Order-Order Transitions in C\textsubscript{60} and C\textsubscript{70}

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Abstract

In recent years enormous effort has been put in understanding the chemical and physical properties of C\textsubscript{60} and C\textsubscript{70}. Order-disorder transition in C\textsubscript{60} 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 \( \approx 10 \) K kbar\(^{-1} \), indicating that pressure favours the ordered state. The DSC and x-ray studies on C\textsubscript{70} 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 C\textsubscript{60} and C\textsubscript{70}. 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 C\textsubscript{60} molecules are known to crystallize in the face centered cubic structure\(^1\) at room temperature with lattice parameters \( a = 14.17 \) Å 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 C\textsubscript{70}. At high temperatures (\( T > 340 \) K), C\textsubscript{70} crystallizes in the face centered cubic structure, and below 270 K, it has a more ordered monoclinic structure. In the intermediate temperature range, C\textsubscript{70} 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 studies\(^2\) 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 pentacont on the neighbouring C_{60} unit.

Heiney et al.\(^6\) 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 studies\(^4\), 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 crystals bulk.

Figure 1: Crystal structure of two nearest neighbor molecules and the surrounding atoms.

The thin film and the number of interactions are about the same, but changes are observed.

The thin film grows with an anisotropy of the surrounding atoms.\(^8,9\)
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Figure 1: (a) Projection along [001] of the ordered C\textsubscript{60} structure at 5K. (b) projection of two neighbouring C\textsubscript{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 studies\textsuperscript{6} of C\textsubscript{60} thin film and C\textsubscript{60} in CS\textsubscript{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\textsubscript{60} are about the same as that in solution, implying very weak solid state intermolecular interactions. The IR line-widths studies as a function of temperature\textsuperscript{7} 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\textsuperscript{8,9}. This potential correctly predicts the low temperature structure to be simple
cubic with space group Pa\(\bar{3}\) and also a phase transition at a temperature of \(\approx 270\) K.

![Graphs](image)

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

\(\text{C}_{70}\) has not been studied as widely as \(\text{C}_{60}\). Its shape is slightly elongated and looks similar to a rugby ball. The shape corresponds to a \(\text{C}_{60}\) molecule with an additional ring of hexagons on the equatorial plane. The phase diagram of \(\text{C}_{70}\) is more complex compared to that of \(\text{C}_{60}\). Prepared at temperatures higher than 340 K, \(\text{C}_{70}\) crystallizes in the face centered cubic structure\(^{10,11}\), with a cell edge of 14.96 Å. 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, \(\text{C}_{70}\) 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 \(<111>\) direction. The final freezing of all the rotations of the \(\text{C}_{70}\) molecules takes place around 270 K. Below 270 K, \(\text{C}_{70}\) has a monoclinic structure with \(a=b=20.04\) Å and \(c=18.53\) Å, and the unit cell contains eight \(\text{C}_{70}\) molecules. As in \(\text{C}_{60}\), in the fully ordered unit cell of \(\text{C}_{70}\) the molecules are orientationally ordered such that the electron rich C-C bond of one \(\text{C}_{70}\) molecule is located at the center of the electron deficient zone.

Using the equation for the thermal expansion of \(\text{C}_{60}\), the thermal expansion coefficient is of 390 am\(^{3}\) per kelvin, which is \(1.9\) \(\times\) \(10^{-5}\) \(\text{K}^{-1}\) at 180 K and 2.3 \(\pm\) \(0.6\) \(\times\) \(10^{-5}\) \(\text{K}^{-1}\) at 340 K.

3 High Pressure Investigations

Applying pressure induces a solid state transition in \(\text{C}_{60}\), and the bulk modulus is \(34\pm 4\) GPa and \(0.17\) GPa.
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deficient pentagon of the neighbouring $C_{70}$ molecule.

The FTIR$^{12}$ and Raman$^{13}$ 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 measurements$^{14}$ 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).](image)

Using constant pressure molecular dynamic calculation$^{15}$ 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 $2.8 \pm 0.3$ and $2.5 \pm 0.3$ kJmol$^{-1}$ which compare well with the experimentally determined values of $2.9 \pm 0.4$ and $2.3 \pm 0.4$ 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 GPa$^{16}$ with an isothermal bulk modulus of $18.1 \pm 1.6$ GPa and a pressure coefficient of bulk modulus of $5.7 \pm 0.6$. Raman and IR vibrational peaks continue to be observable up to about 22 GPa$^{17}$. Extrapolation of the optical band gap measurement in the pressure range of 0-17 GPa indicates that the metallization$^{18}$ 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 \(\sim 3.5 \text{ kbar}\) as seen from Raman spectroscopy\(^{19}\). The pressure coefficient of the Raman peak frequency changes sign at the transition pressure (Fig.5).

![Fig.4](image1)

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

![Fig.5](image2)

**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\(^{61}\), 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\(^{6}\), 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 \(\Delta a_{\sigma}/dP\). 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 Singh\(^{22}\) 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

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by a sharp changes in the resistance. Atake et al.\textsuperscript{23} in their heat capacity measurement have found two transitions centered around 250 and 255 K. Fischer et al.\textsuperscript{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 ($\sim 0.57$ 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.\textsuperscript{22} show that it contains negligible amount of the solvent. Further, the room pressure DSC thermogram showed a single sharp endotherm of width $\sim$ 3 K. These confirm that the two transitions seen in the resistance measurements at high pressures are intrinsic to $C_{60}$. The DSC thermograms\textsuperscript{20} 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\textsuperscript{4,8,8}. Johnson et al.\textsuperscript{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 kbar\textsuperscript{22}. Extrapolated energy gap at room pressure (Fig.8) is 2.0 $\pm$ 0.2 eV which is close to 1.5 eV obtained from the energy band calculations at the Brillouin-zone boundary at X-point\textsuperscript{26}. The measurement of the temperature-dependence of the electrical\textsuperscript{27} conductivity on $C_{60}/C_{70}$ thin films gives an energy gap of 1.9 eV. However, Regueiro et al.\textsuperscript{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: Resistance vs temperature of C_{60} at 6.8 and 12.6 kbar (ref.22).

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

Pressures up to 22 GPa^{17}. 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 transitions^{29}. 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 Greve et al^{4} 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 pressure^{29}. 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^{50} 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 observed^{14} in the DSC, or the temperature obtained by extrapolation to room pressure of the transition temperature data of Ramasesha et al^{59}. In C_{70}, at the 340 K transition, the stacking changes from ABCABC.. (fcc) to

Fig. 9: Transition temperatures marked T_1, T_2 and T_3.

4 Conclusion

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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.

![Graph](image)

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

![Graph](image)

**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\textsubscript{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\textsubscript{60} and C\textsubscript{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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