Sorption of Helium by Fullerite Crystals and Films

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We report sorption isotherms and optical measurements for fullerite C_{60}/C_{70} crystals and C_{60} films exposed to helium. The low temperature isotherms show excess sorption above that expected for surface films. We interpret this as intercalation of helium in the fullerite lattice. Our observations suggest that helium is mobile within the crystal, and opens up the possibility of realizing a new type of three-dimensional quantum fluid. Raman measurements are inconclusive on the issue of intercalation.

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The discovery of a new stable state of molecular carbon in the form of closed structures called fullerenes [1] has generated increased activities along many different directions. Of particular interest among the fullerenes is the very stable form C_{60}. This consists of sixty carbon atoms arranged in a truncated icosahedron configuration. The ability to produce and separate large quantities of this molecule [2] has led to the study of its crystalline form, and a number of discoveries for doped crystals such as conductivity [3], superconductivity [4], and ferromagnetism [5]. We report in this Letter studies to determine the possibility of using fullerene crystals, fullerite, as an intercalation medium for helium atoms. The motivation for this work is the possibility that if helium does intercalate and retain its mobility at low temperatures, then one would realize a new type of quantum system. In a similar way to helium adsorbed on surfaces, most notably graphite, one would have a three-dimensional analog whereby the density of helium could be varied over a wide range. It might be possible then to span the full range from dilute gas to degenerate fluid.

The C_{60} lattice presents a fairly open structure. It is face centered cubic at room temperature and orders orientationally into simple cubic at 249 K [6-8]. This transition should not affect the intercalation process. The lattice constant is about 14 Å with the C_{60} nearest distance of 9.9 Å. The C_{60} radius is about 3.5 Å. If one takes the "size" of ^{4}He as the average interatomic distance in the liquid, ~3.6 Å, the C_{60} lattice is open just enough to allow intercalation without lattice deformation. Whether this will occur for ^{4}He or ^{3}He, given a realistic He-C_{60} interaction, remains to be established.

We report in this Letter measurements of sorption isotherms and Raman studies from fullerite with and without exposure to helium. Data were obtained between 300 and 1.5 K. For the sorption measurements we used a commercial sample with composition of about 80% C_{60} and 20% C_{70} [9]. The crystals in this powder have a distribution of sizes but are typically greater than a few μm. For the sorption we loosely packed 0.479 g of sample in a copper cell. Raman spectra were obtained for the powder sample and films of pure C_{60} on a quartz substrate.

In Fig. 1 we show sorption data for ^{4}He. Six isotherms are plotted here as a function of the ratio of the pressure to the respective saturated pressure. Lines are drawn through these data joining point to point. We have taken three series of measurements in different cryostats in which we gradually improved the temperature stability. It was necessary to obtain data as close as possible to saturation, where temperature stability is important, to verify the trends which we observed. For the data shown in Fig. 1 the temperature was stable to within 20 μK over the period of a complete run. The behavior of the data in Fig. 1 is unusual. Most striking is the fact that at the highest temperature, above a reduced pressure of about 0.3, one obtains a *larger sorption* than one has at lower temperatures. This is counter to what one would expect for surface sorption. What appears as a near collapse of these data at low pressures is shown in greater detail in the inset. In this region, below $P_r \approx 0.18$, the higher the temperature the *smaller the sorption.* This is consistent with surface sorption. One can also see from the inset that the data begin to cross over at different values of P_r

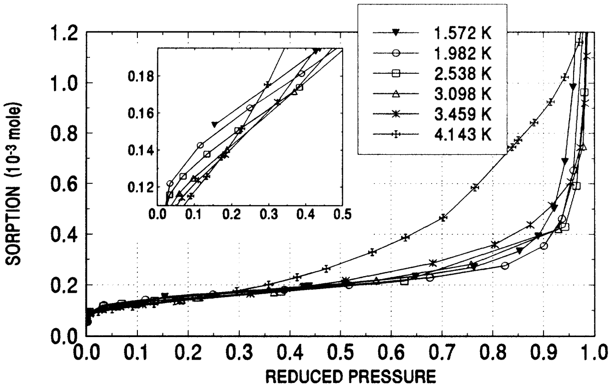

FIG. 1. Sorption isotherms for ^{4}He by C_{60}/C_{70} crystals, as a function of the ratio of the pressure to the saturated vapor pressure at the given temperature. Note the excess sorption at higher versus lower temperatures. The inset shows that at low partial pressure the ordering of the isotherms with temperature is consistent with surface sorption. Random errors in these data are less than the size of the symbols.

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depending on the temperature.

