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Metallic behavior in the potassium-doped fullerene-cubane copolymer

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C_{60} and C_{70} form with cubane (C_8H_8) molecules rotor-stator phases in which the fullerenes are rotating and the cubanes are static. Heating the rotor-stator phase up to 470 K a fulleride copolymer, poly ($C_{60}C_8H_8$), is obtained. Here, we study using microwave conductivity measurements, electron-spin resonance, and superconducting quantum interference device magnetometry the effect of potassium intercalation on the electric and magnetic properties of poly ($C_{60}C_8H_8$). The resulting $K_2C_{60}C_8H_8$ copolymer is metallic for $T>200$ K in contrast to the insulating pristine poly ($C_{60}C_8H_8$) copolymer. At lower temperatures, a disorder-driven Anderson localization of the electrons takes place and the ground state is a magnetic insulator.

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Soon after the discovery of $(C_{60})_x$ the first fulleride polymer,[1] obtained by photopolymerization, AC_{60} (A=K,Rb, Cs) alkali-doped fulleride salts were found to polymerize spontaneously.[2] Both $(C_{60})_x$ and AC_{60} are one-dimensional polymers with a [2+2] cyclo-adduct bonds in which four carbon atoms for each C_{60} molecule are involved.[3] For polymers of C_{60}^{n-} anions with $n \geq 3$, e.g., in linear Na_2RbC_{60} and two-dimensional (2D) Na_4C_{60} (Refs. 4 and 5) single-bond configurations are more stable.[3] Two-dimensional polymeric sheets were observed in the alkaline-earth intercalated fulleride Mg_5C_{60} (Ref. 6) and were also obtained from pure fullerite by applying pressures of a few GPa.[7] Coexistence of single and double interfullerene bonds was found in the 2D polymer Li_4C_{60}.[8,9]

The small bandwidth and the large on-site Coulomb repulsion make electron-electron correlations important in determining the ground state of the alkali-intercalated fulleride polymers. The linear polymers KC_{60} and Na_2RbC_{60} have metallic ground states while RbC_{60} and CsC_{60} have a metal-insulator transition to an antiferromagnetic spin-density-wave ground state.[10,11] The 2D polymer Na_4C_{60} is a strongly correlated metal[5] while Li_4C_{60} is a nonmagnetic insulator.[8]

In this Brief Report, we deal with a three-dimensional alkali-doped copolymer of C_{60} and cubane, $K_2C_{60}C_8H_8$ and show that it is a strongly correlated metal. Recently, it was found that C_{60} or C_{70} crystals intercalated with cubane (C_8H_8) molecules are rotor-stator molecular co-crystals in which the fullerenes rotate while the cubanes are static.[12] The cubane molecule consists of eight carbon atoms sitting at the vertexes of a regular cube and eight C-H bonds directed outward along the body diagonal. At low temperatures, there is an orientational-ordering phase transition where the fullerene rotation stops, at 140 and 150 K for C_{60} and C_{70}, respectively.

The fullerene-cubane co-crystals show an interesting behavior at higher temperatures also. For $T>470$ K, the cubane molecules isomerize into a more stable configuration. This induces a solid-state reaction with the fullerene molecules which results in the formation of a copolymer. In this polymer the two constitutional units C_8H_8 and C_{60} are alternating. A recent study of the vibrational properties[13] showed that interfullerene bonds are absent in the copolymer and indicated dihydropentalene as the most probable isomeric form of the C_8H_8 molecules. The detailed atomic structure of poly ($C_{60}C_8H_8$) copolymer has not been determined. The low-resolution region of its powder pattern can be well described with the fcc structure of the unpolymerized $C_{60} \cdot C_8H_8$.

