THERMAL EXPANSION MEASUREMENTS OF C_{60}/C_{70} MIXED CRYSTALS

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The results of thermal expansion and room temperature powder X-ray diffraction measurements on (C_{60})_{1-x}(C_{70})_{x} fullerene alloys are presented. Samples have been prepared by controlled condensation from the vapor phase. Strong anomalies in thermal expansion occur at the fcc to sc phase transition in C_{60}-rich, and hcp to distorted hcp one in C_{70}-rich crystals, respectively. The phase transition temperature diminishes with rising mixture ratio both on the C_{60}-rich (\sim -4K/1\% C_{70}) and on the C_{70}-rich (\sim -20K/1\% C_{60}) side of the phase diagram. This suggests the existence of an orientational glass phase on the C_{70}-rich side of the phase diagram (in agreement with thermal expansion measurements on sample with 70\% C_{70}, which show no sign of the phase transitions at temperatures above 80 K).

Keywords: A. fullerenes, A. orientational glass, D. thermal expansion.

1. INTRODUCTION

Fullerenes and fullerene-based materials have been the subject of extensive research [1]. The thermodynamics of pure C_{60} and pure C_{70} has been studied in detail with almost every available experimental technique, and rather successful theoretical models for phase transitions in pure C_{60} and pure C_{70} exist.

The C_{60} molecule is in a good approximation an isotropic sphere (symmetry I_h) with diameter 7.1 Å. In the solid there occurs a single thermodynamic phase transition (P.T.) associated with a crossover from quasi-free rotation of the molecules in the high temperature phase (fcc, space group Fm\overline{3}m), to a state where only discrete reorientational jumps are allowed [2, 3] (sc, space group Pa\overline{3}) at T_c = 260 K. At still lower temperatures, the orientational disorder freezes (T_g \approx 90 K), without reaching the ordered ground state.

C_{70} has approximately spheroid form (symmetry D_{3h}), with 2a = 7.22 Å and 2b = 8.52 Å. Consequently, it shows two phase transitions, corresponding to freezing out of the tumbling of the long axis and spinning about that axis [4]. The high temperature phase of C_{70} can be fcc (Fm\overline{3}m) or hcp (P6_3/mmc). Starting from an fcc lattice two phase transitions occur to rhombohedral (R\overline{3}m) and monoclinic phase. hcp-crystals undergo similar transitions, i.e. from a high temperature ideal hcp structure (c/a \approx 1.63) to a distorted hcp(c/a \approx 1.82) where the long molecular axis is aligned along the hexagonal c-axis and finally to a monoclinic structure.

The intermolecular potential of fullerenes is to a large extent due to the Van der Waals interaction between the carbon atoms of different molecules [5]. However, in order to get the correct low temperature structure, spreading of the electron clouds along the bonds between adjacent C atoms must be taken into account by adding additional interaction centers [6, 7]. The expansion of the intermolecular potential in terms of the rotator (or: symmetry adapted) functions has been done for both C_{60} and C_{70} [7–10]. For C_{60}, functions with l=0,6,10... are allowed by symmetry, and functions from the l=10 manifold are responsible for the fcc to sc phase transition. For C_{70}, l=0,2,4... are allowed, and the fcc-rhombohedral P.T. is triggered by l=2 (quadrupolar) part of the potential and translation–rotation coupling.
It has been noticed [11] that the sequence of phase transitions in C_{70} in many aspects resembles the ferroelastic phase transition in mixed crystals of alkali metal halides cyanides, which are well known for forming quadrupolar glasses. If we consider only \( l=0 \) and \( l=2 \) terms in the expansion of the molecular potential, \( C_{60} \) and \( C_{70} \) molecules can be seen as huge atoms of the noble gas; \( C_{60} \) being an isotropic sphere, and \( C_{70} \) having a quadrupolar moment. In this approximation, the \( C_{60}/C_{70} \) system should behave similarly as ortho/para hydrogen, or Ar/N\(_2\) system [12] (at least on the \( C_{70} \) side of the phase diagram). That is: adding \( C_{60} \) to \( C_{70} \) should lower the P.T. temperature, and at larger concentrations a "quadrupolar glass" state should emerge. Additionally, on the \( C_{60} \) side of the phase diagram, a similar lowering of the P.T. temperature can be expected, resulting in a "multipolar glass" (frozen orientationally disordered state with respect to orientation of \( C_{60} \)) for larger concentrations of \( C_{70} \). The simplicity of the \( C_{60}/C_{70} \) system (as compared to mixed cyanides [12]) as well as the fact that fullerene crystals are stable at and above room temperature (unlike "normal" Van der Waals crystals), could make \( C_{60}/C_{70} \) mixtures an almost ideal toy-system for investigations of orientational glasses, and testing the predictions of theoretical models and computational experiments.

