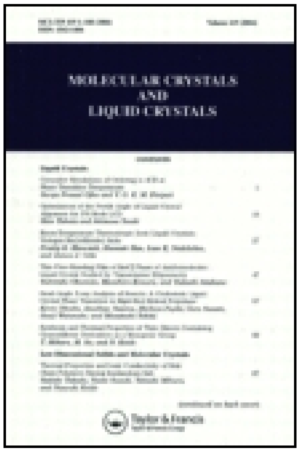

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Alkali Metal - Benzene- Fullerene Ternary Compounds

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$A_x(C_6H_6)_yC_{60}$ (with A = K, Rb and $3<x<6$, $0.5<y<3$) ternary compounds have been prepared. Their structure presents some differences with original A_xC_{60} compounds. Benzene effect on the transition temperature of superconducting phases was investigated by magnetic studies. The most interesting result is that intercalation of C_6H_6 into non superconducting A_6C_{60} led to a superconducting compound.

Keywords: fullerenes; alkali metal; benzene; superconductivity

INTRODUCTION

Alkali metal-doped fullerene phases A_xC_{60} (A = K, Rb, Cs) with x = 3, 4 and 6 exhibiting different crystal structures have been studied in detail. Superconductivity in fcc A_3C_{60} with relatively high transition temperatures from 18 to 40 K has been reported[1-2]. The T_c transition temperature increases with the lattice parameter, provided the symmetry is not changed[1], as it was often observed on various superconducting families such as Chevrel phases. It was therefore tempting to insert species in the structure of A_3C_{60} *without changing* crystalline structure. Then, as it has been shown previously[3], intercalation of ammonia into Na_2CsC_{60} increases T_c from 10.5

to 29.5K. Here are the first results on benzene intercalation in K_xC_{60} and Rb_xC_{60} compounds with x = 3, 4 and 6, and its effect on the superconducting T_C. This molecule has been chosen for its size and its good reactivity towards alkali metals.

EXPERIMENTAL

We used a vapour transport technique for producing A_xC_{60} phases. All the reactions are monitored in pyrex tubes sealed under vacuum. A weighted amount of pure C_{60} (100 mg) is treated with a large excess of alkali metal at 225°C during 10 days. The A_6C_{60} saturation doped compounds obtained are then diluted with C_{60} to give the desired x, and heated at 220–350°C for several days. A_xC_{60} are then immersed in an excess of benzene in a dry box during a few days at ambient temperature. The benzene excess is evacuated by evaporation under argon atmosphere. The $A_x(C_6H_6)_yC_{60}$ ternary compounds synthesized have y/x ratios from 0.25 to 1 and 0.02 to 0.33 for A = K and Rb respectively. They are calculated from the mass uptake of final products.

The magnetic susceptibility was measured in alternating fields at a driving frequency of 337 Hz. The typical amplitude of the modulation field was 1 Oe. Typical sample mass value was between 5 and 20 mg. The magnetization in static field between 0 and 8 T was measured with a SQUID susceptometer. Electron spin resonance (ESR) was conducted at 9.5 GHz.

RESULTS

As expected, benzene intercalation changed the structure of A_xC_{60} binary compounds. However, this evolution is more complex than a simple increase of the cell parameter (Fig.1). No C_{60} was observed by X-ray diffraction measurements in the final products, as already evidenced by the absence of red coloration of the liquid benzene excess phase during the reaction. Moreover, $A_x(C_6H_6)_yC_{60}$ compounds present patterns different from that of A_3C_{60} : additional reflections were observed whereas some A_3C_{60} reflections disappeared. For the $K_6(C_6H_6)_{1.5}C_{60}$ compound, all the reflections can be indexed on the basis of a face centered orthorhombic unit cell with a = 39.90 Å, b = 23.03 Å, c = 31.56 Å. In this structure, it is possible that benzene rings-potassium atoms interaction is similar to that in potassium-benzene-graphite intercalation compounds[4], where the benzene rings are canted against the graphene planes, and potassium atoms are in interaction with both benzene rings and graphene layers. For example, cations may be in interaction with a benzene ring over an hexagon (or a pentagon) of C_{60}.

