The effect of the noncentral impurity-matrix interaction upon the thermal expansion and polyamorphism of solid CO–C\textsubscript{60} solutions at low temperatures

A.V. Dolbin, V.B. Esel'son, V.G. Gavrilko, V.G. Manzhelii, and N.A. Vinnikov

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

G.E. Gadd, S. Moricca, and D. Cassidy
Australian Nuclear Science and Technology Organization, NSW 2234, Australia

B. Sundqvist
Department of Physics, Umea University, SE - 901 87 Umea, Sweden

Received January 4, 2008

Orientational glasses with CO molecules occupying 26 and 90\% of the octahedral interstitial sites in the C\textsubscript{60} lattice have been investigated by the dilatometric method in a temperature interval of 2.5–22 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 $\tau_c(T)$ of the samples. The effect of the noncentral CO–C\textsubscript{60} interaction upon the thermal expansion and the phase transition in these glasses was clarified by comparing the behavior of the properties of the CO–C\textsubscript{60} and N\textsubscript{2}–C\textsubscript{60} solutions.

PACS: 74.70.Wz Fullerenes and related materials.

Keywords: fullerite C\textsubscript{60}, thermal expansion, polyamorphism, carbon oxide (CO).

Introduction

Below $T = 90$ K fullerite C\textsubscript{60} transforms into an orientational glass. According to dilatometric and x-ray structural data [1–7], the gases dissolved in C\textsubscript{60} produce a significant effect on the thermal expansion of the glass and cause a first-order phase transition (polyamorphism) in it. It is interesting to find out how particular molecular parameters of the admixture gas can influence the properties of C\textsubscript{60} lattice as a result of a impurity–matrix interaction. To judge accurately the effect of varying a certain molecular parameter, the gas impurities should be chosen so that they differ mainly in this particular parameter, whilst other molecular parameters that may have an effect on the C\textsubscript{60} lattice are essentially kept the same. For example, we would like to probe the effect on the impurity–matrix interaction of altering the electronic charge distribution within a diatomic gas. The choice of a homo and hetero diatomic gas with similar molecular bond lengths would be a good starting point for investigating this important question. We have conveniently chosen CO–C\textsubscript{60} and N\textsubscript{2}–C\textsubscript{60} solutions. In contrast to O\textsubscript{2}, CO and N\textsubscript{2} molecules do not react chemically with C\textsubscript{60} at the temperatures to which C\textsubscript{60} has to be heated to desorb volatile impurities. These molecules also have practically identical molecular weights ($M$(CO) = 28.0105, $M$(N\textsubscript{2}) = 28.0134) as well as comparable gas-kinetic diameters ($\sigma$(CO) = 3.766 Å, $\sigma$(N\textsubscript{2}) = 3.756 Å) [8], but they differ significantly in electric quadrupole moments $Q$(CO) = $-2.839 \times 10^{-26}$ esu, $Q$(N\textsubscript{2}) = $-1.394 \times 10^{-26}$ esu) [9]. N\textsubscript{2} also does not have a dipole moment whereas CO does. However, as will be discussed further on, it is the quadrupole moment and not the dipole moment, that contributes most to the effect that these impurities have upon...
the low-temperature thermal expansion and polymorphism of $C_{60}$.

The dilatometric data on orientational $C_{60}$ glasses with molar $N_2$ concentrations ($N_2$–to–$C_{60}$ molecule ratio) of 9.9 and 100% has previously been published in Ref. 3, so that this paper extends the studies to include those from CO–$C_{60}$ solutions, followed by comparison of the two data sets.

In this study, we investigate the impurity effect of CO on the properties and phase transformations of orientational $C_{60}$ glasses. Solutions of CO–$C_{60}$ with both 26 and 90 mol. % CO, were investigated.

The impurity ($N_2$, CO) molecules occupy the octahedral interstitial cavities in the $C_{60}$ lattice, of which there is effectively one octahedral cavity per $C_{60}$ molecule. As a result of this, the molar CO and $N_2$ concentrations are equal to the $N_2$ and CO occupancies of the octahedral sites in the $C_{60}$ lattice.

