Specific features of thermal expansion and polyamorphism in CH$_4$–C$_{60}$ solutions at low temperatures

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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 $\tau_1$, reorientation of the C$_{60}$ molecules $\tau_2$, and of the phase transformation between the glasses $\tau'$, have been estimated for these solutions. Both the temperature dependence of $\alpha(T)$ and the characteristic thermalization time $\tau_1$ 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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Keywords: thermal expansion, orientational glass, polyamorphism.

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 ($T \approx 10$ 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 $\tau_1$ 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 $\tau_2$, exceeds $\tau_1$ in all measurement runs. The authors believe that $\tau_2$ 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 $\tau_1$ (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 $\tau_1$ 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 $\tau^*$ of the transition was taken as a characteristic time of the phase transformation. It exceeds both the times of thermalization $\tau_1$ as well as that of reorientation of the matrix molecules $\tau_2$, 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 (1-10$^{-3}$ 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$_4$.**

<table>
<thead>
<tr>
<th>Gas impurity</th>
<th>$n_{mol}$</th>
</tr>
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<tbody>
<tr>
<td>CH$_4$</td>
<td>0.93</td>
</tr>
<tr>
<td>O$_2$+N$_2$</td>
<td>0.06</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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 1·10$^{-5}$ 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$_4$.](image-url)
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 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, $\tau_1$ and $\tau_2$, 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 $\tau_1$ 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 $\tau_1$ 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 $\tau_1$ of the 50 mol. % CH$_4$–C$_{60}$ sample(19,100),(991,993) greatly exceeds $\tau_1$ 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 $\tau_1$. 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 $\tau_2$, of the negative component of the LTED 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 $\tau_2$ 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 $\Delta T$ is no more 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 LTED 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 $\tau'$ 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 $\tau'$, of phase transition, for both CH$_4$–C$_{60}$ solutions, are shown in Fig. 6. The $\tau'$-values are found to be little dependent on the CH$_4$ concentration.
For comparison, Fig. 6 illustrates the corresponding dependence as measured for the N₂–C₆₀ and O₂–C₆₀ solutions, which have linear impurity molecules [4,5].

It is interesting to note that in contrast to the N₂–C₆₀ and O₂–C₆₀ solutions [4,5], the dependence τ′(T) of the orientational CH₄–C₆₀ glasses for both solutions, exhibit no maxima (see Fig. 6). This behavior of the temperature dependence of the characteristic phase transition time τ′(T) for CH₄–C₆₀, may be determined by the rotational dynamics of the CH₄ 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 CH₄ in orientationally disordered C₆₀ at liquid helium temperatures. The thermal expansion of one of the coexisting orientational CH₄–C₆₀ glasses (phase I) was found to contain a negative contribution. Earlier, similar results were obtained on C₆₀ saturated with He, Kr, Xe, H₂, D₂, N₂, O₂ [2–5].

It is first observed that the temperature dependence of the positive component of the thermal expansion and the characteristic time τ₁ 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 C₆₀ lattice by the dissolved CH₄ is also evident from the concentration dependence of this characteristic thermalization time τ₁ for the CH₄–C₆₀ sample.

In contrast to the N₂–C₆₀ and O₂–C₆₀ solutions [4,5], the characteristic phase transformation time τ′ in the CH₄–C₆₀ solutions decreases monotonously with increasing temperature.

The coexisting glasses formed in gas-fullerite solutions differ in the orientation of the C₆₀ molecules. It is therefore reasonable to expect a certain correlation between the characteristic time τ₂ of reorientation of C₆₀ 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 CH₄–C₆₀ either (see Figs. 5, 6). The absence of τ₂ – τ′ correlation agrees with the speculations reached in the theoretical studies [6,8,9]. The authors assume that the characteristic time τ₂ describes only the reorientation of the C₆₀ molecules disposed between the domains, whereas the C₆₀ 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 C₆₀ molecules inside the domains. Thus, τ₂ and τ′ are associated with processes that are not connected directly.

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