Specific features of thermal expansion and polyamorphism in CH_4–C_{60} solutions at low temperatures

A.V. Dolbin[1], V.B. Esel'son[1], V.G. Gavrilko[1], V.G. Manzhelii[1], N.A. Vinnikov[1], G.E. Gadd[2], S. Moricca[2], D. Cassidy[2], and B. Sundqvist[3]

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine
47 Lenin Ave., Kharkov 61103, Ukraine
E-mail: dolbin@ilt.kharkov.ua

[2] *Australian Nuclear Science & Technology Organisation, NSW 2234, Australia*

[3] *Department of Physics, Umea University, SE - 901 87 Umea, Sweden*

The temperature dependence of the linear thermal expansion coefficient $\alpha(T)$ has been investigated in the temperature range of 2.5 to 23 K for two different CH_4–C_{60} solutions in which CH_4 molecules occupied 24 and 50% of the octahedral interstitial sites of the C_{60} lattice. In both cases, $\alpha(T)$ exhibits hysteresis, suggesting the existence of two types of orientational glass associated with these solutions. The temperature of the first-order phase transition between these two glasses was estimated and the behavior of these two glasses compared. The characteristic times of thermalization τ_1, reorientation of the C_{60} molecules τ_2, and of the phase transformation between the glasses τ', have been estimated for these solutions. Both the temperature dependence of $\alpha(T)$ and the characteristic thermalization time τ_1 are found to have features near the phase transition temperature and an explanation has been put forward to explain these observed features.

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Introduction

At temperatures below 90 K, fullerite C_{60} changes into the state of an orientational glass [1]. Investigations of the thermal expansion of such orientational glasses based on C_{60} and at the same time being saturated with atomic and diatomic gases [2–5], has revealed interesting features in their low-temperature behavior, amongst these being the first-order phase transition at around liquid helium temperatures — the so-called phenomenon of polyamorphism [3]. These investigations of the coexisting orientational glasses concentrated primarily on the distinctions between the two glasses, such as the characteristic times of system thermalization and reorientation of the C_{60} molecules but as well as these, the temperature of the phase transition as well as the characteristic time for phase interconversion between the glasses, was also studied.

It was found that the temperature of the first-order phase transition for O_2–C_{60} and N_2–C_{60} glasses occured in the temperature interval of 4.5–6 K, agreeing well with

theoretical estimates ($T \cong 10$ K) [3,6]. Polyamorphism manifests itself as a hysteresis of the thermal expansion of the fullerite saturated with gases. The co-existence of two orientational glasses for a Xe–C_{60} solution has also been found to be supported by x-ray phase analysis [7].

In the solutions investigated, it has been found that the thermal expansion of the more stable glass phase (phase I) at the relatively lower temperatures of the experiment, consisted of both positive and negative contributions. The characteristic time of the positive contribution τ_1 which describes thermalization (the processes of temperature equalization over the sample) was little dependent on either the temperature, or the type or concentration of the dissolved gas. Put in another way, the thermal conductivity of the solutions is mainly determined by the C_{60} matrix, and its structure as an orientational glass. The characteristic time of the negative contribution τ_2, exceeds τ_1 in all measurement runs. The authors believe that τ_2 describes the process of reorientation of the C_{60} molecules and will be essentially dependent on the type of dissolved gas.

The thermal expansion of the phase more stable at relatively high temperatures (phase II) had no negative contribution. The times τ_1 (thermalization) of phases I and II were practically identical, which suggests that their thermal conductivities are very close. It is important that the thermalization times τ_1 had no noticeable features near the phase transition temperature.

The change from the two-phase glass state to the single–phase glass condition was stimulated by thermal cycling of the system in a narrow temperature interval ($\Delta T \sim 2$ K). The characteristic time τ' of the transition was taken as a characteristic time of the phase transformation. It exceeds both the times of thermalization τ_1 as well as that of reorientation of the matrix molecules τ_2, in all measurement events.

