

Interaction between C_{60} and gases under pressure

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Received December 2, 2002

A brief review is given of the interaction between fullerite C_{60} and various gases under elevated pressure. Subjects discussed include the formation of ordered interstitial gas–fullerene compounds, reactions between intercalated gases and fullerene molecules to form new endohedral and exohedral compounds, and changes in the structure and properties of C_{60} because of intercalated gas atoms or molecules.

PACS: 61.48.+c, 62.50.+p, 81.05.Tp, 61.72.Ww

Introduction

Solid fullerites, such as C_{60} and C_{70} , have very interesting physical properties. However, in many cases the understanding of these properties has been hindered or delayed because interactions between the fullerene molecules and their environment have led to significant changes. Although the fullerene molecule is not very reactive, the intermolecular interactions are very weak and many simple properties change easily when the fullerite lattice is structurally deformed, or when small amounts of impurities are introduced.

A particular case in point is the study of fullerites under high pressure [1,2]. Pressure is a very useful parameter in the study of carbon-based materials. Although the graphite sheet structure has a higher interatomic binding energy than diamond, the weak interplane interaction in the three-dimensional graphite lattice implies that graphite is easily deformed by moderate pressures, and the equilibrium pressure between diamond and graphite at room temperature is only about 2 GPa [3]. Similarly, carbon nanotubes in bundles begin deforming radially at similar pressures, about 1.7 GPa [4,5]. Although fullerene molecules do not deform noticeably under these pressures, their orientation and rotation properties change radically with pressure in the range below 2 GPa [1], and many studies have been carried out to map these changes as functions of pressure p and temperature T .

Because C_{60} and other fullerenes are «weak», easily deformable solids, it is important to use a pressure transmitting medium which does not cause a large shear stress in the specimens studied. This is most eas-

ily done using fluid media. However, most fluids that are in the liquid state at room temperature have a rather limited pressure and temperature range before they either crystallize or vitrify into the solid state (at low T or high p), begin breaking down (pyrolyze), or react with the sample material, both usually at high T . In many cases, gases, such as the rare gases, are therefore considered the «ideal» pressure media. Unfortunately, gases often strongly change the properties of fullerites by intercalating into the large interstitials in the lattice.

In this paper I briefly review the interaction of gases with C_{60} , and the changes brought about in the properties of C_{60} when the material has interacted with the gas. The review is mainly motivated by my own need to understand the interactions between fullerites and pressure media, and will be colored by this background, but the subject is also an interesting field of study in itself. The subject has been included before as part of larger reviews [1,6], but since this was some time ago, new material will be presented here. First, a very short introduction is given to the structure of pure C_{60} . This is followed by a review of how solid C_{60} interacts with various kinds of gases by intercalation, chemical reactions, and the formation of endohedral compounds.

Background: the orientational structure of C_{60}

The structure of C_{60} has been very well discussed in the literature [7,8], and only a brief overview will be given here. At low pressures, C_{60} has three structurally different phases which, however, are all very similar.

The room-temperature structure can be described as face-centered cubic (fcc). Both the molecules and the interstitial spaces in the lattice are relatively large, compared to most inorganic atoms or molecules. For each C_{60} molecule in the lattice there are three interstitial sites: two small tetragonal sites with an effective radius of 1.1 Å and one large octahedral site with a radius of 2.1 Å. For comparison, the thresholds or channels between sites have an effective radius of 0.7 Å.

Above $T_0 = 260$ K, the C_{60} molecules carry out quasi-free rotation because of their highly symmetrical shape, and thus the structure can be approximated as a fcc lattice of spherical molecules with a space group $Fm\bar{3}m$. With decreasing T the correlation between the rotation of neighboring molecules increases, and near T_c large, co-rotating clusters are formed. On cooling through T_0 the molecular rotation stops and a simple cubic (sc) phase with space group $Pa\bar{3}$ and a temperature-dependent degree of orientational order is formed. In this phase the molecular rotation has stopped but the molecules can still jump between different molecular orientations. Finally, below the glassy crystal transition at $T_g \approx 90$ K, molecular motion is very slow and the remaining orientational disorder can be considered frozen; an orientational glass is formed. With increasing pressure both T_0 and T_g increase, as might be expected. The phase lines have slopes of $dT_0/dp = 160$ K·GPa $^{-1}$ and $dT_g/dp = 62$ K·GPa $^{-1}$, respectively [1], and on compression of C_{60} at room temperature the fcc–sc (or «rotational») transition occurs already near 0.2 GPa. In practice, almost all high pressure studies are thus carried out on sc (rotationally hindered) C_{60} .