However, very little has been published about the \((C_{60})_{1-x}(C_{70})_x\) alloys. This is what is known, so far:

- Small amounts of \( C_{60} \) dissolved in \( C_{70} \) as well as \( C_{70} \) in \( C_{60} \) cause a lowering of phase transition temperatures. This has been studied by Kniaž et al. [13] and McHie et al. [14] for small concentrations of dissolved molecules.
- Sai Baba et al. [15] have reported the miscibility gap for \( 0.3 < x < 0.735 \) based on partial pressure measurements, and K. Kniaž et al. [13] have reported a very large (0.04 < \( x < 0.95 \)) gap for solution-grown samples. However, they succeeded to grow an \( x = 0.5 \) sample by controlled condensation from the vapor phase, indicating that there is no miscibility gap for sublimated samples.

Except for the miscibility gap, this is exactly the behavior one would expect for a system that forms an orientational glass state. In this work, we present the results of thermal expansion and room temperature X-ray measurements, that show the miscibility of \( C_{60} \) and \( C_{70} \) at larger mixture ratios, and shed more light to the phase diagram of fullerene alloys.

2. EXPERIMENTAL PROCEDURE

 Fullerene alloys were prepared by a controlled sublimation-condensation procedure from the vapor phase. First, the weighted amounts of \( C_{60} \) and \( C_{70} \) were quickly sublimed under dynamic vacuum, to get compact and well-mixed material for crystal growth. The obtained amorphous mixture was then used as a source material for the crystal growth by the method described in [16, 17]. Crystal growth temperature of \( T \approx 810 K \) was used. Starting from the \( C_{60} \) side of the phase diagram, relatively large (\( \gtrsim 1 \text{ mm}^3 \)) single crystals grew up to \( \lesssim 5\% \) \( C_{70} \). At larger concentrations of \( C_{70} \), compact polycrystalline samples grew; the size of the single-crystals gradually became smaller. Finally, at \( C_{70} \) concentration > 15\%, amorphous-looking spherical samples grew. Starting from the \( C_{70} \) side, similar behavior was observed. However, instead of getting compact polycrystalline samples, at higher concentrations of \( C_{60} (\gtrsim 15\%) \), many small crystals grew. At 30\% \( C_{60} \), hedgehog-like structures were obtained, single crystals being performed (length ~ 1 mm, thickness ~ 0.1 mm). The samples were firstly characterized with Raman measurements at \( T \approx 410 K \). By comparing the relative intensities of the \( C_{60} \) and \( C_{70} \) lines in the samples with spectra of the weighted powder mixtures, we determined the mixture ratio of the samples. Secondly, thermal expansion measurements (\( \sim 80 K - 350K \)) were performed using a Thermomechanical Analyser TMA7 (PERKIN ELMER). This apparatus can be used either in the static (TMA-) mode to measure the thermal expansion or in the dynamic mode (Dynamic Mechanical Analysis - DMA7). In the dynamic mode a time dependent force (0.1 Hz - 50 Hz) is applied to the crystal, and the resulting dynamic strain is used to determine the low frequency elastic constant (see e.g. [18]). Finally, the rest of the crystalline material was pulverized, and used for room temperature Guinier powder-diffraction measurements.

3. RESULTS

Almost all of the \( C_{70} \)-rich samples had a morphology of hcp crystals, and in consistence room

\footnotesize

* In this approximation, high temperature phase of \( C_{60} \) and \( C_{70} \), and the first phase transition in \( C_{70} \) (hcp-distorted hcp, i.e. fcc-rhombohedral) can be described.

\footnotesize

† Raman spectra of both \( C_{60} \) and \( C_{70} \) in the high temperature phase is to a large extent due to molecular vibrations. Thus, by comparing the relative intensities of \( C_{60} \) and \( C_{70} \) lines, the concentration can be determined.

‡ Most of the present samples were too small to perform high quality DMA-measurements.