The electronic structure of fullerides can be tuned by alkali intercalation. This motivated us to intercalate with K the copolymer and study the properties of the resulting alkali-fulleride-cubane copolymer, $K_2C_{60}C_8H_8$. Intercalation of the cubic rotor-stator phase directly is not possible as the solid-state reaction is inefficient below the polymerization temperature. According to x-ray diffraction, potassium intercalation does not modify the structure of the copolymer apart from a minor lattice constant change due to the insertion of the K atoms (from 14.8 to 14.9 Å). The electron-spin-resonance (ESR) study reveals, however, a small deviation from the cubic symmetry. We find from microwave conductivity, ESR and superconducting quantum interference device (SQUID) magnetometry measurements that pristine poly ($C_{60}C_8H_8$) is insulating, but $K_2C_{60}C_8H_8$ has a metallic behavior for $T>200$ K. At lower temperatures, a disorder-driven Anderson localization of the electrons leads to an insulating ground state.

The rotor-stator material $C_{60} \cdot C_8H_8$ was prepared from toluene solutions of fullerenes and cubane by evaporating the solvent as described previously.[12] To polymerize the sample, a 36 h long heat treatment was performed at 473 K. Poly ($C_{60}C_8H_8$) was then reacted with stoichiometric amount of K in a steel vessel heated inside a dry box. The reaction mixture was heated at 523 K for two weeks with one intermediate regrinding for homogenization. Infrared spectroscopy and x-ray diffraction measurements were performed after the preparation. The peak in the infrared spectrum of C_{60} derivatives, whose position is the most sensitive to charge transfer and polymerization, is the one derived from the highest frequency T_{1u} mode. This mode is split in poly ($C_{60}C_8H_8$) with the main component at 1424 cm^{-1}.[13] In $K_2C_{60}C_8H_8$ this peak can be found at 1362 cm^{-1}, indicating a charge transfer from the K atoms to the C_{60}'s.[14,15] The x-ray diffraction measurements showed that the K^+ ions occupy the sites related to the tetrahedral ones in the pristine cubic rotor-stator material.

Static susceptibility was measured by a Quantum Design MPMS-5S SQUID magnetometer between 5 and 350 K on 63 mg of $K_2C_{60}C_8H_8$ powder sealed under He atmosphere. Microwave conductivity was measured by a cavity perturbation technique[16,17] on 10 mg of $K_2C_{60}C_8H_8$ mixed in a 1:1 ratio with Mn:MgO powder and sealed under 200 mbar He in a quartz tube. The microwave cavity operates at 10 GHz in the TE011 mode and is kept at RT while the sample temperature is varied between 130 and 400 K. The quality factor of the unloaded cavity was about 15000. The insertion of the sample lowered this value to 13000 at RT. The characteristic grain dimension was much smaller than the microwave penetration depth which is about 100 microns with a resistivity of about 1 mΩ cm of the fulleride metals.[18] In this limit, the microwave losses in the sample are directly proportional to the sample conductivity. Microwave conductivity in fulleride polymers is about equal to dc conductivity as the plasma edge is typically about 1 eV (250 THz).[19] ESR was measured on the same sample used for the microwave conductivity measurements. Mn:MgO (with a Mn concentration of 1.5 ppm) was the intensity and g-factor reference. At 9 GHz, the spectra were obtained with a commercial Bruker Elexsys E500 spectrometer operating between 130 and 330 K. ESR spectra at 225 GHz (which corresponds to 8.1 T for g factor equal to two) were collected in the 4–300 K temperature range with a home built spectrometer.

We first discuss the electric and magnetic properties of the pristine fullerene-cubane copolymer as a reference material. The absence of any measurable losses induced by poly $(C_{60}C_8H_8)$ powder in the microwave cavity indicates that the sample has a low conductivity.

The Curie-like temperature dependence of the spin susceptibility (not shown here) confirms that this polymer is an insulator. The sample has an ESR absorption line which corresponds to a spin concentration of about 0.5 percent per C_{60} molecule assuming $S=1/2$ spins. We attribute these paramagnetic centers to localized defects in the polymeric structure. The full width at half maximum linewidth is mainly due to the dipole-dipole interaction as confirmed by the nearly temperature-independent value of 0.15 mT (see Fig. 1) which is in good agreement with the value of 0.2 mT calculated from the Van Vleck formula[20] for spins localized on the C_{60} molecules.

