to $\alpha(T)$ was absent in the whole range of temperatures.

To prepare a N_2-C_{60} solution with a low N_2 concentration, the measuring cell with the sample was filled

with N_2 up to the pressure 760 Hg mm. The filling was carried out at room temperature. The sample was kept in the measuring cell under these conditions for 20 days. The N_2 concentration in C_{60} equal to the ratio between the number of N_2 molecules and the number of C_{60} molecules was 9.9%. Our method of determining the gas concentration in C_{60} will be described in a special publication.

The measuring cell with the sample was then cooled slowly (for eight hours) down to 65 K. On reaching this temperature, the cell with the sample was evacuated to pressure no worse than $1 \cdot 10^{-5}$ Hg mm and the sample was further cooled for 50 minutes to the boiling point of liquid helium at which the sample was kept for 4 hours before the dilatometric investigation was started.

The function $\alpha(T)$ for the N_2 doped C_{60} sample is shown in Fig. 1. All the curves are averaged over the data of several experimental series. It is seen that the heating and subsequent cooling of the N_2-C_{60} sample at temperatures above 4.5 K cause a hysteresis in $\alpha(T)$. Below 4.5 K the $\alpha(T)$ values taken on heating and cooling coincided.

On heating, the thermal expansion of the 9.9% N_2-C_{60} sample exhibited negative and positive contributions with different characteristic times of relaxation. The negative contribution was only observed in the interval 4.5–8 K. It was not detected, within the experimental error, at higher and lower temperatures. The negative contribution to the thermal expansion was absent when the sample was cooled. Much similar behavior of the thermal expansion coefficient was observed earlier in C_{60} doped with H_2, D_2, Kr, and Xe [3,8].
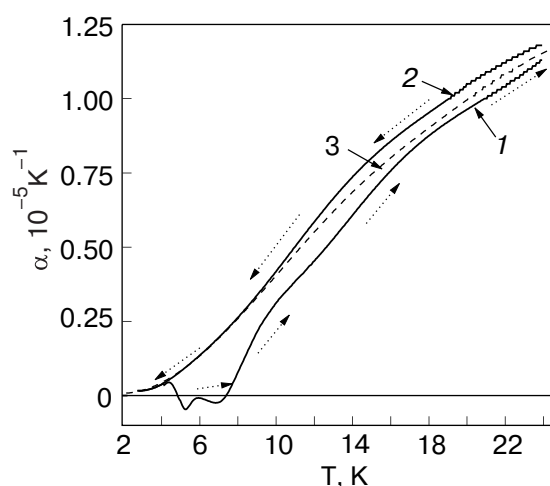

Fig. 1. Temperature dependence of the linear thermal expansion coefficient of pure C_{60} and C_{60} with 9.9% N_2 curve *1* is N_2-C_{60} on heating, curve *2* is N_2-C_{60} on cooling, curve *3* is pure C_{60}.

The experiments with high N_2 concentrations were made on a sample of high-purity (99.99%) C_{60} powder (SES, USA) with the average grain size of about 100 μm.

The C_{60} powder was saturated with N_2 under ~ 200 MPa at $T = 575°C$ for 36 hour at the Australian Nuclear Science and Technology Organization. The thermal gravimetric analysis (TGA) results show that the octahedral cavities were practically completely (100%) occupied by N_2. The N_2-saturated powder was compacted at Umea University, Sweden, using the technique described in [8]. The final sample was a cylinder 8 mm high and 10 mm in diameter.

The sample was delivered to Ukraine by mail. On its way, it was broken into two unequal parts. The investigation was made on the larger part which was worked mechanically into a 4.1 mm high cylinder.

The cylindrical sample was placed into the measuring cell of the dilatometer and cooled to liquid helium temperature by the technique used for C_{60} with low N_2 concentrations (see above).

The obtained temperature dependence of the linear thermal expansion coefficient of C_{60} containing a high N_2 concentration (100%) is shown in Fig. 2. The curves shown are averaged over several series of measurement.

