

Effects of pressure and ambient species on the orientational ordering in solid C₆₀

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The effects of hydrostatic pressure on the orientational ordering transition in solid C₆₀ were investigated using helium, nitrogen, and a 50/50 (by volume) mixture of normal and isopentanes as pressure-transmitting media. The different observed responses in these media and for different samples, as well as some irreversible pressure cycling effects, have provided much insight into the ordering process. Highlights of the work include the following: (1) Lattice compression hinders the librational motion of the C₆₀ molecules in the low-temperature simple cubic (sc) phase, thereby increasing T_c and stabilizing the sc phase; the effect is large; (2) the pressure dependence of T_c , along with the accurately known volume change at the transition, yield 1.7 kcal/mole and 6.5 cal/K mole for the latent heat and discontinuous change in entropy, respectively, associated with the transition; (3) T_c and its pressure dependence are influenced by the presence of ambient species in the interstitial lattice sites. Helium appears to diffuse readily into the lattice, whereas N₂ (and O₂) diffuse less rapidly and occupy octahedral sites; (4) a two-peak structure in differential thermal analysis spectra (also reported in specific-heat measurements) was observed and is believed to be due to the partial occupation of the octahedral sites by species such as N₂ or O₂; (5) solid C₆₀ "reacts" with pentane at pressures ≥ 14 kbar and temperatures > 475 K to yield an irreversible C₆₀/pentane complex similar to that obtained by the cocrystallization of C₆₀ and normal pentane at 1 bar. These results are discussed in terms of proposed models.

I. INTRODUCTION

It is now well established solid C₆₀ exhibits on cooling a reversible phase transition at ~ 250 K from its high-temperature face-centered-cubic (fcc; space group Fm3m) phase to a simple cubic (sc; space group Pa3) phase.¹⁻⁵ The transition involves the development of orientational order of the C₆₀ molecules in the sc phase. Above the transition temperature, each C₆₀ molecule executes continuous motion uncorrelated with the rotational motion of its neighboring molecules, resulting in an orientationally disordered phase. This rotational motion is greatly slowed down on cooling; however, significant motion is observed below the transition.^{3,6} This fact is reconcilable with Pa3 symmetry for the low-temperature phase by the conclusion that the molecules execute jumps between symmetry-equivalent orientations in this phase.

A detailed knowledge of the orientational and rotational properties of the molecules and of the mechanism for the ordering transition is necessary for full understanding of the properties of solid C₆₀. Toward this end, a great deal of experimental and theoretical work is under way.⁷⁻¹⁰ We have recently argued that high-pressure studies can play a significant role in achieving this goal.⁵ 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 C₆₀ 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 an earlier short paper,⁵ we studied the hydrostatic

pressure dependence of the orientational ordering in solid C₆₀ up to 8 kbar using helium gas as the pressure-transmitting medium. It was found that pressure (1) stabilizes the ordered sc phase, (2) greatly reduces orientational fluctuations of the C₆₀ molecules in the sc phase, and (3) enhances a feature in the data which suggested the possible presence of two nearly degenerate configurationally ordered states. We have now extended our studies to higher pressures and examined the above three effects in more detail on different samples using different pressure-transmitting media and obtained important new insights into the ordering process. Significant findings include the large influence of interstitial foreign species and of the pressure-transmitting medium on the ordering process and the discovery of a "new" phase involving the "reaction" of C₆₀ with pentane. In what follows we give the experimental details and then present and discuss the results.

II. EXPERIMENTAL DETAILS

A. Samples

Two different batches of samples, designated in the text by the letters A and B, were used. Batch A was > 99.4 at. % pure C₆₀ powder prepared as follows: Toluene-soluble soot (purchased from Texas Fullerene Co.), typically 1.0 g, was extracted with diethyl ether and then chromatographed on neutral alumina (Brockman activity I, 1.5 kg). C₆₀ eluted first with hexane:toluene (97.3, volumetric ratio) as a distinct purple band on the column. C₇₀ and higher fullerenes were isolated by increasing the concentration of toluene to 30 vol. %. The solution of

C_{60} was reduced *in vacuo* to afford a black solid (0.69 g) which was then annealed at 400 K for 4 h under dynamic vacuum. The material was characterized by infrared, UV, mass, and solid state ^{13}C magic angle spinning (MAS) NMR spectroscopies yielding IR (KBr) bands at 1428, 1181, 575, and 525 cm^{-1} ; UV ($1.2 \times 10^{-5}\text{ M}$ in hexane) bands at 210, 228, 257, 328, 404, 464, and 497 nm; ^{13}C MAS NMR (chemical shift) = 143.7 ppm. Prior to annealing, the x-ray-diffraction pattern had broadened lines as well as a large "foot" on the (111) line, caused by stacking fault defects; the annealing greatly sharpened these lines and removed the "foot."

