Methane-intercalated C_{60}: Preparation, orientational ordering, and structure

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The orientational ordering temperature for methane-intercalated C_{60} is greatly depressed from ~ 260 K in pure C_{60} to ~ 241 and ~ 235 K in the stable compounds C_{60}-CH_4 and C_{60}-CD_4, respectively. ^{13}C NMR shows that the C_{60} molecules have ordered near 200 K while ^2H NMR shows that the CD_4 continues to be completely unoriented and freely rotating. The Rietveld refinement of the structures of C_{60}-CD_4 at 15, 200, and 296 K using time-of-flight neutron powder data as well as least-squares refinement of Mo-K_α x-ray data on C_{60}-CH_4 single crystals are consistent with such rotational disorder. [S0163-1829(97)01145-4]

Early studies of the effect of hydrostatic pressure on the $Fm3m$ (fcc)-$Pa3$ (sc) orientational ordering temperature, T_o, of C_{60} yielded unexpected differences in the pressure dependence of this transition with different pressure media.[1] The observed pressure derivative for this transition was $\sim 30\%$ greater with pentane or nitrogen than with He. This was interpreted as due to penetration of He into the lattice of C_{60}, resulting in less compression than with a nonpenetrating pressure medium. This led to the room temperature (RT) (and below) intercalation of the rare gases into interstices of C_{60}, studied primarily by neutron diffraction.[2–4] He intercalates easily while Ar does not; for Ne, intercalation kinetics may be monitored using lattice parameter vs time following sudden changes in Ne pressure. The fcc-sc transition occurs at a pressure that is highest for He, followed by Ne and smallest for Ar (latter value in agreement with nonpenetrating media values[1,5]). Such RT transitions always occur at the same lattice parameter equal to 14.125 Å (average of the fcc and sc values at the transition).

An unexploited observation of the earlier work by Samara *et al.*[1] consisted of the recoverable pentane C_{60} compound formed near 500 °C at 10 kbar, suggesting the possibility for other compound formation. Recently, Gadd *et al.*[6] employed 400 °C and 1.7 kbar Ar to form the RT stable, stoichiometric fullerene–rare-gas compound, C_{60}-Ar. This paper primarily reports on the formation of similar RT stable, stoichiometric fullerene-gas compounds, C_{60}-CH_4 and C_{60}-CD_4, as well as an attempt to form C_{60}-Xe.

Commercial C_{60} (99.6% nominal purity) was subjected to slow progressive heating in vacuum up to 500 °C for several days in order to remove all solvents and occluded N_2 and O_2. Some material was vacuum sublimed with identical results. Both powder samples and a few single crystals were intercalated and examined. The powdered samples (~ 1.5 g maximum/run) were enclosed in a cylindrical gold foil envelop and loaded into a high-pressure gas cell, previously described in our superconductor-oxygenation studies, and charged by cryopumping so as to completely fill the pressure cell with either CH_4 (Matheson purity grade) or CD_4 (Cambridge Isotope Laboratory, 99% D). Several runs used Xe instead of methane. The cell is sealed off and transferred to a

heated tube furnace (400 C; up to 70 h). The cell was quenched in running cold water. The pressure at temperature in the cell is estimated to be between 1–2 kbar. Weight gains were determined on each of the powdered sample runs and these correspond to a mole ratio of intercalant to C_{60} equal to 0.91(8) and 0.87(8), a value which is of the order of that required for the 1:1 stoichiometric compounds, C_{60}-CH_4 and C_{60}-CD_4, respectively. A C_{60}-CH_4 sample monitored for over several months showed no weight loss, consistent with no out diffusion over that time frame.

Our differential scanning calorimetric (DSC) measurements used a sample ramp of 5 K/min from 190 to 305 K. The thermogravimetric analysis (TGA) samples were heated at ramps of 2 or 5 K/min with an argon purge gas, showing an evolution of the intercalated methane beginning near 346(3) K and continuing to near 700 K. Sample weight losses were consistent with mole ratio of intercalants of 0.84(9), also indicating intercalation to near a 1:1 stoichiometry. Since the samples are stable and show no weight loss at room temperature, various isothermal runs at elevated temperature were performed. Such samples were ramped (at >10 K/min) to temperature and weight loss followed as a function of time.

