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Electron spin resonance study of the polymeric phase of Na_2RbC_{60}

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The structural and electronic properties of the polymeric phase of Na_2RbC_{60} which comprises of C-C bridged C_{60}^{3-} chains have been studied between 410 and 4 K with the electron spin resonance (ESR) technique. On cooling, the polymeric phase starts growing below ~250 K. Its fraction reaches a maximum at ~190 K, where around 55% of the monomeric cubic phase have transformed to the polymer. The temperature dependence of the ESR susceptibility suggests that the Na_2RbC_{60} polymer is conducting down to 4 K. The ESR results exclude the possibility of the existence of a ground-state instability and the formation of either a spin-density-wave (SDW) or a charge-density-wave (CDW) state. [S0163-1829(99)01530-1]

I. INTRODUCTION

Polymerization of C_{60} molecules has been in the focus of fullerene research in recent years. Photoinduced polymerization was first suggested in pristine C_{60}.[1] This was followed by the discovery that neutral C_{60} exposed to moderately high pressures and temperatures[2] can also form C-C bridged polymeric structures. In these polymers, the C_{60} molecules are linked by a characteristic four-membered carbon ring arising from [2+2] cycloaddition. The first examples of polymerization in intercalated C_{60} compounds were found[3] in salts with stoichiometry AC_{60} (A=K, Rb, Cs) in which the same type of bonding between neighboring C_{60} units was encountered. In addition, AC_{60} forms a metastable dimer phase,[4] which exhibits a different bridging structural motif between the C_{60} units, namely a single C-C bond. This type of bonding was later discovered to be present in both the two-dimensional Na_4C_{60} (Refs. 5 and 6) and the one-dimensional Na_2RbC_{60} polymers.[7,8] Thus the charge state of the fullerene molecules appears crucial in determining the bonding mechanism, favoring [2+2] cycloaddition for $(C_{60})_n$ and $(C_{60}^-)_n$ and single carbon-carbon bond formation for $(C_{60}^{3-})_n$ and $(C_{60}^{4-})_n$,[7,9] even though both kinetic and steric factors are also of importance.[8]

The Na_2RbC_{60} polymeric phase appears on very slow cooling below 250 K and, as the temperature is lowered, its fraction increases at the expense of the primitive cubic monomeric phase.[10] However, no full transformation occurs and, even for extremely slow cooling procedures, only about 55% of the cubic phase transform to the polymer.[7,11,12] As a result, at low temperatures Na_2RbC_{60} samples are mixtures of the majority polymer and the minority cubic phases. The polymer crystal structure is derived from the primitive cubic phase by a contraction of 0.6 Å along one of the cube face diagonals and a 0.4° tilt of one of the axes. This results in a monoclinic cell (space group $P2_1/a$) with lattice parameters, $a=13.711$ Å, $b=14.554$ Å, $c=9.373$ Å, and $\beta=133.53°$ at $T=180$ K.[7] The very short C_{60}-C_{60} distance observed along the c axis provides the signature of the formation of the polymer. Ogitsu *et al.*[13] have recently optimized the structure of monoclinic Na_2RbC_{60} using local-density functional (LDF) calculations and obtained its electronic band structure. The optimized geometry compares well with that obtained from the synchrotron x-ray-diffraction data.

The electronic properties of the cubic monomeric form of Na_2RbC_{60}, which can be stabilized to low temperatures by rapid cooling,[10] have been extensively studied. It is found to be a superconductor with an unusually low T_c of 3.5 K.[14] The origin of the suppressed value of T_c has been the subject of extensive work and it may be related to a number of reasons, including either the occurrence of polymerization or the modulation of the Na^+-C_{60}^{3-} interaction with interfullerene spacing.[15,16]

On the other hand, the electronic and magnetic properties of polymeric Na_2RbC_{60} are as yet totally unexplored. It has been shown that it is not superconducting,[10] but it is not known whether it is metallic or not. An important characteristic of molecular conductors is their dimensionality, as low dimensional systems often undergo metal-insulator transitions at low temperatures. These arise from ground-state instabilities, like the formation of spin-density wave (SDW) or charge-density wave (CDW) states. This kind of behavior has been already encountered in the AC_{60} systems which exhibit a metal-insulator transition at ~50 K, accompanied by magnetic ordering of the C_{60}^- ions.[17] The electronic and geometrical structure of the singly bonded fullerene polymer has been studied theoretically in a very recent report in the one-dimensional approximation.[18] For the triply charged C_{60}^{3-} ions, the existence of a small amplitude CDW was predicted, leading to the opening of a gap at the Fermi level. However, as it was pointed out,[18] interchain interactions could easily destroy this CDW state.

