

Order-Disorder Transitions in C₆₀ and C₇₀

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Abstract

In recent years enormous effort has been put in understanding the chemical and physical properties of C₆₀ and C₇₀. Order-disorder transition in C₆₀ occurs around 250 K at ambient pressure. At the transition freely rotating molecules get orientationally ordered in a simple cubic lattice. Application of pressure increases the transition temperature at a rate of $\simeq 10 \text{ K kbar}^{-1}$, indicating that pressure favours the ordered state. The DSC and x-ray studies on C₇₀ indicate two phase transitions, one around 270 K and the other around 340 K at room pressure. These transitions also occur at higher temperatures at higher pressures. Application of pressure is found to lift the degeneracy of the energetically equivalent rotational configurations. The high pressure studies are reviewed in the light of existing literature.

1 Introduction

The new class of compounds, the Buckminster fullerenes, has drawn the attention of physicists and chemists alike. Much effort has been put in synthesizing gram quantities of pure C₆₀ and C₇₀. In the last few years extensive research, both experimental and theoretical, has been carried out to understand the physical and chemical properties of these fullerenes.

The C₆₀ molecules are known to crystallize in the face centered cubic structure¹ at room temperature with lattice parameters $a = 14.17 \text{ \AA}$ and undergoes a structural transition around 250 K to a more ordered simple cubic structure. This transition has been studied widely by many workers using different experimental techniques. Two phase transitions are reported in C₇₀. At high temperatures ($T > 340 \text{ K}$), C₇₀ crystallizes in the face centered cubic structure, and below 270 K, it has a more ordered monoclinic structure. In the intermediate temperature range, C₇₀ has a partially ordered phase with trigonal symmetry.

Fullerenes in the crystalline phase are held together by weak van der Waals forces. There is a shallow barrier for rotation of one fullerene molecule with respect to another. At high temperatures, the molecules are therefore free to rotate independently leading to a plastic crystalline face centered cubic phase. The phase transitions in these compounds occur as a consequence of freezing of this rotational degree of freedom. Application of pressure brings the molecules closer, and thus, hinders the free rotation of the molecules by increasing the intermolecular interactions. This is expected to drastically change the thermal behaviour of these systems at high pressures. The experiments under pressure have brought out many interesting features of these phase transitions. In this article, the effect of pressure on the phase transitions in C_{60} and C_{70} is reviewed in the light of current literature.

2 Ambient pressure experiments

Isolated C_{60} has icosahedron symmetry with 12 pentagons and 20 hexagons. Neutron diffraction studies² show that the C-C bonds fusing two hexagons are shorter (1.391 Å) while C-C bonds connecting a pentagon and a hexagon are longer (1.455 Å). At room temperature, C_{60} molecules rotate freely, and the resulting orientational disorder leads to a face centered cubic crystal structure with Fm3 symmetry. On cooling, the C_{60} molecules in the crystal get locked in orientations such that the pentagon of one C_{60} molecule faces the shorter C-C bond of the adjacent C_{60} unit (Fig.1), and the resulting structure is simple cubic with a cell parameter of 14.04 Å (at 11 K). This is the minimum energy configuration as the electron rich shorter C-C bonds of one C_{60} unit face the electron deficient pentagons on the neighbouring C_{60} unit.

Heiney *et al*¹ reported that the transition at 250 K is first order with a free energy change of 6.7 J/g from DSC measurements. From heat capacity studies, similar data has been reported by Fortune *et al*³ on C_{60} single crystal. In ^{13}C NMR studies⁴, a sharp change in the spin-lattice relaxation time near 243K is observed (Fig.2). At room temperature, the NMR lines are very narrow and continue to be so even below the transition temperature. Above the transition temperature, the molecules appear to execute continuous rotational diffusion, while at lower temperatures, the C_{60} molecules jump between nearly degenerate orientations separated by a potential barriers of ~ 250 meV. A potential barrier of 260 meV has been reported by Yu *et al*⁵ from temperature and time dependent studies of thermal conductivity of C_{60} single