**Samples and measuring technique**

The $C_{60}$ sample with 26 mol. % CO was prepared as follows. Prior to saturation with CO, the sample, which was a pressed cylinder of solid $C_{60}$ powder, 9 mm high and 10 mm in diameter (prepared by a procedure as described in Ref. 2), was kept for 72 hours under dynamic evacuation to remove gas impurities ($P = 1 \times 10^{-3}$ mm Hg, $T = 400 ^\circ C$). The outgassed sample and cell, was filled with CO gas at room temperature to a pressure of 760 mm Hg and sealed. The sample was kept under these sealed conditions for 105 days.

The thermal expansion of the CO–$C_{60}$ solutions was investigated using a low-temperature capacitance dilatometer. Its design and the measurement technique are detailed in Ref. 14.

Immediately before the dilatometric measurement, the measuring cell with the CO–$C_{60}$ sample and which was filled with CO, was cooled slowly to 65 K, which is just below the freezing point of CO at 68 K. The cell was evacuated at this temperature to remove the condensed CO, that was CO that had not been absorbed by the sample. The sample was pumped on further until a base pressure of $1 \times 10^{-5}$ mm Hg was attained, followed by cooling of the sample to the base temperature of 4.2 K. The thermal expansion of the CO–$C_{60}$ sample was measured after a four-hour exposure to this temperature.

After measuring the thermal expansion of the sample, the amount of gas impurities and their compositions were determined qualitatively and quantitatively using a vacuum desorption gas analyzer [12]. It was found that about 26% of the octahedral cavities of the $C_{60}$ lattice were occupied by CO. Most of the CO was desorbed on heating the sample to 300 °C (Fig. 1). The preparation and analysis techniques for the $C_{60}$ sample with 90 mol. % CO are described in Ref. 13.

**Results and discussion**

The temperature dependences of the linear thermal expansion coefficient (LTEC) $\alpha(T)$ of pure $C_{60}$ and of the $C_{60}$ samples with different contents of the CO impurity are shown in Fig. 2. The $\alpha(T)$ values are averaged over several measurement series. Owing to the cubic symmetry of their lattices, the thermal expansion of the samples can be described with 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 which points to a first-order phase transition in the orientational CO–$C_{60}$ glasses. No hysteresis was observed for pure $C_{60}$ (curve 5). From the two different CO–$C_{60}$ samples, it appears that the onset of the hysteresis shifts towards higher temperature with increased impurity concentration, shifting from 3 K for the 26 mol. % CO to 4 K for the 90 mol. % CO. Within the temperature range starting from the lowest measured temperature of 2.5 K to the respective hysteresis onset temperatures, it is found that the $\alpha(T)$ for a particular sample are practically identical for both the heating and cooling curves. Moreover, the LTECs of both the CO–$C_{60}$ samples (26 and 90 mol. % CO) and that of pure $C_{60}$ also coincide within the measurement error. On heating in the interval 4–6 K there is a region of instability with higher experimental errors and local LTEC maxima (Fig. 2), however, the errors are appreciably lower than the maxima heights observed. It is assumed [3–5] that within this interval of temperatures, occurs the first-order phase transition between the two differing impurity doped orientational glasses.

Previous investigations [1–5] show that the thermal expansion of gas-doped $C_{60}$ contains positive and negative components with different characteristic relaxation times ($\tau_1$ and $\tau_2$, respectively). With a temperature
change of the sample, the positive component is attributed [1–5] to the process of temperature equalization over the bulk sample (thermalization), whilst the negative component accounts orientational changes of the C\textsubscript{60} molecules induced by the temperature change of the sample. Since a C\textsubscript{60} crystal is perceived as consisting of domains of different orientational orders of the C\textsubscript{60} molecules, and with these domains in a particular crystal separated by interlayers of C\textsubscript{60}, it has been concluded theoretically [15–17] that the negative component of the thermal expansion observed at these low temperatures studied, results from the C\textsubscript{60} reorientation within these actual interlayers and not in the domains themselves.

The thermal expansion of C\textsubscript{60} samples doped with CO also has two components. They were separated in a similar fashion to the techniques described in Ref. 1. The temperature dependences of the positive and negative components for samples with different CO concentration are illustrated in Fig. 3.