In spite of its high symmetry the C_{60} molecule can be orientationally ordered because it must have 12 carbon atom pentagons, in addition to the «normal» hexagons, in order to have a closed surface. This gives an anisotropic surface charge distribution and thus an electrostatic driving force for orientation. The two possible orientational states will here be denoted descriptively as the P (pentagon) and H (hexagon) orientations, since they correspond to the orientation of a double bond on one molecule towards the center of a pentagon or a hexagon, respectively, on a neighboring molecule [7,8]. At atmospheric pressure the energy difference between these states is only about 12 meV, with the P orientation being lower in energy, but compression of the lattice shifts this energy difference so that at 150 K the two orientations have the same energy near 0.19 GPa [9]. However, the energy threshold for reorientation between these states is quite high, and at atmospheric pressure no orientationally ordered state exists in pure C_{60} . When the material is

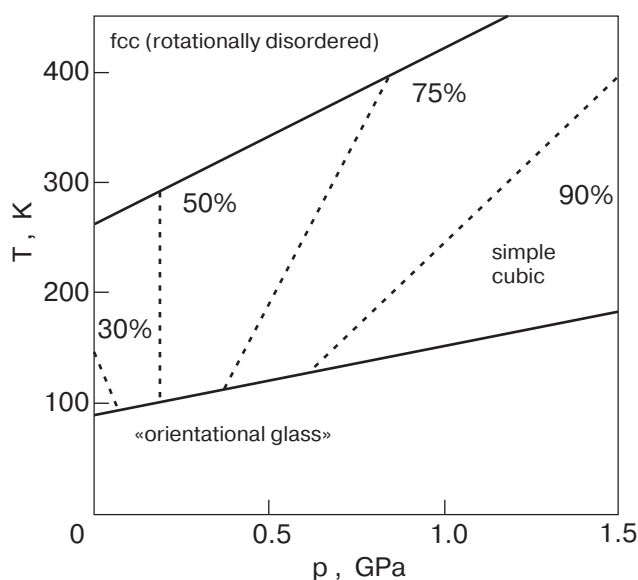


Fig. 1. Pressure–temperature phase diagram of pure C_{60} , showing the three structural phases. In the simple cubic range, the orientational structure under various conditions is shown as calculated from Eq. (1). Numbers indicate the fraction of H -oriented molecules along each of the dotted lines shown.

cooled to below T_0 the orientational order improves with decreasing T , but the glass transition intervenes at about 90 K, when the fraction of P -oriented molecules is still only about 85%. At sufficiently high pressures, however, a completely H -ordered phase should exist.

The evolution of orientational order in the pressure-temperature phase diagram of molecular C_{60} is shown in Fig. 1. This figure shows the fcc–sc phase line and the glass transition line as solid lines. In the fcc phase there is no orientational order, and in the low- T «orientational glass» the orientational structure (i.e., the average number of P - and H -oriented molecules) will be frozen at the particular value present when the sample was cooled through the glass transition line. In the intermediate simple cubic phase, the approximate equilibrium fraction of H -oriented molecules is indicated by several (dotted) lines, corresponding to orientational states with 30, 50, 75 and 90% H -oriented molecules. In the simplest possible model the fraction of H -oriented molecules is given by

$$f(T) = [1 + \exp(-\Delta/k_B T)]^{-1}, \quad (1)$$

where Δ is the energy difference between the two states. Assuming that Δ is linear in p and independent of T , $f(T, p)$ will be constant on lines in the p – T plane. The dotted lines in Fig. 1 have been calculated assuming that the two states have equal energies at

0.19 GPa [9]. (An alternative model, which might be in better agreement with experiment [1], assumes that the energies are always identical at the molecular volume corresponding to 0.19 GPa and 150 K.)