§ We did not have enough \( C_{70} \)-rich samples with fcc morphology to do X-ray measurements on them.
Table 1. Characterization of the $(C_{60})_{1-x}(C_{70})_x$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>x [mol% C_{70}]</th>
<th>Structure (RT)</th>
<th>a</th>
<th>c</th>
<th>r( NN)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{60}</td>
<td>0</td>
<td>fcc</td>
<td>14.160(3)</td>
<td>—</td>
<td>10.013</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>fcc</td>
<td>14.210(3)</td>
<td>—</td>
<td>10.05</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>fcc</td>
<td>14.28(1)</td>
<td>—</td>
<td>10.10</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>fcc</td>
<td>14.35(5)</td>
<td>—</td>
<td>10.15</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>hcp</td>
<td>10.402(8)</td>
<td>16.87(9)</td>
<td>10.40</td>
<td>1.622</td>
</tr>
<tr>
<td>5</td>
<td>95</td>
<td>hcp</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>95</td>
<td>hcp</td>
<td>10.528(14)</td>
<td>17.172(71)</td>
<td>10.53</td>
<td>1.631</td>
</tr>
<tr>
<td>7</td>
<td>96.5</td>
<td>hcp</td>
<td>10.576(17)</td>
<td>17.377(86)</td>
<td>10.58</td>
<td>1.643</td>
</tr>
<tr>
<td>C_{70}</td>
<td>100</td>
<td>distorted hcp</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

With a rate of $-4K/1\% C_{70}$. At higher concentrations of C_{70}, the phase transition gets smeared out, but it still exists for samples with 18% C_{70}. On the C_{70}-rich side of the phase diagram, the hcp-distorted hcp phase transition temperature decreases with much higher rate ($-20K/1\% C_{60}$). No phase transition was observed in C_{60}/C_{70} samples with 70% C_{70} at temperatures above 80K.

4. DISCUSSION

The phase diagram of $(C_{60})_{1-x}(C_{70})_x$ mixed crystals shows a strong decrease of the phase transition temperature with growing concentration of “guest” molecules, especially on the C_{70}-rich side of the diagram. Combined with the fact that at least 30% of C_{60} can be dissolved in C_{70} [13, 15], this suggests a good chance for the observation of a “quadrupolar glass” phase for mixtures with 10 – 30% C_{60}. It is well known, that the freezing process in mixed crystals of alkali metal halides cyanides [12] produces a dynamic anomaly in elastic properties (S_{44}, S_{11}). Also, for pure C_{60}, a dynamic anomaly in the elastic susceptibility due to the glass freezing has been measured [18]. To find out whether a glassy state exists in $(C_{60})_{1-x}(C_{70})_x$ mixed crystals, we have started low frequency (Hz-region) elastic (DMA-) measurements on some of the larger samples. Preliminary results show a dynamic anomaly similar to the one found in pure C_{60} for all the mixed crystals except for pure C_{70}. However, further experiments (X-ray, NMR) and especially DMA-measurements on larger samples are needed to clarify the origin of this anomaly in C_{60}/C_{70} mixtures.

Another interesting question arises in C_{70} rich crystals when we compare our measurements with the DSC measurements of McGhie et al. [14]. Their measurements show that the “second” (rhombohedral to monoclinic) phase transition is much less affected by the presence of C_{60} ($-6K/1\% C_{60}$) than the “first” (fcc to rhombohedral) one. This means that the rhombohedral to monoclinic (i.e. distorted hcp to mono-
Fig. 2. Thermal expansion, C$_{60}$-rich (fcc) samples. Numbers indicate molar percentages of C$_{70}$ in the C$_{60}$/C$_{70}$ mixture.

Fig. 3. Thermal expansion, C$_{70}$-rich (hcp) samples. Numbers indicate molar percentages of C$_{70}$ in the C$_{60}$/C$_{70}$ mixture.

clinic) phase transition can not take place for mixed crystals with more than ~5% of C$_{60}$. Although their results were obtained for fcc crystals, similar results can be expected for hcp crystals, as well. We are preparing a set of DSC and temperature dependent X-ray measurements to clarify this question.

There is also a question left whether fullerenes are miscible in any ratio, as reported by Kniaž et al., or not (Sai Baba et al.). Our results so far are in the favor of the latter. However, it is possible that crystals with higher mixture ratios can be grown at higher temperatures.

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REFERENCES