Complete pentagon orientational ordering in C_{60} fullerite charged with NO

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Solid C_{60} was stored in NO under high pressure and the gas molecules NO were found to diffuse into the octahedral interstitial sites in its fcc crystal lattice. Its ^{13}C NMR MAS spectra composed of a primary resonance at 143.7 ppm, accompanied by two minor peaks shifted 0.4 and 0.8 ppm downfield respectively. The dopant was found to depress its phase transition temperature at 260 K in pure C_{60}, and to reduce substantially the drop $\Delta\varepsilon'$ at the phase transition temperature. Furthermore, the spectral features associated with relaxation during glass transition at lower temperature, as observed in impedance spectra, were smeared. The fraction of P-orientation below T_c has been calculated, that is larger than 11/12. These results show that a completely P-oriented phase has occured in $(NO)_{0.1}C_{60}$, and this phase is favored by a negative pressure on C_{60} lattice exerted by NO, as well as the electrostatic interaction between the two.

This work has been supported by a grant from the NSF of China (Grant N 10074031), and another from The Jiangsu Province Fuondation of Natural Science (Grant N BK2001027). M. Gu thanks the Crocher Foundation of Hong Kong for the Fellowship at HKBU.

Gases accommodated interstitially in C_{60} fullerite have exerted significant influence on its order-disorder phase transition [1–4]. As we known, the C_{60} fullerite accommodates a rotational disorder of C_{60} molecules and adopts a face-centered cubic (fcc) lattice, but below $T_c = 260$ K, the structure changes to simple-cubic (sc) when the random rotations lock into specific orientations with fluctuations characterized by discrete jumps over an energy barrier. After C_{60} fullerite has been charged with gases under high pressure condition, the consequential changes in the critical temperature for the ordered phase have been examined. In the case of argon the shift is $\Delta T = -10$ K [2], and oxygen produces a large shift of -20 K [1,3]. CO was also found to depress fcc-sc transition temperature T_c from the normal value by as much as 12 K [5–7]. Likewise CO causes a slight expansion of the lattice [8]. But no subsequent changes in the lattice symmetry have yet been observed. Being a paramagnetic molecule with a permanent electronic-dipole moment, NO has been selected as a dopan to form a candidate system, C_{60} doped with NO. To attain greater clarification of the roles of foreign molecules in the lattice, we have further studied the dielectric responses vs. temperature of the C_{60} solids charged with NO, characteristics that are sensitive to their orientation order. Meanwhile, the extent of NO in the C_{60} solids has been estimated from the solid ^{13}C NMR of C_{60}. These experimental findings may also contribute towards a deeper understanding of the order-disorder transition phenomenon itself.

1. Experimental details

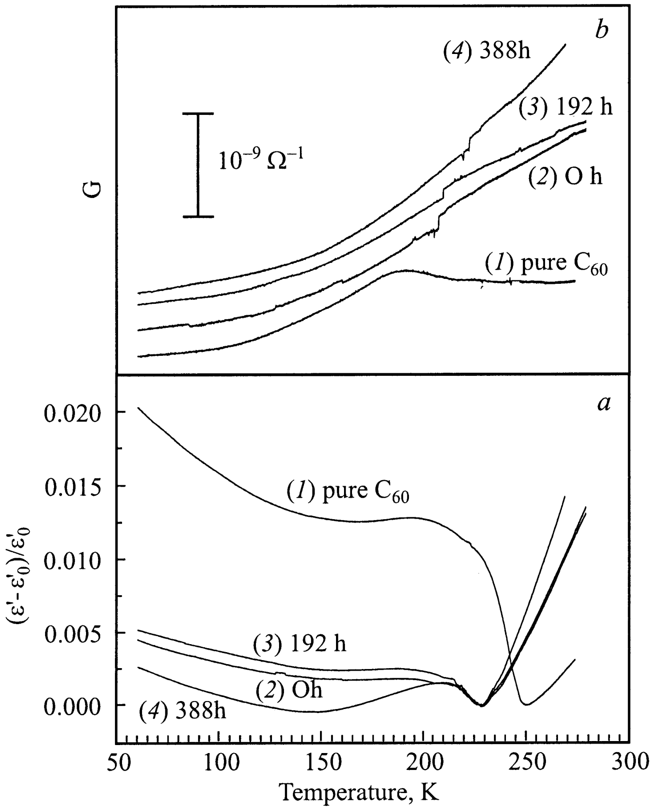
The C_{60}, of purity better than 99.9%, was annealed at 280°C in dynamic vacuum for 72 h to have solvent removed. Rigid pellets of $6 \times 7 \times 0.7$ mm in dimensions were then fabricated from by unixial compaction in an evacuated mold under a pressure of 7 kbar for 10 min. Some powder was crushed from the pellets for ^{13}C NMR and DSC experiments. One batche each of powder and pellets was subjected to NO, at 30 bar for 24 hours at 200°C.