At a high N_2 concentration the hysteresis in $\alpha(T)$ is much larger than in the case of a low N_2 concentration. On heating the thermal expansion of this sample also exhibited negative and positive contributions. However, the negative contribution was observed in a broader interval (2.8–20 K). At low N_2 concentrations it was 4,55–8 K (see Fig.1). The negative contribution was not found on cooling C_{60} with a high N_2 con-
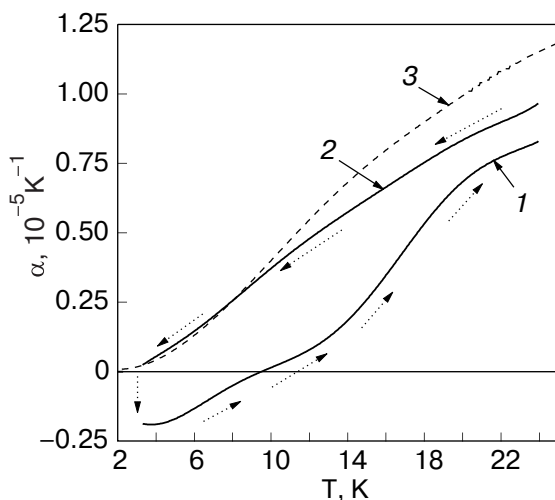
centration. It is interesting to consider some features of the $\alpha(T)$ behavior observed in the C_{60} sample with a high N_2 concentration.

1. To change from the condition of curve 2 (cooling to the lowest temperature of the experiment $T = 2.8$ K) to subsequent heating when the dependence $\alpha(T)$ is described by curve 1, the sample was kept at $T = 2.8$ K at least for 2.5 hours.

2. If the sample is not warmed above 4.6 K, the negative contribution is observable both on the heating and cooling of the sample. However, after heating the sample above 6.5 K, the negative contribution disappears when the sample is cooled.

Discussion

The hysteresis in the dependence $\alpha(T)$ observed in gas–fullerite solutions is caused by the co-existence and mutual transformations of different orientational glasses N_2–C_{60} [3,8,13] .

In solutions with high and low N_2 concentrations the low temperature glass phase (phase I) is in equilibrium at least in the interval 2.8–4.6 K. For C_{60} with a high N_2 concentration this is evident from the fact that after the first-order phase transition at $T = 2.8$ K the cycling of the sample within the interval 2.8–4.6 K does not cause a hysteresis in $\alpha(T)$. The dependence $\alpha(T)$ of C_{60} with a low N_2 concentration has no hysteresis in this temperature interval. The dependence $\alpha(T)$ of phase I is described in Figs. 1 and 2 by curves 1.

In solutions with high and low N_2 concentrations, the «high temperature» phase (phase II) is in equilibrium at least in the interval 6–24 K. The function $a(T)$ for phase II is described in Figs. 1 and 2 by curves 2. There is certain evidence for the equilibrium state of phase II. The α is values that fall on curves 2 in this temperature interval still hold their positions after sign — alternating variations of temperature by 1–3 K (cycling). As for the α is values on curves 1, several cycles are sufficient to shift them to the corresponding curves 2. The reproducibility of the measured data was poor in the interval 4.6–6 K. This region of instability may suggest the presence of two phases here. We can assume that this interval includes the temperature of the phase transition, which corresponds well with theoretical estimates [8].

The derived information can be used to specify the features of phases I and II. As was mentioned above, on heating the sample by ΔT, the time dependence of the thermal expansion exhibits two processes with different characteristic times.

At constant temperature the dependence $\alpha(T)$ measured on cooling can be described by

Fig. 2. Temperature dependence of the linear thermal coefficient of pure C_{60} and C_{60} with a high N_2 concentration. curve *1* is N_2–C_{60} on heating, curve *2* is N_2–C_{60} on cooling. curve *3* is pure C_{60} on heating and cooling.

$$\alpha(t) = \frac{1}{\Delta T} \frac{\Delta L}{L} = A(1 - \exp(-t/\tau_1)) +$$

$$+B(\exp(-t/\tau_2) - 1) \qquad (2)$$

where the first and second terms on the equation's right-hand side describe the positive and negative contributions, respectively; A and B are the absolute values of the corresponding contributions at $t \to \infty$; and τ_1 and τ_2 are the characteristic relaxation times for these contributions.

Using the data processing procedure of [3], we evaluated the positive A and negative B contributions and the characteristic times of the processes responsible for the thermal expansion of the N_2–C_{60} samples as a function of temperature.