Batch B was 99.5 at. % pure C_{60} obtained from Texas Fullerene. We subsequently annealed this sample under dynamic vacuum at 500 K for 8 h before characterization by ^{13}C MAS NMR spectroscopy. The annealing sharpened the x-ray-diffraction lines and removed the "foot" on the (111) line which was present in the as-received material. Even after this thermal treatment, high-resolution solid-state proton (^1H) MAS NMR gave evidence for some remaining H-containing solvent impurities (specifically toluene) in this sample. After annealing, both samples were exposed to air during handling, but kept in a desiccator when not in use. The pressure experiments were performed several weeks after the anneals.

B. Techniques

The ordering transition was studied by differential thermal analysis (DTA). The sample and an adjoining inert reference material (NaCl or SiO_2 powder) were encapsulated and enclosed inside one of two pressure cells. One cell was a 10-kbar cell situated inside a low-temperature cryostat and employed either helium or nitrogen gas as the pressure-transmitting medium. The second cell was a 30-kbar apparatus which employed a 50:50 (vol.) mixture of normal and isopentanes as the pressure-transmitting medium. This cell is massive and cannot be operated below room temperature. The pressure was measured to an accuracy of better than 1% by calibrated manganin gauges. Temperature change was measured to better than 0.1 K by a thermocouple placed near the sample, and the DTA scans were run at a heating rate of 10 K/min. At this relatively rapid heating rate, the temperature inferred from the DTA peak on heating is somewhat higher than the equilibrium T_c ; however, this difference does not affect the relative changes in T_c and the shift of T_c with pressure, which are accurately determined and are the effects we seek.

Complementary ^{13}C NMR experiments were performed at 1 kbar on samples recovered from annealing in oxygen at pressures up to ~ 2 kbar. The results clearly revealed the fact that oxygen can occupy the octahedral interstitial sites.¹¹

III. RESULTS

A. Samples A

Our earlier results to 8 kbar on samples from batch A using helium as the pressure-transmitting medium re-

vealed three principal, reversible pressure effects which can be summarized as follows: First, the ordering transition temperature T_c shifts to higher temperatures with pressure at the rapid rate of 10.4 K/kbar. This shift can be intuitively understood on the basis of the hindrance of the rotational-orientational motions of the C_{60} molecules on decreasing the intermolecular separations. The large size of the shift reflects the weak van der Waals intermolecular bonding and the concomitant high compressibility of the C_{60} lattice as well as the high sensitivity of the orientational barriers to the intermolecular separations. Second, the broad (in temperature) precursor on the low-temperature side of the transition, seen in both the DTA spectra^{1,5} and x-ray diffraction,¹ which is attributed to orientational fluctuations in the ordered sc phase, decreases markedly with pressure. This is a manifestation of increased motional correlations and the stabilization of the sc ordered phase with pressure. Third, there was a hint (asymmetry) in the 1-bar (≈ 0 -kbar) scan that there could be a second feature on the low-temperature side of the peak. With increasing pressure, this feature evolved into a well-defined shoulder, suggesting the presence of two nearly degenerate configurational states even at 1 bar. Because of its relatively large size and pressure dependence, it was thought possible that this feature could be intrinsic and not due to trace impurities or residual solvent (hexane-toluene) in the sample; however, we could not completely rule out the possible involvement of impurities.

The above results suggested the desirability of extending the measurements to higher pressures as well as the need to examine samples prepared under different conditions. We have now carried out both of these aspects. Going to higher pressures necessitated the use of the 30-kbar apparatus which uses the pentane mixture as the pressure-transmitting medium.

Figure 1 shows the temperature-pressure phase diagram of solid C_{60} . The $sc \rightleftharpoons fcc$ phase boundary up to 8 kbar in helium is from our earlier work.⁵ The large pressure-induced stabilization of the sc phase is evident. The results with the 50/50 mixture of normal and isopentane as the pressure-transmitting medium are remarkably different from the results with helium. Two sets of data with pentane are shown. In both cases the C_{60} used was from the same preparation (batch A) but different samples and different DTA cell designs and inert reference materials were employed for the two sets. The reproducibility of the results is very good, as shown by the solid circles and open triangles, the systematic differences between the T_c 's for the two sets of data being due to different placements of the thermocouples relative to the samples in the two cells. Up to ~ 14 kbar, the pressure effects are reversible upon lowering the pressure; however, at ≥ 14 kbar an irreversible change takes place, as discussed below. It is seen that in pentane the $sc \rightleftharpoons fcc$ phase boundary is much steeper than in helium, the slope dT_c/dP being 15.9 ± 0.3 K/kbar. Thus, the presence of pentane causes additional hindrance of the motion of the C_{60} molecules, and, at any given pressure, additional thermal energy is needed to cause orientational disordering.

