

## Low Temperature Magnetic Instabilities in Triply Charged Fulleride Polymers

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The electronic properties of the  $C_{60}^{3-}$  polymer in  $Na_2Rb_{0.3}Cs_{0.7}C_{60}$  were studied by X-band and high field (109.056 GHz) ESR. They are characteristic of a strongly correlated quasi-one-dimensional metal down to 45 K. On further cooling, a pseudogap of magnetic origin opens at the Fermi level below 45 K with three-dimensional magnetic ordering occurring below  $T_N \approx 15$  K, as confirmed by the observation of an antiferromagnetic resonance mode. The  $Na_2Rb_{1-x}Cs_xC_{60}$  family of polymers offers a unique way to chemically control the electronic properties, as the opening of the gap in this system of predominantly itinerant electrons is an extremely sensitive function of the interchain separation.

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An important characteristic of organic molecular conductors is the sensitivity of their electronic properties to their dimensionality. Electronic instabilities are often encountered in low-dimensional systems at low temperatures, leading to broken symmetry ground states [for instance, spin-density wave (SDW), charge-density wave (CDW), or superconducting states] and the opening of a gap in the single particle excitation spectrum [1]. However, 3D fluctuations can lead to the opening of a pseudogap, even above the transition temperature. This is the case of the prototypical SDW material  $(TMTSeF)_2PF_6$ , in which the opening of a pseudogap is reflected in the decrease of the spin susceptibility at 20 K, far above the SDW transition temperature of 11.5 K [2]. Systematic investigation of the impact of varying dimensionality on the electronic properties of molecular conductors thus represents one of the most interesting aspects of these materials.

Polymerization of  $C_{60}$  molecules in alkali fullerenes,  $A_nC_{60}$  ( $n = 1, 3, 4$ ) has led to the isolation of a diversity of phases with a rich variety of structural and physical properties, evidently controlled by the charge state of the  $C_{60}$  units and the type of the alkali metal involved. This is well exemplified by the  $AC_{60}$  ( $A = K, Rb, Cs$ ) family [3], in which the polymer chains are comprised of singly charged  $C_{60}^-$  ions bridged by two single C-C bonds. While  $KC_{60}$  is an almost isotropic strongly correlated metal [4,5], the physical properties of  $RbC_{60}$  and  $CsC_{60}$  are characteristic of quasi-one-dimensional metals which, below 50 K, undergo a transition to a magnetically ordered [3] state whose precise nature is still a matter of debate [6,7]. On the other hand, polymerization of  $C_{60}^{3-}$  ions in  $Na_2RbC_{60}$  is characterized by extremely slow kinetics and never goes to completion [8]. It results in a different structural motif [9], involving a single C-C bridging bond. As a result, the  $C_{60}$ - $C_{60}$  intrachain distance ( $\sim 9.35$  Å) in  $Na_2RbC_{60}$  is longer than that in  $RbC_{60}$  ( $\sim 9.11$  Å). Recent X-band ESR studies of the  $Na_2RbC_{60}$  polymer [10,11] have shown that it remains metallic down to 4 K. No magnetic

or electronic instabilities were identified, a situation reminiscent of the  $KC_{60}$  polymer. Partial replacement of Rb by Cs to give  $Na_2Rb_{1-x}Cs_xC_{60}$  ( $0 \leq x \leq 1$ ) allows the formation at ambient or elevated pressure of a family of isostructural polymer phases [12,13] in which the chain-chain separation can be controlled. For instance, the  $C_{60}$ - $C_{60}$  interchain distance increases by  $\sim 0.22\%$  from 9.966 Å in  $Na_2RbC_{60}$  to 9.988 Å in  $Na_2Rb_{0.3}Cs_{0.7}C_{60}$  at 200 K—an effect reminiscent of the analogous expansion encountered in  $AC_{60}$  when K is replaced by Rb or Cs.

In this Letter, we present an electron spin resonance (ESR) investigation of the electronic properties of the  $Na_2Rb_{0.3}Cs_{0.7}C_{60}$  polymer. The temperature evolution of the intensity and linewidth of the conduction electron spin resonance (CESR) signal is consistent with metallic behavior in analogy with  $Na_2RbC_{60}$ , while the observed uniaxial  $g$ -factor anisotropy implies the quasi-one-dimensional character of the electronic structure. However, in contrast to the behavior of  $Na_2RbC_{60}$ , the spin susceptibility disappears below  $\sim 45$  K, providing evidence for a low-dimensional instability in the electronic structure.