It appears that the positive contribution $\alpha(T)$ to the thermal expansion of phase I coincides within the experimental error with the thermal expansion $\alpha(T)$ in phase II. Thus, the low frequency excitations (phonons and librons) contribute equally to the thermal expansions in phases I and II. This is quite natural if we recall that there is only a minor distinction between the molar volumes of the phases [14]. At the same time the processes of C_{60} molecule reorientation which determine the negative contribution to the thermal expansion manifest themselves only in phase I.

The temperature dependences of the ratio between the negative and positive contributions to the thermal expansion of phase I with low and high concentrations of nitrogen are shown in Fig. 3.

Figure 4 illustrates the dependence of the negative contributions B to the thermal expansion of C_{60} samples with high and low N_2 concentrations. It is seen that the negative contribution (B) and the interval of

Fig. 4. The negative contribution to the thermal expansion of C_{60} sample with a high (solid line) and low (broken line) N_2 concentration.

its existence increase when the N_2 concentration grows. We can assume that at growing N_2 concentrations more and more C_{60} molecules are involved in the process of reorientation and the potential barriers impeding reorientation become suppressed. The first factor is responsible for the increase in B. The other leads to the broadening of the band of the tunnel C_{60} rotation spectrum and hence to extension of the temperature interval where the negative thermal expansion is observable.

As was found in [3,8], the negative contribution to the thermal expansion of C_{60} is largely determined by the diameter of the dissolved molecules rather than by their mass. It is therefore interesting to compare the dependence $B(T)$ of the N_2–C_{60} solution with the corresponding dependence for C_{60} containing equal concentrations of other gas. It is convenient to start with a solution having a low content of impurity, where the interference of the interaction between the impurity particles is negligible. In our previous investigations [1–3,6–8] low concentrations of the dissolved gases were undetectable. In this study we tried the technique [8] used to saturate pure C_{60} with deuterium and then measured the D_2 concentration. It was 12.9%, i.e., very close of the N_2 concentrations measured in this study. This justifies our comparison of $B(T)$ measured in the N_2–C_{60} and D_2–C_{60} solutions. We see in Fig. 5 that the dependence $B(T)$ of the N_2–C_{60} solution resembles that of the D_2–C_{60} solution but is shifted towards high temperatures and stretched along the T-axis. The explanation can be as follows. The introduced N_2 molecules push apart the neighboring C_{60} molecules more vigorously than the smaller D_2 molecules can do. The distance between the C_{60} molecules increases and their non central interaction attenuates, which suppresses the barriers impeding the reorientation of the C_{60} molecules. This in turn broadens the band of the tunnel rotation spec-
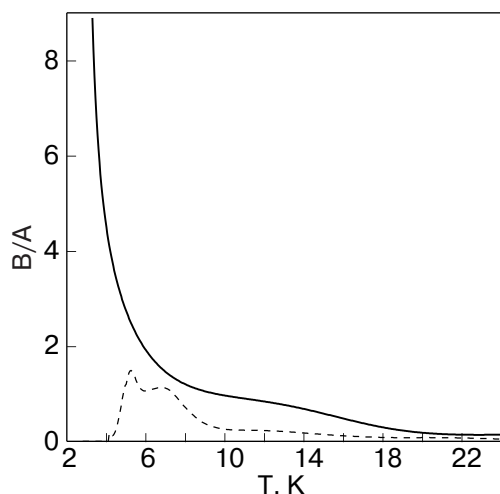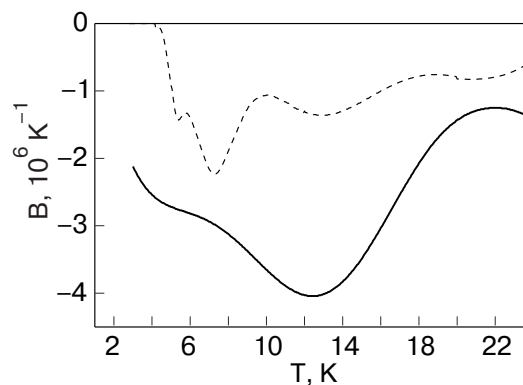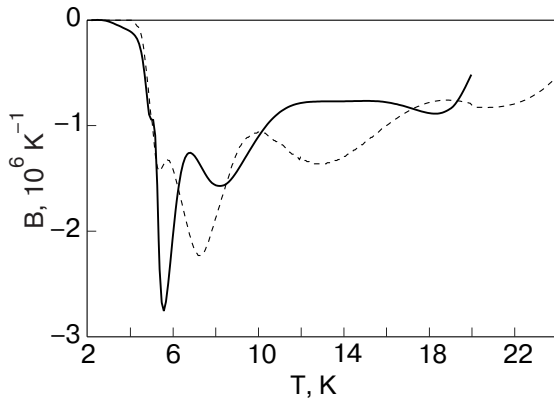