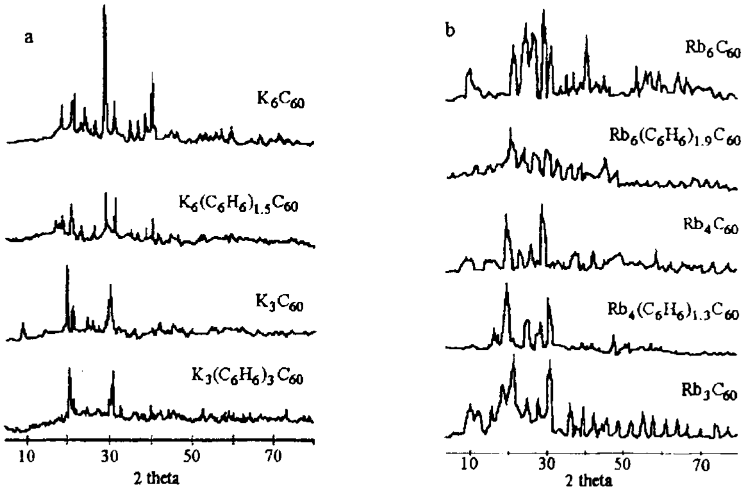

FIGURE 1 X-ray diffraction patterns with Cu K_α radiation.

The magnetic susceptibility was measured in alternating fields between 4 and 50K. No thermal hysteresis is observed while cooling or heating the samples. Benzene intercalated compounds exhibit a superconducting characteristic behaviour (Figures 2 and 3a). For $K_6(C_6H_6)_{1.5}C_{60}$, the superconducting transition is between 16.8 and 17.2K. Note that the T_c for K_3C_{60} is about 18K (Fig. 2b). The magnetization in static field between 0 and 8 T was also measured for the same sample (Fig. 3b). Below 0.2 T at 4K clear diamagnetism is observed. By increasing the field up to 8 T the magnetization becomes positive showing existence of paramagnetism. The paramagnetic contribution flattens at 8 T but does not saturate. It should be associated to localized magnetic moments with low spin values. Then, the magnetic moment value at 4K is 2600 emu.mol^{-1}. That leads to an average value close to 0.5

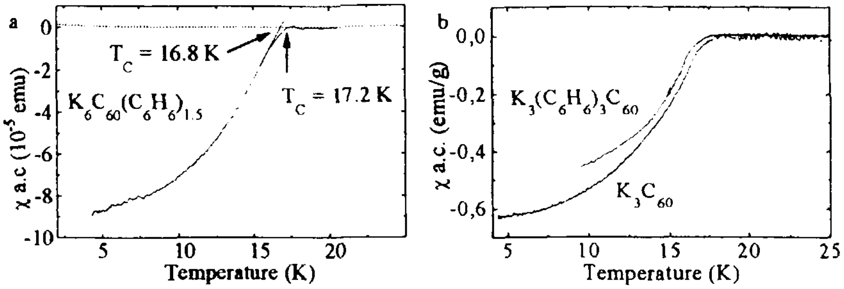

FIGURE 2 Real part suceptibilities of $K_x(C_6H_6)_yC_{60}$ compounds.

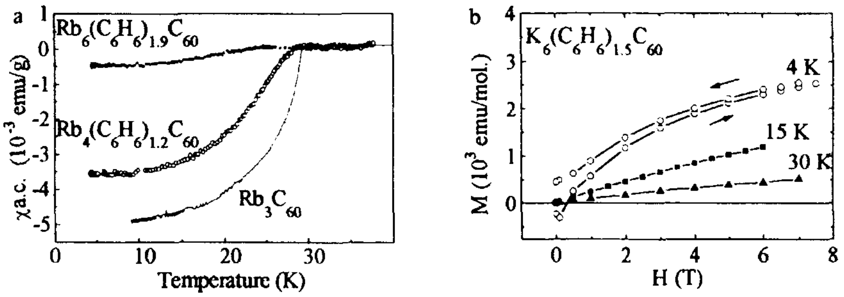

FIGURE 3 Susceptibility real part (a) and magnetization versus field (b).