From nitrogen adsorption measurements at 77 K, which show no excess sorption and can be analyzed using the Brunauer-Emmett and Taylor equation [10], we obtain a surface area for our sample of 4.2 m^2. We use this to compare our data with adsorption of helium on other substrates. At 4.2 K, and P_r near 0.02, adsorption ranges from about 30 to about 12 μmole/m^2, the largest being associated with strong binding substrates such as graphite [11], and the lowest with noble-gas preplated substrates [12]. For the fullerite we obtain at 4.2 K about 22 μmole/m^2. This, in addition to the correct trend with temperature in this region, suggests that the low pressure data are quite "normal." We thus interpret Fig. 1 as follows. At low partial pressures the dominant behavior is the formation of a surface layer on the fullerite crystals. After this, helium shows appreciable intercalation in the lattice. This latter, unlike surface sorption, is done more efficiently at higher temperature and pressure, and results in the inversion of the ordering of the isotherms. This interpretation can be put on firmer grounds by comparing these data with those on other substrates, and considering sorption as a function of chemical potential rather than pressure.

If one is dealing with surface sorption, and if the helium film builds up uniformly with pressure, then different isotherms for the same substrate should collapse on a universal curve when plotted as a function of the difference in chemical potential, $\Delta\mu$, between unsaturated and saturated conditions. $\Delta\mu$ can be calculated most easily from the properties of the gas by using

$$\frac{\Delta\mu}{R} = -T\ln\left[\frac{\rho_0}{\rho}\right] + 2\frac{BP_0}{R}\left[\frac{P}{P_0}-1\right], \qquad (1)$$

where R is the gas constant and $B = (23.05 - 421.17/T)$ cm^3 mole^{-1} is the second virial coefficient [13]. For the densities ρ, ρ_0 we use the virial equation of state. We show this analysis in Fig. 2 with existing data for adsorption of helium on jewelers' rouge [14] along with the data for fullerite. The data for rouge, scaled to 4.2 m^2, can be seen to collapse quite well. The exception is the 4.21 K data. These could be made to collapse in a further refinement whereby the smaller density of the liquid at this temperature is taken into account. All of the rouge data are shifted 0.08 m mole to avoid overlap.

The fullerite data behave differently. They join a universal curve at large negative values of $\Delta\mu$, but show excess sorption as $\Delta\mu$ goes toward zero, i.e., saturation (see inset). This trend is more obvious and systematic than in Fig. 1 where the data are plotted as a function of the reduced pressure. Equation (1) should apply to a situation where a film builds uniformly on a substrate. It fails if anywhere along the isotherm the surface is modified, as by compression or registry of the adsorbed layers, or *if new sorption sites become more readily accessible as a function of pressure and temperature.* This we believe is the interpretation of the region where the data move away from the universal curve. The excess sorption for the 4.143 K isotherm is many times what would be expected on the basis of a surface film. It cannot be explained by compression of the underlying layers or capillary condensation. For capillary condensation in particular, we note that the surface tension of ^{4}He decreases as the temperature increases, from 0.33 to 0.1 erg/cm in the region of data shown in Fig. 1. Thus, if capillarity were a problem, it would enhance the low temperature isotherm rather than the high. It would be the opposite of what we observe.

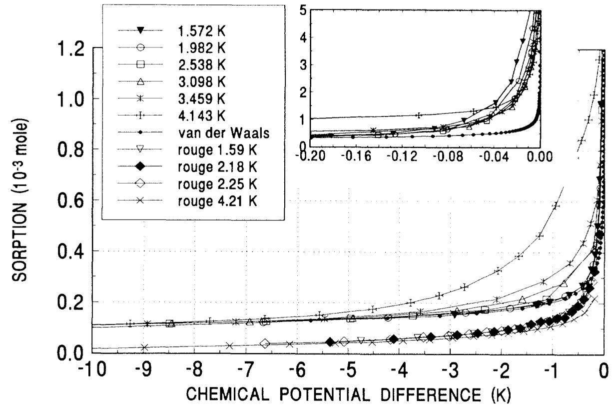

FIG. 2. Same data as in Fig. 1, plotted as a function of the chemical potential difference from saturation, $\Delta\mu$, calculated with Eq. (1). Note the systematic excess sorption in these data as the temperature increases. Also data for adsorption on jewelers' rouge. The latter, contrary to the C_{60}/C_{70} data, collapse on a universal curve. The dots are a calculation of $\Delta\mu$ using Eq. (2). The inset shows that near saturation the C_{60}/C_{70} data again merge.