The effect of potassium doping poly $(C_{60}C_8H_8)$ is evident in both microwave conductivity and magnetic measurements. As shown in Fig. 2, the temperature dependence of the microwave conductivity of the $K_2C_{60}C_8H_8$ polymer is characterized by a broad maximum at about 400 K. At higher temperatures, the conductivity decreases linearly with T as in metals in which the electron-phonon coupling is the main relaxation mechanism. At lower temperatures the behavior is activated-like. For $T<250$ K, the conductivity of the sample is too low to induce measurable losses.

In Fig. 3 the temperature dependence of the static susceptibility measured by SQUID and 9 GHz ESR is shown. The absolute values obtained by the two different techniques agree within experimental precision. For $T<200$ K a gradual change from a Pauli to a Curie-like behavior is found with the lowering of the temperature. The Pauli contribution to the susceptibility, $\chi_P=8\times10^{-4}$ emu/mole, measured for $T>200$ K is large. It is comparable to that of orthorhombic KC_{60} (Ref. 21) and cubic K_3C_{60} (Ref. 19) which are well-known strongly correlated fulleride metals. The high value of χ_P indicates a large electron-electron correlation enhancement with respect to the free-electron susceptibility. In a free-electron model, the measured susceptibility would correspond to a Fermi temperature of 400 K only, in contradiction with the observed temperature independence. Below 40 K, the susceptibility rises rapidly with decreasing temperature. At the lowest temperatures, it corresponds to about 10 percent of C_{60} having an $S=1/2$ spin.

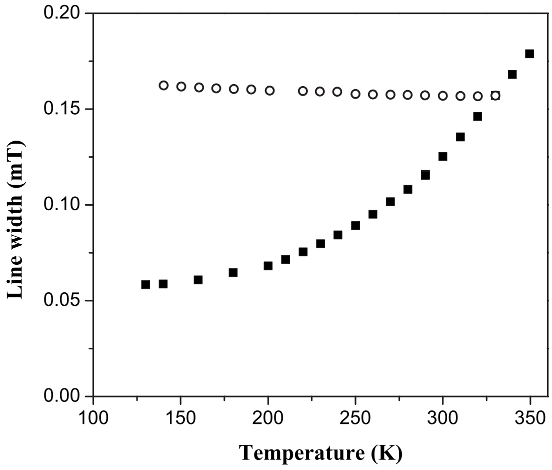

FIG. 1. Temperature dependence of the 9 GHz ESR linewidth of pristine poly $(C_{60}C_8H_8)$ (circles) and $K_2C_{60}C_8H_8$ (squares) polymers.

The intensity of the 9 GHz RT ESR signal of $K_2C_{60}C_8H_8$ is two orders of magnitude higher than in the pristine polymer confirming the charge transfer from K to the C_{60} molecules. The ESR linewidth increases with temperature from 0.05 mT at 100 K to 0.18 mT at 350 K (Fig. 1). For temperatures higher than 300 K, the increase is linear with T as

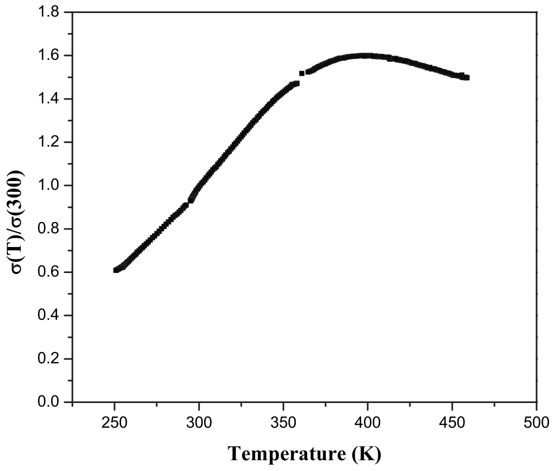

FIG. 2. Temperature dependence of the microwave conductivity, $\sigma(T)$, of $K_2C_{60}C_8H_8$ normalized to the RT value. At 400 K the conductivity changes reflect a transition from a metal to a semiconducting behavior.

