An internal-friction study of C_{60} crystal intercalated with O_2

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Abstract. After a C_{60} crystal was intercalated with O_2, the internal-friction peak due to the orientational relaxation of the C_{60} molecules shifted to a lower temperature. Also, the activation energy decreased, by 26 meV. These results indicate that the depth of the orientational potential well is changed by the O_2 intercalation. This change is assumed to be due to the electrostatic interaction between O_2 and C_{60} molecules. The decrease of the order–disorder phase transition temperature, which is by about 20 K, can also be explained using this model.

At around 260 K, there is an order–disorder phase transition in C_{60} crystal, which has been detected in a lot of experiments [1–4]. Below 260 K, the crystal is in an orientationally ordered phase. In other words, every C_{60} molecule will be in one specific orientational state. But thermally excited jumps between two nearly energetically equivalent orientations still occur; this is always regarded as 'orientational relaxation'. Some scientists [4–7] have used the internal-friction method to study the phase transition and the orientational relaxation of C_{60} crystal. Shi *et al* [4] reported that for C_{60} single crystal, an attenuation peak associated with an elastic anomaly due to the orientational relaxation appeared at ~ 160 K, and found the activation energy $U = 241$ meV. Schranz *et al* [5] get the activation energy $U = 300 \pm 10$ K. These results coincide with the data measured by other methods [8–10]. So, through an internal-friction measurement, the activation energy of the orientational relaxation can be detected accurately.

When a C_{60} sample is intercalated with gas molecules (O_2, He, Ne, Ar, etc), the order–disorder phase transition shifts to a lower temperature [11–14]. For the inertial gas, the shift is not very dramatic, and can be explained through 'negative-pressure effects'. But when the C_{60} crystal is intercalated with O_2 molecules, the phase transition temperature will decrease by about 20 K [13, 14], which has not so far been explained. In this paper we will study the influence of O_2 molecules on the phase transition and the orientational relaxation of C_{60} by the internal-friction method.

The C_{60} powder that we used was prepared by the method proposed by Kratschmer *et al* [15], and purified by a column liquid chromatography method [16] to a purity of $>99.9\%$. The C_{60} powder was evaporated in a vacuum of 10^{-5} Torr, and deposited on SiO_2 substrates with the dimensions $0.25 \times 4.0 \times 40.0$ mm^3. The substrate temperature was carefully controlled at 200 ± 10 °C (sample 1 and 2) and 100 ± 10 °C (sample 3). The average thickness of the C_{60} films was about 10 nm. Through transmission electron

microscopy, the average grain size of samples 1 and 2 was found to be more than 500 nm. The average grain size of sample 3 was about 150 nm.

The internal friction of the sample was measured by means of a free–free bar apparatus, in which a combination of an electrostatic drive and capacitor microphone detection was used [17]. The internal friction of the composite sample was found to be $\delta = \delta_s + (3t/d)(E_f/E_s)\delta_f$, where t and d represent the thicknesses of the film and of the substrate, δ_f and E_f represent the internal friction and the Young modulus of the film, and δ_s and E_s denote the same quantities for the substrate. The frequencies f of the composite sample are related to the frequencies f_s of the bare substrate by the expression $f^2/f_s^2 = 1 + (t/d)(3E_f/E_s - \rho_f/\rho_s)$, where ρ_f and ρ_s are the densities of the film and the substrate, respectively. A 10^{-2} Torr vacuum was maintained in the sample chamber. The internal friction was measured for samples 1, 2 and 3 from 100 K to 300 K at a frequency of $\sim$1 kHz after they were prepared. Then we exposed samples 1 and 3 to an O_2 atmosphere at a pressure of 0.15 kbar for 72 hours at room temperature, and then removed them to measure the internal friction. We exposed sample 2 to a He atmosphere at a pressure of 0.14 kbar for 72 hours, and then measured its internal friction too.
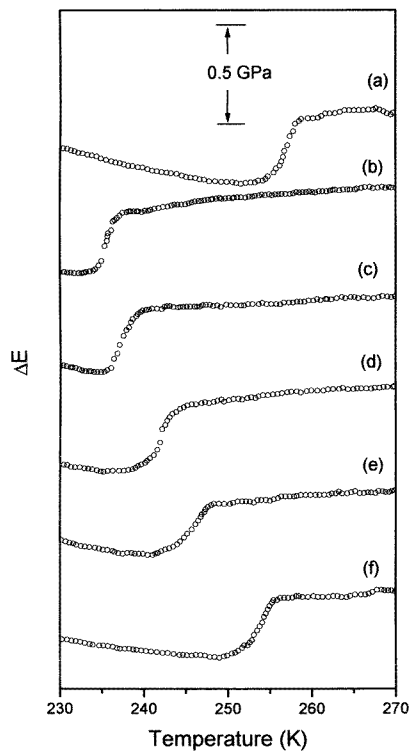
Figure 1. The modulus of the C_{60} film (samples 1, 2) versus temperature. Curve (a) corresponds to pure C_{60} film. Curves (b), (c), (d) and (e) indicate the modulus when the sample was removed from the O_2 atmosphere for less than 1 h, and for 24 h, 48 h, and 72 h, respectively. Curve (f) indicates the modulus when the sample was removed from the He atmosphere for less then 1 h.