The ^2H and ^{13}C NMR experiments employed a Bruker AMX-400 spectrometer with a 4 mm magic angle spinning probe. The relaxation times for both nuclei were determined as a function of temperature using a saturation recovery pulse sequence. Delay times ranged from 1 to 60 s for ^2H and from 0.1 s to 100 s for ^{13}C nucleus. In addition, the signal intensity of the ^{13}C was recorded as a function of temperature using a delay time of 10 s. Eight scans for each delay time were accumulated for ^2H experiments and 1 scan for each delay time was accumulated for the ^{13}C experiments.

The single crystals employed were grown by vapor transport.[7] These were treated in a similar manner to the powders, subjected to either cryopumped CH_4 or Xe and then heated (400 °C; ~ 100 h). These crystals were too small to be measured for weight gain and were examined by the usual single-crystal techniques. Extensive intensity data sets (just over 5000 different hkl's) were measured to 50° 2Θ
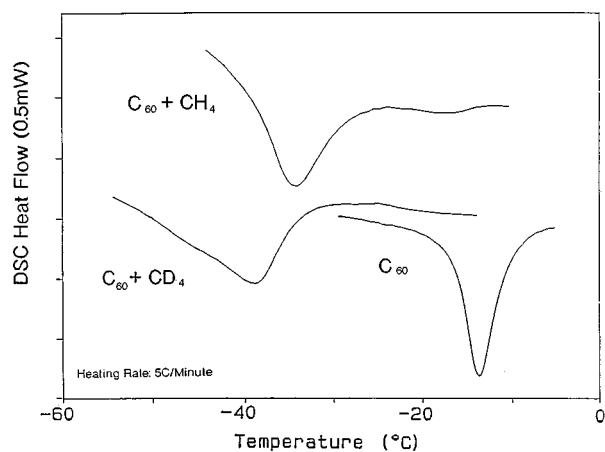
FIG. 1. DSC heat flow as a function of temperature of pure C_{60}, C_{60}-CH_4, and C_{60}-CD_4, showing the depression upon intercalation of T_o.

FIG. 2. Weight of a sample of C_{60}-CH_4 ramped to and held at 473 K as a function of time.

(Mo-K_α) on each of the C_{60} crystals intercalated with CH_4 or Xe. For each set, the symmetry equivalent reflection were averaged, yielding near 165 unique values, and these data were used for the usual least-square refinement of several structural models discussed below.

Comparison of the RT x-ray diffraction patterns on powders of pure and methane intercalated C_{60} show only very small differences, primarily the appearance just above background of the 002 peak not observed in pure C_{60}. The lattice parameter increases slightly from 14.153(3) to 14.179(3) Å. Neutron powder-diffraction data for the ~ 3 g C_{60}-CD_4 sample were collected at the intense pulsed neutron source (IPNS) at 15, 200, and 296 K for 6.7, 2.8, and 4.9 h, respectively (beam current ~ 14 μamp).

For the least-squares refinement of the structure models using the neutron data, the time-of-flight Rietveld code[8] available at IPNS was used. We previously modified this code to include the use of molecular spherical shell scattering form factors for the rotating molecules as well as for a contribution to the background derived from the expected large diffuse scattering arising from C_{60} disorder.[3] For the single-crystal x-ray data, we modified the appropriate parts of the crystallographic computer codes in the XTAL system[9] so that spherical form factors could be used.

