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Metallic conductivity and metal-insulator transition in $(A\mathrm{C}_{60})_n$ (A=K, Rb, and Cs) linear polymer fullerides

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Magnetic spin susceptibility and optical conductivity from 1 to 100 meV and at 9 GHz are presented for the recently discovered alkali-metal fulleride linear polymers, $(A\mathrm{C}_{60})_n$ (A=K, Rb, and Cs). We find that $(\mathrm{KC}_{60})_n$ is a metal with an enhanced Pauli susceptibility and a low-frequency conductivity decreasing with increasing temperature. $(\mathrm{RbC}_{60})_n$ and $(\mathrm{CsC}_{60})_n$ are also conducting at high temperatures but have a metal-insulator transition at 50 and 40 K, respectively. The data are suggestive of a quasi-one-dimensional instability towards a condensed spin-density-wave state.

Alkali-metal fulleride linear polymers, $(A\mathrm{C}_{60})_n$ with A=K, Rb, and Cs are members[1–3] of the already rich family of C_{60} derivatives. Like in iodine-doped polyacetylene the polymer chains are charged and there is one electron per C_{60} forming an unfilled band. The $(A\mathrm{C}_{60})_n$ polymers are formed spontaneously below 400 K from the monomer $A\mathrm{C}_{60}$ salts. The crystal structure[1,2,4] of the polymer suggests a strongly anisotropic electronic structure. Along the chains the center-to-center distance between C_{60} ions is short, 9.1 Å, and two pairs of nearest-neighbor carbon atoms form the interfulleride covalent bonds. In the other directions the separation is 10 Å, i.e., it remains about the same as in the usual monomer compounds. Chauvet *et al.* suggested[4] from magnetic measurements that $(\mathrm{RbC}_{60})_n$ is a quasi-one-dimensional (1D) conductor with a spin-density wave (SDW) ground state, developing at about 50 K. Little is known about the electrodynamic response of the fulleride polymers. Mid-infrared (MIR) optical studies on $(\mathrm{RbC}_{60})_n$ (Refs. 5–7) and on $(\mathrm{KC}_{60})_n$ (Ref. 7) indicated a metallic behavior at ambient temperature.

In this paper, we present data on the frequency-dependent conductivity and on the magnetic spin susceptibility of $(A\mathrm{C}_{60})_n$ polymers with A=K, Rb, and Cs. All three materials appear to be conducting at ambient temperature but with an unusually strong frequency dependence in the far infrared (FIR). $(\mathrm{KC}_{60})_n$ is a poor metal with a slowly decreasing low-frequency conductivity from 4 K up to the depolymerization temperature of 400 K. $(\mathrm{RbC}_{60})_n$ and $(\mathrm{CsC}_{60})_n$ are also conductors at ambient temperatures but in contrast to $(\mathrm{KC}_{60})_n$ display metal-insulator transitions at 50 and 40 K, respectively. At the lowest temperatures, the optical conductivity is depressed below 15 and 30 meV, indicating a vanishing density of states (DOS) at the Fermi level. Thus, although they are isostructural,[1] the electronic properties of the three polymers are widely different. Small changes in the interchain separation correlate with a decrease of the dimensionality in the order of K, Rb, and Cs. We argue that the K polymer is an anisotropic, but not quasi-1D, strongly correlated metal while the Rb and Cs polymers are quasi-1D with a transition to a SDW state.

Powder samples were prepared by solid-state reaction of stoichiometric mixtures of high-purity C_{60} powders and alkali metals in a sealed quartz capillary at 260 °C for 80 days. Single crystals were prepared by doping pure C_{60}. Some samples were exposed to air, in order to eliminate residual contribution of the superconducting $A_3\mathrm{C}_{60}$ phases (for Rb and K). Moreover, care was taken to avoid phase segregation of the K compound[8] which occurs in a narrow temperature range around 400 K. The phase purity of our specimens (i.e, the full polymerization at ambient pressure) was checked by x-ray diffraction and electron spin resonance (ESR).

The spin susceptibility measured by integrating the ESR line at 9 GHz is presented in Fig. 1. At high temperatures, the susceptibility of the monomer fcc phase is Curie-like for all three materials (measured up to 800 K for K and Rb). A similar temperature dependence was observed in the NMR shift,[9] as well. The magnitude of χ is close to that of a paramagnetic system with localized $S=\frac{1}{2}$ spins. In all three materials the polymerization is marked by a drop in the susceptibility at $T_0 \sim 350$ K.