It is seen from Fig. 2,\textit{b} that all the LTEC curves are lower than the LTEC of pure C\textsubscript{60} over this temperature range, with the heating and cooling curves of the 90 mol. %
CO and the heating curve of the 26 mol. % CO, being markedly lowered. From Fig. 2, we can conclude that this lowering scales with increases in the concentration of the CO impurity. Above 8 K, although the heating and cooling LTEC curves for the 90 mol. % CO and the heating curve of the 26 mol. % CO appear lowered even further than the corresponding LTEC curve of pure C_60, the cooling curve of the 26 mol. % CO is more or less identical with that of pure C_60. However if we consider just the positive component to this curve, as shown in Fig. 3, it is seen to also be lower than that of pure C_60 (which only exhibits a positive component). In N_2–C_60 solutions this lowering effect of the LTEC curves, exists only at high N_2 concentrations and is much less [3]. This lowering effect is explained as follows. Over the temperature range spanned in our experiments (2.5–22 K), the thermal expansion of pure C_60 is determined by the changes with temperature that occur in a range of phenomena, which predominantly include the translational lattice vibrations, the C_60 librations and the soft modes and two-level systems of the C_60 glasses, and in particular those associated with the changing of the relative orientations of the C_60 molecules with respect to each other. The admixed gas molecules within the octahedral sites can affect the above contributors as well as making their own contribution to the thermal expansion of the solid CO–C_60 solution, through its own thermal motions.

As noted above, the thermal expansion coefficients of pure C_60 and the CO–C_60 solutions coincide at the lowest temperatures of the experiment. This means that at these temperatures the CO impurity has little effect on the dominant contributors to the thermal expansion that being the translational lattice vibrations, the two-level systems and the soft modes [18]. The weak effect of the impurity on the translational vibrations of the C_60 lattice is quite natural because CO adds little to the effective molecular weight of the CO–C_60 solutions and changes the lattice constant of C_60 at most by 0.15 % [19]. As the temperature rises, the contributions of the C_60 librations and the motions associated with the CO molecule (translational, rotational and internal vibrational) increase significantly. But any contribution from the CO through its increased thermal motion can only lead to higher LTEC values. Therefore, the lower LTECs of the CO–C_60 solutions in comparison with those of pure C_60 must be attributed to the diminished contribution of the C_60 librations. This arises from the fact that the CO molecules at T ≤ 77 K are oriented in a particular fashion within the octahedral interstitial sites of C_60 [11,20,21] so that there is a noncentral interaction between the impurity and the surrounding C_60 molecules and which is not nullified by any rotation of the CO molecules within the sites. The CO molecule has both dipole and quadruple electrical moments although the dipole moment is rather weak [22], so that the noncentral CO–C_60 interaction is mainly determined by the quadrupole moment of the CO molecule. This CO orientational induced noncentral force interaction acting on the C_60 molecules tends to increases the frequency of their librations. As a result, the contribution of the C_60 librations to the positive component of the thermal expansion for these CO–C_60 solutions, and over the studied temperature range, is reduced as compared to that of the pure C_60 sample. Only at higher temperatures will their effect be realized as their contribution increases with temperature as they become more and more thermally activated. This effect is weaker for the N_2–C_60 solutions as the quadrupole moment of N_2 molecules is much smaller and this is clearly seen in Fig. 4 that compares the positive and negative components of the thermal expansion for samples with 90 mol. % CO and 100 mol. % N_2. We have chosen these two samples to compare, because the effects of impurities upon the thermal expansion of doped fullerites are most evident at their high concentrations.