The features of C_{60} glasses have been interpreted theoretically in [3,6]. Some models with mechanisms have been proposed [8,9] to explain the reorientation of the classical C_{60} molecules at low temperatures. The thermodynamics of the processes in C_{60} glasses was also considered in [6].

The aim of these recent studies was to investigate the effect of an impurity consisting of tetrahedral molecules (CH_4) upon the properties and interconversion kinetics of orientational C_{60} glasses. To carry this out, CH_4–C_{60} solutions were prepared with molar CH_4 concentrations of both 24 and 50%.

The choice of CH_4 as an impurity was also motivated for the following reasons. Firstly, the effect of admixed tetrahedral symmetric molecules upon the thermal expansion of fullerite had so far until these studies, not been investigated. Secondly, it is naturally to be expected that molecular symmetry would play a vital role in determining the interaction between the impurity and host C_{60} molecules and hence the properties of the solid C_{60} matrix. Also in the case of CH_4, this interaction would be maximized on account of that the effective diameter of the CH_4 molecule is comparable in size to the octahedral voids, which the dissolved molecules occupy in the crystal lattice of fullerites [10–12]. It is therefore expected that the CH_4 impurity would deform the C_{60} lattice considerably, affecting not only the lattice parameter, but also the glass phase transition temperature, as well as other properties of fullerite matrix.

Measurement technique and samples

The C_{60} sample (cylinder 10 mm in diameter and 5,27 mm high) with 24 mol.% CH_4 was prepared and analyzed as follows. Prior to saturation with CH_4, the sample was kept under the condition of dynamic evacuation ($1 \cdot 10^{-3}$ mm Hg, $T = 300$–$400°C$, $t = 10$ days) to remove gas impurities. The pure C_{60} sample desaturated by this procedure was placed into the measuring cell of the dilatometer. The cell was then filled with CH_4 at room temperature to the pressure 760 mm Hg. The sample remained under this condition for 69 days. Owing to this doping procedure, the CH_4 molecules occupied about 24% of the octahedral voids in the C_{60} lattice.

The composition and concentration of the gasses dissolved in the C_{60} sample were determined using a low-temperature vacuum desorption gas analyzer (for design and operation details see [13]). The results of the analysis of the gas desorbed after the dilatometric measurements as a result of stepwise heating of the CH_4–C_{60} samples to $300°C$ are shown in Fig. 1 and the overall composition is summarized in the Table. It is seen that most of the CH_4 was desorbed by a temperature of $100°C$.

Table 1. The composition of the gas mixture (molar fractions n_{mol}) desorbed from the C_{60} sample with 24 mol.% CH_4.

Gas impurity	n_{mol}
CH_4	0.93
O_2+N_2	0.06
CO_2	0.01

The methods of preparation and analysis of the C_{60} sample with 50 mol. % CH_4 are described elsewhere [14].

The thermal expansion of the CH_4–C_{60} solutions was investigated using a low temperature capacitance dilatometer (for details of the dilatometer design and measuring technique see [15]). Immediately before the dilatometric investigation, the measuring cell with the CH_4–C_{60} sample was cooled slowly down to 70 K. At this temperature the CH_4 that remained unabsorbed by the sample was removed from the cell. The further cooling and the subsequent investigations were performed under a vacuum of no worse than $1 \cdot 10^{-5}$ mm Hg. The thermal expansion was measured after a four-hour exposure of the CH_4–C_{60} sample to the temperature of liquid helium.
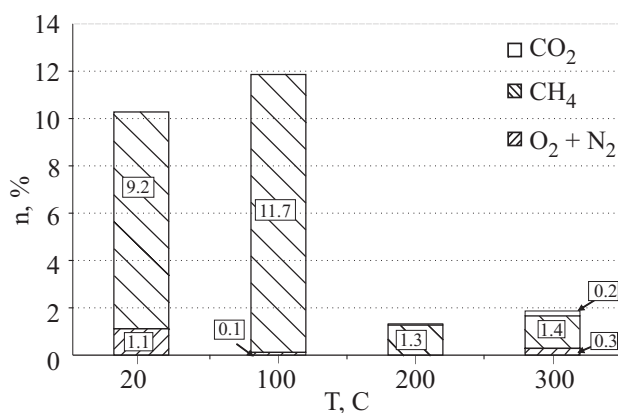