The ESR spectrum below T_0 of the K polymer is characteristic of a metal with a narrow band. The spin susceptibility is temperature independent down to 4 K and its value of $\chi = 5.0\times10^{-4}$ emu/mol indicates a strong exchange enhancement and a large DOS of 15 states/eV per KC_{60}. The Fermi temperature would be unrealistically low, $T_F = 800$ K, in a free-electron interpretation. The linewidth continuously increases from 4.5 G at 25 K to 6.6 G at 300 K as in metals

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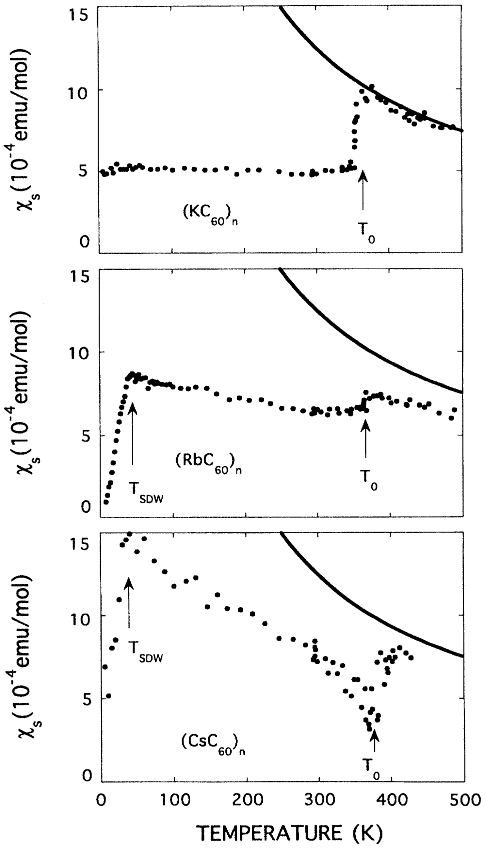

FIG. 1. Spin susceptibility measured by ESR. The fcc-orthorhombic structural phase transition at $T_0 \sim 350$ K has a large hysteresis and the data are shown here for the cooling run. The solid line is the Curie dependence of a free $S=\frac{1}{2}$ system with one spin per mole. In the magnetically ordered state ($T<T_{\mathrm{SDW}}$) the ESR data do not correspond to the static susceptibility.

where the spin lifetime is limited by phonons. In contrast, the ESR spectra of the Rb and Cs compounds show a transition at $T_{\mathrm{SDW}} \sim 50$ and 40 K, respectively, from a paramagnetic state to a ground state in which there is no ESR at $g=2$. It has been suggested for $(\mathrm{RbC}_{60})_n$ that the ground state is due to the formation of a SDW condensate which forms at low temperatures in quasi-1D metals with strong electron-electron interactions.[10] The present data show that $(\mathrm{CsC}_{60})_n$ behaves similarly. Moreover, in the paramagnetic regime the susceptibility of $(\mathrm{RbC}_{60})_n$ is weakly, while that of $(\mathrm{CsC}_{60})_n$ is more strongly temperature dependent, indicating that the band may be very narrow.

The quasi-1D electronic structure may be the reason for the relatively narrow ESR linewidths in the Rb and Cs polymer fullerides.[11] Spin-orbit interaction in two- or three-dimensional metals, containing elements with large atomic numbers, broadens the conduction electron spin resonance already at low temperatures, while it is known to be ineffective in one dimension. This is well demonstrated by the linewidths of 18 G for $\mathrm{K}_3\mathrm{C}_{60}$ and 600 G for $\mathrm{Rb}_3\mathrm{C}_{60}$. Such a difference is due to the different atomic numbers of K and Rb. On the other hand, the linewidths for $(\mathrm{KC}_{60})_n$ and $(\mathrm{RbC}_{60})_n$ are practically equal (i.e., 6.5 and 6 G, respectively), in spite of the difference in atomic numbers. Therefore, it is safe to conclude that the dramatic reduction of the linewidth in the Rb system is due to the 1D nature of the polymeric compound. Also $(\mathrm{CsC}_{60})_n$ has a narrow linewidth (50 G at 300 K). In the same line of reasoning as for the Rb compound, we can safely state the 1D nature of the Cs polymer, as well. On the other hand, in the case of the K systems, comparable linewidths [i.e., 6.5 and 18 G for $(\mathrm{KC}_{60})_n$ and $\mathrm{K}_3\mathrm{C}_{60}$, respectively] suggest that the $(\mathrm{KC}_{60})_n$ remains quasi-3D. The change in dimensionality can be further supported by the increase of the nearest-neighbor interchain distance in the order of K, Rb, and Cs.[1,2,12]

