Electron spin resonance of $N@C_{60}^{6-}$ in the fulleride salt Rb_6C_{60}

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Abstract. The use of $N@C_{60}$ as a spin probe is demonstrated in the ionic fulleride salt Rb_6C_{60}. The salt contains a few ppm of $N@C_{60}$ and was synthesised using a low temperature reaction. The electron spin resonance of $N@C_{60}^{6-}$ of this compound at 225 GHz (g=2 at 8.1 T) shows a small diamagnetic shift of 88±15 ppm with respect to pure $N@C_{60}$.

INTRODUCTION

N atoms encapsulated into fullerenes has a great potential for magnetic probes in Electron Spin Resonance (ESR) spectroscopy[1]. Since the N atoms are only weakly interacting with the surrounding cage, ESR lines are narrow. Recently, it has been shown that the endohedral N atom can be a sensitive indicator of molecular distortions[2]. In this paper we show that $N@C_{60}$ may be incorporated into fulleride salts. We successfully synthesised Rb_6C_{60} starting from dilute $N@C_{60}:C_{60}$. The observation of the $N@C_{60}^{6-}$ ESR proves that the endohedral compound survives ionization to the hexaion with the N atom remaining at the center of the cage.

EXPERIMENTAL

Endohedral $N@C_{60}$ was produced in an electric discharge tube following the method of Pietzak et al.[3]. The typical concentration of $N@C_{60}$ in C_{60} after purification is between 10^{-6} and 10^{-5} as measured by ESR at X band. During the discharge a nitrogen gas pressure of 1 mbar was maintained and typically a current of 0.2 mA was applied between electrodes placed about 10 cm apart. The tube is heated above 500 °C and the C_{60} powder placed at the bottom is continuously sublimated into the discharge. The endohedral $N@C_{60}$ is produced in the gas and is collected at a water cooled surface. C_{60} is heavily damaged at that part of the cathode where discharge is intense. However, damage to C_{60} is small at cooled surfaces a few centimeters away from the visible discharge and here most of the C_{60} is recovered after purification. We showed that it is not neccessary to collect the product at the cathode; similar N concentrations are obtained at other cooled surfaces. N ions were not implanted in significant amounts into C_{60} which has been condensed onto the surface before the discharge was turned on. This also shows that $N@C_{60}$ is predominantly formed in the gas.
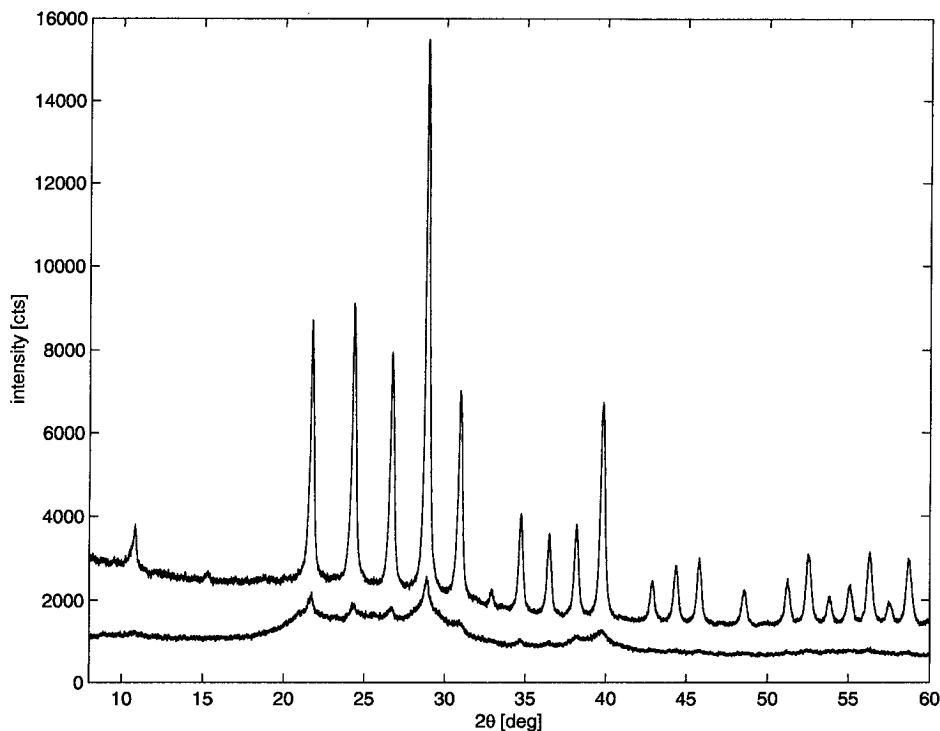
Figure 1. X-ray diffraction spectra of Rb_6C_{60} produced at low temperature. Lower trace: after synthesis and drying at 120 °C. Upper trace: after anneal at 300 °C.

Since N atoms escape the cage at elevated temperatures, a low temperature method was devised to produce the Rb_6C_{60} salt doped with $N@C_{60}$. 0.1 mmol of $N@C_{60}$ doped C_{60} was dissolved in 70 ml of toluene (purified by trap to trap distillation from liquid Na/K alloy). Stoichiometric amount of Rb was added to the solution in a reaction tube and the mixture was sealed in vacuum. The reaction was carried out at 55 °C with sonication for 1 hour. The solution became colorless after sedimentation of the black precipitate formed. The material was filtered in a glove box and dried in dynamic vacuum at 120 °C for 4 hours.