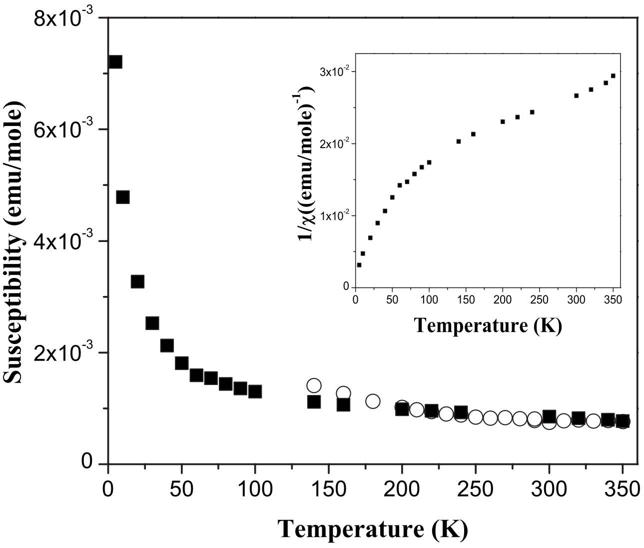

FIG. 3. Temperature dependence of the static susceptibility of $K_2C_{60}C_8H_8$ measured by SQUID (squares) and 9 GHz ESR (circles). Inset: temperature dependence of the inverse of the susceptibility. Note the non-Curie-Weiss behavior.

in metals in which the main spin-relaxation mechanism is due to the electron-phonon coupling.[22] For $T<320$ K, the linewidth is smaller than in the pristine polymer. The dipole-dipole interaction effective in the pristine polymer is narrowed in the intercalated material by the diffusion of the conducting electrons.

The 225 GHz ESR spectrum of $K_2C_{60}C_8H_8$, shown in Fig. 4, is a characteristic three-axial g-factor anisotropy powder spectrum with three singularities ($g_1=2.00464$, $g_2=2.00462$, $g_3=2.0044$) at all temperatures. The narrowness of the intrinsic linewidth excludes that the material consists of segregated phases like observed in other alkali-doped fulleride systems as KC_{60} (Ref. 23) and Na_2C_{60}.[24] The presence of more phases would result in a splitting or inhomogeneous broadening of the high-frequency ESR absorption line. The g-factor anisotropy indicates the presence of well-defined crystallites with dimensions comparable to the spin-diffusion length, typically 200 nm in conducting fullerenes.[19] The g-factor anisotropy is very small and the deviation from the cubic structure is too small to be detected by x-ray diffraction.

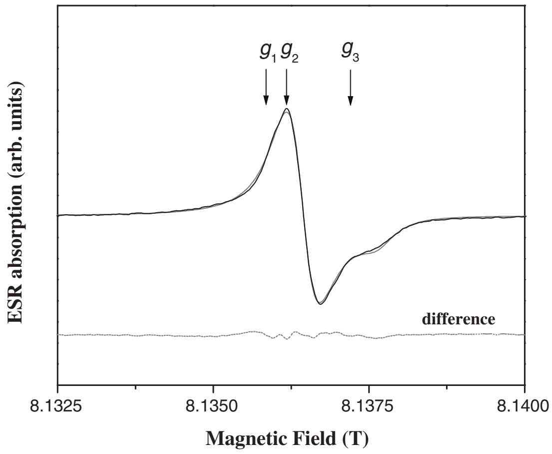

FIG. 4. 225 GHz ESR spectrum of $K_2C_{60}C_8H_8$ measured at 120 K. The fit (gray line) assumes a three-axis g-factor anisotropy with g_1, g_2, and g_3 given in the text. The difference between the fitted and the measured spectrum is also shown.