A decrease in the g factor and a strong increase of the linewidth at the transition[4] are typical fingerprints of a transition to an antiferromagnetic state. Similar effects were observed in the organic charge transfer salt $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (Ref. 13) (where TMTSF is tetramethyltetraselenafulvalene), up to date the best studied quasi-1D system with a static three-dimensionally ordered SDW ground state. The SDW instability, inferred from the magnetic results, motivated us to study the electrodynamic response of the fulleride polymers by measuring the optical reflectivity on a very broad frequency interval. The broad spectral range form the FIR up to the visible and ultraviolet has been covered by a combination of three spectrometers with overlapping frequency intervals.[14] We have measured both pressed-pellet and single-crystal specimens, which gave equivalent and similar results. Kramers-Kronig transformations were applied to the reflectivity spectra, in order to obtain the optical conductivity $[\sigma_1(\omega)]$.[14] The temperature dependence of the conductivity at 9 GHz was also measured on loose powders by the cavity perturbation technique with the sample at the maximum rf magnetic field. In all measurements an orientational average is obtained.

Figure 2 displays the frequency dependence of the real part of the optical conductivity σ_1 at selected temperatures, while Fig. 3 shows the temperature dependence of σ_1 at 9 GHz. At 300 K the reflectivity (not shown here) increases with decreasing photon energy for all three compounds and approaches total reflection as ω tends to zero. This is the typical optical fingerprint for metallic behavior. At ambient temperature, the K compound has the largest conductivity. Both the FIR and the microwave data show that this compound is a metal in the full temperature range with a continuously increasing conductivity down to 4 K.

The FIR conductivity of the Rb and Cs polymers and the 9-GHz microwave conductivity of the Rb polymer clearly show a transition to an insulating state at low temperatures associated with the magnetic transition. At temperatures above 50 K the optical conductivity may be phenomenologically divided into a Drude term $\sigma_{1\mathrm{Drude}}=\omega_p^2\Gamma_D/(\omega^2+\Gamma_D^2)$ describing the conductivity at the lowest frequencies and a set of harmonic oscillators for the phonon and electronic excitations. The experimental data are well reproduced by such a description, although the plasma frequencies ω_p are unusually small, of the order of 0.1 eV for $(\mathrm{KC}_{60})_n$ and even less for the other two compounds, and the scattering relaxation times $\tau \sim 1/\Gamma_D$ are also unusually long. Furthermore, a strong peak appears in the FIR-MIR range. A similar peak was found in $A_3\mathrm{C}_{60}$ as well[14] and it was ascribed to Coulomb correlation effects. At high frequencies (not shown on the

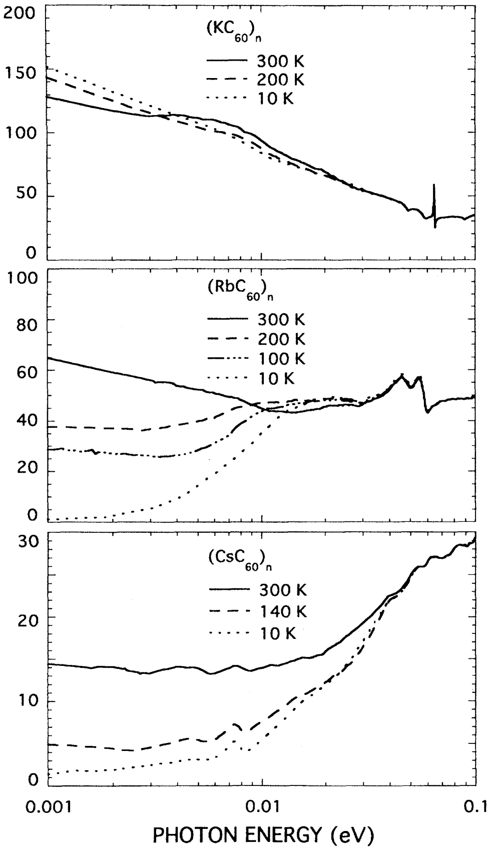

FIG. 2. Optical conductivity of $(AC_{60})_n$ polymers in the FIR and MIR range. $(KC_{60})_n$ is a metal at all temperatures, while $(RbC_{60})_n$ and $(CsC_{60})_n$ have an insulating ground state.

figure) $\sigma_1(\omega)$ is dominated by an intensive absorption peaked at about 1 eV which is in the range of the electronic interband transitions.[14] A full account of the experimental data and a detailed analysis in terms of the Lorentz-Drude dispersion theory will be presented in a forthcoming publication. Here, we just observe that for $(KC_{60})_n$ Γ_D decreases with decreasing temperature, while for $(RbC_{60})_n$ and $(CsC_{60})_n$ the Drude term decreases and drops to zero below 50 K. As shown in Figs. 2 and 3, unlike the magnetic transition, the low-frequency conductivity disappears smoothly over a broad temperature scale. The smearing of the transition could have several origins, like anisotropy and disorder, or eventually fluctuation effects. The importance of the fluctuation effects was recognized by Tycko *et al.* with the enhanced ^{13}C NMR spin lattice relaxation rate in the metallic phase of RbC_{60}.[9] Moreover, the phase transition at 50 K is not of first order since $\rho(T)$ displays a broad upturn to the insulating regime (Fig. 3).