Bohr magneton per C_{60} molecule. While decreasing the field, irreversibility of the isothermal magnetization is observed between 4 and 15K in agreement with superconductivity in the presence of vortex pinning. For each isotherm at a given field, the average value of the magnetization obtained while sweeping the field up and down is plotted as a function of H/T (Fig. 4a). The averaged magnetization gives then a good approximation of the magnetic part. Figure 4a shows that all isotherms, except that obtained at 4K, lie on the same curve. It shows that the positive contribution should be a sum of Brillouin functions. ESR measurements were carried out between 300 and 12K. At these two temperatures, 13 and 3 G width symmetrical signals, respectively, are monitored at g = 2 (Fig. 4b). The g factor slightly changes from 2.0016 to 2.002 at 12K. We can therefore assume that there is no anisotropy field experienced by the spins. The narrowest line has the highest amplitude at low temperature but its integrated intensity corresponds to only 10-15 % of the whole absorbed intensity. For both lines, intensity increases as temperature decreases, indicating localized spins in agreement with the magnetization data. The magnetization at 4K gives an average spin concentration of one spin for two C_{60}'s. It is 15 times the values reported for K_3C_{60} and Rb_3C_{60}[5] and 5 times that of supercon-ducting Cs_xC_{60} phase[6]. In order to calculate the superconducting volume, it is necessary to compare the paramagnetic susceptibility part to the total sus-ceptibility. The positive part has a Curie like behaviour (from ESR). The Curie constant of $C \approx 3.10^{-6}$emu.K is estimated from the slope of the magnetization at 30K (well above T_c). The corresponding Curie law (Fig. 2a : discontinuous line) shows that the total susceptibility is mainly due to the diamagnetic part. The volumic mass 1 g/cm^3 (1.9 g/cm^3 for K_3C_{60}), calculated from the orthorhombic cell parameters, leads to a shielding volume fraction of 9-10 %.

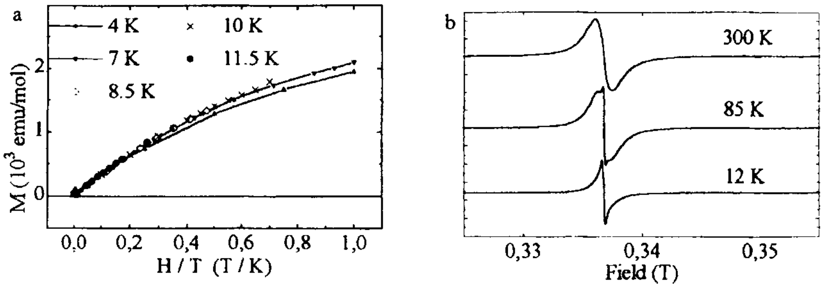

FIGURE 4 Magnetization versus H/T parameter (a) and ESR signals (b) for $K_6(C_6H_6)_{1.5}C_{60}$ compound.

DISCUSSION

Although benzene intercalation in the binary x = 6 compounds does not raise the transition temperature of the A_3C_{60} phases, we can point out that this new family of ternary intercalation compounds exhibits interesting properties like superconductivity and magnetism due to charge transfer. Diffraction data and relatively important shielding fraction, for example 9 % in the case of $K_6(C_6H_6)_{1.5}C_{60}$, are not consistent with the presence of A_3C_{60}. Given the supposed lattice cell parameters, it can be surprising that the transition temperature of the $A_6(C_6H_6)_yC_{60}$ compounds is only 2 and 5K lower than that of K_3C_{60} and Rb_3C_{60}, respectively. Although superconductivity mostly occurred in cubic fullerides, the list of superconducting compounds with lower crystalline symmetry is actually growing. There are at least three examples : superconductivity was reported at 6 and 8K respectively in $Yb_{2.75}C_{60}$[7] and Sm_3C_{60}[8] rare earth fullerides, which have an orthorhombic believed structure as well as $K_3NH_3C_{60}$[9] ($T_c = 28K$ under 15 Gpa pressure). This indicates that cubic symmetry is not an essential ingredient for superconductivity in C_{60} intercalation compounds. Yildirim et al.[10] demonstrated recently that, provided a cubic symmetry, the superconductivity is strongly suppressed in Pa3 and Fm3m phases when the average C_{60} molecular valence, x, deviates from 3. The strong paramagnetic contribution observed in $K_6(C_6H_6)_{1.5}C_{60}$ suggests that a charge transfer occurs between the different species, but it is still not possible to have an idea of the molecular valence of this compound.

To conclude, we have prepared new alkali-C_{60} compounds containing C_6H_6. Some of insulator binary compounds became superconductor with benzene intercalation. In all cases, the critical temperature of the superconducting transition is not enhanced with respect to that of A_3C_{60}. Further studies, including diffraction data refinement measurements are under way.Iit would be also interesting to determine the C_{60} molecular valence of each compound.

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