Fig. 3. The absolute value of the ratio between negative and positive contributions to the thermal expansion of C_{60} sample with a high (solid line) and low (broken line) N_2 concentration.

Fig. 5. Absolute values of negative contributions B to the linear thermal expansion coefficient of C_{60}+ 9,9% N_2 (broken line) and C_{60}+12.9% D_2 (solid line).

trum of C_{60} molecules. As a result, the dependence $B(T)$ appears to be shifted towards high temperatures and stretched along the T-axis. Meanwhile, in both N_2–C_{60} and D_2–C_{60} solutions the behavior of $B(T)$ remains practically unaffected by the rather large difference between the masses of N_2 and D_2 molecules.

Figure 6 shows the temperature dependences of the characteristic times of the positive τ_1 and negative τ_2 contributions to the thermal expansion of C_{60} with low and high N_2 concentrations. τ_1 is actually the characteristic time during which the temperature equalizes over the sample. τ_1 is sensitive to the size and thermal resistance of the sample. The influence of gas impurities upon the thermal resistance of C_{60} is
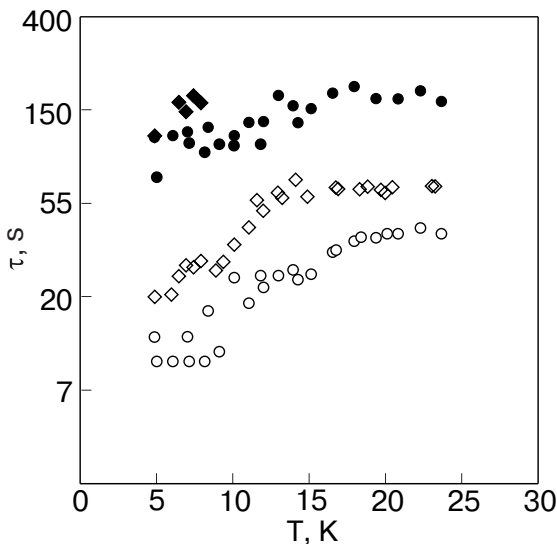
rather weak against the background of the high thermal resistance of compressed pure samples of C_{60} [3,8]. The higher τ_1 is values obtained for C_{60} with a low N_2 content may be due to the large size of the sample (9 mm). The size of the sample with a high N_2 concentration was 4mm.

We did not observe any significant dependence of τ_2 on the concentration of the gas impurity in [3,8], which can be due to the much smaller difference between the gas concentrations in the samples. Nevertheless, in this study there were only minor distinctions between the τ_2 is values of the samples with 9,9% N_2 and 100% N_2 (see Fig. 6). τ_2 is the characteristic time of reorientation of C_{60} molecules. It is rather strongly dependent on the type of gas impurity [3,8]. Figure 7 illustrates the characteristic times τ_2 for C_{60} with high and low concentrations of N_2 and 12,9 % D_2. The comparison of the negative contributions $B(T)$ to the thermal expansion coefficients of the N_2–C_{60} and D_2–C_{60} solutions shows that because of the larger sizes of N_2 molecules the probability of C_{60} reorientation is higher in the N_2–C_{60} solution. The lower τ_2 — values in the N_2–C_{60} sample in comparison to those in the D_2–C_{60} system reflect the higher probability of C_{60} reorientation in the N_2–C_{60} solution.