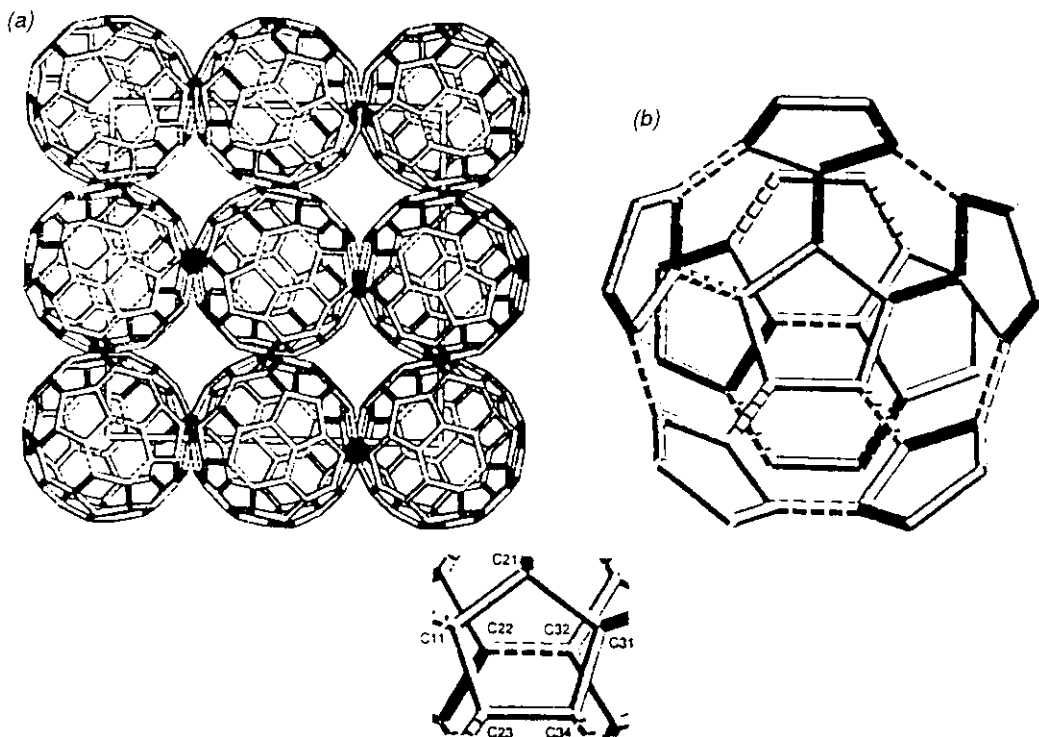


Figure 1: (a) Projection along $[001]$ of the ordered C_{60} structure at 5K. (b) projection of two neighbouring C_{60} units along $[110]$. The hatched bonds are the short C-C bonds and the solid bonds are the long C-C bonds (ref.2).

crystals below 260 K. The high resolution IR and Raman spectroscopic studies⁶ of C_{60} thin film and C_{60} in CS_2 have shown that the vibrational peaks are very narrow in both the cases and the differences in frequencies are also small. In a polycrystalline sample, one should expect inhomogeneously broadened vibrational lines because of the large number of accessible environments. However, the line-widths in polycrystalline C_{60} are about the same as that in solution, implying very weak solid state intermolecular interactions. The IR linewidths studies as a function of temperature⁷ show marked changes across the phase transition (Fig.2).

The theoretical models have been developed employing Lennard-Jones potentials with an additional term to account for the charge on the bonds between the carbon atoms^{8,9}. This potential correctly predicts the low temperature structure to be simple

cubic with space group $\text{Pa}\bar{3}$ and also a phase transition at a temperature of $\simeq 270$ K.