The thermograms show that T_o is depressed upon intercalation from 260 K for pure C_{60}.[5] For the CH_4 intercalated powders, this ordering temperature is near 241 K; however, usually a two peak structure is obtained with a small peak just below the position for pure C_{60}, suggesting that the samples are not completely intercalated. The ratio of the two peak structure correlates with the location of the sample position along the gold envelope (indicating a possible temperature gradient within the pressure cell); however, various runs never yielded as clean of a single peak as that obtained for the CD_4 samples. This suggests that in the case of CD_4, a more complete intercalation must have occurred. The latter shows T_o near 235 K, a bit lower than our CH_4 samples. Figure 1 shows examples of our DSC curves. Our different pure C_{60} preparation runs showed an ordering temperature of 259.5(4) K while the CH_4 and CD_4 intercalated materials
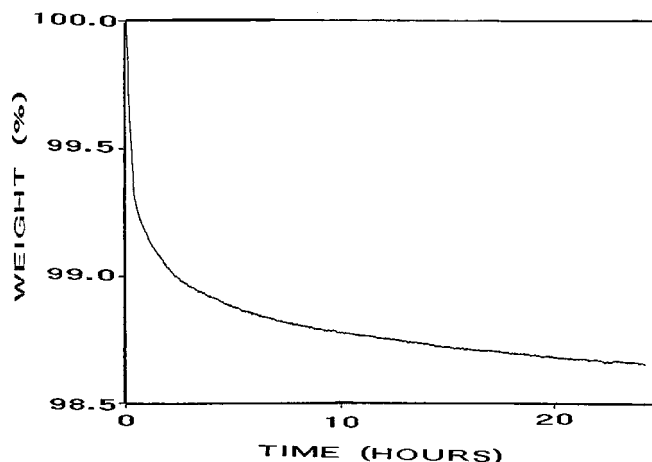
showed 241.9(17) K, with the larger spread due to possibly some contribution from the two peak structure, and 234.8(5) K, respectively.

Figure 2 shows a sample held at 473 K for 24 h; the gas release behavior is similar to that of some of the other much smaller intercalates studied, though such studies were usually at room or lower temperatures.[10] The limited data were insufficient to allow the determination of an activation energy for the process as our complementary studies on other gases.[11]

The RT structure models in space group $Fm3m$ consisted of a spherically disordered C_{60} with the octahedral sites occupied by either a spherically disordered CD_4 molecule, or positionally disordered CD_4 (D fixed in 8-fold positions along the four 3-fold axes 1.118 Å from the C) or, in the case of the Xe intercalated C_{60} crystal, a Xe atom. At low temperatures in space group $Pa3$, the previously determined coordinate values on our pure C_{60} sample were employed for the positions of the ten carbon atoms necessary to define the C_{60} molecule together with either spherically or positionally disordered CD_4 molecules. In all cases, the intercalant was assigned a fractional site occupancy (or population) parameter, f. (The tetrahedral site was also examined and found not to have any scattering density associated with it.) In the case of our Rietveld refinement of the powder neutron data, d spacings to 1.0 Å^{-1} were included. On these data collected at 15, 200, and 296 K, the corresponding lattice parameters were 14.0585(1), 14.1105(11), and 14.1762(1) Å, respectively.

Just as in our neutron-diffraction study[3] on Ne intercalated C_{60}, f for the intercalant is highly correlated with respect to its thermal (displacement) factor, U. Various refinements were attempted with similar results with the models and on the materials studied, including the choice of independently refining C coordinates for the C_{60} in $Pa3$ or using the coordinates previously determined on a pure C_{60} sample. These refinements also showed that if the intercalant thermal parameters were constrained to be equal to that for the single value used for the C_{60} (or to the single value for the corresponding C atoms for the $Pa3$ structure) a lower value for the intercalant f than possibly exists is obtained. For the present comparisons, we have constrained the intercalant f

value to 0.80, the lowest value consistent with the weight gains and TGA results above.

For the Rietveld refinements, the 296 K neutron data yielded 0.0017(3) and 0.224(11) Å^2 for the U values of the C_{60} and CD_4, respectively, for the spherically disordered CD_4 model, with a significantly better fit ($\chi_R = R_p/R_{exp} = 1.443$) than that obtained using the positionally disordered model ($\chi_R = 1.472$). Our 200 K data were taken over a shorter run time that should result in more statistical error. For the spherically disordered model, $U = 0.0120(8)$ and 0.125(28) Å^2 for the C_{60} and CD_4, respectively ($\chi_R = 1.838$); for the positionally disordered models, $U = 0.0102(8)$ and 0.135(25) Å^2 for the C_{60} and CD_4, respectively ($\chi_R = 1.840$). Both of these models gave essentially the same fit and no choice in the models can be made on a statistical basis.[12] For the 15 K data, U for the C_{60} was set to 0.0001 Å^2 so that it remained positive for all refinements. These data gave a CD_4 U value of 0.145(12) Å^2 for the spherically disordered model ($\chi_R = 2.198$). For the positionally disordered model, if the U values for the C and the D are constrained equal to each other, $U = 0.127(9)$ Å^2 ($\chi_R = 2.189$); if these two are not constrained, U values of 0.112(10) Å^2 for the C atom and 0.255(29) Å^2 for the D are obtained ($\chi_R = 2.181$). Though the latter choice can almost be made on a statistical basis,[12] it is the more plausible model since those values are consistent with the CD_4 oscillating about its center.