We also investigated the kinetics of phase transformations in the orientational glasses N_2–C_{60}. The characteristic time τ' of the phase transition was found through sign — alternating variations of temperature by 1–3 K (thermocycling) in the nonequilibrium phase. During thermocycling the α — value varied approach-
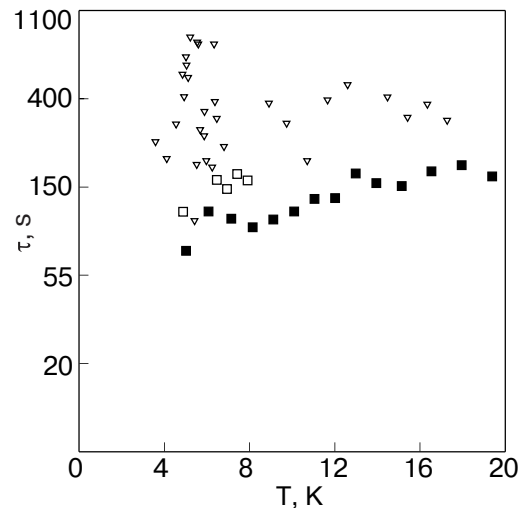

Fig. 6. Characteristic times of positive and negative contributions to the thermal expansion of N_2–C_{60} sample. Positive contributions: $\Diamond$ — C_{60} with low N_2 concentration; $\bigcirc$ — C_{60} with high N_2 concentration; Negative contributions: $\blacklozenge$ — C_{60} with low N_2 concentration; $\bullet$ — C_{60} with high N_2 concentration.

Fig. 7. Characteristic times of negative contributions to the thermal expansion of C_{60} doped with N_2 and D_2: $\square$ — C_{60} with low N_2 concentration; $\blacksquare$ — C_{60} with high N_2 concentration; ∇ — D_2–C_{60}.

ing the thermal expansion coefficient of the equilibrium phase. The characteristic time τ' was obtained from the time dependence $\alpha(t)$. The experimental technique and data processing are detailed elsewhere [8]. Figure 8 shows τ' versus the average temperature of thermocycling. In the whole interval of temperatures the results on τ' obtained for C_{60} with a low N_2 concentration are reliable to within the experimental error. The dependence $\tau'(T)$ taken on C_{60} with high N_2 concentration has a maximum at $T \approx 11.5$ K. τ' was only slightly dependent on the N_2 concentration.

The phases of the orientational glasses of C_{60} saturated with gases differ mainly in the orientational order of the C_{60} molecules [8]. It is therefore interesting to compare the characteristic times τ' (phase transformation) and τ_2 (C_{60} reorientation). In the N_2-C_{60} solution τ' is about an order of magnitude higher than τ_2. Note that in this solution the correlation between τ' and τ_2 is observed only at one temperature, $T = 11.5$ K [8].

The above facts suggest the following conclusions.

1. In the temperature interval 2.2–24 K, fullerite C_{60} doped with gases exhibits coexistence of several types of orientational glasses, each of them having its characteristic molar volume.

2. A change in the temperature condition of sample leads to mutual phase transformations of tunnel character. We have estimated the temperature dependence of the characteristic time of such transformations (Fig. 8).

3. For the systems investigated there is a certain limiting temperature T_c below which one of the orientational glass phases becomes the main contribu-
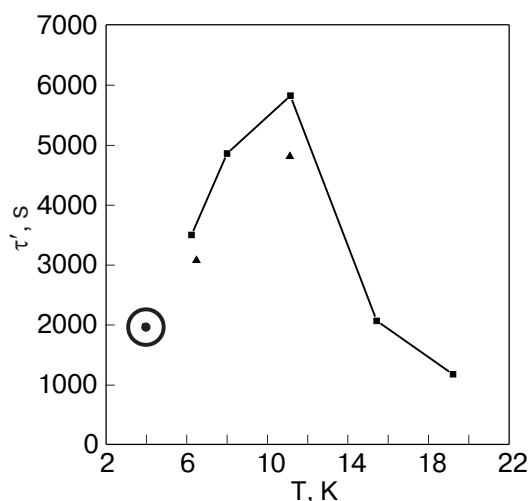
tor to the thermal expansion. This is $T_c \approx 4.5$ K for the N_2-C_{60} systems investigated in this study.

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Fig. 8. Temperature dependence of characteristic time τ' of phase transformation in orientational N_2-C_{60} glasses. Change from phase I to phase II: ▲ — C_{60} with low N_2 concentration; ■ — C_{60} with high N_2 concentration. Change from phase II to phase I: ⊙ — C_{60} with high N_2 concentration.