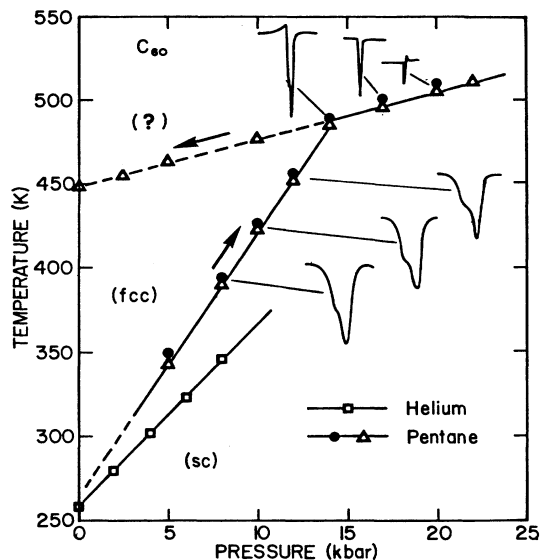


FIG. 1. Temperature-pressure phase diagram for solid C_{60} (sample A) contrasting the responses of the sc-fcc transition in helium and a 50/50 (by volume) mixture of normal and isopentanes. Shown also is the variation of the DTA signal with pressure. A qualitative, irreversible change occurs at ≥ 14 kbar in pentane. This change appears to involve a reaction between C_{60} and pentane. As such, it is not strictly proper to include the upper line (boundary) on an equilibrium phase diagram for solid C_{60} . We include this line in the figure for contrast with the behavior at pressures ≤ 14 kbar.

The insets in Fig. 1 show the evolution of the DTA spectrum with pressure. The 8-, 10-, and 12-kbar spectra depict the continued evolution in the intensity of the shoulder on the low-temperature side of the peak similarly noted in our earlier data up to 8 kbar in helium (see Fig. 1, Ref. 5). The two-peak nature of the spectrum is clearly evident. By splitting the spectrum into its two components, we find the peak separation to be ~ 5 K and approximately independent of pressure.

On going to still higher pressure, the DTA spectrum changes drastically at ≥ 14 kbar, becoming much narrower and sharper, as shown. This new spectrum, which signifies the formation of a new pressure-induced "phase," decreases in intensity and shifts to higher temperature with pressure, but the slope,

$$dT_c/dP = 2.8 \pm 0.2 \text{ K/kbar},$$

is only about $\frac{1}{3}$ that below 14 kbar. The new phase is irreversible upon lowering the pressure below 14 kbar, and its "transition" temperature, as defined by the sharp DTA peak, follows the upper phase boundary, as depicted in Fig. 1. The new phase can be recovered at 1 bar and appears to be stable (at least over the period of several weeks of our observations). At 10 kbar on the release cycle, only the sharp DTA spectrum of the new phase is observed, as shown; however, by holding the pressure at ≤ 5 kbar for several hours, the DTA spectrum exhibits two peaks, the lower-temperature peak corresponding to the original sc-fcc transition and the

higher-temperature peak corresponding to the upper phase boundary. Thus, below ~ 5 kbar there is some recovery of the original cubic C_{60} phase.

The material recovered from > 14 -kbar experiments in pentane is of mixed phase: its 1-bar DTA spectrum exhibits the original sc-fcc peak at 259 K as well as a peak at 450 K. We have begun to examine the recovered new phase. Early x-ray-diffraction results will be discussed below.

B. Samples B

The large difference between the helium and pentane results on samples from specimen A suggested that the pressure-transmitting medium could permeate the C_{60} lattice and influence the orientational motion of the molecules. To explore this point further and to examine the possible involvement of impurities or residual solvent in the observed two-peak DTA spectrum on specimen A, we studied a completely different C_{60} specimen (batch B) using helium and nitrogen as pressure-transmitting media.

The 1-bar DTA spectrum of a virgin sample from specimen B is shown in Fig. 2(a). This spectrum is remarkably different from that of specimen A. First, the spectrum shows a distinct shoulder (or second peak) even at 1 bar. Second, whereas for specimen A the shoulder was on the low-temperature side of the major peak, the shoulder for specimen B is on the high-temperature side of this peak, which is observed at 258.5 K. We shall return to this contrast later.

Figure 3 summarizes results in helium and nitrogen on a sample from specimen B. Striking differences between the helium and nitrogen results are evident and there are also other important features in the data which we now discuss.

The helium results were obtained first and are from two different runs which agree well. The slope above 1 kbar is

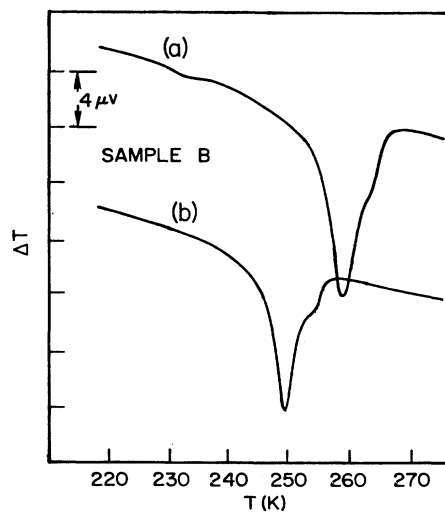


FIG. 2. (a) DTA spectrum of virgin sample B (upper trace) and (b) immediately after repeated cycling in helium pressure up to 8 kbar and 400 K (lower trace).