These U values for the CD_4 are large since the intercalant is not ordered at 296 or 200 K (see NMR below). The octahedral site together with the channels leading to the tetrahedral sites, along which the D are located, are sufficiently large in size to allow small displacements in positions, which lead to the apparent large U values in the refinements of the diffraction data. In addition, the harmonic approximation for thermal vibrations employed in the diffraction model may not be completely appropriate for the displacements actually occurring.

In our RT single-crystal x-ray study, we have no other basis for establishing the stoichiometric ratio of $CH_4:C_{60}$ than the diffraction data itself. Various models were attempted and we report here the refinements in which the intercalant and host U values were constrained equal to each other. This as mentioned above leads to a lower f value than possibly exists.[13] The CH_4 intercalated C_{60} data gave essentially the same value, $f = 0.24(3)$, with $U = 0.027(1)$ Å^2 for all the models tested with essentially statistically indistinguishable fits ($R_w \sim 0.051$), based on R ratio testing.[12] This probably results from the low scattering factor of the H relative to C in the x-ray studies compared with the corresponding D and C neutron cross-section values in the powder studies. The lower value for f probably results from the incomplete intercalation due to the several orders of magnitude size differences of the crystals compared with the average powder crystallites even though a longer time at temperature was used. Since no other basis is available to constrain f to a value, it is impossible to evaluate U values for the C_{60} and CH_4 independently. For the corresponding Xe intercalated single-crystal data, essentially no Xe appears present, with $f = 0.011(8)$, a value less than 2 esd's (or estimated standard deviations).

The ^{2}H spin-lattice relaxation time, T_1, of CD_4 in the C_{60} lattice were measured as a function of temperature between 213–300 K. The T_1 shows little change as a function of temperature and does not appear to undergo a transition. The relationship between T_1, 17.9(1.8) s, and the molecular reorientation time τ_θ is given by[14]

$$1/T_1 = \tfrac{3}{8}(e^2qQ/\hbar)^2\tau_\theta, \qquad (1)$$

where $(e^2qQ/\hbar)$ is 2π times the quadrupole coupling constant in Hz. Assuming a quadrupole coupling constant of 180 kHz,[15] this relationship predicts that τ_θ is only 0.12 ps. This value is 80 times shorter than the τ_θ measured for the C_{60} molecule at RT.[16,17] These results show that the CD_4 is rotating freely down to 213 K.

Equation (1) assumes that the CD_4 molecule reorients by small step Brownian diffusional motion. Bopp[18] has defined a parameter, χ, which tests this assumption:

$$\chi = (\tfrac{5}{18}D_r)(kT/I)^{1/2}, \qquad (2)$$

where D_r is the rotational diffusion coefficient equal to $\tfrac{1}{6}\tau_\theta$ and I is the moment of inertia of the molecule. If $\chi \gg 1$ then the molecule reorients by small steps whereas if $\chi \sim 1$ then large-angle inertial reorientation occurs. At RT χ equals 1.2 that indicates that large-angle inertial effects dominate the rotational motion of the CD_4 molecule. This contrasts with the rotational motion of pure C_{60} that has a value for χ of 3.4 that indicates moderate rotational step sizes.

The C T_1 of the C_{60} molecule could be described by a single exponent at temperatures of 243 K and above and at temperatures of 208 K and below. Between these temperatures, however, the saturation recovery curve of the magnetization was biexponential. Biexponential behavior has been seen previously between the temperatures of 240 K and 260 K for pure C_{60} by Tycko.[16] He attributes this behavior to the transition from an ordered to a disordered phase. The biexponential behavior of the C_{60} with intercalated CD_4 has shifted to lower temperatures and occurs over an extended temperature range. Both of these features are consistent with the DSC results that indicate that the ordering transition has broadened and shifted to lower temperatures.