Intercalation of C_{60} with gases

Atomic (rare) gases

The chemical reactivity of the fullerene molecules is low, and many atomic or molecular species can diffuse into the cavities in the fullerite lattice without forming chemical bonds with individual fullerene molecules. As might be expected, there is also a strong correlation between the dimensions of the intercalant atoms or molecules and their ability to intercalate into the interstitial sites in the fullerite lattice. Very careful neutron scattering studies of the intercalation of rare gases into these sites have been carried out by Morosin et al. [10,11]. At room temperature they were unable to measure the very high diffusion rate of He, which has an effective atomic radius of 0.93 Å and probably fills all available sites. While He is reported to penetrate the lattice completely within a few minutes, even at quite low applied pressure, Ar, with a radius of 1.54 Å, did not intercalate noticeably even after six days at 0.6 GPa. Ne, as expected, is an intermediate case because of its atomic radius of 1.12 Å, and, as such is an excellent model substance to illustrate the general behavior of many gases. The presence of Ne atoms in the octahedral sites leads to a small expansion of the lattice. Using neutron diffraction, Morosin et al. were able to use this effect to show that Ne diffuses into the lattice with a time constant of a few hours, finally reaching a saturated state in which the Ne occupancy in the octahedral sites was about 20% at atmospheric pressure and increased to about 100% above 0.2 GPa [10]. Interestingly, the rate of Ne diffusion into the C_{60} lattice depends very strongly on the applied Ne pressure. In the fcc phase the diffusion time constant increases linearly from a few minutes (as for He) at zero pressure to about 90 min at 0.2 GPa, while in the sc phase the time constant for diffusion is approximately 5 h, independent of p over the range studied [11]. It should be noted that while pressure increases the driving force for diffusion, it also decreases the size of the interstitials and channels, but this decrease is much too small to explain the changes in the diffusion rate. On relieving of the Ne pressure, the diffusion of Ne out of the C_{60} lattice was always very rapid except at very low temperatures (200 K).

To explain these observations, Morosin et al. suggest that the main transport mechanism for the Ne atoms is a paddlewheel effect [11]. Ne atoms are

slightly too large to pass through the «static» channels in the structure, but when the C_{60} molecules rotate, Ne atoms may follow the movement and be swept in. In particular, it is speculated that Ne atoms may attach to the electron-poor centers of the pentagons and hexagons, which form dimples or buckets in the molecular structure and which would temporarily afford larger space for atomic transport through the intermolecular channels during rotation. Such a mechanism would explain the observation that Ne transport slows down significantly with increasing pressure, which leads to a larger interaction between the C_{60} molecules and thus to a slowing down of the molecular rotation. In the sc phase, diffusion slows down even more because rotation is replaced by a stepwise, much slower ratcheting movement of the molecules. On relief of the external pressure, the presence of Ne atoms in the interstitial sites should result in a larger lattice parameter than normal and thus also a smaller molecular interaction, a more rapid molecular rotation, and a very large diffusion coefficient.

The same model should be applicable over a large interval in T , and also to other gases that interact weakly with the fullerene molecules. We would expect the diffusion rate to be high and to increase very strongly with increasing T in the fcc phase (with «free» molecular rotation) and to be smaller and decrease very rapidly with decreasing T in the sc phase as the orientational ratcheting dies out. These predictions agree well with experimental results. At temperatures below 180 K, even He diffusion becomes too slow to be detectable over several hours or days even at 0.5 GPa [12], and at temperatures above 475 K the heavy rare gases (R=Ar, Xe, and Kr) may all diffuse into C_{60} at 0.17 GPa to form compounds [13] R_xC_{60} with $0.6 < x < 1$. After cooling and pressure relief these compounds are stable over long times at room temperature.