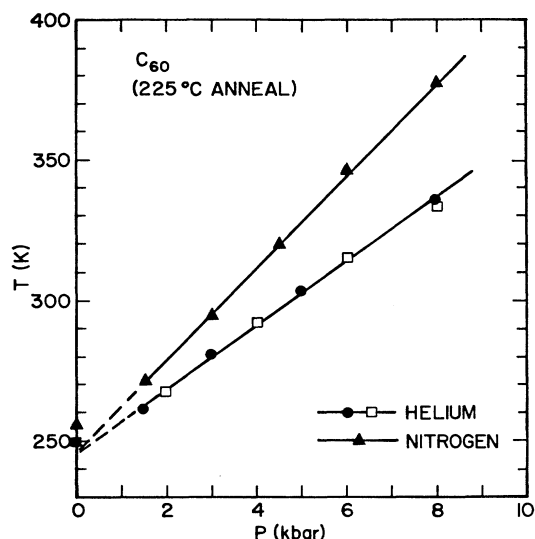


FIG. 3. Temperature-pressure phase diagram of solid C_{60} (sample B) contrasting the behavior in helium and nitrogen as the pressure-transmitting media.

$$dT_c/dP = 10.9 \pm 0.4 \text{ K/kbar},$$

which is comparable to the $10.4 \pm 0.2 \text{ K/kbar}$ for specimen A. The recovered sample after the first pressure run to 8 kbar in helium (open squares in Fig. 3) had a $T_c = 249 \text{ K}$ at 1 bar (represented by the solid square), i.e., the sample exhibited an irreversible effect after exposure to helium at high pressure. A second run in helium (solid circles) reproduced the first run very well as shown. On releasing the pressure from this run, T_c was again $= 249 \text{ K}$ at 1 bar, i.e., the same as after the first run. The 1-bar DTA spectrum after pressure cycling in helium retains the well-defined shoulder on the high-temperature side of the peak observed in the virgin sample B (i.e., before pressure cycling) as shown in Fig. 2(b); however, the large shift in T_c due to pressure cycling is evident.

In marked contrast with the helium data, the results in nitrogen (which were obtained on the same sample after cycling in He) yielded a much steeper sc-fcc phase boundary, as shown by the solid triangles in Fig. 3. The slope in nitrogen above $\sim 1 \text{ kbar}$ is

$$dT_c/dP = 16.4 \pm 0.2 \text{ K/kbar},$$

which is about the same as that in pentane for specimen A. Thus, contrasted with helium, nitrogen causes considerable additional hindrance of the orientational motion of the C_{60} molecules. The recovered sample from the nitrogen pressure run had a T_c of 256 K (the solid triangle at zero pressure in Fig. 3).

IV. DISCUSSION

A. Effects of ambient species on the ordering process

The above observations on the irreversible pressure-cycling effects on T_c and the different responses in

different pressure-transmitting media, as well as the differences between samples A and B, contain much insight, which we now discuss. The results in Fig. 2 on sample B provide a significant clue. The $\sim 10\text{-K}$ decrease in the 1-bar T_c of this sample after high-pressure cycling in helium suggests that helium exchanged for or removed some other species that was incorporated in the sample. We suspected the presence of either oxygen (O_2) or nitrogen (N_2) or both. Our ^{13}C NMR results on a virgin sample from batch B taken under MAS conditions and shown in Fig. 4(a) revealed the presence of a minor resonance at 144.4 ppm in addition to the well-known monotonically narrowed primary resonance at 143.7 ppm which is due to the rapidly rotating C_{60} molecules in the solid. Detailed NMR studies in our laboratories showed that the minor resonance is associated with molecular oxygen, and, furthermore, the O_2 occupies octahedral interstitial sites next to a given C_{60} in the lattice.¹¹ In the virgin sample, the NMR spectrum shows that there is only one O_2 adjacent to some C_{60} molecules (i.e., only one of the six octahedral sites next to a given C_{60} is occupied by O_2) leading to the observed one minor resonance. However, exposure of the sample to modest high pressure (0.5 kbar) oxygen¹¹ resulted in some filling of all six octahedral sites with O_2 molecules, as clearly demonstrated by the six minor resonances in Fig. 4(b).

That O_2 can be readily accommodated in the octahedral sites is consistent with intuitive expectations based on molecular size considerations. The lattice parameter of solid C_{60} at normal conditions⁴ is $a_0 = 14.17 \text{ \AA}$ yielding a van der Waals radius of 5.01 \AA for the C_{60} molecule. The minimum octahedral site spacing is then 4.15