^{13}C NMR measurements proceeded at room temperature in a Bruker MSL-300 spectrometer equipped with a 7-T field and having a resonance frequency of 75 MHz, under the condition of magic-angle spinning (MAS) at the rate of 2.0 kHz and with a delay time of 60 s. In dielectric spectral studies, silver films were evaporated onto the two surfaces of the pellet in question, for measurement via the three-terminal method, with the help of an HP 4284 A multimeter. For DSC, two batches were studied. The first consisted of powder prepared from crushing pellets, and the second from pellets that had been subjected to high-pressure NO. Samples of 25–30 mg in mass were examined at the same scanning rate of $10\,\mathrm{K} \cdot \mathrm{min}^{-1}$ under in a Setaram DSC 92 instrument.

2. Results

The high-resolution ^{13}C NMR spectrum of pristine crushed powder exhibited a primary resonance at 143.7 ppm, related to freely rotating C_{60}, in agreement with previous studies [3,9]. Furthermore, charging with NO at 30 bar and 200°C for 24 hours led to the introduction of two secondary resonances which shifted 0.4 and 0.8 ppm downfield respectively. Calculated from the height of each resonance [9], the value of octahedral occupancies of NO reaches to 0.10. After exposing in air for over 800 hours, however, their intensities remained same.

The Figure depicts the dielectric constant and conductivity, $\varepsilon' \propto (\varepsilon' - \varepsilon'_0)/\varepsilon'_0$ and G respectively, in a representative pellet charged with NO; here ε'_0 stands for the minimum value obtained of ε' which is indicative of the fcc-sc structure transition. The measurement was repeated after the pellet had sat in air for various lengths of time. The permittivity in the "fresh" pellet, upon heating, dropped to a minimum



Reduced dielectric constant (*a*) and conductivity (*b*) at 50 kHz measured for pristine C_{60} (curves *1*) and the pellet charged with NO after various lapses of time: 0 (*2*), 192 (*3*), 388 hours (*4*).

value at 230 K, as curve (*2*) in the figure shows, and with longer exposure, this minimum remained the same: (*3*) and (*4*).

The conductivity G of the pellet, in its pristine state, exhibited upon heating a peak at 170 K, and its dielectric constant ε' showed a step, at the same temperature T_p (curves *1* in the Figure). These relaxation features related to a glass transition, disappeared entirely after the sample was charged with NO at 30 bar and 200°C for 24 hours (curves *2–4* in the Figure, *b*). Meanwhile, the magnitude of the drop in $\Delta\varepsilon' = (\varepsilon' - \varepsilon'_0)$ that was induced by fcc-sc transition, reduced substantially.

DSC scan for a freshly NO charged sample shows a broad endothermic peak whose position shifted down 20 K, compared with that of pristine C_{60}.

3. Discussion

In low-temperature phase, the C_{60} molecules have two possible orientations and their difference in energy is very small and the fraction of molecules in the more stable orientation P is only about 60% near 260 K, increasing to about 84% near $T_g = 90$ K. Below T_g the reorientational jumps of molecules are frozen to creation an orientation glass. A Debye-like relaxational peak from this glass transition probed by dielectric method [10], was observed and confirms that there exists orientational disorder of C_{60} molecules in the sc phase, and these molecules adopt both H and P orientations following the usual thermal distribution.

In our case, solid C_{60} was stored in NO under high pressure and the gas molecules NO were found to diffuse into the octahedral interstitial sites in its fcc crystal lattice. The downfield shifts of the two minor peaks in its ^{13}C NMR MAS spectra were attributed to the Fermi-contact interaction between paramagnetic NO and the carbon atoms of nearest neighbour C_{60}. The shift in temperature of DSC peak for $(NO)_{0.1}C_{60}$, compared with that for pristine C_{60}, arises from the doping of these gas molecules, solely. Moreover, the dielectric spectrum in the Figure was seen to be virtually nearly identical with that of DSC. Furthermore, the spectral features of the pristine C_{60} at 170 K (curves *1* in the Figure), were smeared by the interstitial NO (curves *2–4* in the Figure).

In the sample of $(NO)_{0.1}C_{60}$, the interstitial NO may exert a negative pressure on the C_{60} lattice, in analogue to dilated lattice of $(CO)_xC_{60}$ by CO. Furthermore, the interstitial NO would change orientation of the nearest C_{60} molecules to P-orientation and decrease quantity of intrinsic permanent dipoles. This viewpoint is testified by our experimental data. We had calculated the fraction of P-orientation for the sample charged with NO from the drop of dielectric constants near T_c and found that a fraction of P-orientation reached to over 93%. Because the fraction of orientational defects is lower than 1/12, it is insufficient to induce a dipole on essentially all molecules, therefore too few dipoles (density n) to contribute to the dielectric response. That is the reason why the peak at $T_p = 170$ K disappeared after the sample charged with NO. Meanwhile, below T_c the fraction of P-orientation is larger than 11/12, so a comletely P-oriented phase had occured in $(NO)_{0.1}C_{60}$.

So, a phase with almost completely P-oriented molecules exists in solid C_{60} containing NO of molar ratio exceeding 0.10.

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