First, the internal friction of the pure C_{60} sample (sample 1) was measured. As shown in figure 1(a), at $\sim$257 K, a soft modulus was detected, which was due to the order–disorder phase transition [4–7]. But the internal-friction peak corresponding to the phase transition
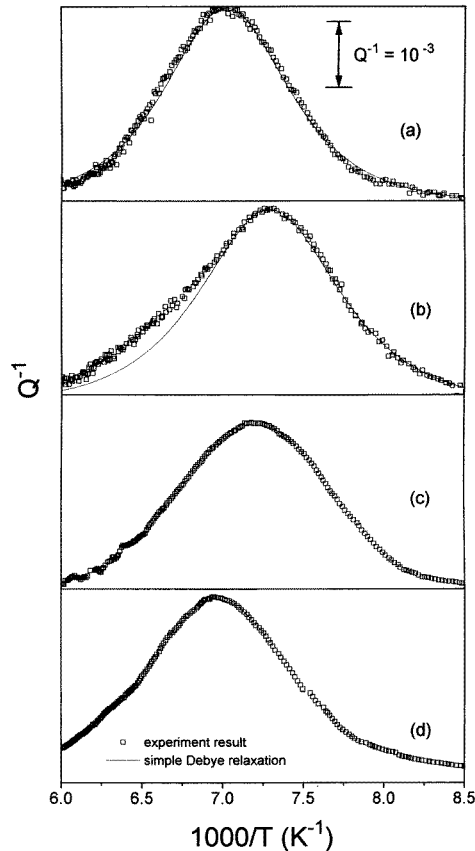
Figure 2. The internal friction of the C$_{60}$ film (samples 1, 2) over the temperature range from 110 K to 170 K. The small squares show the experimental results. The solid line is the fit for simple Debye relaxation. (a) indicates the internal friction of the pure sample. (b) and (c) indicate the internal friction when the sample was removed from the O$_2$ atmosphere for less than 1 h and for 24 h, respectively. (d) indicates the internal friction when the sample was removed from the He atmosphere for less than 1 h.

was not detected, which was perhaps due to the large grain size and the high background against which the internal friction was measured [7]. In the low-temperature range, an internal-friction peak was measured, as shown in figure 2(a). The peak temperature is 142.8 K. The modulus showed no dramatic variation over the temperature range. For sample 2, all of the results were identical to those for sample 1, so we did not present these in the figures.

After sample 1 had been exposed to an O$_2$ atmosphere for 72 hours, we promptly took the sample out, put it in the sample chamber, and cooled it to about 100 K. This complete procedure took less than one hour. Then we measured the internal friction of sample 1 from 110 K to 170 K at a heating rate of 1 K min^{-1}. As shown in figure 2(b), we found that the internal-friction peak shifted to lower temperature and the peak shape became asymmetric. The peak temperature is 137.2 K. Then we heated the sample quickly to 210 K, and then heated it slowly at a constant rate of 1 K min^{-1}. At 237 K, a modulus softening was detected, as shown in figure 1(b). After keeping the sample in a vacuum for 24 hours at