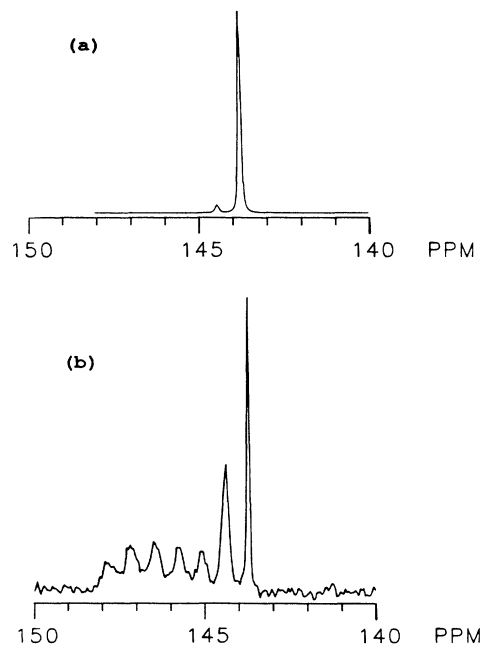


FIG. 4. High-resolution ^{13}C NMR spectra for sample B (a) before and (b) after exposure to high-pressure (1 kbar) oxygen for 1.75 h.

Å. By comparison, the interatomic separation in O₂ is 1.208 Å with an effective van der Waals radius of ~1.4 Å for O₂.¹² Thus, O₂ is readily accommodated in the octahedral sites,¹³ and, we believe, can readily tumble within these sites. The observed limit of six minor resonances in Fig. 4(b) denotes that only one O₂ occupies a given octahedral site.

For every octahedral site in the fcc lattice there are two tetrahedral sites. The effective van der Waals radius of these latter sites is ~1.13 Å, suggesting that O₂ cannot be accommodated in them, a conclusion consistent with the maximum of six minor resonances in the NMR spectrum.

Molecular nitrogen has a slightly larger size than O₂. Specifically, while the interatomic separation in N₂ is 1.095 Å, which is slightly smaller than for O₂, the effective van der Waals radius is ~1.5 Å. (The most dense forms in the solid state have effective volumes of 35.5 and 44.9 Å³ for O₂ and N₂, respectively, illustrating how the shorter triple bond of N₂ spreads the remaining electron cloud.) Thus, we expect N₂ to be also readily accommodated in the octahedral, but not in the tetrahedral, sites.¹³ Helium, on the other hand, has an atomic radius of 0.95 Å, and can be accommodated in both sites, but probably cannot permeate the C₆₀ molecules themselves.¹³

With the above considerations in mind, we can now postulate plausible explanations for the effects described in Sec. III. Virgin samples B clearly contain a small amount of O₂ (from NMR, ~0.4%) and possibly N₂ (which is not detected by NMR), whose presence and tumbling motion in the octahedral sites can be expected to influence the rotational-orientational motion of the C₆₀ molecules in the lattice. The high value of the 1-bar T_c (258.5 K) and the relative sharpness of the main peak in the DTA spectrum [Fig. 2(a)] suggest that there is sufficient O₂ (and N₂) which is uniformly distributed in the sample and which hinders the motion of the C₆₀ molecules—hence, the high T_c . Upon repeated cycling in He pressure up to 8 kbar and up to 400 K, we believe He exchanges for the O₂ (and N₂). Being small and spherical, we do not expect He in either the octahedral or tetrahedral sites to influence appreciably the motion of the C₆₀ molecules. Thus, the disordering transition in the presence of He can be expected to occur at a lower temperature than in the presence of O₂ (or N₂). The observed T_c of 249 K after He pressure cycling is consistent with this view.

Sample B was next repeatedly cycled in N₂ at pressures up to 8 kbar and temperatures up to 400 K and, after recovery at 1 bar, had T_c = 256 K, which is 2.5 K lower than T_c of the virgin sample. This result can be understood in terms of N₂ reentering octahedral sites, hindering the rotational motion of the C₆₀ molecules and hence the ~7-K-higher T_c . The 2.5-K-higher T_c of the virgin sample compared with the N₂-containing sample remains somewhat of a puzzle but may be due to the presence of other impurities (most likely solvent) which are removed during He and N₂ cycling. As already noted, solid-state

¹H NMR data gave evidence for some H-containing solvent impurities (toluene) in the sample. The toluene molecule, being large, cannot of course permeate the C₆₀ lattice, but it can be trapped between grains and its CH₃ group can in principle permeate to some extent the surface octahedral sites of the fine powder grains. If we presume that the transition from the sc to the fcc phase involves the correlated, cooperative rotational motion of the C₆₀ molecules, then any hindrance of the motion of the near-surface C₆₀ molecules by the presence of toluene can hinder the motion of the majority of the molecules in each grain, hence causing a higher T_c .

It is tempting to explain the large difference in the pressure dependence of T_c in He and N₂ (Fig. 3) 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 C₆₀, resulting in smaller octahedral sites. (The size of the C₆₀ molecules should remain about the same.) The presence of N₂ (or O₂) in a smaller site would cause additional hindrance of the rotational motion of the C₆₀ molecules—hence still higher T_c . The observed much higher slope dT_c/dP in N₂ 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 C₆₀'s.