The C T_1 is 35 s at 243 K, immediately above the order/disorder transition. This value is very close to that predicted by the extrapolation shown by Tycko[16] for measurements on pure C_{60} at the same field strength. Thus the CD_4 molecule has not caused a substantial change in the dynamics of the C_{60} molecule, although it has reduced the transition temperature. Our 10 s delay time was chosen because it is several times longer than T_1 of the ordered C_{60} phase (3.4 s) while it is only a fraction of the T_1 of the disordered phase. Thus the magnetization of the ordered phase will be 95% recovered while the magnetization of the disordered phase will be only 25% recovered. The measured value of the magnetization between these two values indicates the extent to which the sample has undergone the ordering transition. These results are shown in Fig. 3. The position and breadth of the transition approximates that measured by DSC for C_{60}-CD_4.

From the NMR data, the reorientational correlation times of the CD_4 and C_{60} molecules in a sample of CD_4 intercalated in C_{60} differ by nearly two orders of magnitude. While the CD_4 molecule undergoes large reorientation steps, the
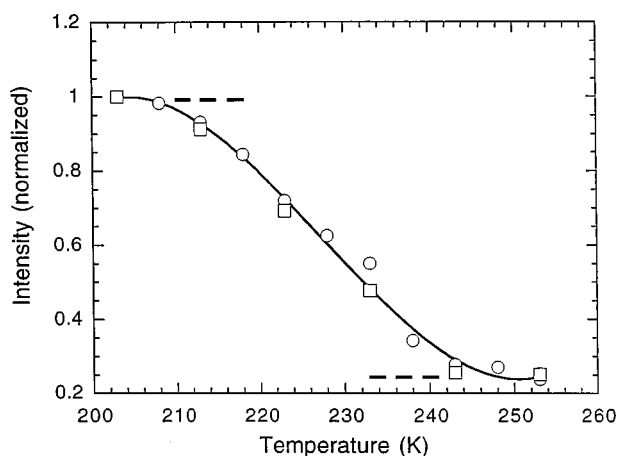
FIG. 3. The relative intensity of the ^{13}C signal as a function of temperature for C_{60}-CD_4. A pulse saturation sequence followed by a delay time of 10 s was applied before signal acquisition. Circles/squares were data taken with increasing/decreasing temperature.

C_{60} molecule undergoes small step diffusional motion. The motion of the CD_4 molecule remains relatively unrestricted down to 213 K while the C_{60} molecule undergoes the order/disorder transition between 208 and 243 K. Both the magnitudes of the correlation times and the difference in the temperature behavior of the two components prove that the rotational motions of CD_4 and C_{60} are not strongly coupled to each other.

In the present refinements of the diffraction data, the high correlation of the thermal parameter and the site occupancy does not allow the direct determination of both parameters. Arbitrarily constraining the U values of the C_{60} and CD_4 to be identical leads to a lower limit for the occupancy of the intercalants than probably exists. This is an unrealistic choice

since at 296 and 200 K the motion of the CD_4 remains relatively unrestricted as determined by the ^{2}H NMR measurements. The refinement of the 200 K neutron data are consistent with such unrestricted motion for the CD_4. At 15 K, the neutron data give a better fit with a positionally disordered CD_4; the latter, however, is undergoing oscillations which result in the large U values. The real potential or confinement normal to the C-D bond is of trigonal symmetry so that the harmonic approximation for thermal vibrations employed in the diffraction model may not be completely appropriate. Samples were remeasured following our neutron-diffraction study and gave essentially identical results as first measured, a single peaked DSC and sample weight loss near 2%, and such values were included in averages reported above. Thus the large CD_4 U values are not the result of any out diffusion of CD_4.

The lattice parameters of solid CH_4 (6.221 Å) and Xe (6.2023 Å) near 75 K may be used to suggest that the two intercalants should behave in a similar manner.[19] It is noted that at lower temperatures solid CH_4 undergoes a phase transition so that its relative volume becomes less than that for Xe. The molar volumes suggest that the two should act similarly at higher temperatures, so that the fact that CH_4 intercalates while Xe does not must result from the nonspherical nature of the CH_4 molecule. The dynamics of the C_{60} and the interactions both with itself and the intercalant must also play an important role in determining T_o as previously shown with N_2 and O_2.[10]

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