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Glass and phase transitions in solid C_{60} charged with Ar, Ne, He, and O_2

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C_{60} pellets, charged respectively with He, Ne, Ar, and O_2 under high pressure, have been studied with complex impedance spectroscopy. The latter two were found to depress the temperatures for both phase change (T_c) and glass transition (T_g), although in time shifts stayed almost constant in the Ar, but decreased in the O_2, case. The effective barriers for the glass transition were determined as 218 ± 15 in $Ar_{0.49}C_{60}$, and 182 ± 20 meV in$(O_2)_{0.5}C_{60}$. In contrast, neither He nor Ne had discernible influence on these materials parameters. These observations could be explained as follows. (1) Interstitial Ar causes a reduction in energy barrier and a weakening in the restorative force of the cage libration mode, thereby depressing T_c. (2) For $(O_2)_{0.5}C_{60}$, a coupling between the cage libration and the tumbling of an O_2 di-atomic molecule further weakens the restorative force, so that a larger temperature shift results. (3) Its tumbling motion makes O_2 more susceptible to the "paddle wheel" action of rotating C_{60}, and more easy to diffuse even under ambient conditions.

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C_{60} fullerite displays a first-order phase transition [1] from face-centered cubic (fcc) symmetry above $T_c = 260$ K, to simple cubic (sc) when the random rotations of C_{60} lock into specific orientations. In the ordered phase, these are two possible orientations obtained by rotating the molecules by either 38 or 98° around the unit cell diagonal [1]. Further freezing of re-orientational jumps lead to an orientational glass; dielectric measurements revealed revealed a Debye-like relaxational peak near 165 K at 10 kHz [2].

Gases doped interstitially offer the advantages of not altering the structure of the host lattice, yet significantly affecting the C_{60} interaction potential. In the case of argon, T_c is shifted by $\Delta T = -10$ K [3], whereas for oxygen $\Delta T = -20$ K [4,5]. Now, the glass transition is also highly sensitive to details of the potential, but its relation to gas intercalation has been little studied. We have therefore selected the van der Waals gases He, Ne and Ar as well as the diatomic gas O_2 as guest molecules, and correlated the phase and the glass transition temperatures with the potential barriers, as determined with complex impedance spectroscopy.