room temperature, we measured the internal friction through a second heating cycle at the same heating rate. We found that the internal-friction peak became symmetric, and that the peak temperature shifted to 138.9 K, as shown in figure 2(c). The phase transition temperature increased as shown in figure 1(c). Then we repeated the experiment every 24 hours. After several heating cycles (with the sample held in a vacuum for more than six days), the measurement results were approximately identical to those for the pure sample.
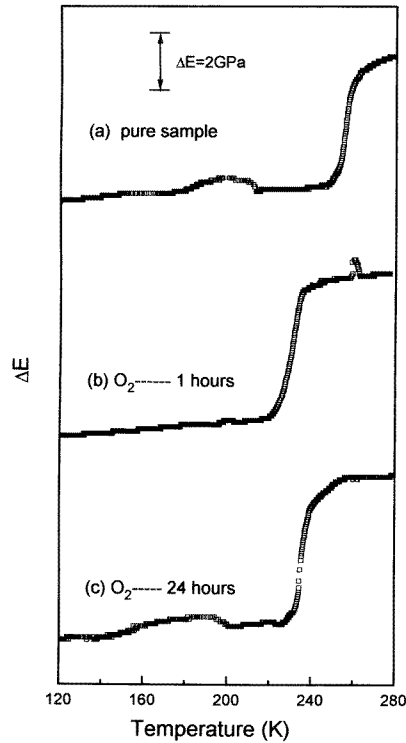
Figure 3. The modulus of a C_{60} film (sample 3) versus temperature. Curve (a) corresponds to the pure C_{60} film. Curves (b) and (c) indicate the modulus when the sample was removed from the O_2 atmosphere for less than one hour, and that when it was removed for 24 hours, respectively.

So the O_2 molecules are seen to influence the orientational relaxation dramatically. But it is not clear whether the O_2 diffuse out during the measurement process, especially from 110 K to 170 K, which can also influence the peak shape. We have carried out an experiment to investigate this. After sample 1 was removed from the O_2 atmosphere, we cooled it to 100 K, then heated it at a rate of 1 K min^{-1} to 170 K, and we obtained an internal-friction peak as shown in figure 2(b). Then we cooled it to 100 K, and performed the internal-friction measurement again at a heating rate of 1 K min^{-1}. We obtained the same internal-friction peak. So the O_2 out-diffusion in the experiment below 170 K can be neglected.

As shown in figure 2(a), the internal-friction peak can be fitted with a simple Debye relaxational process equation: $Q^{-1} = \Delta\omega\tau/(1 + \omega^2\tau^2)$, where $\Delta = \delta E/E_0$ (δE is the relaxation of the modulus). τ is the relaxation time. The relation between $1/\tau$ and the temperature T can be expressed as $1/\tau = (1/\tau_0)e^{-U/kT}$, where U is the activation energy.

Here, the activation energy $U = 252$ meV, and $\tau_0 = 2.11 \times 10^{-13}$ s.

After the sample was intercalated with O$_2$, the relaxational peak became asymmetric in the first heating cycle, as shown in figure 2(b). The data for the low-temperature side of the peak can be perfectly simulated with a simple Debye relaxational peak. The activation energy $U = 226$ meV, and $\tau_0 = 7.93 \times 10^{-13}$ s. But the high-temperature side of the peak is a little broader, and is higher than the calculation data. We assume that this is due to out-diffusion of oxygen molecules near the surface of the C$_{60}$ film. Though the sample was kept in a vacuum at room temperature for only a few minutes, the oxygen molecules near the surface could easily diffuse into the vacuum. So the relaxational time of C$_{60}$ molecules near the surface was longer than those for other molecules. As a result, on the high-temperature side, the peak became broader.

In the second heating cycle, the relaxational peak became symmetric. But it cannot be simulated with a simple Debye relaxational process, and shows a slight broadening on both sides, as shown in figure 2(c). We think that this is due to the heterogeneous distribution of O$_2$ molecules in the sample. Since the sample was kept in a vacuum for 24 hours at room temperature, a large amount of O$_2$ had diffused into the vacuum. Regions nearer the surface had lower O$_2$ concentrations. As a result, the relaxational process exhibited a distribution of relaxational times. However, we assume that the distribution of the relaxational times was symmetric, which would explain why the relaxational peak remained symmetric. In the next few heating cycles, the relaxational peak remained symmetric, and it could not be simulated with a simple Debye relaxational process until the O$_2$ was completely diffused into the vacuum.

The internal friction of sample 3 was measured by a similar process. As the grain size was about 150 nm, the internal-friction peak was very high, as has been explained in another paper [7]. As shown in figure 3 and figure 4, a modulus softening associated with a high internal-friction peak was detected at 254 K before the sample was intercalated with O$_2$. After sample 3 was removed from the O$_2$ atmosphere, the modulus softening and the internal-friction peak shifted to 231 K in the first heating cycle. In the second heating cycle, the peak temperature shifted to 237 K. So the order–disorder phase transition temperature of sample 3 also decreased by about 20 K immediately after the sample was removed from O$_2$. The internal-friction peak due to orientational relaxation was not detected, even for the pure sample.