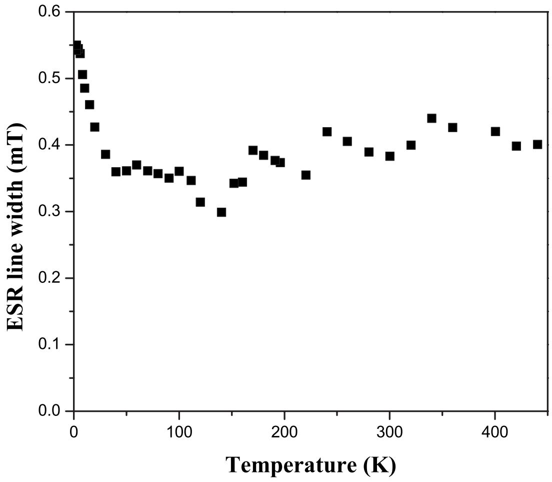

FIG. 5. Temperature dependence of the 225 GHz ESR linewidth. Note the line broadening at temperatures below about 40 K.

As shown in Fig. 5, between 40 and 5 K the intrinsic linewidth extracted from the fit of the high-field ESR powder spectra increases from 0.35 to 0.55 mT at 5 K with lowering of the temperature.

As mentioned above, both susceptibility and microwave conductivity show metallic behavior in the intercalated copolymer. The susceptibility has a Pauli-like behavior for $T>200$ K. Conductivity shows the presence of delocalized conducting electrons in the same temperature range but is metallic for $T>400$ K only. The gradual transition from a metal to an insulator cannot be attributed to the development of a spin gap at low temperatures. In that case, the conduction-electron magnetization would decrease exponentially at temperatures below E_g/k_B, where E_g is the value of the gap and k_B is the Boltzmann constant. In $K_2C_{60}C_8H_8$, the decrease in the conductivity with temperature is accompanied by an increase in the spin magnetization down to the lowest temperature (5 K). The Mott-Hubbard transition usually has a well-defined transition temperature and the ground state is magnetically ordered, which is not observed here. For these reasons, we suggest that $K_2C_{60}C_8H_8$ is an Anderson-localized system[25,26] similar to the Mg_5C_{60} fulleride polymer.[6] In these systems, the structural disorder induces a mobility edge, E_C, in the electron band above the Fermi level. At temperatures higher than E_C/k_B, electrons thermally excited above the mobility edge contribute to the conductivity. On the other hand, for temperatures lower than this threshold value, electrons and spins are localized at disordered positions.

In disordered materials the size of the spatial regions in which the conducting electrons diffuse increases with temperature. At low temperatures the electrons diffuse in small islands embedded in an insulating matrix. Since only these conducting islands contribute to the ESR, the susceptibility appears metallic. On the other hand, in the same temperature range, the conductivity is dominated by electron hopping between the islands and is therefore activated. At higher temperatures an interconnected pattern of metallic domains forms and both the conductivity and ESR appear metallic. The increase in the ESR linewidth at 225 GHz for $T < 40$ K may be a signature of growing antiferromagnetic interactions between the localized spins. A magnetically ordered ground state is not yet established at 5 K.

$K_2C_{60}C_8H_8$ fulleride copolymer has a metallic electronic structure with an electron-electron interaction enhanced temperature-independent susceptibility above about 200 K. The conductivity is more sensitive to the morphology and disorder and is metallic above 400 K only. For lower temperatures, microwave conductivity and ESR measurements show a gradual transition to a paramagnetic insulating state, which we attribute to Anderson localization driven by the high degree of disorder in the crystalline structure.

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