In the context of the above consideration, the negative component of the thermal expansion is determined by the probability of reorientation of the C_60 molecules in the domain interlayers. It is found that the magnitude of the negative component of the LTEC for the CO–C_60 solutions decreases considerably as the CO concentration increases from 26 to 90% (Fig. 3). The absence of a negative component in the thermal expansion of pure C_60 prompts us to conclude that on dissolution of CO in the C_60 lattice, the probability of C_60 reorientation in the do-

![Fig. 4. The temperature dependences of the positive and negative components of the linear thermal expansion coefficient are shown for both CO–C_60 (solid lines) and N_2–C_60 (dashed lines) [3] solutions. The positive components are the curves 1 — 90 mol. % CO and 2 — 100 mol. % N_2, whilst the negative components are the curves 3 — 90 mol. % CO and 4 — 100 mol. % N_2. Again pure C_60 which only has a positive contribution is shown as the dotted line (5).](image-url)
main interlayers must first increase with impurity concentration up to a certain impurity concentration but increasing the impurity concentration past this, it must start to decrease again and Fig. 3 even suggests it contribution is reduced to zero contribution at 100% occupancy with CO. By contrast, for N₂–C₆₀ solutions, in which the noncentral interaction between the N₂ and the C₆₀ molecules is weaker, there is an opposite trend with the negative contribution to the thermal expansion being much greater at higher N₂ concentrations than at lower ones. It should be noted that a change from a low to a high impurity concentration will reduce the temperature interval of the negative contribution for the CO–C₆₀ solution but in contrast increases it for the N₂–C₆₀ solution [3].

It is of our opinion that these observations of the thermal expansion behavior for the CO–C₆₀ and N₂–C₆₀ solutions suggests that in both cases, there is a competition between two contrasting mechanisms. On the one hand, we have the CO and N₂ impurities introduced into the interstitial sites of C₆₀ pushing the neighboring C₆₀ molecules farther apart. This mechanism tends to reduce the effect from the noncentral interaction between the C₆₀ molecules but promote their reorientation. This increases the negative contribution to the thermal expansion. On the other hand, their introduction also results in a noncentral interaction between the impurity and the neighboring C₆₀ molecules that 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.

It is expected that the noncentral interaction between the impurity and C₆₀ matrix can affect the characteristic time of C₆₀ reorientation (τ₂) within the interlayers between the domains. As seen in Fig. 5, the τ₂ values have been extracted from the negative component of the LTEC are much longer for the CO–C₆₀ solution than for the N₂–C₆₀ one, indicating that the CO molecules with the substantially larger quadrupole moment than that of N₂ greatly depress on account of this enhanced noncentral CO–C₆₀ interaction, the probability of C₆₀ reorientation.

The local maxima in the temperature dependences of the positive components of the LTECs for the CO–C₆₀ samples may indicate that within the interval of 4–5.5 K occurs the temperatures associated with the phase transformations between the orientational CO–C₆₀ glasses. This assumption is supported by the analysis of the temperature dependences of the relaxation time τ₁(T) associated with thermal equilibration of the CO–C₆₀ solution, and obtained from the positive component of the LTEC. As shown in Fig. 6, this extracted thermalization time τ₁ of the sample, increases sharply in the temperature interval of the local LTEC maxima because the heat supplied to the sample during heating is partially consumed by the phase transformation in the orientational glass.

In contrast to the CO–C₆₀ solutions, the dependences α(T) and τ₁(T) of the N₂–C₆₀ solution have no distinct maxima. The glasses coexisting in gas–fullerites solutions differ only in the orientational order of the C₆₀ molecules [2,15–17]. Since the noncentral interaction between the impurity and matrix molecules is stronger in the CO–C₆₀ solution, we can assume that the latent heat of the phase transformation between the glasses and associated with this change in the orientational order is much larger for this solution, up as maxima in the α(T) and τ₁(T) plots.

It is known that gas impurities of high concentrations can often cause microcracking and even fracture of the C₆₀ samples [2,3,5,23]. The higher τ₁ values for the sample with the high CO concentration can be attributed to

![Fig. 5.](image-url)  
*Fig. 5. The characteristic time τ₂ for C₆₀ reorientation extracted from the negative components of the thermal expansion: CO–C₆₀ with 90 (×) and 26 (□) mol. % CO; and N₂–C₆₀ with 100 mol. % N₂ (▲).*

![Fig. 6.](image-url)  
*Fig. 6. The characteristic times τ₁ of the positive components of thermal expansion from 90 (▲) and 26 (△) mol. % CO–C₆₀.*
The authors thank Prof. A.S. Bakai for helpful discussions. The authors are also indebted to the Science and
Technology Center of Ukraine (STCU) for the financial support of this study (Project Uz-116).