The  $Na_2Rb_{0.3}Cs_{0.7}C_{60}$  sample was prepared by the reaction of stoichiometric amounts of Na, Rb, and Cs with  $C_{60}$ . Phase purity was established by high-resolution synchrotron x-ray powder diffraction measurements. X-band ESR measurements were performed with a Bruker E580 spectrometer equipped with an Oxford liquid He cryostat (temperature stability  $\pm 0.2$  K). High field ESR experiments were run on a homebuilt spectrometer using a Gunn diode as a frequency source with oversized waveguides and a single pass transmission probe [14]. In order to maximize the amount of the polymer phase formed on cooling, we followed the protocol established in earlier works [8], with the sample cooled from 285 to 200 K at a rate of 20 K/h, and then kept at 200 K for 1 h. Below 200 K, the cooling rate was increased to 50 K/h. Measurements were performed on cooling.

Figure 1 compares X-band ESR spectra of  $Na_2Rb_{0.3}Cs_{0.7}C_{60}$  recorded in the cubic phase at

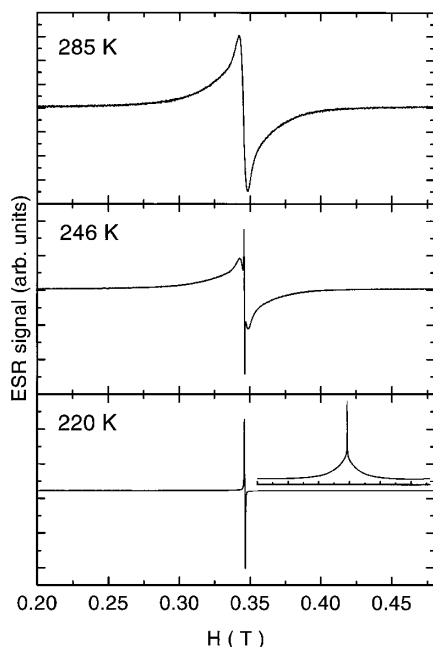


FIG. 1. X-band ESR spectra of  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$ , recorded on slow cooling. The broad line at 285 K is due to the CESR of the high temperature monomer phase, while the narrow line, which appears below 250 K is attributed to the polymer phase. The inset at 220 K shows the integrated ESR spectrum in which the broad line is still evident.

285 K (before the onset of polymerization), at 246 K (just below the monomer-polymer phase transition), and at 200 K (when a substantial fraction of the polymer phase has essentially formed). The CESR line of the cubic monomer phase observed at 285 K has a nearly Lorentzian line shape. Its CESR susceptibility is  $4.4(2) \times 10^{-4}$  emu/mol, a value which straddles those measured for  $\text{Na}_2\text{RbC}_{60}$  [ $3.4(2) \times 10^{-4}$  emu/mol] and  $\text{Na}_2\text{CsC}_{60}$  [ $5.0(2) \times 10^{-4}$  emu/mol] [10,11,15]. Slow cooling results in the sudden appearance below 250 K of a very sharp line, superposed on the existing broad line attributed to the monomer (Fig. 1). The new line is characteristic of the polymer phase and has been observed before below the monomer-polymer transition temperature in  $\text{Na}_2\text{RbC}_{60}$  [10,11]. Further cooling leads to a continuous increase in the intensity of the narrow line, as the polymer fraction grows. At 220 K, the narrow signal completely dominates the measured spectra with the broad cubic CESR line now buried in the background. However, its presence is still evident in the integrated ESR spectra (inset of the 220 K spectrum in Fig. 1).

The polymerization of  $\text{C}_{60}^{3-}$  in  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$ , identified before by x-ray diffraction, is thus confirmed and the polymer line is unambiguously assigned. Figure 2 displays the temperature dependence of the ESR signal to low temperatures at 9.622 GHz (X band) and 109.056 GHz. The line appears considerably asymmetric, with a line shape characteristic of uniaxial  $g$ -factor anisotropy [16], as expected in highly anisotropic polymeric phases. This contrasts with the absence of such anisotropy in the  $\text{RbC}_{60}$