Fig. 1. The composition of the gas mixture (percentage of octahedral void occupancy) desorbed from the C_{60} sample with 24 mol.% CH_4.

Measurement results. Discussion

The temperature dependences of the linear thermal expansion coefficient (LTEC), $\alpha(T)$ taken from the C_{60} samples with 24 mol. % CH_4 and 50 mol. % CH_4, are shown in Fig. 2. The dependences were obtained by averaging the results of several series of experiments.

It is seen that on heating (curves *1, 2*) and subsequent cooling (curves *3, 4*) the LTEC has a hysteresis at $T > 4$ K (24 mol. % CH_4) and $T > 3.5$ K (50 mol. % CH_4). This hysteresis points to the first-order phase transition between the orientational glasses. Below either of these respective temperatures, the measured values of $\alpha(T)$ for heating for and cooling of the respective solutions, are practically identical. On heating, the thermal expansion of the CH_4–C_{60} samples consisted of both positive and negative components with different characteristic times, τ_1 and $\t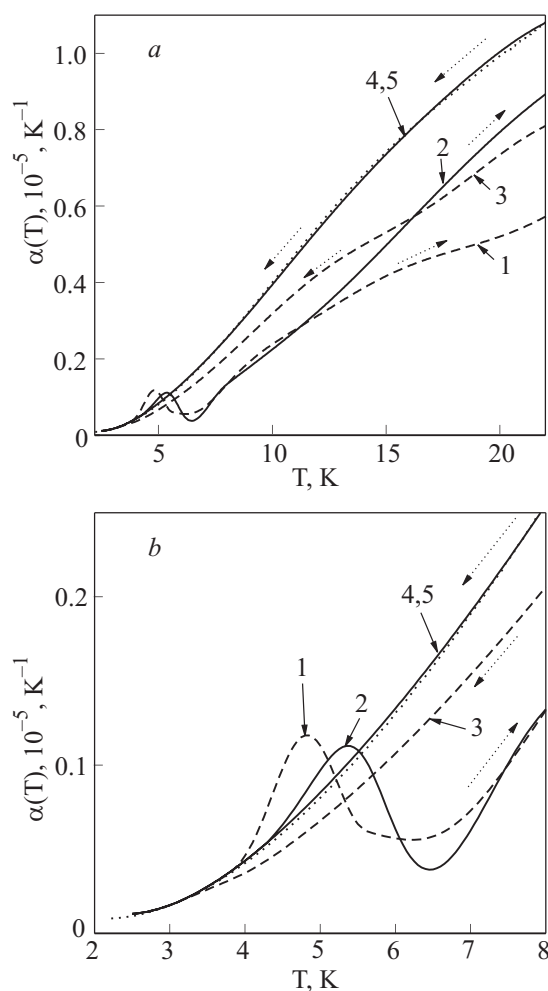au_2$, respectively. These components were separated using the method described in [2,3]. The temperature dependence of the positive and negative contributions to the LTEC for the samples with 24 mol. % CH_4 and 50 mol. % CH_4 are shown in Fig. 3. In contrast to heating, the thermal expansion measured on cooling the samples down from the highest temperature of the experiment showed only a positive contribution (curves *3* and *4* in Fig. 2).