The purpose of this paper is to present a detailed study of the stability and conducting and magnetic properties of the polymer phase of Na_2RbC_{60}. The electron spin resonance (ESR) technique has been proven before to be a very efficient method for the study of the conducting and magnetic properties of alkali fullerides.[17,19–21] We followed this approach to study both the high-temperature monomeric phase and the monomer→polymer phase transition of Na_2RbC_{60} in the temperature range 410–4 K. We have found that the Na_2RbC_{60} fulleride is conducting both in the monomeric and the polymeric phases. The spin susceptibility, χ_s of the latter, as measured by the ESR technique, is strongly enhanced at low temperatures.

II. EXPERIMENTAL

Na_2RbC_{60} was prepared by the reaction of stoichiometric quantities of C_{60}, Na, and Rb, contained in a sealed Ta cell inside a sealed glass tube filled with He to 500 Torr at 480 K for 3 h, 570 K for 12 h, and 620 K for 72 h; after an intermediate regrinding, the sample was annealed at 673 K for 25 days. The sample was characterized by synchrotron x-ray and neutron powder diffraction, solid-state NMR and superconducting quantum interference device magnetometry. *X*-band ESR experiments were performed on a commercial Bruker ESP 300 E spectrometer equipped with an Oxford liquid-helium cryostat, operating in the temperature range between 410 and 4 K. The temperature stability was better than ±0.2 K. In order to achieve maximum conversion of the cubic to the polymer phase, particular attention was paid to the cooling procedure below 280 K. Thus cooling between 280 and 190 K was performed over a period of 48 h at a rate of 1.8 K/h. ESR spectra were recorded automatically every 30 min.

III. RESULTS AND DISCUSSION

The full temperature dependence of the ESR spectra of the powder Na_2RbC_{60} sample taken at *X* band (9.6 GHz) is shown in Figs. 1 and 2. As it is apparent from Fig. 1(a) and 2(a), the room temperature ESR lines are significantly asymmetric. However, for a fine grained powder metallic sample, like that used in these experiments, the particle size is small compared to the skin depth. Under these circumstances, the conducting electron spin resonance (CESR) signal is entirely independent of the diffusion of the conducting electrons through the skin depth and the CESR line shape takes the simple Lorentzian form.[22,23] In order to explain the observed asymmetric line shape, we recall that the ESR spectra of many other alkali fullerides are asymmetric and are composed of a broad and a narrow line.[20] The linewidth of the narrow line is commonly ~5 G, while that of the broad line depends strongly on the alkali metal present, varying from 25.5 G in K_3C_{60} to 744 G in Rb_3C_{60}.[19] A similar situation is also encountered for the Na_2AC_{60} family, with the observed linewidths of the broad component being 381 G for Na_2CsC_{60}, 15.8 G for Na_2KC_{60} and 28.9 G for Na_2RbC_{60}.[20]

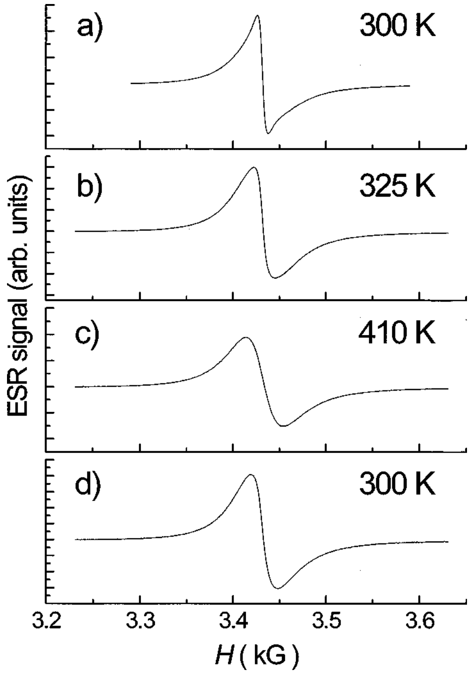

FIG. 1. Temperature dependence of the *X*-band ESR spectra of Na_2RbC_{60}, showing the evolution of the ESR signal in the course of a thermal cycle from 300 K (upper spectrum) to 410 K and then back to 300 K (bottom spectrum). Note the difference between the two spectra taken at 300 K before and after the heat treatment.