To support our interpretation of the data, we can also calculate the value of $\Delta\mu$ using the properties of the liquid under the assumption that it does form a uniform film. We use the following semiempirical expression which includes retardation effects [15]:

$$\Delta\mu = -\frac{\alpha}{z^3}\left[1+1.64\left(\frac{z}{d_{1/2}}\right)^{1.4}\right]^{-1/1.4}. \qquad (2)$$

This is expected to work for a planar surface where z is the thickness of the film and $d_{1/2}, \alpha$ are constants appropriate for the helium-substrate interaction. We have used, respectively, 180 Å and 1900 K Å^3, values which apply to graphite [15]. Equation (2) is found to successfully describe helium adsorption on films up to hundreds of Å thick [15]. This equation is plotted in Fig. 2 as the solid black dots, labeled van der Waals. There are *no parameters* in this calculation since the film thickness is fixed, given the amount adsorbed, the area of the substrate, and the density of liquid ^{4}He which is taken as constant in this calculation. One can see from Fig. 2 that Eq. (2) describes the data over a limited range and does better for low temperatures than for high. It eventually fails for all temperatures near saturation as can be seen in the inset. By contrast, an equivalent expression can be written for rouge to describe the data over the full range shown in this figure. The inset in Fig. 2 shows also that for small $\Delta\mu$ the various isotherms again collapse. They do so within ± 0.001 K near 99.5% saturation.

In Fig. 3 we show a series of isotherms for ^{3}He. An even more striking and systematic behavior than ^{4}He is observed. At large negative values of $\Delta\mu$ the isotherms collapse, but they systematically show excess sorption at higher temperatures as one moves toward saturation. The inset shows, as in Fig. 1, that the region of collapse corresponds to the normal temperature ordering at low P_r. This we associate predominantly with surface sorption. We note again, on the issue of capillarity, that the surface tension decreases as the temperature is increased. This would produce the opposite effect from what we observe. Taken together the ^{3}He and ^{4}He isotherms span a range of surface tension from 0.33 to 0.01 dyn/cm^2. We also note in Fig. 3 that the 3.265 K isotherm has been measured in two runs in sorption and one in desorption (although only one datum is shown in the range of data plotted in this figure). These data, as well as other obtained with ^{4}He, reproduce within our resolution and show no evidence of hysteresis. Thus, the movement of helium in the sorption sites does not seem to involve the tunneling through a potential barrier. This argues against micropores or cracks which are typically accessible through such a barrier [16]. The amount of helium sorbed exceeds one atom per fullerene molecule (there are $\sim 0.64\times 10^{-3}$ mole of fullerene in our sample). This also argues strongly against the possibility that this excess is due to microcracks in the crystals. The density of such cracks would have to be excessive. We find that a simple model can be used to describe the *start* of the excess sorption in the region where the isotherms begin to cross. We assume that the helium in the crystals is in a constant potential above the vacuum, and in equilibrium with a two-dimensional gas at the surface. This model yields isotherms which are linear in P_r with a slope dependent on the volume of the crystals, the surface area, and the potentials. We find that a reasonable value for the crystal potential is 4–10 K above the vacuum. This explains the start of the excess sorption at low P_r for various temperatures, but it is clearly too simple a model to describe the whole isotherm as P_r increases.

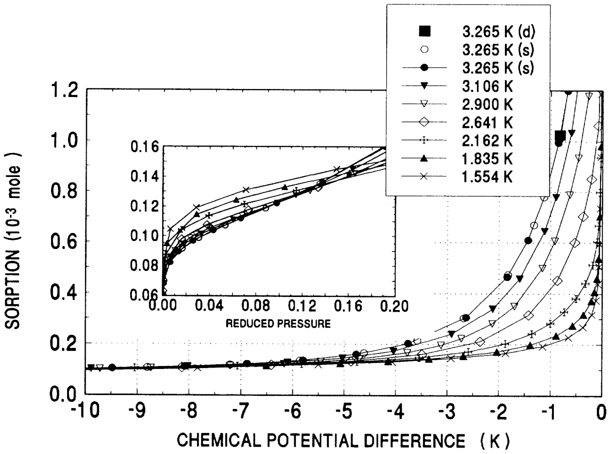

FIG. 3. Sorption of ^{3}He as a function of the chemical potential difference from saturation. These data collapse on a single curve in the region where at the same reduced pressure (see inset) the isotherms show the expected higher sorption at lower temperature. This order reverses rather dramatically at higher levels of sorption in the same way as for ^{4}He. Three runs are shown for 3.265 K, two for sorption (s) and one for desorption (d) (only one datum is visible in the range shown). No difference is seen among these data.

