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EFFECTS OF PRESSURE ON THE ORIENTATIONAL ORDERING
AND PHASE TRANSITIONS IN SOLID C₆₀ AND C₇₀

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ABSTRACT

The temperature-pressure phase diagrams of solid C₆₀ and C₇₀ have been determined and compared. A significant finding is the large influence of interstitial species and of the pressure transmitting medium on the orientational ordering processes. The pressure results reveal different, nearly degenerate configurations in both solids, which are believed to be due to hindered molecular rotations by interstitial species, and possibly different stacking modes in C₇₀.

INTRODUCTION

The identification of the molecular structures of C₆₀ and C₇₀ and their subsequent synthesis and separation have generated tremendous interest in these exciting forms of carbon. Currently broad research efforts are being aimed at determining and understanding the properties of these van der Waals solids and at identifying potential applications. Toward these ends, detailed knowledge of the orientational and rotational properties of the molecules in the solids and of the orientational ordering transitions that have been observed¹⁻⁶ in both crystalline C₆₀ and C₇₀ are necessary.

We have recently argued that high pressure studies can improve our understanding of the orientational properties and phase transitions of solid fullerenes.^{3,7} Specifically, pressure is the only variable which allows the delicate and continuous tuning of the strength of the intermolecular potentials and rotational barriers which control the motions of the molecules. Thus, results from high pressure studies can provide new insights into the ordering process as well as vital data for testing proposed intermolecular potentials and models for the transition.

In earlier papers³ we presented and discussed the hydrostatic pressure dependence of the orientational ordering in solid C₆₀. A significant finding of this earlier work is the large influence of interstitial foreign species and of the pressure-transmitting medium on the ordering process. We have since obtained additional results on C₆₀ and extended the work to C₇₀. In this paper we summarize the C₆₀ results, present new results on C₇₀ and compare and discuss these findings and the pressure-temperature phase diagrams for the two materials.

EXPERIMENTAL DETAILS

The ordering transitions were studied by differential thermal analysis in hydrostatic pressure apparatus using helium, nitrogen or a 50:50 mixture (vol.) of normal- and iso-pentanes as the pressure transmitting medium. Details on apparatus and techniques as well as on C₆₀ sample preparation can be found elsewhere.³ Nominally 99.5% pure C₇₀ obtained from Texas Fullerene and subsequently annealed under a dynamic vacuum at 500 K for 8 hours, as well as vapor-grown samples prepared from this starting material were used in the present study.

RESULTS AND DISCUSSION

Solid C₆₀

Solid C₆₀ exhibits on cooling a reversible phase transition at ~ 250 K from its high temperature face-centered-cubic (fcc; Fm3m) phase to a simple cubic (sc; Pa3) phase.¹⁻³ Above the transition temperature, each C₆₀ molecule executes continuous rotational diffusion uncorrelated with the rotational motion of its neighboring molecules resulting in an orientationally disordered phase. This rotational motion is significantly slowed down on cooling, and below the transition temperature the soccerball-shaped molecules develop orientational order resulting in the sc (Pa3) phase. It has been suggested² that an optimized ordering scheme results in nesting of the short (1.391Å) electron-rich *h*-pentagon bonds against the electron-poor pentagon faces of neighboring molecules. This nesting represents an effective bonding mechanism which locks the molecules into their ordered positions.

In this section we summarize some of our pressure results on C₆₀. More details can be found elsewhere.³ Effects of Pressure and Ambient Species. Figure 1 shows the temperature-pressure phase diagram of solid C₆₀ obtained using helium and nitrogen as the pressure transmitting media. Two remarkable features in the data are clearly evident. First is the large pressure-induced stabilization of the ordered sc phase, and second is the large influence of the pressure medium on the slope of the sc-fcc phase boundary. Specifically, the slope in helium above ~ 1 kbar is $dT/dP = 10.7 \pm 0.4 \text{ K/kbar}$ and that in nitrogen is $16.2 \pm 0.4 \text{ K/kbar}$. Thus, compared to helium, nitrogen causes considerable additional hindrance of the orientational motion of the C₆₀ molecules and further stabilization of the sc phase. In pentane, the slope is $15.9 \pm 0.3 \text{ K/kbar}$, essentially the same as nitrogen.