We thus tried to simulate the anisotropy in the ESR spectra by assuming that the observed line shape at 9.6 GHz and

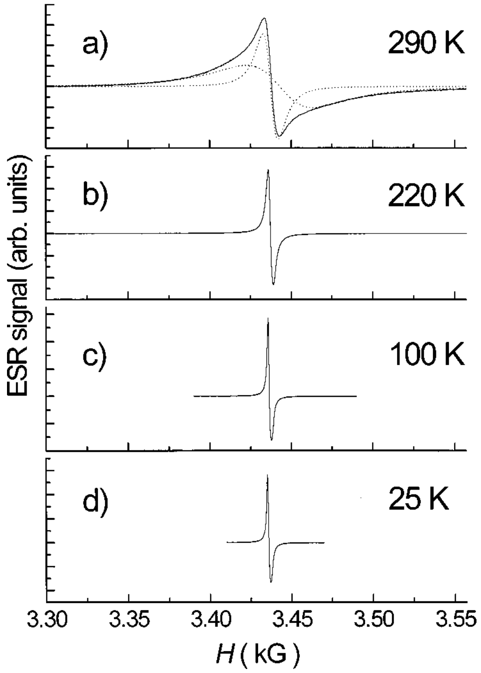

FIG. 2. Temperature dependence of the *X*-band ESR spectra of Na_2RbC_{60} below room temperature. The cooling rate from 280–190 K was 1.8 K/h. The dashed lines in (a) represent the deconvolution of the spectrum into two components [Eq. (1)].

290 K [Fig. 2(a)] is composed of two Lorentzian components:

$$f(H)=C_a\frac{2[\gamma(H-H_{0a})T_{2a}]}{\{1+[\gamma(H-H_{0a})T_{2a}]^2\}^2}+C_b\frac{2[\gamma(H-H_{0b})T_{2b}]}{\{1+[\gamma(H-H_{0b})T_{2b}]^2\}^2}. \qquad (1)$$

Here T_{2a}, T_{2b} are the spin relaxation times, H_{0a}, H_{0b} are the centers of the two components, γ is the electronic gyromagnetic ratio, and C_a and C_b are the fitting parameters, which depend on their susceptibility. The fit is reasonably good with values of $2T_{2a}^{-1}/(\sqrt{3}\gamma)=\Delta H_{pp}(a)=9.1\,\mathrm{G}$ and $2T_{2b}^{-1}/(\sqrt{3}\gamma)=\Delta H_{pp}(b)=39.5\,\mathrm{G}$ at 9.6 GHz and 290 K for the narrow and broad components, respectively. The centers of the two components are split by 4.3 G, leading to g factors for the narrow and broad components of $g_a=2.0025(2)$ $(H_{0a}=3437.3\,\mathrm{G})$ and $g_b=1.9999(2)$ $(H_{0b}=3441.6\,\mathrm{G})$, respectively.

The two-component structure of the ESR line can thus satisfactory explain the asymmetry of the room-temperature data. However, the origin of the two lines still remains an open question. The broad component of the observed ESR line with a characteristic $g_b=1.9999$ can be ascribed to the conducting electron spin resonance of the C_{60}^{3-} electrons, by analogy to other A_3C_{60} systems. However, the presence of the narrow component with a spin only g value, $g_a=2.0025$ needs to be discussed further. Tanigaki *et al.* postulated[19] that the narrow component, observed in the A_3C_{60} series and found to display Curie-like temperature dependence, originates from defect-type spins trapped in the crystal. Similar narrow ESR signals have been also observed in AC_{60} systems with their origin attracting a number of alternative explanations;[24] for instance, it was proposed that they could arise as a result of (i) rapid electron exchange between C_{60} and C_{60}^- units, (ii) thermal population of low-lying ^2A excited states, or (iii) aggregation of C_{60}^- ions to form $(C_{60})_2^{2-}$ dimers. Thus, by analogy, an attractive explanation for the appearance of the narrow component in the ESR spectra of Na_2RbC_{60} is that it reflects precursor effects to polymerization and, as a consequence, it forms as a result of the presence of $(C_{60})_2^{6-}$ dimers or larger $(C_{60})_n^{3n-}$ aggregates. Non-Curie-like temperature dependence of the intensity of the narrow component would lend support to this explanation and militate against its impurity origin.