The first-order phase transition of the orientational glasses formed in the O_2–C_{60} and N_2–C_{60} systems occurs in the temperature interval 4.5–6 K [4,5] (see the Introduction). This was evident from the unstable behavior of the thermal expansion in this region. On heating the CH_4–C_{60} samples, $\alpha(T)$ showed a distinct maximum at 4–5.5 K (Fig. 2) and the measured values were rather poorly reproducible. No such signs of these first-order phase transition have been observed in other C_{60} — based orientational glasses prior to above reported ones.

Fig. 2. Temperature dependences of linear thermal expansion coefficient for 24 mol. % CH_4–C_{60} and 50 mol. % CH_4–C_{60} samples in the intervals 2.5–23 K (*a*) and 2.5–8 K (*b*): *1* – heating (50 mol. % CH_4); *2* – heating (24 mol. % CH_4); *3* – cooling (50 mol. % CH_4); *4* – cooling (24 mol. % CH_4); *5* – pure C_{60} (dotted curve).
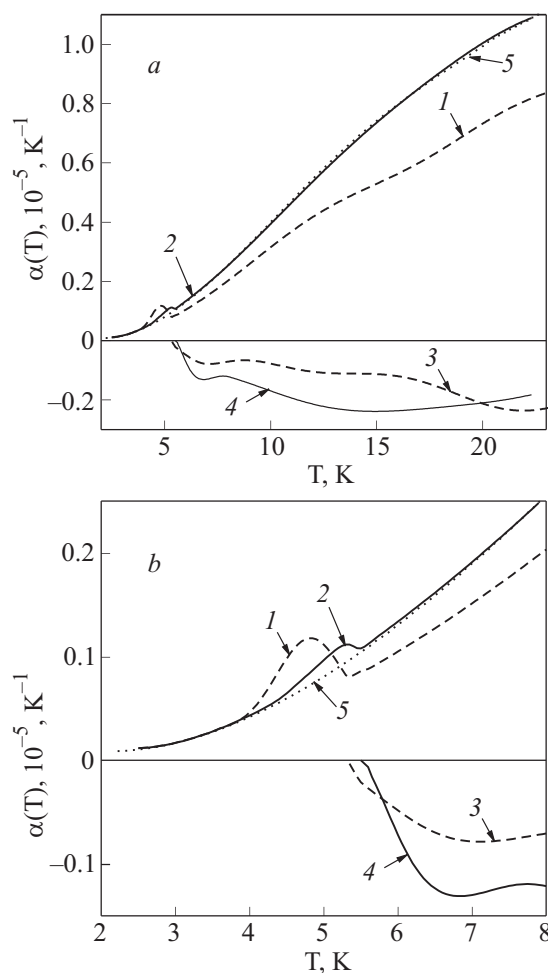
Fig. 3. Temperature dependence of the positive and negative contributions to the linear thermal expansion coefficient, with heating , for 50 mol% and 24 mol%, CH_4–C_{60} solutions: $T = 2.5$–23 K (*a*), $T = 2.5$–8 K (*b*): *1* – positive contribution (50 mol % CH_4); *2* – positive contribution (24 mol. % CH_4); *3* – negative contribution (50 mol. % CH_4); *4* – negative contribution (24 mol. % CH_4); *5* – pure C_{60} (dotted line).

Note that the above feature exists only for the positive contribution to the thermal expansion (Fig. 3). It is therefore reasonable to expect that the temperature dependence of the characteristic time τ_1 of the positive contribution to thermal expansion also will have a feature in this temperature region. This assumption is indeed supported by the analysis of the T dependence of $\tau_1(T)$ and $\tau_2(T)$. Since the positive component characterizes thermalization of the sample [2,3], its characteristic time τ_1 increases drastically near the temperature of the orientational phase transition because the formation of the new phase consumes heat and thus prolongs the time for temperature equalization over the sample volume (Fig. 4).