We have also tried to determine if helium intercalates in the C_{60} lattice at 300 and 77 K. For these measurements we have pressurized the sorption cell to about 1 atm and measured the relaxation of the pressure as a function of time. Or conversely, in a more sensitive measurement, we have determined the rate of evolution of gas after the crystals have been exposed to helium for a period of several days. This is shown as a function of time in Fig. 4. What is plotted here is the pressure increase in a fixed volume as the gas evolves from the crystals after the pressure of helium is removed. After an initial short transient, the pressure has a characteristic relaxation which settles to a rate of 0.003 torr/h. This is the background pressure rise in our gas handling system. From these measurements one can obtain the exponential approach to equilibrium. This is shown in Fig. 4 on the right-hand axis. The characteristic relaxation times are 15 and 10 h at 300 and 77 K, respectively, for ^{4}He, and 10 h at 300 K for ^{3}He. These times are too long to be attributed to a surface process. The diffusion of helium into the crystals at 300 K is not surprising. O_2 and H_2 have been shown to intercalate in fullerite for pressures in the range of 0.1 to 1 kbar [16]. Helium is also known to diffuse through glass and plastics with a diffusion constant $D\sim 10^{-11}$–10^{-14} cm^{2}sec^{-1}. From our data, tak-

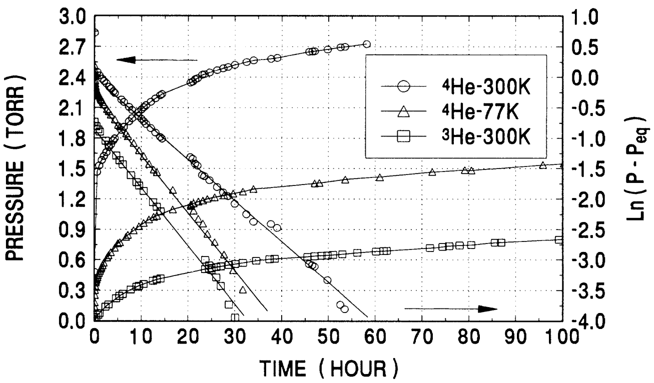

FIG. 4. Desorption of ^{4}He and ^{3}He at 77 and 300 K from C_{60}/C_{70} after exposure to about 1 atm of helium. On the left-hand side is plotted the pressure increase as the gas evolves in a constant volume. On the right-hand side the ln of the difference of the pressure from equilibrium as a function of time. See text.

ing about 3 μm as a typical crystal size, we obtain $D \sim 0.7\times 10^{-12}$ cm^{2}sec^{-1}. This is quite reasonable. What is unusual for the C_{60}, however, is that this value increases at 77 K where helium diffusion should become negligibly small. At lower temperatures yet, this diffusion takes place even more readily as evidenced from the isotherms. It seems reasonable to us that if the helium intercalates within the lattice without deformation, then the lower the temperature, where lattice vibrations are not as important, the easier this process should become.

In other experiments we studied the Raman spectra [17] of the fullerene to see if there was an effect associated with the intercalation of helium. It is known that upon doping the C_{60} crystal with potassium a substantial shift in the charge sensitive $A_g(2)$ mode takes place due to electron transfer [4,18]. We do not expect a charge transfer in the case of helium; however, there might be higher order effects. We have studied the Raman signal from pure C_{60} films deposited on quartz and from the powder sample we used in the isotherm studies. These data show no effect upon helium exposure. We have looked at other lines as well; however, the $A_g(2)$ line, which is the strongest, gives us the best resolution. We were forced, to avoid heating of our sample, to work at relatively low power densities, 0.1–0.4 W cm^{-2}. Heating was noted by monitoring the increase of pressure in the cell when the laser was turned on. Without this constraint other molecular modes would have been more appropriate to see an effect. We have also measured interband transmission in the near infrared through the film samples with and without exposure to helium. The incident power for this measurement is much less than in the case of the Raman method. This method, however, would not seem to have the sensitivity for seeing subtle effects associated with helium intercalation. The null results from the Raman spectra can have several explanations. The effect could be too small to be seen. This is actually supported by the isotherm measurements which indicate a very weak interaction of helium with the fullerene, i.e., helium is not bound to a molecule upon intercalation. This would be a very positive interpretation relative to the physics which we are trying to study, i.e., a dilute mobile quantum fluid. Another possibility, however, is that at the power levels we used, even though there was no observable heating of the cell, helium desorbs locally; thus the null result.

We note measurements by two other groups with C_{60} films *vis-à-vis* ^{4}He intercalation [19,20]. Both of these studies concluded that ^{4}He did not intercalate in the films. These experiments were done at lower temperatures than ours, and in one case, at pressures below saturation. It is quite possible that if there is lattice expansion upon intercalation, then intercalation in the film might not be favored. This might be prevented because of the constraint of the substrate.

In summary, we have reported measurements to explore the possibility of helium intercalation in the fullerite lattice. We conclude from the sorption isotherms by C_{60}/C_{70} crystals that this indeed takes place at low temperatures and in a reversible fashion. The character of this intercalated helium remains to be explored.

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