In order to check this, we followed the temperature dependence of the ESR spectra of cubic Na_2RbC_{60} above room temperature. If the narrow component originates from the presence of dimers, trimers or larger sections of the polymeric chains already existing in the cubic monomeric phase, then it should rapidly disappear on heating, as the bridged $(C_{60})_n^{3n-}$ aggregates revert to monomers. The temperature dependence of the ESR spectra of the Na_2RbC_{60} powder sample measured first on heating from 290–410 K and then on cooling back to 290 K is shown in Fig. 1. It is immediately apparent that the narrow component almost completely disappears on heating to 325 K, and thus we can discard the possibility that in the present case it originates from impurities. We also note that in this temperature region the low-temperature simple cubic phase of Na_2RbC_{60} transforms to an orientationally disordered fcc phase. The possibility that the two signals may come from the ordered and disordered cubic phases, respectively, can be ruled out by analogy to the case of CsC_{60} which exhibits the same phase transition, but no change in linewidth and intensity of the ESR signal.[25] Finally, on cooling from 410–290 K, we see no reappearance of the narrow component with only the broad line present for the annealed sample.

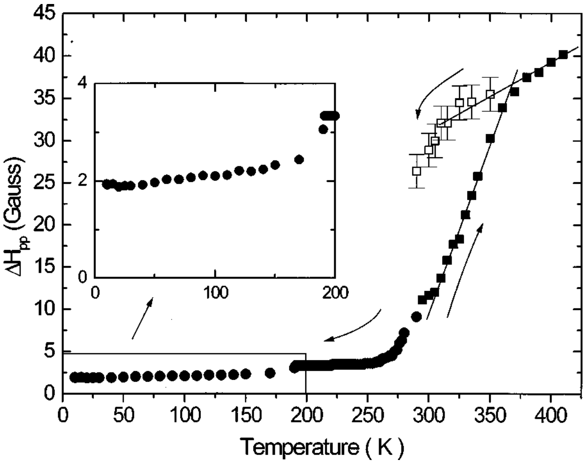

FIG. 3. The temperature dependence of the derivative peak-to-peak ESR linewidth. The solid circles represent the results obtained in the slow cooling experiment from 290–4 K, the solid squares those obtained during heating of the sample from 290–410 K, and the open squares those obtained on cooling the annealed sample from 410–290 K. The inset shows the expanded region between 4 and 200 K.

The changes in the ESR spectra above room temperature are most clearly seen in Fig. 3, which displays the temperature dependence of the peak-to-peak ESR linewidth ΔH_{pp} before deconvolution into the two components. As the narrow component gradually disappears with increasing temperature, ΔH_{pp} also increases linearly. The slope of the temperature dependence of ΔH_{pp} shows a drastic change above 360 K that we take as the signature of the complete disappearance of the narrow component. Finally, we find a large hysteresis in the temperature dependence of the linewidth of the annealed sample when it is cooled from 410 K to room temperature (Fig. 3), reflecting the delayed growth of the narrow component of the ESR line on cooling. These observations provide strong support that in our sample the presence of the narrow component in the ESR spectra of unannealed samples [Figs. 1(a) and 2(a)] reflects polymerization precursor effects, arising through the formation of molecular aggregates.

The effect of the polymer formation on the ESR spectra is even more pronounced below room temperature. Slow cooling of the unannealed sample at a rate of 1.8 K/h below 280 K leads to a gradual change in the line shape below 250 K (Fig. 2) with the narrow component of the ESR line now becoming dominant. At the same time, the intensity of the total ESR signal increases by a factor of 2.5 between 250 and 190 K (Fig. 4). These results can be compared with those obtained when the sample is cooled rapidly (at a rate much larger than 10 K/h) when polymer formation is suppressed and the metastable primitive cubic phase survives to low temperatures. Under these circumstances, no significant

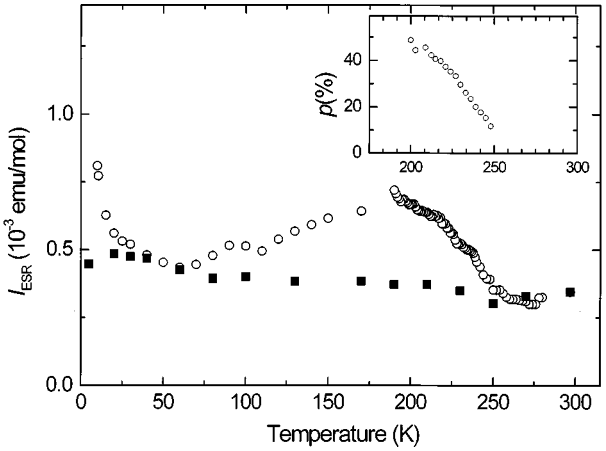

FIG. 4. The temperature dependence of the normalized ESR intensity, as obtained during the slow (open circles) and the rapid (squares) cooling experiments. The inset shows the temperature dependence of the fraction p of the polymer phase, obtained from synchrotron x-ray-diffraction measurements (Ref. 12).