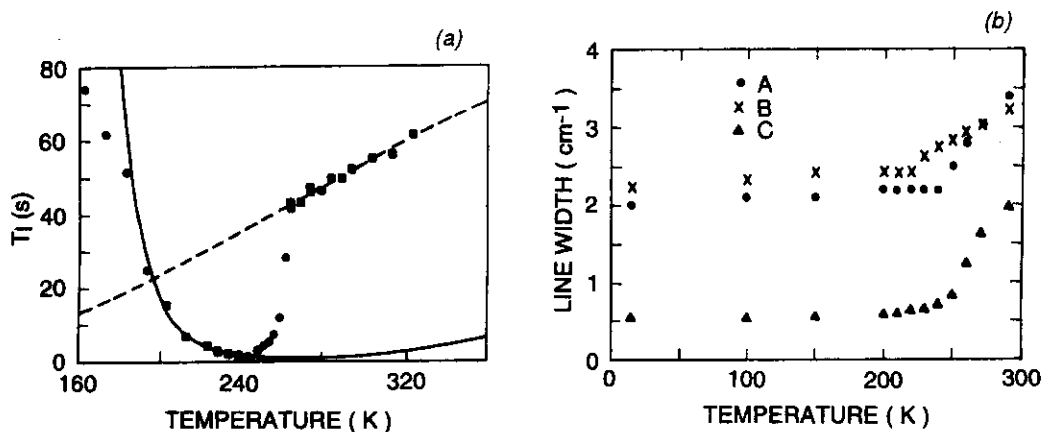


Figure 2: (a) Spin relaxation time vs temperature in C_{60} (ref.4). (b) IR linewidth as a function of temperature. A- 576 cm^{-1} ; B- 1183 cm^{-1} ; C- 527 cm^{-1} (ref.6).

C_{70} has not been studied as widely as C_{60} . Its shape is slightly elongated and looks similar to a rugby ball. The shape corresponds to a C_{60} molecule with an additional ring of hexagons on the equatorial plane. The phase diagram of C_{70} is more complex compared to that of C_{60} . Prepared at temperatures higher than 340 K, C_{70} crystallizes in the face centered cubic structure^{10,11}, with a cell edge of 14.96 \AA . Although the hcp phase is energetically similar to the fcc phase, and can most likely be nucleated by a number of effects like the solvent, powder-grain surfaces, crystal domain boundaries etc., samples prepared by the sublimation method invariably crystallize in the fcc phase, with fully disordered orientation of the molecules in the unit cell. Around room temperature, C_{70} has a hcp structure wherein the freely rotating molecules are partially frozen, and the free rotation is only around their long axis (five fold axis). The five fold axes are oriented with a distinct tilt of $\sim 18^\circ$ with respect to the unique $\langle 111 \rangle$ direction. The final freezing of all the rotations of the C_{70} molecules takes place around 270 K. Below 270 K, C_{70} has a monoclinic structure with $a=b=20.04\text{ \AA}$ and $c=18.53\text{ \AA}$, and the unit cell contains eight C_{70} molecules. As in C_{60} , in the fully ordered unit cell of C_{70} the molecules are orientationally ordered such that the electron rich C-C bond of one C_{70} molecule is located at the center of the electron

deficient pentagon of the neighbouring C_{70} molecule.

The FTIR¹² and Raman¹³ spectroscopic studies carried out as a function of temperature indicate changes in line widths (Fig.3) and Raman phonon frequencies across these transition temperatures. The DSC measurements¹⁴ indicate two endotherms at 280 and 337 K corresponding to the two transitions (Fig.4). The Debye temperature calculated from the specific heat measurements on C_{70} is 145 K.

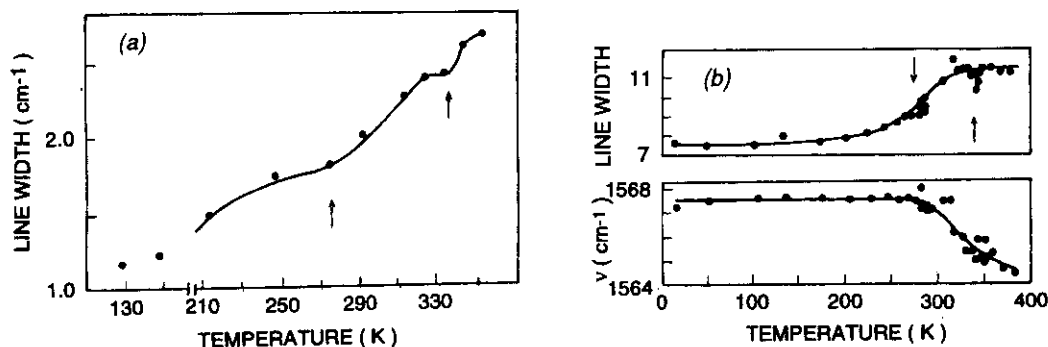


Figure 3: (a) FWHM of IR line at 643 cm^{-1} as a function of temperature in C_{70} (ref.12); (b) Changes in the Raman peak position and FWHM of 1566 cm^{-1} line across the two transitions (ref.13).