X ray diffraction verified that the stoichometry of the material was indeed Rb_6C_{60} (Figure 1). The spectra were recorded with a Huber G670 Image Plate Guinier camera and Cu $K\alpha 1$ radiation. The crystallinity of the as received material was poor, weak and broad diffraction lines of Rb_6C_{60} were sitting on an amorphous background. An overnight annealing at 300 ^{0}C dramatically improved crystallinity. Rietveld analysis proved that the stoichometry corresponded well to the chemical formula and no trace of a minority phase was present.

200

The electron spin resonance was observed in the poorly crystalline material at 225.00 GHz between 2 and 25 K. The spectra were taken with the superconducting magnet in the persistent mode and the millimeter wave Gunn diode oscillator locked to a quartz 100 MHz reference oscillator. To sweep the field a current was added to the modulation coil wound around the sample. Although the pure $N@C_{60}$ and $N@C_{60}^{6-}$ spectra were not taken simultaneously, the magnet remained in the persistent mode while the samples were exchanged to ensure precision in determining the g-factor.

RESULTS AND DISCUSSION

Figure 2 shows a spectrum at 10 K of $N@C_{60}^{6-}$ in the fulleride salt Rb_6C_{60} compared to $N@C_{60}:C_{60}$. As expected, the N hyperfine splittings of the neutral and charged systems are equal (0.56 mT) within the experimental accuracy of a few %. The intrinsic linewidths of the pure system are very narrow and the ESR is distorted by saturation at 10 K in spite of a mm wave power less than a milliwatt and that there is no cavity. Under the same conditions the $N@C_{60}^{6-}$ ESR in Rb_6C_{60} is not saturated. The N lines of the doped Rb_6C_{60} system are relatively broad, about 0.2 mT and independent of temperature. The ESR of the N atom in the hexaion is slightly shifted to higher fields by 0.7 mT at 8 T thus the relative shift is $\Delta B/B_0 = 88 \pm 15$ ppm with
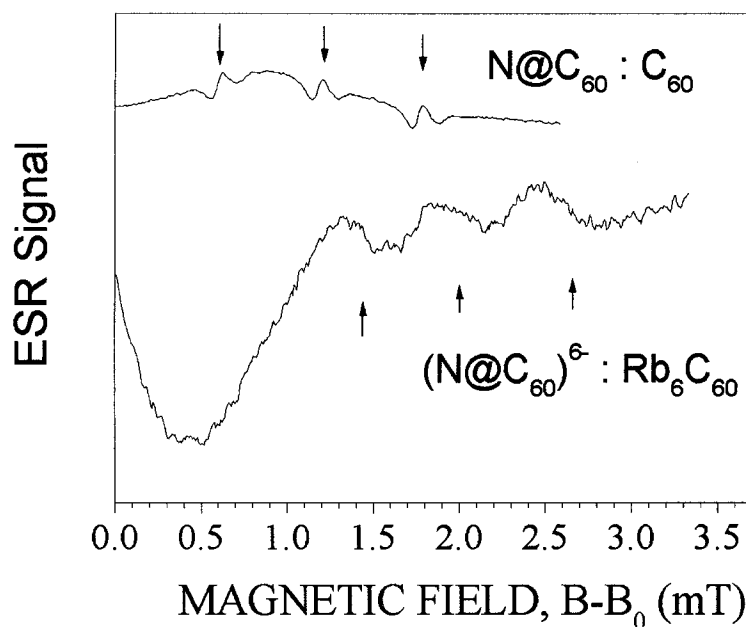

FIGURE 2. Comparison of the ESR spectra of $N@C_{60}$ and $N@C_{60}^{6-}$ at temperature of 10 K and exciting frequency 225 GHz. $B_0=8.07$ T.

201

respect to the neutral $N@C_{60}$. This corresponds to a diamagnetic shielding of the external magnetic field at the N atom by the sixfold charged cage with respect to the shielding due to the neutral cage. The temperature independent linewidth is explained by dipolar hyperfine coupling of the S=3/2 nitrogen electrons to ^{85}Rb and ^{87}Rb nuclei. We find for the second moment of the linewidth $M_2 = 0.22$ mT using the Van Vleck formula and the known structure[4] of Rb_6C_{60}. The 24 first Rb neighbours are responsible for most of the linewidth.

CONCLUSIONS

Since N atoms encapsulated in neutral C_{60} cages and in C_{60}^{6-} fulleride hexaions are stable and remain at the center of the fullerene molecule it is almost certain that $N@C_{60}^{n-}$ is stable in solids for all n between 0 and 6. Thus N encapsulated C_{60} may be an attractive ESR probe in both neutral and ionic fullerenes to measure distortions, molecular motion and internal fields. For example it may be interesting to study the A_4C_{60} compounds which are close to a metallic state. In paramagnetic compounds, like A_3C_{60} superconductors in the normal state, interaction of the S=3/2 N spin with the electrons on the cage (or with conduction electrons) is expected to be strong and it is unlikely that the ESR of the N atom is observable.

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