Although NMR shows that the intermolecular interactions and molecular dynamics of intercalated C_{60} differ little from those of the pristine material, intercalation into the interstitial sites still changes the lattice properties of the material in several subtle ways. In general, the presence of foreign atomic or molecular species in the lattice makes both the central interactions between the C_{60} molecules and the orientational interaction weaker, because intercalation expands the C_{60} lattice. The effects are particularly large in the case of the heavy rare gases and molecular gases. For Kr_xC_{60} and Xe_xC_{60} this leads to a decrease in T_0 from 260 K for pure C_{60} to 240 K and 200 K, respectively. Compressibility studies on C_{60} using the (intercalating) lighter rare gases as pressure media showed that the presence of intercalated atoms (He or Ne) made

the lattice less compressible [14]. However, the fcc–sc transition still occurred at approximately the same molecular volume as for pure C_{60} (i.e., at a slightly higher pressure), showing that the orientational interaction had changed little. This was not the case for compounds with the heavy rare gases, for which T_0 at atmospheric pressure occurred at a larger molecular volume than for pure C_{60} , indicating a more complicated effect on the intermolecular potential. As mentioned above, the orientational state in the lattice changes with pressure (or, equivalently, volume) in such a way that compression favors the H orientation [1,9]. Conversely, expansion should favour the P orientation, and in principle the expanded lattices should have a higher fraction of P -oriented molecules at low T than pure C_{60} . This effect has not been observed in rare gas compounds, but we return to this question below.

Because intercalation changes the intermolecular interaction it also affects the low-energy vibrations and librations in the lattice, and thus the low-temperature properties. Aleksandrovskii et al. have carried out extensive studies of the low-temperature thermal expansion of C_{60} , which, surprisingly, shows a large negative peak [15] below 4 K. The magnitude of this effect is also very sensitive to the presence of intercalated gases, even rare gases [16], showing again that intercalation leads to subtle effects in the lattice properties of C_{60} .

Molecular gases

Many other gases have molecules small enough to diffuse into the C_{60} lattice, especially under low pressures at high temperatures. Many studies have been carried out on the atmospheric components N_2 and O_2 , because of their obvious presence in most practical experiments. Other gases that form stable intercalation compounds with C_{60} are, for example, H_2 , CH_4 , CO , CO_2 , and NO .

Gases with relatively large molecules show many interesting effects, when confined to the octahedral interstitial sites in C_{60} . Complete filling of the octahedral sites is usually not observed, except for [17] H_2 above 75 MPa, but all gases expand the original C_{60} lattice, and both molecular shape and size are important in determining the properties of the intercalated material. While the very symmetrical CH_4 (or CD_4) molecules continue to rotate freely inside the C_{60} interstitial sites [18] even at 210 K, far below the «freezing» temperature T_0 for the C_{60} lattice, the linear CO_2 molecules must be oriented along the $\langle 111 \rangle$ directions of the C_{60} lattice to fit inside the cavities at all, and the interaction between the C_{60} and the rod-like CO_2 molecules induces large structural differ-

ences [19] between pure C_{60} and the intercalated compound at low T . The smaller H_2 , CO and NO molecules are also free to vibrate and rotate in their cavities. The dynamic behavior of CO has been observed by NMR and IR spectroscopy over large ranges in temperature and pressure (or «prison cell» volume), and the interaction between the guest molecules and the C_{60} host lattice has been analyzed in detail. With a decrease in temperature the motion gradually changes from basically free rotation at room temperature to tunneling between a few orientational states at low temperatures [20], and with an increase in pressure a similar restriction in the motion is observed as the available volume decreases [21]. At the highest pressures studied, 3.2 GPa, the molecules must take up oriented positions in the C_{60} lattice in much the same way as does CO_2 , and theoretical calculations indicate that the observed spectra agree well with a purely H -oriented C_{60} lattice. The dynamic behavior of trapped H_2 in C_{60} has also been studied [17]. Studies of the interaction between hydrogen and the carbon atoms in C_{60} are important from the point of view of understanding fully the interaction of hydrogen with carbon-based storage media, but C_{60} itself is not a practical storage host since only one H_2 molecule can be stored interstitially per C_{60} molecule, limiting the maximum storage capacity to well below one percent in pure C_{60} .