When the gas molecules intercalate in the C$_{60}$ crystal, the order–disorder phase transition temperature will decrease. This has been interpreted as a 'negative-pressure' effect [13]. Put simply, when a high pressure is applied to a C$_{60}$ crystal, the order–disorder phase transition temperature will increase (the value of dT_0/dP is 11.5 K kbar^{-1} [18]). So when the gas molecules intercalate into the crystal, they will induce a negative pressure and decrease the phase transition temperature. But for O$_2$, the theory fails: since only 0.15 kbar of pressure was applied, a shift of $\sim$2 K at most would be predicted, but in fact $\sim$20 K was observed, and the actual shift was probably larger just before the sample was removed from the O$_2$ atmosphere.

To test for the 'negative-pressure' effect, we performed an internal-friction measurement on sample 2, which was exposed to a 0.14 kbar He atmosphere for 72 hours. In the first heating cycle, we found the modulus softening shift to 255 K—a little below the position for the pure C$_{60}$ sample. The internal-friction peak corresponding to the orientational relaxation process appeared at 143 K. The peak shape underwent little change compared with that of the pure C$_{60}$ sample. So the effect of He molecules on C$_{60}$ crystal can be approximately explained by the 'negative-pressure' theory.

But why can the influence of oxygen molecules not be explained by the 'negative-
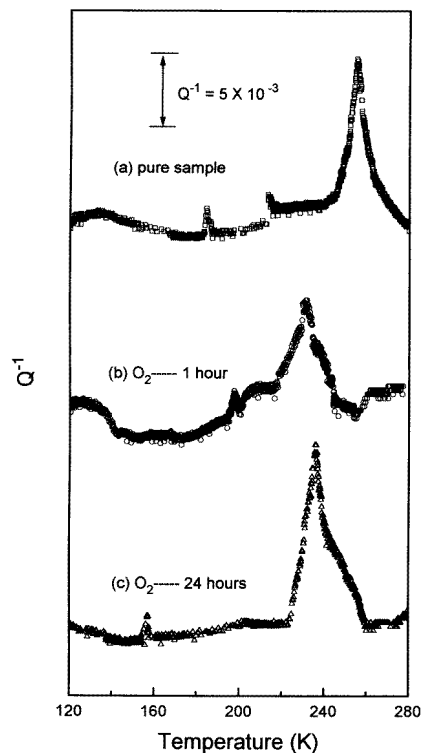
Figure 4. The internal friction of a C_{60} film (sample 3) versus temperature. Curve (a) corresponds to the pure C_{60} film. Curves (b) and (c) indicate the internal friction when the sample was removed from the O_2 atmosphere for less than one hour, and that when it was removed for 24 hours, respectively.

pressure' theory? We assumed that this was due to the different molecular shapes of O_2 and He. The He molecule is a one-atom molecule, while the O_2 molecule is a two-atom molecule. The electron cloud of a He molecule has spherical symmetry, so the He molecules could not interact electrostatically with the neighbouring molecules. However, the electron cloud of an O_2 molecule has a shape like a dumb-bell, so O_2 molecules will interact electrostatically with the neighbouring C_{60} molecules, because the C_{60} molecule has a heterogeneous distribution of electron density on its surface.

The C_{60} molecule has the same shape as a soccer ball, consisting of 12 pentagons and 20 hexagon faces. Sixty carbon atoms are distributed at sixty different vertices. The edge between two hexagon faces corresponds to an electron-rich short C=C bond. At the centres of both the pentagon and hexagon faces, the electron density is comparatively low. In the orientationally ordered phase (below $\sim$260 K), due to the electrostatic interaction, electron-deficient pentagon or hexagon centres will face an electron-rich short C=C bond of the neighbouring molecule. When the molecule enters an orientational state with the pentagon centres facing C=C bonds, the energy is lower. The C_{60} molecules will be in one of two orientational states which are separated by a potential barrier. Thermally excited jumps between two states, corresponding to a relaxational process, have been detected in several experiments [4, 5]. The exciting energy U is equal to the height of the potential barrier. When He molecules are interpolated into the crystal, they will induce a negative

pressure and increase the lattice constant. As a result, the height of the potential barrier decreases. In other words, the orientational potential wells become shallow. So the phase transition temperature and the relaxation peak will shift to a lower temperature. But as a He molecule does not interact electrostatically with C$_{60}$ molecules, the orientational potential well changes only with the increase of the lattice constant. So the influence of the He molecule can be explained by the 'negative-pressure' effect. But as regards the influence of O$_2$, O$_2$ molecules do interact electrostatically with neighbouring C$_{60}$ molecules, so the depth of the orientational potential well changes both with the electrostatic interaction and with the increase of the lattice constant due to the 'negative-pressure' effect. We assumed the exciting energy of the first cycle to be the height of the energy barrier when the C$_{60}$ crystal is interpolated with O$_2$ molecules.

