Superconductivity of doped Ar@C$_{60}$

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The synthesis of a mg amount of pure argon containing fullerene allowed the synthesis of the first endohedral superconductors with critical temperatures lower than expected, an indication of the strong influence of the argon atom on the C$_{60}$ cage.

The wealth of novel properties and functions produced by the capture of different atoms inside the fullerene cage has led to much interest in endohedral fullerenes. Endohedral C$_{60}$ compounds[1] are compounds with non-ionic-interacting elements such as nitrogen,[2] phosphorus[3] or noble gas atoms[4,5] and are inert. There is little charge transfer between the inserted atom and the cage, in marked contrast to metal endohedral fullerenes, for instance La- or Y-doped C$_{82}$.[6] While the study of these materials is appealing, the synthesis of endohedral fullerenes is generally very difficult because of low yield and difficult synthetic conditions,[7] including the use of high-pressure and high temperatures.[8]

The superconductivity of doped C$_{60}$ has been studied by changing the inter-cage distance through intercalation of various metals.[9,10] For the case of endohedral compounds, we present evidence of the important influence of the inserted atom on the superconductivity despite the fact that, traditionally, little change is expected for a *van der Waals* system. We chose to study Ar@C$_{60}$ because it can be obtained on a large scale in a HIP device.

The synthesis of Ar@C$_{60}$ is similar to that described previously (ref. 11): 2000 mg of [60]fullerene (>99.5%) was ground up together with 600 mg of potassium cyanide (*Warning: KCN is highly toxic; all manipulations must be done under appropriate conditions*) to obtain a finely powdered mixture. This was put in a "Hot Isostatic Pressure" vessel (Kobelco HHP100) with Ar gas as the pressure medium, at 650 °C and 400 MPa for 22 h. The resulting powder was ground in a mortar and extracted with toluene (the residual solid contains cyanides, careful manipulation and waste disposal must be ensured).

Multi-stage HPLC was employed with the use of a large preparative Cosmosil Buckyprep [3-(1-pyrenyl)propyl] column (28 × 250 mm), a UV-Vis detector, recycling, and toluene as eluent at a flow rate of 50 ml min^{-1}. The sample was dissolved in toluene and 24 ml was injected at a time. A five-time-recycling process was conducted for each injection. After recycling, unreacted C$_{60}$ eluting at 43.8 min was separated, the remainder was collected and re-injected. This procedure was repeated eight times to yield better than 98% pure Ar@C60 (Maldi-TOF, HPLC). By using this procedure we obtained more than 1 mg of pure Ar@C$_{60}$.

Comparison of the ^{13}C-NMR spectra for Ar@C$_{60}$ (143.38 ppm) and C$_{60}$ (143.21 ppm) indicates the slight effect of Ar on the electronic states of the C$_{60}$ cage. An argon atom inside C$_{60}$ causes a downfield shift of 0.17 ppm. The single resonance indicates that Ar@C$_{60}$ has, as expected, the same symmetry as C$_{60}$, *i.e.* I_h. In other endohedral fullerenes, Kr@C$_{60}$ and Xe@C$_{60}$, the resonance is shifted downfield by 0.39 ppm[11] and 0.96 ppm[12], respectively, due to the effect of the encapsulated atom on the C$_{60}$ cage. While UV-Vis spectroscopy did not show any differences between Ar@C$_{60}$ and pristine C$_{60}$, the IR and Raman spectra showed a complex behaviour with a blueshift for the frequencies lower than 600 cm^{-1} and a redshift for the higher frequencies. These shifts are quite small, 2 to 4 cm^{-1}; they are consistent with a change in the rigidity of the C$_{60}$ cage, this work is in progress.

Having established that pure Ar@C$_{60}$ was obtained, we explored possible superconductivity by doping it with potassium obtained by the thermal decomposition of KN$_3$.[13]

The temperature dependent magnetization of K$_3$Ar@C$_{60}$ under a field of H = 10 Oe, Fig. 1, shows a clear diamagnetic signal below 17.8 K which was ascribed to superconductivity. The K$_3$C$_{60}$ sample, prepared under the same conditions, showed a T_c of 19.2 K and is shown in the same figure. The hysteresis between the zero
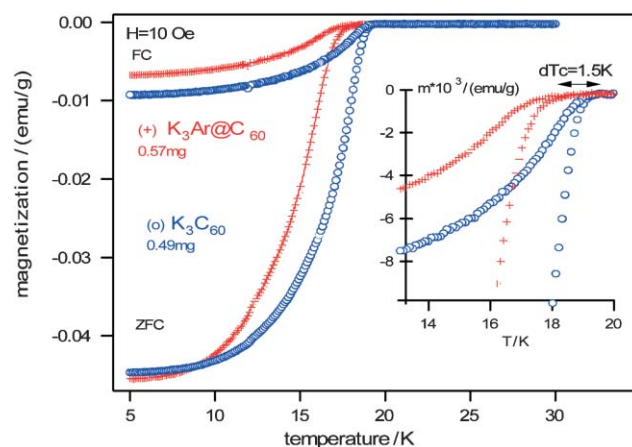
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Fig. 1 Temperature dependent magnetization of K$_3$Ar@C$_{60}$ and K$_3$C$_{60}$ in an applied field of 10 Oe.

field cooled and the field cooled data indicates type II super-conductivity. The zero field signal corresponds to 11% and 13% of perfect diamagnetism for $K_3Ar@C_{60}$ and K_3C_{60}, respectively.