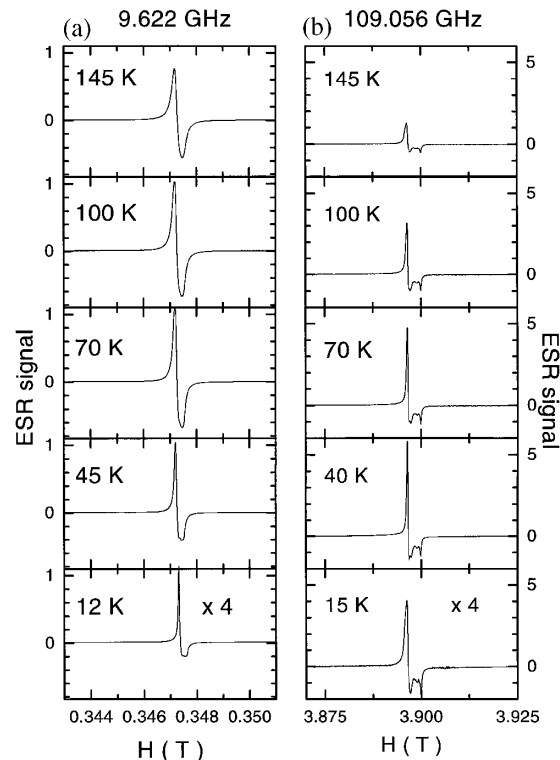


FIG. 2. X-band (9.622 GHz) and (b) HF (109.056 GHz) ESR spectra of  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$  at selected temperatures. The horizontal (field) scale is expanded for clarity. Note the change in intensity at base temperatures.

polymer [6]. Line shape analysis leads to  $g_{\parallel} = 1.9915(2)$  and  $g_{\perp} = 1.9896(2)$ .

Figures 3(a) and 3(c) display the temperature dependence of the susceptibility  $\chi_{\text{ESR}}$  of the polymer phase at 9.622 and 109.056 GHz, respectively, normalized to its value at 130 K. Three temperature regions can be distinguished. At high temperatures,  $\chi_{\text{ESR}}$  increases gradually with decreasing temperature down to 160 K. As  $\chi_{\text{ESR}}$  is proportional to the product of the molar susceptibility,  $\chi_m(T)$ , and the fraction of the polymer phase,  $p(T)$ , the observed increase principally reflects the growth in  $p(T)$  with decreasing temperature. The temperature evolution of  $p(T)$  was determined by Rietveld refinements of synchrotron x-ray powder diffraction patterns, collected following analogous cooling protocols [17].  $p(T)$  is found to approach a value of  $\sim 0.19$  at 200 K, leading to estimates of the molar susceptibility of the polymer,  $\chi_m(200 \text{ K}) = 7.5 \times 10^{-4}$  emu/mol and of the density of states at the Fermi level,  $N(E_F) = 11 \text{ states eV}^{-1} (\text{C}_{60} \text{ spin})^{-1}$ . The increased  $\chi_m$  of the polymer is consistent with its correlated metallic nature. At lower temperatures, the polymer fraction does not change further and the temperature dependence of  $\chi_{\text{ESR}}$  now reflects that of  $\chi_m(T)$ . In this intermediate temperature region,  $\chi_{\text{ESR}}$  increases only slightly, reaching a maximum between 45 and 50 K. Below this temperature  $\chi_{\text{ESR}}$  suddenly drops and almost completely vanishes below 10 K providing evidence of the opening of a gap at the Fermi level.