1. Experimental details

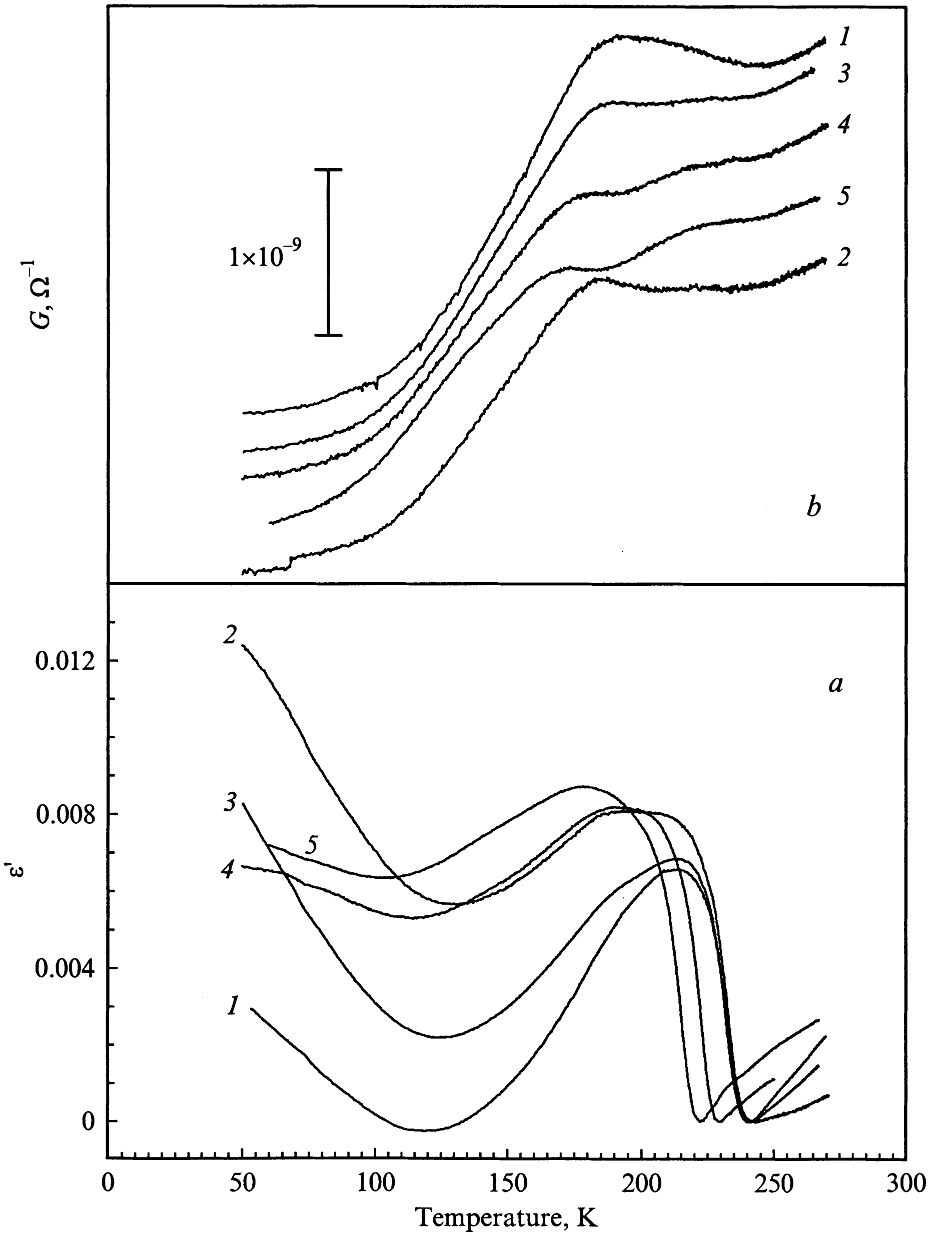
C_{60} of $3N$ purity was annealed at 510 K in dynamic vacuum for 60 h before being compacted uniaxially under 6.5 kbar in an evacuated mould for 15 min. Rigid pellets thus produced measured $6 \times 7 \times 0.7$ mm. One batch was charged with He at 0.115 kbar after storage for 3 days inside a steel vessel at room temperature, another with Ne at 0.12 kbar. The molar concentration (octahedral sites occupancy) as calculated from fractional mass increase was $x = 1.00 \pm 0.01$ for He, and $x = 0.62 \pm 0.01$ for Ne. A third batch was treated with Ar for 3 days at 300°C, the gas pressure reaching 0.16 kbar at that temperature, to reach $x = 0.49 \pm 0.01$, which remained constant for months at room temperature, even in vacuum, as indicated by weighing. The last batch of pellets was charged with 0.15–kbar O_2 for 7 days at room temperature, whence $x = 0.50 \pm 0.01$.

Silver films were evaporated onto the two large surfaces of each pellet. AC impedance was recorded via the three-terminal method, using an HP 4284A pricision multimeter under computer control, as the pellet was heated at the rate of $1\,\mathrm{K\,min^{-1}}$.

2. Results

In the Figure, panel a presents the reduced dielectric constant $\varepsilon' \equiv (\varepsilon - \varepsilon_0)/\varepsilon_0$ and panel shows the conductance G of a representative sample from each batch, ε_0 denoting the minimun value obtained of ε. The position of $\varepsilon = \varepsilon_0$ or $\varepsilon' = 0$ corresponds to the fcc-sc phase transition. For HeC_{60} and $Ne_{0.62}C_{60}$ (curves *2* and *3*), T_c was unchanged from the undoped case (curve *1*), but the intercalation of Ar (curve *4*) shifted it by -13 K, and ΔT remained the same after exposing the pellet to vacuum at room temperature up to 50 days (curve omitted for clarity). In $(O_2)_{0.5}C_{60}$ (curve *5*), there was a larger shift of -20 K, but ΔT decreased as the pellet spent longer time in vacuum. These indications are consistent with our previous observation [4] that, at room temperature, Ar does not diffuse out of C_{60} significantly, but O_2 does.