While tempting, this explanation is not supported by two observations. First, the T_c versus P data in N₂ extrapolate to the same T_c value at 1 bar as the data in He (see Fig. 3). This would not be expected to be the case if sufficient N₂ entered the octahedral sites. Second, we believe that the kinetics of N₂ diffusion into and out of solid C₆₀ are so slow that it is unlikely that sufficient permeation of the C₆₀ lattice by N₂ can occur on the time scale (hours) of our DTA experiments. Specifically, we find that the half-life for oxygen diffusion out of C₆₀ is in on the order of 160 h for a sample in which 25% of the sites had been filled by exposure to oxygen at 1 kbar for 116 h. Nitrogen diffusion appears to be slower than that of oxygen.

On the basis of these observations, we conclude that the most likely explanation for the difference in dT_c/dP between the N₂ and He results is as follows: The $T_c(P)$ results in N₂ represent the *intrinsic* hydrostatic pressure response of solid C₆₀, i.e., compression of the C₆₀ lattice in the absence of sufficient permeation of N₂ into the octahedral sites. Helium, on the other hand, is expected to permeate easily both the tetrahedral and octahedral sites on the time scales of the experiment, and, under pressure, it renders the C₆₀ 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 N₂.

On the above scenario, we still have to explain the T_c = 256 K at 1 bar (Fig. 3) value obtained on sample B after pressure and temperature cycling in N₂. This T_c was obtained after the sample was held at normal conditions in air for several days. Under these conditions, we believe that a sufficient amount of N₂ and O₂ permeated

the sample to cause this higher T_c . It is possible to test our proposed explanation by a series of experiments in which we measure T_c and its pressure dependence on a sample containing significant amounts of N_2 and/or O_2 achieved by loading the C_{60} lattice for extended periods of time under suitable pressure and temperature conditions. Such experiments are under way.

The T_c versus P results in pentane (Fig. 1) support the above view. As noted above, the dT_c/dP slopes in N_2 and pentane are essentially the same within experimental error (16.4 ± 0.2 versus 15.9 ± 0.3). Thus, the pentane results (as do those of N_2) reflect the intrinsic response of solid C_{60} to pressure.

The above considerations also provide a plausible explanation for the different values of T_c (248 to 260 K) reported in the literature, namely, the variation is most likely due to impurities or residual solvents in the solid. As noted, there was residual solvent in our sample B even after vacuum annealing at 500 K for 8 h. We suspect that residual solvent was also present in sample A which was annealed at a lower temperature (400 K) and for a shorter time (4 h). Unfortunately, we did not perform 1H NMR measurements on sample A before it underwent the irreversible reaction with pentane.

B. Nature of the transition

As noted in the Introduction, in the orientationally disordered high-temperature fcc ($Fm3m$) phase, each C_{60} molecule undergoes uncorrelated random-walk rotational diffusion, but below T_c the molecules form an orientationally ordered sc ($Pa3$) phase. A neutron-diffraction study of the $Pa3$ phase revealed that the molecules are rotated in an anticlockwise manner around the $[111]$ direction by $\sim 98^\circ$ from the ideal $Fm3m$ configuration.⁴ It has been suggested that this seemingly arbitrary rotation results from an optimized ordering scheme in which there is nesting of the short (1.391-Å) electron-rich inter-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. The 98° rotations about $[111]$ ensure that all 12 nearest-neighbor interactions are optimized in this way.⁴

In a neutron-scattering study, Neumann *et al.*¹⁴ observed low-frequency librational modes (2–3 meV) at low temperatures. The librational energy softens by about 35% and the peak broadens by a factor of 6 between 20 and 250 K (just below T_c); concomitantly, the librational amplitude increases from $\sim 2^\circ$ to $\sim 7^\circ$. The authors suggest that the transition occurs when the amplitude of the libration exceeds a certain fraction of the relevant angle within a molecule (here, the angle of $\sim 23^\circ$ subtended by near-neighbor C atoms at the center of the C_{60} molecule). In this view, the transition is regarded as a rotational analog to displacive melting, which in the Lindemann picture occurs when atomic displacements exceed $\sim \frac{1}{5}$ of the interatomic distances.¹³ On “melting,” translational diffusion occurs in the case of liquids and rotational diffusion in the case of C_{60} .

Michel *et al.*¹⁰ have developed a microscopic theory to

describe the orientational dynamics and phase transition in C_{60} . The order-parameter variables for the transition are molecular rotator functions. In the language of soft modes, the transition to the ordered phase results from the condensation of a multipolar mode of T_{2g} symmetry at the boundary (X point) of the Brillouin zone.¹⁰ The first-order nature of the transition (discontinuous change in lattice parameter at T_c) is a clear indication of coupling between the orientational and elastic degrees of freedom in solid C_{60} . The coupling is between the square of the order parameter and the longitudinal lattice strain, and the theory accounts for the sign of the change in lattice parameter at T_c .