As in the case of heavy rare gases, intercalation of molecular gases leads to significant downward shifts in T_0 , usually down to 240–250 K, and to large increases in the bulk moduli [22]. The lattice expansion should also in principle improve the orientational order, as discussed above, and such an effect has indeed been observed in C_{60} intercalated with CO [23] and NO [24]. For NO , Gu, Tang, and Feng [24] claim to identify a completely pentagon-oriented lattice with $T_0 = 230$ K from dielectric measurements, but no structural evidence is shown. However, a very careful structural study on CO shows [23] a significant enhancement of the fraction of P -oriented molecules at both intermediate (150 K) and low temperatures. The improved order is believed to arise from a combination of three effects. In addition to the lattice expansion effect already discussed, the glass transition temperature is depressed by about 5 K, and the CO molecules are structurally correlated with the C_{60} molecules at low T through electrostatic interactions. The dipolar CO molecule prefers to bind weakly to the electron-poor single C–C bonds on P -oriented C_{60} molecules, resulting in an almost completely P -oriented structure.

Because of its practical importance, the interaction of C_{60} with N_2 and O_2 has received much attention.

Early NMR studies showed that oxygen diffused reversibly into the octahedral sites at atmospheric pressure and room temperature with equilibrium filling fractions of at most a few percent [25,26]. At high pressures, 10–100 MPa, both O₂ and N₂ diffuse slowly into the C₆₀ lattice, so that they may fill a large fraction of the octahedral sites over a time of several days [27,28]. However, for N₂ an elevated temperature (500 K) is needed to reach high filling fractions. Because diffusion is slow (and slower for nitrogen than for oxygen), grain size is important, and finely ground powder reaches the highest filling fractions, while the inner parts of crystallites probably always have a lower filling fraction. Evacuation at slightly elevated temperature (see the next Section) is reported to restore the C₆₀ to a pure state. The intercalation compounds of oxygen have been studied by many methods. NMR can give information on the average number of filled octahedral sites [25–27,29] and also shows that the oxygen resides at the center of the interstitial sites with no sign of charge transfer or chemical bonding [26]. Inelastic neutron scattering and Raman scattering also shows that although some vibration modes of the intercalated molecules soften appreciably when the molecules are confined within the C₆₀ interstitial sites, this has no measurable effect on the vibrational and librational properties of the C₆₀ lattice [28]. In spite of this, calorimetry, structural studies, and dielectric studies [27–29] all show that the rotational transition temperature T_0 is strongly depressed by both O₂ and N₂, by up to –20 K in (O₂)_xC₆₀ and –22 K in (N₂)_xC₆₀ [28]. Again, these figures are much larger than can be explained by the intercalation-induced lattice expansion (the «negative pressure effect» [27]). To explain this anomaly, Gu et al. [29] suggest that the local strain set up by diffusing intercalant molecules enhances fluctuations in the order parameter close to T_0 , while Renker et al. [28] suggest that the observed slowing down of molecular motion in the guest molecules transfers energy to the C₆₀ lattice by anharmonic interaction with librational modes, thus reducing the effective height of the energy threshold for molecular rotation.

Reactions with intercalated gases

As reported above, treatment of intercalated C₆₀ under vacuum usually removes the intercalated gas and restores the material to a pure state. However, this is not true for all gases, and in particular reactions may occur between the C₆₀ and the gas if the temperature is raised. Two gases are particularly likely to react, hydrogen and oxygen. Hydrogen easily intercalates into C₆₀ under pressure, but is also easily desorbed by pumping at room temperature [17]. How-

ever, if a high hydrogen pressure is applied to C₆₀ at elevated temperature, a reaction occurs between C₆₀ and intercalated hydrogen, transforming the material into an intercalation compound of H₂ in C₆₀H_x. At a pressure of 600 MPa and a temperature of 620 K, $x \approx 24$ has been reported [30]. The intercalated hydrogen could again be removed by pumping, leaving the new compound behind, and with a long enough reaction time the conversion of C₆₀ into hydrofullerite was more or less complete.