The large slope reflects the weak van der Waals intermolecular bonding and the concomitant high compressibility of the C₆₀ lattice as well as the high sensitivity of the orientational barriers to the intermolecular separations. Interpreted in terms of our current understanding of the microscopic view of the transition, this result can be understood in terms of pressure-induced enhancement of the nesting of neighboring molecules and stiffening of the orientational potential which results in the

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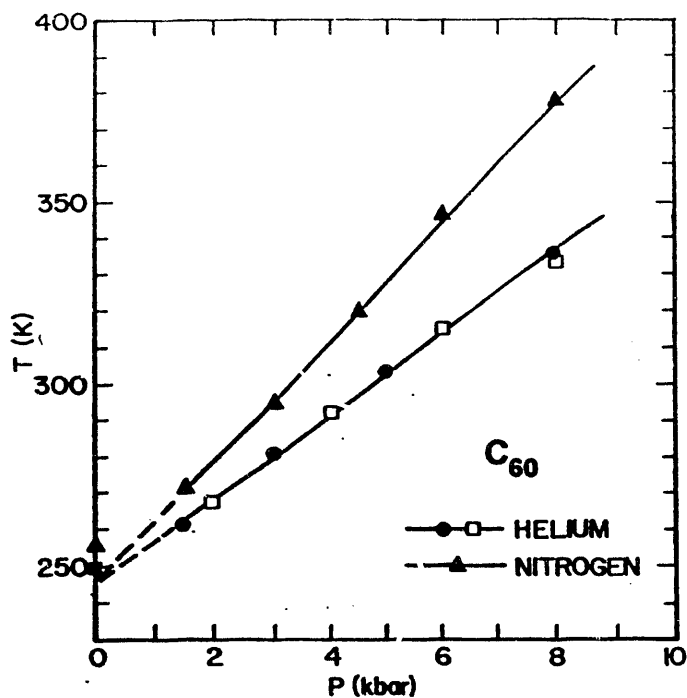


Fig. 1 Temperature-pressure phase diagram of solid C_{60} contrasting the behavior in helium and nitrogen.

octahedral sites. Helium, on the other hand, is expected to easily permeate both the tetrahedral and octahedral sites on the time scales of the experiment, and, under pressure, it renders the C_{60} lattice less compressible than in its absence. The resulting lower compression of the lattice for a given applied pressure in the presence of He thus leads to a lower T_c than for N_2 . In the above view, the pentane results (as those of N_2) reflect the intrinsic response of solid C_{60} .

The Two-Peak Structure The DTA spectra of our samples exhibited a two-peak structure (~ 5 K apart) in the region of the sc-fcc phase transition; however, there were remarkable differences among samples, as illustrated in Figure 2. In sample A, a shoulder is observed on the low-temperature side of the main DTA peak while in sample B the shoulder is on the high-temperature side of the main peak. In other samples there were other differences in the relative intensities of the two peaks. This two-peak structure is not seen in all DTA scans, but it has been observed in high resolution specific heat data.³

The two-peak structure clearly suggests the possibility of two nearly degenerate orientational configurations of the molecules in the sc phase. The fact that the two-peak structure is not seen in all solid C_{60} samples further suggests that this feature may be caused by impurities in the lattice. Our finding concerning the influence of ambient species on the transition³ leads us to propose a plausible explanation. In the absence of foreign species such as O_2 and N_2 in the interstitial (particularly the octahedral) lattice sites, the rotational motion of the C_{60} molecules is unhindered; however, the presence of such species hinders this motion and shifts the sc \rightarrow fcc transition to higher temperatures. When only some of the interstitial sites are occupied, the sample exhibits both

lowering (raising) of the librational amplitude (frequency) of the molecules in the sc phase.³

It has been demonstrated that gaseous species, such as N_2 and O_2 permeate the C_{60} lattice and influence the rotational motion of the molecules.³ It is thus tempting to explain the large difference in the pressure dependence of T_c in He and N_2 (Fig. 1) on the basis of the occupation of the interstitial sites by these two gaseous species. The main effect of pressure at the modest pressures of the present experiments is to reduce the lattice parameter of C_{60} resulting in smaller octahedral sites. The presence of N_2 in a smaller site would cause additional hindrance of the rotational motion of the C_{60} molecules, hence still higher T_c . The observed much higher slope dT_c/dP in N_2 compared with He would be consistent with this view, since He, for the reasons cited above, should have very little influence on the motion of the C_{60} s.