The metal-insulator transition observed in the conductivity supports the idea that the electronic structure is quasi-1D with a condensation of spin-density waves at low temperatures. The mean field gap is related to the transition temperature as in BCS superconductors, $2\Delta = 3.5 k_B T_{\mathrm{SDW}}$, i.e., it is expected to be about 16 meV. This is in the middle of the frequency range at which the low-temperature conductivity increases to a temperature-independent value (Fig. 2). One interpretation of the data is that the observed decrease of $\sigma_1(\omega)$ in the range below 20 meV reflects directly the decrease of DOS in that same range. Moreover, the materials might be in the clean limit $2\Delta > \Gamma_D$ for which the gap does not appear as an increase of the conductivity at $\omega = 2\Delta$. For a SDW, the oscillator strength, removed as the Drude term disappears, should reappear in the spectrum of collective excitations. For the best studied SDW system, $(TMTSF)_2PF_6$, a similar phenomenon occurs: the gap is not seen in the optical data at 2Δ and at least some of the oscillator strength appears in the phason spectrum.[15] In the alkali polymer fullerides no additional oscillator strength is observed above approximately 50 meV, suggesting therefore the existence of low-frequency excitations. It remains to be seen whether collective SDW excitations with low pinning energy (which would incorporate the missing spectral weight, removed from the Drude term) exist in the polymers or not. Such excitations appear in high-purity incommensurate systems. $(RbC_{60})_n$ and $(CsC_{60})_n$ have formally a half-filled conduction band if the degeneracy of the lowest unoccupied molecular orbitals of the $C_{60}{}^{-}$ ion is sufficiently lifted by the distortion along the chain direction. In an ideally 1D system this would lead to a doubling of the unit cell and a strong commensurability gap. The interchain electronic overlap is, however, not extremely small since the isostructural K polymer does not appear to be one dimensional. Therefore, the Fermi surface is warped and the nesting vector may not point along the chain direction. Consequently, the fulleride polymers might well be incommensurate.

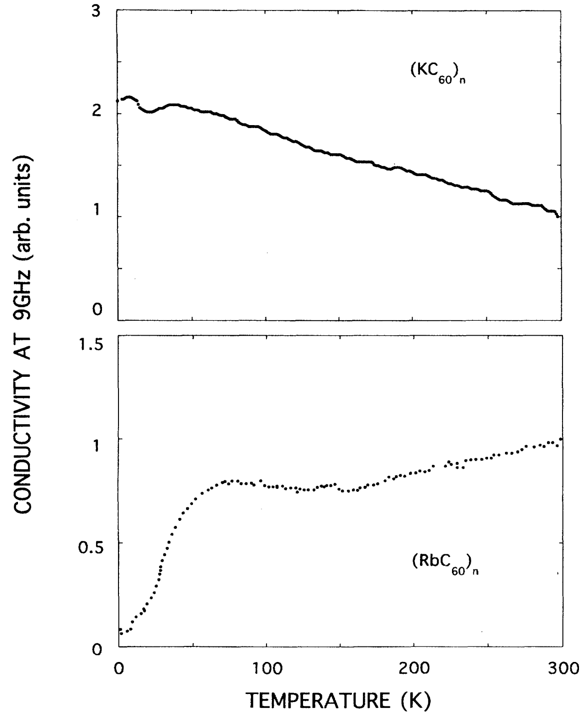

FIG. 3. Microwave conductivity at 9 GHz of $(KC_{60})_n$ and $(RbC_{60})_n$ vs temperature normalized at 300 K.

In conclusion, the magnetic data and the frequency-dependent conductivity of the $(AC_{60})_n$ polymers provide unambiguous evidence for a new class of fulleride conductors. Up to date the superconducting A_3C_{60} compounds were the only other known conducting fullerides. Since the electron density is low and the bandwidth in the polymers is probably small, strong electron correlations are expected. The Mott-Hubbard insulator ground state predicted for fullerides with an integer number of electrons per unit cell is, however, not realized in the polymers. $(KC_{60})_n$ is a metal with a large Pauli susceptibility down to 4 K. The magnetic and electrodynamic properties of the $(RbC_{60})_n$ and $(CsC_{60})_n$ polymers are indicative of a quasi-1D electronic structure. At high temperatures, these latter compounds are poor conductors, undergoing at about 50 K a second-order phase transition to an insulating ground state which is presumably a condensed SDW.

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