change in the ESR intensity is observed around 250 K. The latter is only weakly temperature dependent and increases slightly with decreasing temperature (Fig. 4). As a result, the increase in the ESR intensity below 250 K in the slow cooling experiment can be attributed to the gradual formation of the polymer phase, in agreement with the results of synchrotron x-ray and neutron-diffraction experiments.[12]

As already mentioned, the transformation from the cubic to polymeric phase is not complete even after extremely slow cooling procedures. In order to analyze quantitatively the temperature dependence of the ESR intensity, we assume that the total ESR intensity, I_{total} can be expressed as a sum of the intensities arising from the cubic and the polymeric fractions:

$$I_{\mathrm{total}}=(1-p)I_{\mathrm{cubic}}+pI_{\mathrm{poly}}. \tag{2}$$

Here p is the fraction of the polymer phase, and I_{cubic} and I_{poly} are the intensities of the ESR signal of the cubic and polymeric phases, respectively. The latter are directly proportional to the spin susceptibilities of the respective fractions. The temperature dependence of p is known from synchrotron x-ray and neutron powder diffraction experiments which clearly reveal macroscopic coexistence of the monomeric and polymeric phases (Fig. 4 inset),[12] while the temperature dependence of I_{cubic} can be taken from the results of the fast cooling experiment. Combining these data and using Eq. (2), we can now extract the temperature dependence of I_{poly} which is shown in Fig. 5.

The intensity of the ESR signal arising from the polymer phase, I_{poly} is temperature independent in the temperature range between 250 and 190 K, implying that the polymeric phase is also conducting. We also note the significantly different relative magnitudes of I_{cubic} and I_{poly} with I_{poly} found to be equal to 0.95×10^{-3} emu/mol—a factor of 2.8 larger than I_{cubic}. In low dimensional systems with narrow electronic bands, correlation effects are expected to lead to the enhancement of the Pauli susceptibility,[26] an effect characteristic of correlated metals. However, as pointed out by Mott[27] correlations between conducting electrons can result in a number of different phenomena at low temperatures, like the appearance of a Mott-Hubbard transition and the stabilization of magnetic or even superconducting ground states. In order to search for additional phase transitions at lower temperatures, we then continued the ESR measurements down to 4.4 K.

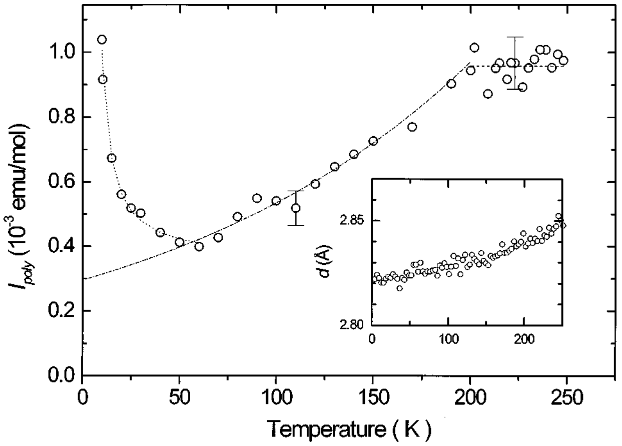

FIG. 5. The temperature dependence of the normalized ESR intensity I_{poly} of the polymeric phase of Na_2RbC_{60}, as determined from Eq. (2). The dash-dotted line represents the fit in the temperature range between 200 and 60 K to Eq. (3), with $\alpha=3.2\times10^{-4}$ states/eV/C_{60}/Å, $\beta=0.25$ Å, and $I=0$. The dotted line is a fit of the low-temperature phase to Eq. (4) with $\theta=5.1\pm1.2$ K. The inset shows the temperature dependence of the interfullerene separation d in the ab plane of the monoclinic cell (Ref. 10).