While tempting, this explanation is not supported by three observations. First, the T_c vs. P data in N_2 extrapolate to the same T_c value at 1 bar as the data in He (see Fig. 1). This would not be expected to be the case if sufficient N_2 entered the octahedral sites. Second, the kinetics of N_2 diffusion into and out of solid C_{60} are so slow that it is unlikely that sufficient permeation of the C_{60} lattice by N_2 can occur on the time scale (hours) of our DTA experiments.⁷ Third, the $T_c(P)$ slope in pentane is the same as in N_2 , and pentane cannot be accommodated in interstitial sites.

A more plausible explanation for the difference in dT_c/dP between the N_2 and He results is as follows.³ The $T_c(P)$ results in N_2 represent the *intrinsic* hydrostatic pressure response of solid C_{60} , i.e., compression of the C_{60} lattice in the absence of sufficient permeation of N_2 into the

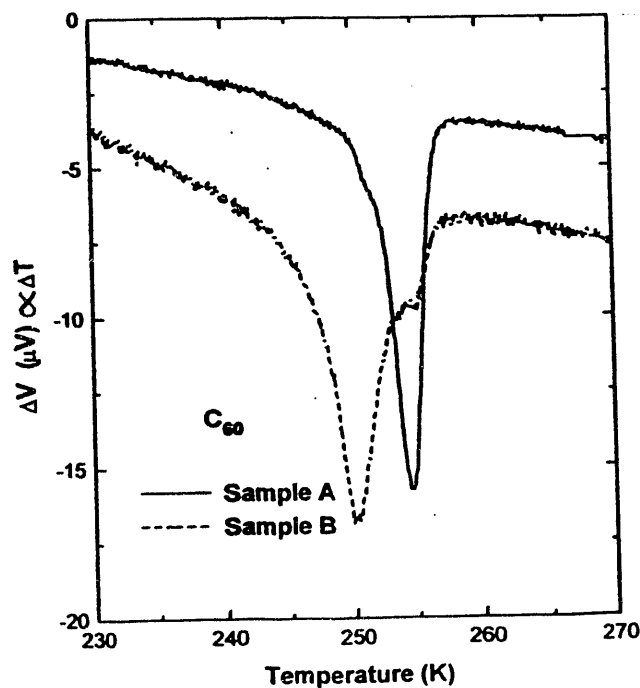


Fig. 2 DTA spectra of two C_{60} samples showing the two-peak structure and remarkable differences.

unhindered as well as hindered rotations, and this situation leads to the two-peak structure. In this scenario, the intensities of the two peaks can be expected to depend on the relative populations of unhindered and hindered rotational states which are ~ 5 K apart in energy.

Based on a symmetry analysis of the ordered phase it has recently been suggested⁸ that the sc-fcc transition may be a two-step process: (1) a continuous $Fm\bar{3}m \rightarrow Fm\bar{3}$ transition driven by a scalar order parameter at the Γ -point, i.e., without any change in unit cell, and (2) a first-order transition described by a six-component order parameter and belonging to the X_5 irreducible representation of $Fm\bar{3}m$. While the experimental evidence favors foreign interstitial species as the cause of the two-peak structure, as discussed above, this proposed two-step model is interesting and deserves further study.

Solid C_{70}

Because of C_{70} 's elliptical (rugby ball) molecular shape, orientational ordering in solid C_{70} can be expected to be more complex than that in C_{60} . Indeed, as many as five crystalline phases have been identified.^{5,6}

As-grown, C_{70} crystals occur in both the fcc and the ideal hexagonal close packed ($P6_3/mmc$, $c/a = 1.63$) structures^{5,6} in both of which the C_{70} molecules rotate freely and are oriented randomly. On heating, the crystals first transform (irreversibly) to a rhombohedral phase and then to fcc. On lowering temperature they transform to a deformed hcp phase ($c/a = 1.82$) at ~ 340 K where the initially free random rotations of the molecules are reduced to free rotations around their long axis which becomes oriented along the 6-fold hexagonal axis. On further cooling a second transition occurs at ~ 275 K to a monoclinic phase where the free rotations around the c-axis are frozen-in. In this phase there is a doubling of one of the hexagonal a axes, and the unique monoclinic axis is along the former hexagonal c-axis. On cooling, the fcc phase transforms to the rhombohedral phase (unknown transition temperature) which remains stable down to 77 K.