There is another interesting feature that was not registered in previously studied C_{60} solutions, namely that the τ_1 of the 50 mol. % CH_4–C_{60} sample far exceeds τ_1 of pure C_{60}. It is natural to assume that the high-concentration CH_4 can deform the C_{60} lattice significantly producing micro cracking in the sample, which in turn can increase the thermal resistance of the sample and hence the thermalization time τ_1. Note that the thermal expansion of a cubic-symmetry sample is isotropic and indifferent to micro cracking in the sample.

In contrast to the above, the characteristic time τ_2, of the negative component of the LTEC is found to be weakly dependent on temperature (see Fig. 5), which is consistent with the theoretical conclusions reached in [3]. In this study, we observed for the first time a strong dependence of τ_2 on the concentration of the gas dissolved in C_{60}.

To investigate the relative stability of the orientational CH_4–C_{60} glasses at different temperatures T, we measured the time dependence of the thermal expansion coefficient of the CH_4–C_{60} samples in the process of thermal cycling in a narrow interval $T \pm \Delta T$, where ΔT is no more
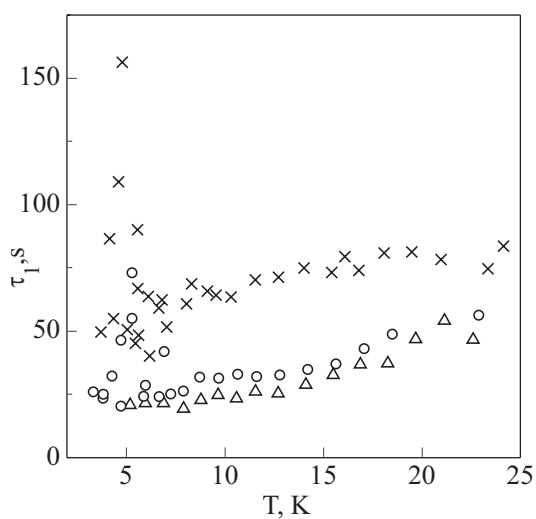

Fig. 5. Characteristic time τ_2 of negative contributions to thermal expansion of C_{60} samples with 50 mol. % CH_4 (▼) and 24 mol. % CH_4 (●).

than 2 K. The details of the technique are described previously [2,3]. The thermal cycling in the interval 5.5–23 K shifted the LTEC values from curves *1* and *2* to curves *3* and *4*, respectively (Fig. 2), which suggests a higher stability of the «high-temperature» phase II, over this thermal cycling interval.

We have also estimated the characteristic time τ' of the phase transition between the two orientational CH_4–C_{60} glasses. The technique of estimation has previously been described in [2,3]. The obtained temperature dependence of the characteristic time τ', of phase transition, for both CH_4–C_{60} solutions, are shown in Fig. 6. The τ'-values are found to be little dependent on the CH_4 concentration.

Fig. 4. Characteristic time τ_1 of positive contributions to the thermal expansion of CH_4–C_{60} samples with 50 mol. % CH_4 (x), 24 mol. % CH_4 (O) and pure C_{60} (△).
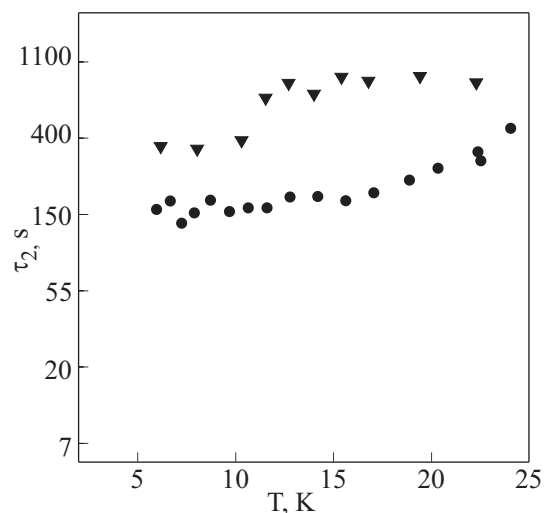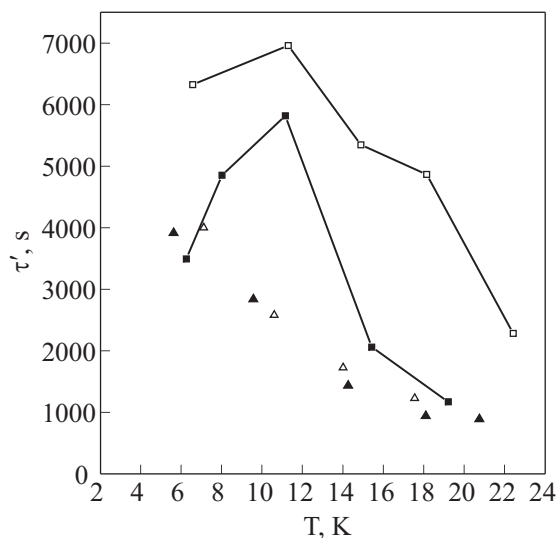