Further cooling below 190 K leaves the fraction of the polymer phase unchanged ($p\approx0.55$),[7,12] while the X-band ESR intensity I_{poly}, as obtained from Eq. (2), decreases (Fig. 5). Such temperature dependence has been also observed in other cubic alkali fullerides[6,20,21] and it has been interpreted in terms of the decrease of the density of states at the Fermi level, $N_b(E_F)$ with temperature, as a result of lattice contraction. Robert *et al.*[28] modeled this dependence by employing the exponential functional form, calculated by Satpathy *et al.*:[29]

$$N_b(E_F)=\frac{\alpha}{d}\exp\left(\frac{d}{\beta}\right). \tag{3}$$

Here $N_b^{-1}=N_\chi^{-1}+I$ is the bare density of states at the Fermi level, enhanced by the Stoner parameter, I. d is the C_{60}-C_{60} distance which is given in the cubic alkali fullerides by $d=a/\sqrt{2}-D$, with a being the unit-cell length and D the C_{60} diameter. α and β are empirical fitting parameters. In the case of the Na_2RbC_{60} polymer, however, the situation is more complicated, as this shows strong anisotropic behavior on cooling, with the thermal contraction along the C-C bridging monoclinic c axis being negligible ($d\ln c/dT=1.0(5)\times10^{-6}\,\mathrm{K}^{-1}$).[10,12] Instead, we attempted to fit the ESR intensity between 200 and 50 K by assuming that the temperature dependence of $N_b(E_F)$ is modulated by the interfullerene separation in the ab plane. An excellent fit (Fig. 5) was obtained by using the parameters, $\beta=0.25$ Å and $I=0$, essentially identical to those employed by Robert *et al.*[28] This result provides support for the importance of the interchain interactions in polymeric Na_2RbC_{60} that make its character less one-dimensional than the AC_{60} systems.[17]

Below 50 K, the fit fails to describe the experimental data due to the upturn in the temperature dependence of the ESR intensity. Such behavior could imply that at low temperatures, the Stoner enhancement factor becomes nonzero, an effect also encountered in other fulleride systems, described as strongly correlated metals, like the two-dimensional Na_4C_{60} polymer.[5,6]

The observed increase in the susceptibility of the polymeric phase at low temperatures could be also analyzed in terms of the occurrence of a metal/insulator transition. In such a case, the susceptibility could be well described below 60 K as a constant plus the Curie term (Fig. 5, dashed line)

$$\chi_{\mathrm{poly}}=\mathrm{const}+C/(T-\theta) \tag{4}$$

with a positive Curie temperature, $\theta=5.1\pm1.2\,\mathrm{K}$. However, this scenario also necessitates that a change in the ESR linewidth should occur around 60 K; no such change is observed (Fig. 3). The linewidth shows a drastic narrowing from $\Delta H_{\mathrm{pp}}=9.1\,\mathrm{G}$ at room temperature to $\Delta H_{\mathrm{pp}}=2.7\,\mathrm{G}$ at 210 K with a further smaller reduction to 1.9 G at around 190 K. Below this temperature, the linewidth is only very weakly temperature dependent, displaying a metal-like small, but positive, slope with increasing temperature (Fig. 3 inset).

Since the changes in the ESR intensity, I_{poly} are not as pronounced as, for instance, those in (TDAE)C_{60} (TDAE=tetrakis-dimethylamino-ethylene),[30] $NH_3K_3C_{60}$,[31] or RbC_{60},[17] and since no change in the ESR linewidth is observed, we conclude that no long-range magnetically ordered state develops in Na_2RbC_{60} down to 4 K, despite the presence of strong magnetic correlation effects below 60 K. Instead, the temperature dependence of the ESR linewidth suggests that polymeric Na_2RbC_{60} remains conducting down to 4 K. The observed behavior is also quite different from that observed in the one-dimensional charge-transfer salt TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethanide) which shows transitions to CDW states. It is likely that the importance of the interchain interactions identified in Na_2RbC_{60} prevent the occurrence of a transition to a CDW state, as it was pointed out in Ref. 18.

IV. CONCLUSION

In conclusion, we have studied the process of polymerization in the Na_2RbC_{60} fulleride by the *X*-band ESR technique. In agreement with earlier x-ray-diffraction data, we have determined that the polymerization sets in, on cooling, around 250 K and that the maximum fraction of the polymerized phase is about 0.55. The polymeric phase is found to be conducting down to 4 K. The temperature dependence of the spin susceptibility, as measured by ESR, suggests that interchain interactions are important and the Na_2RbC_{60} polymer shows less pronounced one-dimensional character than the AC_{60} compounds. The results at low temperatures are similar to those observed for the Na_4C_{60} polymer.

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