The above evidence reveals a complicated phase behavior in solid C_{70} . All the observed transitions occur in a relatively small temperature range ($\Delta T < 100$ K) indicating small energy differences between the various configurations. The available literature^{5,6} reveals substantial variability in the transition temperatures and suggest that not all of the transitions are observed in all samples. The occurrence of these transitions appears to be affected by crystalline defects, crystalline morphology, strains and, as we shall see later, the incorporation of atomic or molecular species in the interstitial lattice sites.

We have investigated the effects of pressure on the DTA spectra of solution- and vapor-grown samples. On heating the solution-grown sample exhibited a well-defined peak at 275 K (T_{C1}) which we associate with the monoclinic \rightarrow deformed hcp transition and a weak peak at ~ 335 K (T_{C2}) which we associate with the deformed hcp \rightarrow ideal hcp transition. This latter peak exhibited a very large shift to higher temperatures with pressure, but its dT_{C2}/dP

could not be determined sufficiently accurately because of smearing. The shift of T_{C1} is linear up to 8 kbar with $dT_{C1}/dP = 14$ K/kbar (in helium).

The DTA spectrum of the vapor-grown sample is shown in Figure 3. On heating at 1 bar it exhibited two peaks: a lower temperature peak at 286 K (T_{C1}) with a shoulder at the high temperature side, which is most likely due to hindered rotations caused by interstitial species, and a higher temperature peak at 367 K. We attribute this peak to the deformed hcp \rightarrow a free rotor phase which could be either the ideal hcp or the rhombohedral (or fcc) phase. The first choice follows the expected sequence of transitions according to Verheijen et al⁶ and is favored, but its T_C is considerably larger than the usual stated value (~ 340 K) for T_{C2} which could be due to the presence of some unknown impurities which hinder the onset of free rotations of the C_{70} molecules. The second choice is favored by the higher observed T_C but disfavored by the fact that we find the transition to be reversible, whereas the hcp \rightarrow rhombohedral (or fcc) transition is said to be irreversible.⁶

Figure 3 shows the large shifts of the two peaks with pressure (in helium) and the reversibility of the pressure effects. Some of the spectra in Figure 3 and others not shown reveal the presence of shoulders which seem to occur somewhat randomly. These features reflect different orientational configurations which are most likely associated with lattice defects and/or interstitial species.

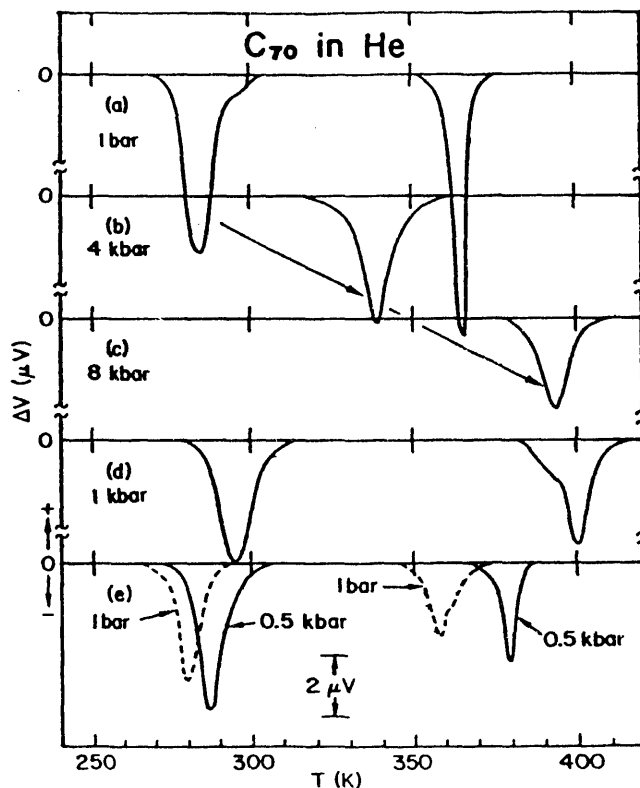


Fig. 3 Variation of the DTA spectrum of C_{70} with increasing and then decreasing pressure.