The increase of T_c with pressure can be qualitatively understood in terms of the above microscopic picture. By decreasing the intermolecular distances, pressure enhances the nesting condition, stiffens the orientational potential, and thereby lowers (raises) the librational amplitude (frequency). Consequently, a higher temperature is needed to disrupt the nesting, i.e., a higher T_c . This conclusion can be made quantitative by a high-pressure neutron-scattering study which should reveal the expected increase in librational frequency. In the theory of Michel *et al.*,¹⁰ the degree of orientational order is proportional to lattice strain. Specifically, negative strain (as is produced by pressure) increases the orientational order, and hence T_c .

Very recently, Lu, Li, and Martin⁹ developed a model in which the intermolecular interactions in C_{60} consist of dominant van der Waals-type interactions between C atoms on different molecules and a secondary short-range Coulomb interaction to account for a small amount of charge transfer between the electron-deficient single bonds and the electron-rich double bonds in C_{60} . The authors used the model to calculate the pressure dependence of T_c and find

$$dT_c/dP = 11.5 \pm 0.7 \text{ K/kbar},$$

which is in close agreement with our result using He as the pressure-transmitting medium and with a similar result by Kriza *et al.*,¹⁵ but is somewhat smaller than what we believe to be the intrinsic value of 16 K/kbar, as discussed above.

From the thermodynamic point of view, the pressure dependence of T_c of a first-order phase transition is given by the Clausius-Clapeyron equation

$$dT_c/dP = \Delta V/\Delta S = T_c \Delta V/Q,$$

where ΔV and ΔS are the discontinuous changes in unit cell volume and entropy, respectively, at the transition and Q is the latent heat associated with the transition. Both dT_c/dP and ΔV for the transition are accurately known, and thus we can calculate ΔS , or Q . David *et al.*'s high-resolution lattice parameter versus temperature data^{7(a)} allows us to calculate $\Delta V = 28.74 \text{ \AA}^3/\text{unit cell}$ on going from the sc to the fcc phase. This ΔV and our value of $dT_c/dP = 16 \text{ K/kbar}$ yield $Q = 7.0 \text{ kJ/mol}$ ($= 1.7 \text{ kcal/mol}$) and $\Delta S = 27.0 \text{ J/K mol}$ ($= 6.5 \text{ cal/K mol}$). Both Q and ΔS are relatively large, characteristic of order-disorder transitions. Heiney *et al.*^{7(b)}

also determined ΔV from detailed x-ray- and neutron-diffraction measurements. Their data yield $\Delta V = 26.35 \text{ \AA}^3/\text{unit cell}$. Use of this value would reduce our calculated Q and ΔS values by 4%. The experimentally reported entropy discontinuity at the transition ranges from the rough estimate of Heiney *et al.*¹ of 2.1 R (=4.2 cal/K mole) to Atake's¹⁶ 3.7 R (=7.3 cal/K mole) determined from accurate specific-heat data. Our calculated value is in good agreement with Atake's results.

C. The two-peak structure

The DTA spectra of both samples A and B exhibited a two-peak structure in the region of the $sc \rightleftharpoons fcc$ phase transition; however, there were remarkable differences between the two samples. In sample A, a slight asymmetry on the low-temperature side of the main DTA peak was observed at 1 bar and evolved into an increasingly well-pronounced shoulder with increasing pressure. In sample B, a well-pronounced shoulder was observed even at 1 bar, but on the high-temperature side of the main peak (Fig. 2). This two-peak structure was not seen in either the original 1-bar differential calorimetry scan by Heiney *et al.*¹ or the high-pressure data of Kriza *et al.*,¹⁵ both carried out on samples grown from solvents, or in Li *et al.*'s specific-heat measurements on vapor-grown C_{60} crystals.^{17(a)} However, two peaks were observed in Atake *et al.*'s high-resolution specific-heat data.¹⁶ Splitting our DTA spectrum into its constituent two peaks shows that the two peaks are $\sim 5 \text{ K}$ apart, as is true of Atake *et al.*'s specific-heat peaks and recent crystallographic evidence.^{17(b)}

The origin of the two-peak structure is not known at present, but 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 findings concerning the influence of ambient species on the transition discussed in Sec. IV A above leads us to propose the following 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, as well as other impurities, 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 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 $\sim 5 \text{ K}$ apart in energy. Thus, for our two samples, hindered rotations are dominant in sample A, while unhindered rotations dominate the motion in sample B. This behavior is consistent with the fact that virgin sample B was vacuum annealed at higher temperature (500 versus 400 K) and longer (8 versus 4 h) than virgin sample A. The increase in the intensity of the low-temperature shoulder (or peak) with He pressure in the case of sample A reflects the increase in the population of

unhindered rotations as He substitutes for larger interstitial species which hinder C_{60} rotations. In further support of this view, we note that within experimental error, the major DTA peak in sample B [spectrum (b) in Fig. 2] occurs at the same temperature as the shoulder in sample A, whereas the shoulder in sample B occurs at the same temperature as the major peak in sample A.

While the above arguments seem plausible and consistent with other observations, more needs to be done to understand this interesting two-peak structure. Experiments on both highly pure and especially intercalated solid C_{60} could provide more definitive answers.