We have also synthesized K_3C_{60} and $K_3Ar@C_{60}$ by using the standard reaction of C_{60} with potassium metal. The critical temperatures in this case were 17.5 K and 19.1 K for $K_3Ar@C_{60}$ and K_3C_{60}, respectively, and showed about 10% diamagnetism.

We also synthesized the Rb superconductors (by RbN_3 procedure) and we observed that the depression of the T_c for $Rb_3Ar@C_{60}$ compared with Rb_3C_{60} was 2.5 K (26.8 K and 29.3 K respectively). In relative values the decrease of the T_c is similar for the K and Rb doped compounds, this is about 8% of the T_c of the pristine C_{60} superconductors. This decrease was observed for all three experiments. The results indicate a rather pronounced influence of the argon atom on the superconductivity of these materials.

We measured X-ray powder diffraction data for C_{60}, $Ar@C_{60}$, K_3C_{60} and $K_3Ar@C_{60}$ at the SPring-8 synchrotron from 300 K to 100 K. Two sets of diffraction experiments, for two independent C_{60} and $Ar@C_{60}$ samples, were performed.

The peculiarities of the solid state structure and dynamics of C_{60} and related materials are well documented.[14] Rietveld[15] analysis allowed us to conclude that the solid state behaviour of $Ar@C_{60}$ is similar to that of C_{60}, that is, there is a rotational disorder at room temperature. The refined fractional occupancy for the Ar atom was 97.8%.

Interestingly, the refined unit cell parameters for C_{60} and $Ar@C_{60}$ were different. Silicon was used as internal standard[16] so the obtained results have enough accuracy to detect even small differences, Fig. 2. The $Ar@C_{60}$ unit cell parameter is 0.022 Å larger at room temperature but the decrease with lowering the temperature is more pronounced than that of pristine C_{60}. This striking result indicates the *influence of the inserted atom on the lattice parameter* and possibly on the cage dimension.

Rietveld analysis was not possible for the data of K_3C_{60} and $K_3Ar@C_{60}$ because of impurities, disorder and stacking faults common in these systems. However, analysis of the patterns indicates a lattice parameter 0.07 Å smaller for $K_3Ar@C_{60}$ comp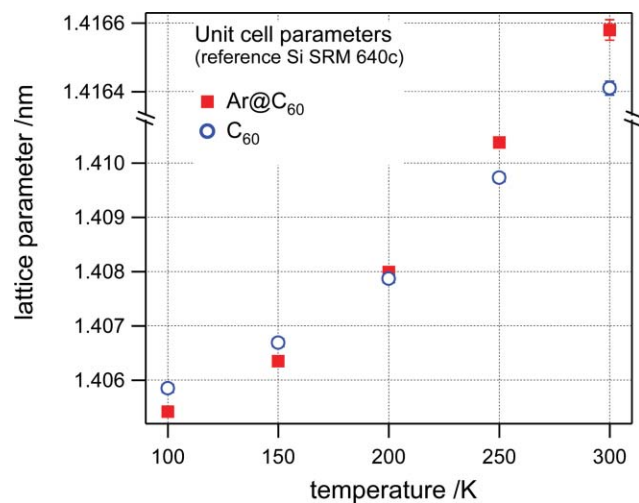ared to K_3C_{60}, at room temperature. This effect may be due to sample nonstoichiometry, inhomogeneities or possibly the effect of the inserted Ar atom on the lattice.

We suggest that the important T_c decrease for the endohedral superconductors is related to the influence of the inserted atom on the C_{60} cage and not to the presence of impurities.[17] In support of this is the fact that doping pristine C_{60} by the same procedure and at the same level (less than 1 mg and down to 0.15 mg samples) showed, reproducible, critical temperatures consistent with previous results.

There are two main factors which should be considered when discussing the critical temperatures for these compounds: (i) *phonon spectra distribution* and (ii) *density of states*. For (i), the endohedral fullerenes have slightly different phonon spectra by considering the mass effects and the influence of the rattling mode vibration. The influence of these effects on the superconductivity properties are difficult to estimate at this time but it should be rather small considering the small IR/RAMAN shifts we observed. For (ii), changes in the density of states must be considered. It is unlikely, in such a van der Waals system where no or little charge transfer occurs, that the electronic density states at the Fermi level are directly modified. However, a subtle change in the *inter-molecular interactions* triggered by the inserted atom should alter the band width. Note that only a small change in the unit cell is enough to affect the superconductivity.[18] We therefore propose that the changes in the critical temperatures observed for these compounds are related to indirect changes in the density of states together with, to a lesser extent, changes in the phonon spectra. Further work is required to determine the change in the superconductivity of endohedrals, particularly for larger atoms like krypton and xenon where this effect should be more pronounced. The possibility that indirect changes of the density of states at the Fermi level are induced by the inserted atoms suggests that an increase in the T_c of these materials is possible.
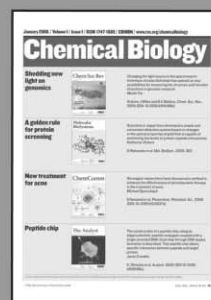
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Fig. 2 Unit cell parameters as a function of temperature for C_{60} and $Ar@C_{60}$.

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