The curves show also a peak in conductivity and a step in dielectric constant, at almost the same temperature for each sample, but which increased with frequency ω of the applied field. This relaxational feature points to the glass transition, and its activation energy may be calculated from respective Arrhenius plots of $\log \omega$. Again, our data indicatae that charging with He or Ne did not shift T_g, but with Ar and O_2 T_g was depressed, and that the activation energy was virtually identical to that for undoped C_{60} in the first two cases, but much smaller for Ar and O_2 (see Table).



Reduced dielectric constant (*a*) and conductance (*b*) at 50 kHz, for (*1*) undoped C_{60}, (*2*) HeC_{60}, (*3*) $Ne_{0.62}C_{60}$, (*4*) $Ar_{0.49}C_{60}$ and (*5*) $(O_2)_{0.5}C_{60}$.

3. Discussion

In fcc solid C_{60}, the voids belong to geometrical categories: octahedral (radius 2.06 Å) and tetrahedral (1.13 Å); the latter lacks room for a rare-gas atom [6,7]. Ar atoms (1.54 Å) are charged into the octahedral sites under high pressure [8]. Neutron-diffraction reveals no modification in lattice symmetry, but an expansion in lattice parameter from 14.218 to 14.230 Å [3]. The resulting extra "free volume" enables the C_{60} molecules to rotate more easily. Indeed, $Ar_{0.49}C_{60}$ has an effective barrier determined as 218 ± 15 meV, some 70 meV lower than in pristine C_{60}. That explains our observation that its T_g is depressed. For T_c the suppression is usually attributed to negative "chemical pressure". However, $\Delta T = -13\,\mathrm{K}$ would invoke a pressure of 1.2 kbar [9], whereas the pressure actually applied reached merely 0.16 kbar. We therefore propose that the suppression

Effective barrier energy

Sample	Barrier, meV
Pristine C_{60}	291 ± 10
HeC_{60}	314 ± 30
$Ne_{0.62}C_{60}$	282 ± 30
$Ar_{0.49}C_{60}$	218 ± 15
$(O_2)_{0.5}C_{60}$	182 ± 20

is enhanced by the reduction in effective barrier for molecule re-orientation. The consequential weakening in the restorative force for the cage libration mode decreases T_c beyond what is expected from the negative pressure.

Being a di-atomic molecule, O_2 has additional degrees of freedom, in rotation and vibration. It executes a tumbling motion inside the octahedral void [6], with a frequency close to that of the cage libration mode [10], so the two may couple below T_c. This interaction will further weaken the restorative force in cage libration. Indeed, the largest $\Delta T = -20\,\mathrm{K}$ and the lowest effective barrier $= 182 \pm 20\,\mathrm{meV}$ have been determined for $(O_2)_{0.5}C_{60}$.

In molecular weight and radius, oxygen differs little from argon (32 *vs* 39; 1.40 Å *vs* 1.54 Å), but the former diffuses readily whereas the latter does not. Our explanation is as follows. The intercalation of a gas involves its passage through a channel of radius ~ 0.82 Å between adjacent octahedral sites [8]. The centre of each pentagonal face on C_{60} molecules being ~ 0.29 Å inside the surface defined by the molecular radius, as molecules rotate the channel size can increase to ~ 1.11 Å. This still does suffice for argon or oxygen to pass, but there is a further consideration. They are envisaged to undergo random-walk rotational diffusion uncorrelated with the motion of neighbours [1], and based on this picture, a "paddle wheel" model has been proposed for the intercalation of Ne [8]. For oxygen, its tumbling will accentuate the "paddling" and accounts for its fast diffusion at room temperature. This diffusivity has significant implications for practical applicability of fullerenes.

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