When C$_{60}$ crystal is exposed to an O$_2$ atmosphere, the O$_2$ will diffuse into and occupy the octahedral sites of the C$_{60}$ crystal [13, 19]. When the diffusion reaches equilibrium, the distribution of O$_2$ is approximately homogeneous. What percentage of the octahedral sites are occupied by O$_2$? We cannot precisely measure it. Schirber *et al* [13] have exposed C$_{60}$ crystal to 1 kbar of O$_2$ for 48 h at room temperature, and then investigated it by differential scanning calorimetry (DSC). They found two endothermic peaks, at $\sim$260 K and $\sim$240 K. These results were clearly showing that the sample was composed of two parts. One part (part I) was interpolated with O$_2$ and reached equilibrium under the applied O$_2$ pressure. The other part (part II) was the pure C$_{60}$ crystal. As the decrease of the phase transition temperature of our sample has the same value of that of their sample, we assume that in our sample the O$_2$ content was not lower than that of part I of their sample. But our sample was exposed to 0.15 kbar of O$_2$, while their sample was exposed to a pressure of 1 kbar. So the O$_2$ contents of the two samples had reached saturation. In other words, almost 100% of the octahedral sites were occupied by O$_2$.

When the O$_2$ intercalation reaches saturation, around every C$_{60}$ molecule there are six O$_2$ molecules. It can be assumed that, in the orientationally ordered phase, the depth of the orientational potential well will vary, for every C$_{60}$ molecule, by the same amount under the influence of O$_2$ molecules. We think that the shift of the order–disorder phase transition temperature is also due to the variation of the depth of the potential well.

To estimate the shift of the transition temperature under the influence of O$_2$ molecules, we employ a mean-field argument that involves calculating the free energies [20]. Above the order–disorder phase transition, we approximate each C$_{60}$ molecule as a three-dimensional free rotor. The free energy is the sum of the static energy E_{fcc} and the free energy of three-dimensional rotors at temperature T:

$$F_{\mathrm{fcc}}(T) = N[E_{\mathrm{fcc}} - k_B T \ln 8\pi^2 (I k_B T / 2\pi\hbar^2)^{3/2}]$$

where $I = 1.0 \times 10^{-43}$ kg m^2 is the moment of inertia of the C$_{60}$ molecule. The static energy E_{fcc} is calculated by averaging over random configurations. In the orientationally ordered phase, each molecule vibrates around its optimal orientation. So the free energy is the sum of the static energy $E_{Pa\bar{3}}$ and that of three-dimensional harmonic oscillators at temperature T:

$$F_{Pa\bar{3}}(T) = N[E_{Pa\bar{3}} + 3k_B T \ln(1 - \mathrm{e}^{-\hbar\omega_0/k_B T})]$$

where $\omega_0 = 1.86 \times 10^{12}$ s^{-1} [20] is the average frequency of the librons. The phase transition happens at the temperature for which the two free energies are equal.

Because E_{fcc} is the potential energy calculated by averaging over random directions, the part of E_{fcc} that is due to the electrostatic interaction approximately equals $-U/2$. Here, we assume that at the top of the energy barrier the potential energy equals zero.

The electrostatic interaction part of $E_{Pa\bar{3}}$ corresponds to the energy at the bottom of the potential well and equals $-U$. In the first heating cycle after the sample is removed from the O_2 atmosphere, the depth of the potential well decreased by $\Delta U = 26$ meV. So the energy difference between E_{fcc} and $E_{Pa\bar{3}}$ decreased by $\Delta U/2 = 13$ meV. We assume that ω_0 does not change when O_2 molecules are intercalated. So we can calculate the shift of the phase transition temperature: $\Delta T \approx -28$ K. In our experiment. the decrease of the phase transition temperature is about 20 K. So the influence of O_2 on the phase transition temperature can be substantially explained using the theoretical model.

In conclusion, when O_2 molecules were intercalated into C_{60} crystal, the depth of the orientational potential well changed dramatically; this is assumed to be due to the electrostatic interaction between O_2 and C_{60} molecules. The influence on the order–disorder phase transition temperature, which decreased by about 20 K, can also be explained through the depth variation of the orientational potential well.

Acknowledgments

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