Fig. 6. Temperature dependences of the characteristic time τ' of phase transition in orientational CH_4–C_{60}, N_2–C_{60} and O_2–C_{60} glasses [4,5]. I–II phase transition: 50 mol. % CH_4–C_{60} (▲), 24 mol. % CH_4–C_{60} (△), 100 mol. % N_2–C_{60} (■), 80 mol. % O_2–C_{60} (□).

For comparison, Fig. 6 illustrates the corresponding dependence as measured for the N_2–C_{60} and O_2–C_{60} solutions, which have linear impurity molecules [4,5].

It is interesting to note that in contrast to the N_2–C_{60} and O_2–C_{60} solutions [4,5], the dependence $\tau'(T)$ of the orientational CH_4–C_{60} glasses for both solutions, exhibit no maxima (see Fig. 6). This behavior of the temperature dependence of the characteristic phase transition time $\tau'(T)$ for CH_4–C_{60}, may be determined by the rotational dynamics of the CH_4 impurity in the octahedral voids of the crystal lattice of fullerite [16].

Conclusions

The first-order phase transition was observed in the solutions formed by dissolving CH_4 in orientationally disordered C_{60} at liquid helium temperatures. The thermal expansion of one of the coexisting orientational CH_4–C_{60} glasses (phase I) was found to contain a negative contribution. Earlier, similar results were obtained on C_{60} saturated with He, Kr, Xe, H_2, D_2, N_2, O_2 [2–5].

It is first observed that the temperature dependence of the positive component of the thermal expansion and the characteristic time τ_1 of phase I have maxima which are interpreted as indications of the first-order phase transition between the orientational glasses. The significant deformation of the C_{60} lattice by the dissolved CH_4 is also evident from the concentration dependence of this characteristic thermalization time τ_1 for the CH_4–C_{60} sample.

In contrast to the N_2–C_{60} and O_2–C_{60} solutions [4,5], the characteristic phase transformation time τ' in the CH_4–C_{60} solutions decreases monotonously with increasing temperature.

The coexisting glasses formed in gas-fullerite solutions differ in the orientation of the C_{60} molecules. It is therefore reasonable to expect a certain correlation between the characteristic time τ_2 of reorientation of C_{60} molecules and the characteristic time τ' of the mutual glass phase transition. However, this sort of correlation was not found in previous investigations [2–5]. There is no evidence of such correlation for CH_4–C_{60} either (see Figs. 5, 6). The absence of $\tau_2 - \tau'$ correlation agrees with the speculations reached in the theoretical studies [6,8,9]. The authors assume that the characteristic time τ_2 describes only the reorientation of the C_{60} molecules disposed between the domains, whereas the C_{60} molecules disposed inside the domains have a certain invariant orientation. The characteristic times of the phase transition τ' describe the changes in the orientation of the C_{60} molecules inside the domains. Thus, τ_2 and τ' are associated with processes that are not connected directly.

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