Using constant pressure molecular dynamic calculation¹⁵ with similar potentials as in C_{60} , the phase transitions in C_{70} have been predicted with transition temperatures of 390 and 200 K. The calculated heats of transitions are 2.8 ± 0.3 and 2.5 ± 0.3 kJmol^{-1} which compare well with the experimentally determined values of 2.9 ± 0.4 and 2.3 ± 0.4 kJmol^{-1} , respectively.

3 High pressure experiments

Application of pressure has brought out many interesting aspects of order-disorder transitions in C_{60} and C_{70} . C_{60} is found to be stable up to 20 GPa¹⁶ with an isothermal bulk modulus of 18.1 ± 1.6 GPa and a pressure coefficient of bulk modulus of 5.7 ± 0.6 . Raman and IR vibrational peaks continue to be observable up to about 22 GPa¹⁷. Extrapolation of the optical band gap measurement in the pressure range of 0-17 GPa indicates that the metallization¹⁸ should occur around 33 GPa in C_{60} .

As discussed in the introduction, isothermal application of pressure should also bring about the phase transition in these materials because of the increase in the intermolecular interaction. The fcc \rightarrow sc transition at room temperature indeed occurs at ~ 3.5 kbar as seen from Raman spectroscopy¹⁹. The pressure coefficient of the Raman peak frequency changes sign at the transition pressure (Fig.5).

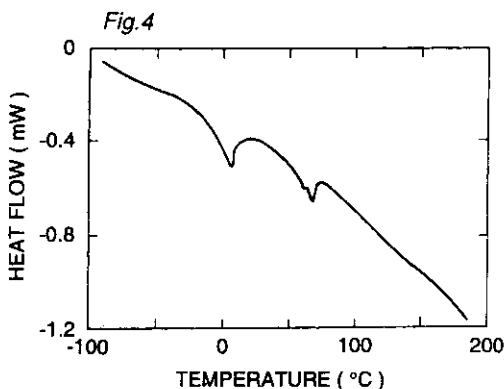


Figure 4: DSC thermogram of C_{70} (ref.14).

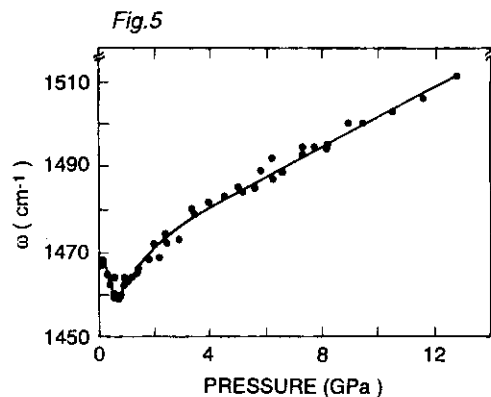


Figure 5: Peak position of Raman peak at 1468 cm^{-1} in C_{60} as a function of pressure at room temperature (ref.19).

Samara *et al*²⁰ and Kriza *et al*²¹, from DSC measurements, found that the sc \rightarrow fcc phase transition temperature increased with increasing pressure at a rate of 10.4 and 11.7 K kbar⁻¹, respectively. Thus, pressure tends to preserve the high symmetry phase to much higher temperatures. Lu *et al*⁸, based on their model have calculated the compressibility to be 5.175 Mbar⁻¹ which yields a value of 0.024 Å kbar⁻¹ for da_o/dP . Assuming that the only effect of pressure is to vary the lattice constant, the calculated dT_c/dP is found to be 11.5 ± 0.7 K/kbar which is close to the experimentally observed value.

Ramesesha and Singh²² have tracked down the transition by monitoring the electrical resistivity as a function of temperature at different pressures (Fig.6). The resistance is of the order of 10^8 ohms and decreases by two orders of magnitude between room temperature and 425 K. There are two well separated transitions, marked