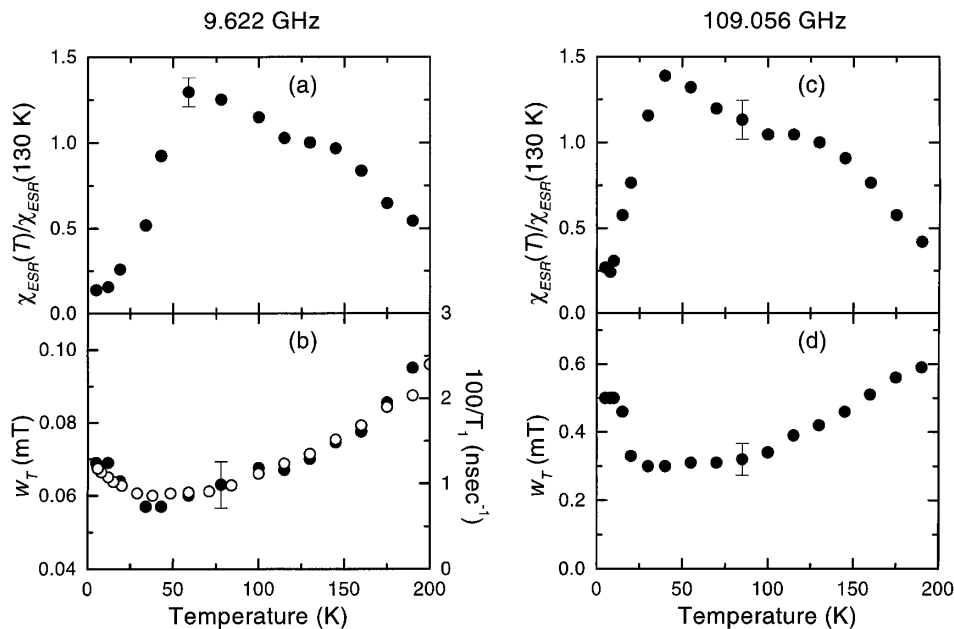


FIG. 3. Temperature dependence of (a) the X-band ESR intensity, (b) the X-band homogeneous linewidth  $w_T$ , (c) the HF ESR (109.056 GHz) intensity, and (d) the HF homogeneous linewidth  $w_T$ . The ESR intensity has been normalized to its value at 130 K. In (b), we also include the temperature dependence of the inverse spin-lattice relaxation time,  $T_1^{-1}$  (empty circles), measured with the inversion recovery pulse sequence.

The observed changes in  $\chi_{\text{ESR}}$  are also accompanied by changes in the temperature dependence of the homogeneous linewidth, shown in Figs. 3(c) and 3(d). In analyzing the spectra, we take into account two effects, which may lead to broadening: (a) inhomogeneous broadening  $w_f$  due to  $g$ -factor anisotropy, which is field dependent and remains temperature independent within experimental error and (b) homogeneous broadening  $w_T$ , which in metals is proportional to the spin-lattice relaxation rate  $1/T_1$  [4,18]. Contrary to  $w_f$ ,  $w_T$  changes considerably with temperature, decreasing almost linearly with decreasing temperature between 200 and 45 K, where it reaches a minimum. Below 45 K, the trend is suddenly reversed and  $w_T$  starts to increase.

We have also measured the electron spin-lattice relaxation time  $T_1$  as a function of temperature using the standard inversion recovery pulse sequence  $\pi$ - $t_1$ - $\pi/2$ -FID and monitoring the height of the free induction decay (FID) as a function of  $t_1$ . The temperature dependence of  $1/T_1$  [Fig. 3(c)] mirrors that of the homogeneous linewidth, also reaching a minimum around 45 K.

The nearly linear decrease of the homogeneous linewidth with decreasing temperature in the temperature range 200 to 45 K is characteristic of normal metals where the linewidth is determined by spin-lattice relaxation. Its small value ( $<0.1$  mT) implies low-dimensional character for the polymeric phase and is significantly smaller than that in  $\text{Na}_2\text{RbC}_{60}$  ( $w_T > 0.2$  mT) [10,11]. Thus the transfer integrals perpendicular to the polymer chains are further reduced in  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$  when compared with  $\text{Na}_2\text{RbC}_{60}$ , consistent with the larger chain-chain separation and a quasi-one-dimensional

electronic structure. The temperature dependence of the ESR susceptibility between 200 and 45 K and its strongly enhanced value with respect to the spin susceptibility of the cubic phase are also characteristics of a correlated quasi-one-dimensional metallic system.

Below  $\sim 45$  K, the spin susceptibility suddenly disappears. Since the data at higher temperatures are consistent with a quasi-one-dimensional electronic conductor, the observed behavior provides evidence for a low-dimensional instability in the electronic structure. The increase in the homogeneous linewidth at the same temperature might also signal the onset of antiferromagnetic fluctuations at the Larmor frequency. The situation is strikingly similar to the low temperature magnetic transition in  $\text{RbC}_{60}$  [3]. However, contrary to  $\text{RbC}_{60}$ , we do not find any changes in the  $g$ -factor anisotropy either in X-band or in the HF experiments within experimental error.