All forms of carbon, including diamond and fullerenes, burn in oxygen at sufficiently high temperatures. Although no oxidation of C₆₀ seems to occur at room temperature, measurements at 370 K shows that reactions have occurred and that oxides have formed [31]. At higher temperatures the oxidation increases rapidly. At 470 K strong IR evidence for oxidation is seen, with traces of trapped CO and strong absorption bands from C–O and C=O bonds. The fullerene molecules have started breaking down or have been transformed into C₆₀O_x. At 570 K, the material breaks down further with the formation of both oxides and amorphous residues from broken cages; in simple terms, it slowly burns. Any fullerite sample exposed to air should thus be kept at temperatures well below 400 K to protect it from permanent changes by oxidation.

C₆₀ can also react with oxygen without heating. In the discussions above, it has implicitly been assumed that the material has been protected from visible or UV light, since it is well known that both C₆₀ and C₇₀ polymerize if irradiated with such light in an oxygen-free environment [32]. Oxygen inhibits this polymerization process, but C₆₀ irradiated in the presence of oxygen shows other characteristic changes («photo-transformation») [33,34]. First, radiation with visible or UV light enhances the oxygen diffusion rate in C₆₀ by at least an order of magnitude, so that thin films in air rapidly become oxygen saturated (most octahedral sites filled, at least within the light penetration depth), or oxygen-rich films lose oxygen in a vacuum. Films (or, equivalently, the surface layers of irradiated bulk material) irradiated for a short time do not differ from the materials discussed above, i.e., the oxygen interacts only weakly with the lattice. After longer times, however, an increasing amount of photo-induced oxidation of C₆₀ to C₆₀O_x becomes evident. After «long time» exposure the films become insoluble in toluene like photo-polymerized C₆₀, suggesting the presence of cross-linked carbon–oxygen clusters in the film. Fullerenes should therefore also be protected from light, whether in air, vacuum, or under inert gas.

Formation of endohedral compounds

Fullerenes like C₆₀ and C₇₀ are hollow shells, which can be used as containers for other atoms, and several methods have been found to produce such materials. Here it will only be noted that the formation of such endohedral compounds has been reported during treatment of fullerenes under reasonably high rare-gas pressure at high temperatures. Saunders et al. [35] reported that under 0.3 GPa at temperatures near 925 K, about 0.1% of the C₆₀ molecules captured rare-gas guest atoms such as He, Ne, Ar, and Kr. The larger Xe molecule, however, did not enter into C₆₀. At high temperatures, C–C bonds on the C₆₀ molecules are believed to break spontaneously and the rare-gas atoms then have a chance to enter and get trapped inside when the «window» closes. Endohedral compounds are usually stable for long times under ambient conditions. The method, the properties of the resulting endohedral compounds, and their possible applications have been thoroughly discussed in Ref. 36.

Conclusions

Intercalation of atomic and molecular gases gives rise to many novel and interesting phenomena in fullerite lattices. Some of these are well understood, while for others our understanding is still only in the early stages. Because intercalation may lead to significant changes in the properties of fullerite materials both directly and, in some cases, through chemical reactions induced by temperature or pressure, it is important to understand these effects in order to sort out which properties are intrinsic to C₆₀ or other fullerenes and which depend on the presence of intercalated impurity atoms or molecules. Since intercalation can also be used as a physical tool to study the properties of single molecules or their interactions with carbon or each other, research into intercalation compounds of fullerenes will probably continue to be of interest for many years to come.

I would like to thank the Swedish Research Council and the Royal Swedish Academy of Science for funding our work on fullerenes, and Acad. V.G. Manzhelii and Dr. A.N. Aleksandrovskii for discussions on the effects of gases trapped in the lattice of C₆₀.

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