by a sharp changes in the resistance. Atake *et al*²³ in their heat capacity measurement have found two transitions centered around 250 and 255 K. Fischer *et al*²⁴ from DSC studies at ambient pressure have reported that samples containing hydrogen up to 6 atom % show a split signal at the transition temperature with the splitting of about 3 K while those containing negligible amount of hydrogen (~ 0.57 at %) show a single sharp peak at the transition. Thus it appears that at ambient pressures, observing split peaks corresponding to the transition is an artifact due to the presence of the solvent. However, FTIR studies on the sample used in ref.22 show that it contains negligible amount of the solvent. Further, the room pressure DSC thermogram showed a single sharp endotherm of width ~ 3 K. These confirm that the two transitions seen in the resistance measurements at high pressures are intrinsic to C_{60} . The DSC thermograms²⁰ at higher pressures (> 4 kbar) show a clear shoulder on the lower temperature side of the main peak. It is quite possible that high pressure delineates two energetically comparable states at the ambient. Existence of such nearly degenerate orientations separated by small energy gaps have been proposed based on experimental and theoretical studies^{4,5,8}. Johnson *et al*²⁵ measured the reorientational correlation time from the magnetic field dependence of spin lattice relaxation time. Below T_c , a second phase with much longer reorientation time was observed. It was proposed that for $T < T_c$, the C_{60} molecules ratchet between symmetry equivalent configurations. The energy-spread of these degenerate states, as determined from resistance measurements, increases with increasing pressure (Fig.7).

Activation energy, obtained from $\log R$ versus $1/T$ plots (by fitting a single straight line through all the data points ignoring the small difference in slope between the sc and fcc phase), decreases with increasing pressure in the pressure range up to 13 kbar²². Extrapolated energy gap at room pressure (Fig.8) is 2.0 ± 0.2 eV which is close to 1.5 eV obtained from the energy band calculations at the Brillouin-zone boundary at X- point²⁶. The measurement of the temperature-dependence of the electrical²⁷ conductivity on C_{60}/C_{70} thin films gives an energy gap of 1.9 eV. However, Regueiro *et al*²⁸ from their resistivity data on a mixture of 80 % C_{60} and 20 % C_{70} between 50 and 250 kbar and $T < 300$ K obtained a value of 0.45 eV for the room pressure band gap. The studies of Regueiro *et al* indicate that the behaviour and the extrapolation from high pressure studies to ambient pressures is not reliable.

From Raman and optical reflectivity studies, C_{70} is also found to be stable under

Fig.6

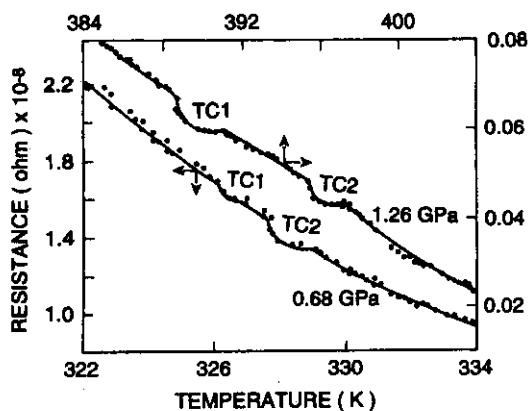


Fig.7

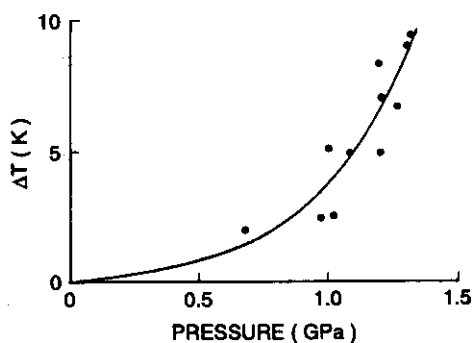


Figure 6: Resistance vs temperature of C_{60} at 6.8 and 12.6 kbar (ref.22).

Figure 7: Temperature difference between the two transitions in C_{60} as a function of pressure (ref.22).

pressures up to 22 GPa¹⁷. Only two phase transitions in C_{70} were earlier reported. However, a typical R vs T plot of C_{70} at 8.5 kbar shows three distinct jumps in resistivity (Fig.9) indicating the occurrence of three phase transitions²⁹. As in C_{60} , here also there are small but clear changes in resistance at these transitions. The change in resistance at T_2 is much smaller than that at T_1 and T_3 . The DSC data of Grevei *et al*¹⁴ also shows a well defined shoulder on the lower temperature side of the 300 K transition (Fig.4), although its presence has not been explained by the authors. All the three transition temperatures show an increase with increase in pressure²⁹. The transition temperatures T_1 , T_2 , and T_3 increase at a rate 8.4, 5.3 and 6.8 K kbar⁻¹ respectively, the zero pressure intercepts for these are found to be 268, 326 and 339 K, respectively (Fig.10). Intercepts of T_1 and T_3 agree well with reported transition temperatures at room pressure. Sworakowski *et al*³⁰ in their heat capacity measurements on C_{70} have seen a small peak at 307 K which may be attributed to the third transition, though this temperature is much lower than the temperature at which the shoulder is observed¹⁴ in the DSC, or the temperature obtained by extrapolation to room pressure of the transition temperature data of Ramasesha *et al*²⁹. In C_{70} , at the 340 K transition, the stacking changes from ABCABC.. (fcc) to