Figure 4 shows the temperature-pressure phase diagram in helium. There is some irreversibility in the zero pressure values of the T_c 's: for the virgin sample T_{c1} and T_{c2} were 286 and 367 K but after repeated temperature-pressure cycling up to 400 K and 8 kbar these T_c 's decreased to 280 and 358 K, respectively. A similar effect was observed in C_{60} which we attributed to helium exchanging for some O_2 and N_2 present in the virgin sample. The presence of these two species in interstitial lattice sites hinders the rotational/orientational motion of the C_{70} molecules and raises the T_c 's. Being small and spherical, interstitial helium does not have an appreciable influence on the motion, and the T_c 's can be expected to occur at lower temperatures.

The phase boundaries in Figure 4 are linear with $dT_{c2}/dP = 14.9 \pm 0.4 \text{ K/kbar}$ and $dT_{c1}/dP = 42 \pm 1 \text{ K/kbar}$. Both of these shifts are large reflecting the extreme sensitivities of the orientational potentials to intermolecular separations. Their relative magnitudes are consistent with intuitive expectation: a given decrease in intermolecular separations can be expected to more strongly hinder the free rotations of the molecules than the rotations along the long axes. The fact that these shifts are much larger than that of T_c of C_{60} is also intuitively clear: the orientational motion of elliptical molecules is more strongly hindered by decreasing intermolecular separations than that of spherical molecules.

Figure 4 also shows the T_{c1} phase boundary in nitrogen where $dT_{c1}/dP = 30.5 \pm 1.0 \text{ K/kbar}$. The much larger shift of T_{c1} in nitrogen compared to helium is qualitatively similar to what we observed in C_{60} , and we suggest a similar explanation.

CONCLUDING REMARKS

The different observed pressure responses of the order-disorder transitions of solid C_{60} and solid C_{70} in different pressure media have provided much new insight into the orientational ordering processes. We have determined the temperature-pressure phase diagrams for both solids and elucidated the role of interstitial foreign species in their lattices. The pressure results have revealed different, nearly degenerate (in energy) configurations which are related to hindered molecular rotations and possibly to different stacking modes in C_{70} . Additionally, these results along with the compressibilities of the two solids are crucial for testing proposed models and orientational potentials, as has been already demonstrated⁹ for C_{60} .

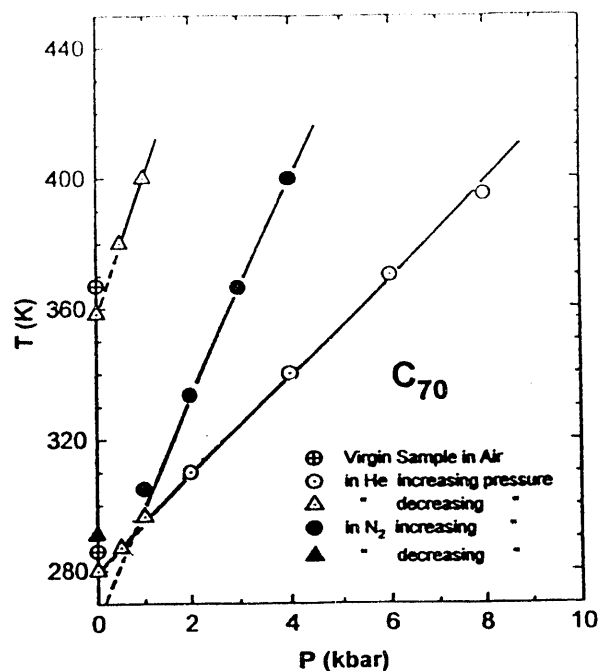


Fig. 4 Temperature-pressure phase diagram of solid C_{70} contrasting the behavior in helium and in nitrogen.

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