D. Reaction with pentane at high pressures

As noted in Sec. III (see Fig. 1), a partially irreversible "transformation" of solid C_{60} occurs at $\geq 14 \text{ kbar}$ and $\sim 475 \text{ K}$ in the presence of a 50/50 (by volume) mixture of normal and isopentanes as the pressure-transmitting medium. We have initiated a study of the "new phase" recovered at 1 bar and 295 K. Our initial observations are based on x-ray-diffraction measurements and are as follows.

The recovered material shows broadened x-ray-diffraction lines. Though the pattern is somewhat limited, it contains lines different from the pure C_{60} pattern (or that expected for a hexagonal-close-packed arrangement of pure C_{60}). We compared this pattern with that obtained on material grown at 1 bar from the same 50/50 isopentane-*n*-pentane mixture used in the pressure experiments. The general features of the x-ray powder diffraction patterns are similar, but differ in detail. Our larger single crystals grown from the solvent mixture were shown not to be stable, changing over a period of several months; therefore, only qualitative comparisons could be made. We found that after three months at ambient conditions, these single crystals yielded patterns similar to those obtained in an earlier study in which C_{60} was crystallized from CS_2 .¹⁸ With long exposure to x-ray radiation, these $C_{60}CS_2$ crystals undergo an orthorhombic to a tetragonal-like lattice transformation with broadened peaks. We believe that solvent removal is enhanced by the irradiation. Our observations indicate that the pentane-mixture-grown crystals are less stable at ambient conditions than those grown from CS_2 .

It should be noted, however, that we have confirmed long-term stability of crystals containing other solvent species. In a complementary study on single crystals similar to that of Fleming *et al.*,¹⁹ we have determined the packing arrangement of C_{60} and toluene in the lattice. Pentane molecules could easily be placed in the same cavity of this lattice in place of the toluene. What would be required is that the pentane's five carbons would have to occupy a somewhat more disordered, slightly elongated position, with pentane's easily bent structure essentially fitting upon the seven carbon positions of the flat and rigid toluene molecule. This may account for the similarity in the diffraction pattern of our freshly prepared pentane-grown materials and that obtained from the single crystal of the toluene study.²⁰ Unfortunately, a detailed comparison may not be possible.

The similarity of the diffraction patterns leads us to believe that above 14 kbar and 475 K, the C_{60} structure reorganizes to form the solvent-containing complex. This material appears to be recoverable in large part at ambient conditions, but is of sufficient structural complexity to prevent a detailed analysis in the powder form. Single crystals, specifically grown for comparison proved not to be stable for conventional single-crystal diffraction studies.

V. CONCLUDING REMARKS

In this work we investigated the effects of hydrostatic pressure on the order-disorder transition in solid C_{60} . The different observed responses in different pressure media and for differently prepared samples as well as some irreversible pressure cycling effects have provided much insight into the orientational ordering process. Additionally, the pressure results along with the known compressibility of solid C_{60} are crucial for testing proposed models and orientational potentials. The highlights of the work can be summarized as follows.

(1) Lattice compression hinders the rotational-orientational motion of the C_{60} molecules in the solid, thereby increasing T_c and stabilizing the ordered sc phase. The intrinsic effect is large with $dT_c/dP = 16$ K/kbar. 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 the electron-rich interpentagon bonds against the electron-poor pentagon faces of neighboring molecules and stiffening of the orientational potential, which results in the lowering (raising) of the librational amplitude (frequency) of the molecules in the sc phase.

(2) Given that the transition is first order, we have used our accurate value of dT_c/dP and the accurately known value of the discontinuous volume change at the transition to calculate the latent heat (Q) and discontinuous entropy change (ΔS) associated with the transition. The results are $Q = 1.7$ kcal/mol and $\Delta S = 6.5$ cal/K mol, which agree with, but are probably more accurate than, values deduced from specific-heat measurements.

(3) T_c and its pressure dependence are influenced by the presence of interstitial species in the lattice. Specifically, helium appears to easily permeate the lattice, and the present results along with complementary pressure-loading experiments at our laboratories indicate that O_2 and N_2 diffuse into the octahedral interstitial sites.

(4) The two-peak structure in the DTA spectrum observed in the present work and in reported specific-heat data is most likely related to the partial occupancy of the octahedral sites by impurities. This occupancy can be expected to lead to the presence of both hindered and unhindered librational states with different transition temperatures.

(5) Solid C_{60} "reacts" with pentane at pressures ≥ 14 kbar and temperatures ≥ 475 K to yield a C_{60} -pentane complex which is partially reversible upon release of pressure. Preliminary x-ray-diffraction results suggest that the recovered material is related to that obtained by cocrystallizing C_{60} with pentane at 1 bar.

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rameters $a = 10.34$, $b = 31.53$, and $c = 10.18$ Å. The C₆₀ are centered at 0, 0.1396, $\frac{1}{4}$ on fourfold *mm* sites, while toluene resides in similar symmetry sites disordered so as to lie in both *ab* and *bc* planes.