ABAB.. (hcp). Application of pressure could hinder this transition and a polytypic stacking of the type ABCAB.. could occur at intermediate temperatures which may manifest as a weak transition at T_2 , between the two major phase transitions. This phase could persist over a wider temperature range at higher pressures.

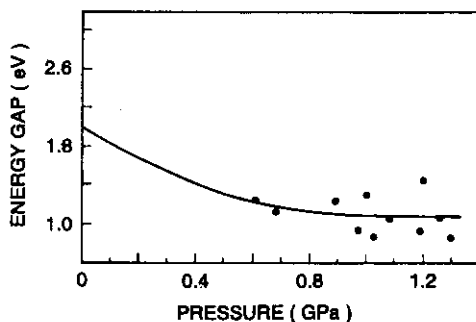


Figure 8: Variation of energy gap as a function of pressure in C_{60} (ref.22).

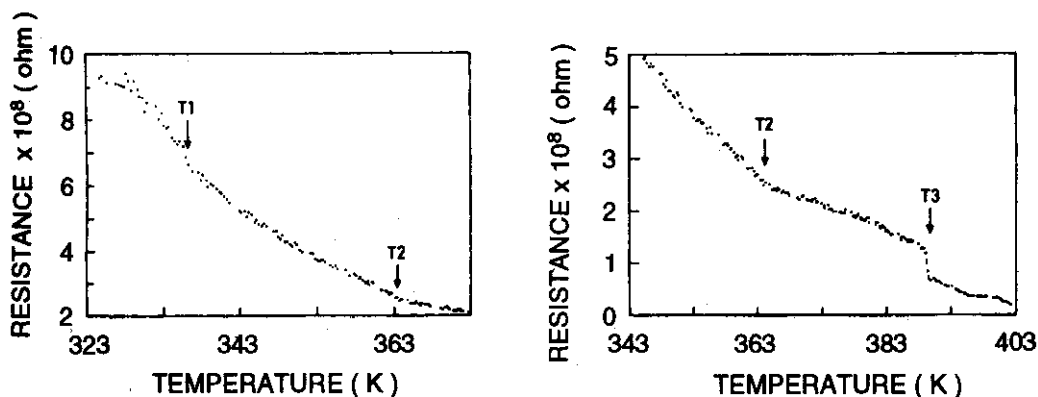


Figure 9: Resistance of C_{70} at 8.5 kbar vs temperature. The three transitions are marked T_1 , T_2 and T_3 . (ref.29).

4 Conclusions

The high pressure experiments have played a significant role in understanding the properties of fullerenes. Because of weak intermolecular bonding, fullerenes have

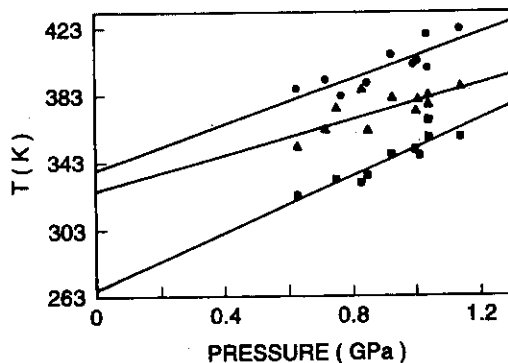


Figure 10: Variation of the three transition temperatures as a function of pressure in C_{70} . The solid lines are the straight lines fitted to the data (ref.29).

large compressibility coefficients. The nearly degenerate rotational configurations separated by small potential barriers become non-degenerate at moderately high pressures due to increased strength of the intermolecular interactions. This hinders the rotation of the fullerene molecules in the solid state. When the C_{60} and C_{70} molecules are cooled from the completely disordered high-temperature phase, some of the rotations are preferentially frozen before going to the fully ordered phase. These intermediate phases are thermodynamically stable over wider temperature ranges at higher pressures. This renders the high-pressure studies useful in the unambiguous detection and characterization of these phases.

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