There are three possible scenarios, which can lead to a vanishingly small ESR susceptibility in  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$ : (a) 3D ordering of the spin density waves, as originally suggested for  $\text{RbC}_{60}$  [3], (b) antiferromagnetic (AFM) ordering as seen in  $\text{NH}_3\text{K}_3\text{C}_{60}$ , the only  $\text{C}_{60}^{3-}$  system discovered so far with a magnetic transition [12,19], or (c) transition to a nonmagnetic CDW state, as theoretically suggested for polymeric  $\text{Na}_2\text{RbC}_{60}$  [20]. If SDW or AFM ordering is the case, the low temperature state has a well-defined magnetic character and one expects the appearance of an additional antiferromagnetic resonance (AFMR) mode at high frequencies [6,7]. A closer inspection of the low temperature integrated HF ESR spectra of  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$  reveals a new line emerging on the low field side below 15 K. This is absent in the X-band

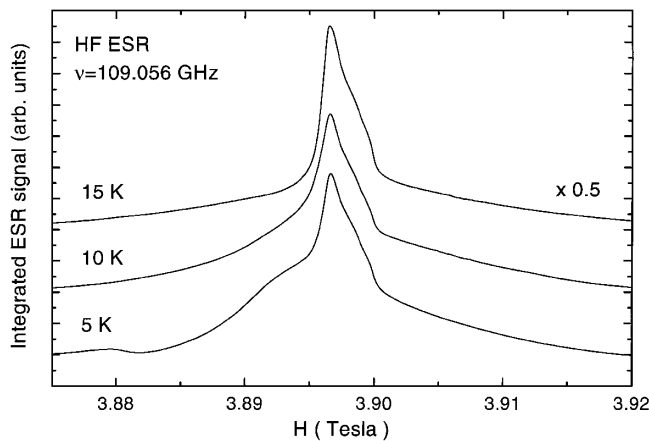


FIG. 4. Integrated ESR signal measured at 109.056 GHz, showing the appearance of a new line in the low field side of the spectrum at low temperatures.

data. The broad background seen in the spectrum at 15 K (Fig. 4) arises from the CESR signal of the untransformed cubic phase. A low field shift and a broadening of the new line with decreasing temperature are characteristic of both the AFMR and the resonance in spin glasses [7]. In  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$ , the low field shift,  $\Delta M_1$  is  $\sim 5.2$  mT and the linewidth is  $\sim 4.4$  mT. In a uniaxial antiferromagnet, these are determined by the anisotropy ( $H_A$ ), exchange ( $H_E$ ), and external ( $H$ ) fields:

$$\{\Delta M_2\}^{1/2} \approx \Delta M_1 \approx \frac{H_A H_E}{H}. \quad (1)$$

leading to a spin flop field,  $\sqrt{H_E H_A} \approx 0.3$  T, a value comparable to that found in  $\text{RbC}_{60}$  ( $\sim 0.34$  T) [6,7]. This supports the assignment of the new line to an AFMR mode, confirming the magnetic origin of the observed transition and discarding the possibility of a small-amplitude CDW state. We note that the AFMR line appears below 15 K, while the ESR susceptibility starts to decrease at a much higher temperature. It is possible that a pseudogap opens below 45 K due to 3D fluctuations, which reduce the magnetic susceptibility [6] with the true Néel temperature being  $\sim 15$  K.

Preliminary ESR results on the  $\text{Na}_2\text{Rb}_{0.5}\text{Cs}_{0.5}\text{C}_{60}$  polymer have shown the absence of any instabilities with the metallic state surviving down to 4 K, in analogy with  $\text{Na}_2\text{RbC}_{60}$ . It thus appears that the opening of the gap in the system of predominantly itinerant electrons in  $\text{Na}_2\text{Rb}_{1-x}\text{Cs}_x\text{C}_{60}$  is an extremely sensitive function of  $x$ , which presumably controls the interchain separation. These systems lie very close to the metal-insulator transition and provide a unique opportunity for the chemical control of the electronic properties.

In conclusion, we find that polymerization of  $\text{C}_{60}^{3-}$  units in  $\text{Na}_2\text{Rb}_{0.3}\text{Cs}_{0.7}\text{C}_{60}$  is initiated below 250 K. The

electronic properties, as measured by ESR, are suggestive of quasi-one-dimensional metallic behavior above 45 K. Below 45 K, a pseudogap opens at the Fermi level causing an abrupt drastic reduction of the ESR susceptibility. An AFMR resonance line appears below 15 K at high fields. Our data are consistent with 3D magnetic ordering below  $T_N \approx 15$  K.

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