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tetrakis(dimethylamino)ethylene-C-60  
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Slaven Garaj\*  
Andrzej Sienkiewicz\*\*

Takashi Kambe†  
Motoyasu Fujiwara††

László Forró‡  
Kokichi Oshima‡‡

\*Institute of Physics of Complex Matter, École Polytechnique Fédérale de Lausanne

†Graduate School of Natural Science and Technology, Okayama University

‡Institute of Physics of Complex Matter, École Polytechnique Fédérale de Lausanne

\*\*Institute of Physics, Polish Academy of Sciences

††Graduate School of Natural Science and Technology, Okayama University

‡‡Graduate School of Natural Science and Technology, Okayama University

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**Polymer phase of the tetrakis(dimethylamino)ethylene-C<sub>60</sub> organic ferromagnet**Slaven Garaj,<sup>1</sup> Takashi Kambe,<sup>1,2</sup> László Forró,<sup>1</sup> Andrzej Sienkiewicz,<sup>3</sup> Motoyasu Fujiwara,<sup>2</sup> and Kokichi Oshima<sup>2</sup><sup>1</sup>*Institute of Physics of Complex Matter, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*<sup>2</sup>*Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima, Okayama 700-8530, Japan*<sup>3</sup>*Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland*

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High-pressure electron spin resonance (ESR) measurements were performed on tetrakis(dimethylamino)ethylene (TDAE)-C<sub>60</sub> single crystals and stability of the polymeric phase was established in the  $P$ - $T$  parameter space. At 7 kbar the system undergoes a ferromagnetic to paramagnetic phase transition due to the pressure-induced polymerization. The polymeric phase remains stable after the pressure release. The depolymerization of the pressure-induced phase was observed at a temperature of 520 K, revealing an unexpectedly high thermal stability of the polymer. Below room temperature, the polymeric phase behaves as a simple Curie-type insulator with one unpaired electron spin per chemical formula. The TDAE<sup>+</sup> donor-related unpaired electron spins, formerly ESR silent, become active above a temperature of 320 K, which demonstrates that the magnetic properties are profoundly defined by miniscule reorientation of TDAE molecules.

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**I. INTRODUCTION**

The organic charge-transfer compound TDAE-C<sub>60</sub> [where TDAE is tetrakis(dimethylamino)ethylene] is a ferromagnet with a Curie transition temperature of  $T_C = 16$  K (Ref. 1). This is the highest temperature onset of ferromagnetic behavior for a purely organic material. The first measurements on powder samples raised the controversy about the nature of the ground state (itinerant ferromagnetism,<sup>2</sup> superparamagnetism,<sup>3</sup> spin glass,<sup>4</sup> weak ferromagnetism<sup>5</sup>). However, thorough studies on single crystals by means of ferromagnetic resonance,<sup>6,7</sup> and magnetization,<sup>8,9</sup> measurements firmly established that TDAE-C<sub>60</sub> is an isotropic Heisenberg ferromagnet with an extremely small anisotropy field  $H_A \approx 30$  G.

The TDAE molecule, a strong electron donor, transfers one electron<sup>10</sup> to the lowest unoccupied molecular orbital of C<sub>60</sub> in a similar way as it is found in alkali metal C<sub>60</sub> charge transfer salts. Likewise, the valence band in TDEA-C<sub>60</sub> mainly originates from the triply degenerate  $t_{1g}$  orbital of the C<sub>60</sub> molecule.<sup>11</sup> Although the single-charged C<sub>60</sub> alkali salts A<sub>1</sub>C<sub>60</sub> ( $A = \text{K, Rb, Cs}$ ), reveal metallic properties in a wide temperature range,<sup>12</sup> the TDAE-C<sub>60</sub> system was found to be nonmetallic.<sup>13,14</sup> The insulating ground state of TDAE-C<sub>60</sub> was explained theoretically assuming the combined effects of Jahn-Teller distortion and enhanced Mott-Hubbard localization.<sup>15,16</sup>

Upon the charge transfer from TDAE to C<sub>60</sub>, both cations and anions are expected to carry an unpaired spin density. However, electron spin resonance (ESR) results<sup>8,17</sup> showed that the TDAE-C<sub>60</sub> system has only one  $S = 1/2$  magnetic moment per chemical formula unit, giving rise to a single ESR line well above  $T_C$ . This is consistent with the magnetic susceptibility measurements.<sup>2,17,18</sup> From the ESR  $g$ -factor analysis it was concluded that the spins are mainly localized on C<sub>60</sub><sup>-</sup> (Ref. 17). The TDAE<sup>+</sup> donors remain ESR silent, which is probably due to spin-singlet pairing resulting from

the dimerization shift of the neighboring TDAE<sup>+</sup> molecules.<sup>5</sup> Recently, nuclear magnetic resonance (NMR) data<sup>19</sup> and electron spin echo envelope modulation measurements<sup>20</sup> confirmed that the unpaired spin density on <sup>14</sup>N in TDAE<sup>+</sup> is very small.

The early inconsistency in assessing the nature of the ground state of TDAE-C<sub>60</sub> can be explained by the strong dependence of magnetic properties of the material on the miniscule structural changes and on the thermal history of the sample. Single crystals freshly grown below 10 °C are antiferromagnetic down to the temperature of 1.7 K ( $\alpha'$  phase),<sup>8,21</sup> whereas the samples annealed at 350 K show a long range ferromagnetic order below 16 K ( $\alpha$  phase). Both modifications have the equivalent monoclinic crystal structure,<sup>22</sup> space group  $C2/c$ , and four formula units per unit cell.<sup>5</sup> Although the two forms appear structurally indistinguishable at room temperature, a small difference between the orientation of the C<sub>60</sub> molecules in the two phases show up in structural measurements below 50 K (Refs. 8, 15 and 23).

The observed ferromagnetism is explained assuming the charge-transfer stabilized intramolecular Jahn-Teller (JT) distortion (JTD) of the C<sub>60</sub> balls, and their collective antiferro-orbital ordering.<sup>16,24</sup> The opposite case of ferro-orbital ordering leads to a simple antiferromagnetic ground state equivalent to the one expected from the single-band Mott-Hubbard insulator. Therefore, the interplay of the two orbital configurations can give rise to both the ferromagnetic  $\alpha$  phase and the antiferromagnetic  $\alpha'$  phase. Indeed, NMR observations of the JT distortion and an asymmetric charge distribution on the C<sub>60</sub> balls have recently been reported.<sup>25</sup> Furthermore, the NMR results of Arcon *et al.*<sup>19</sup> suggest that the  $\alpha$  phase contains the C<sub>60</sub><sup>-</sup> molecules with both ferromagnetic and antiferromagnetic configurations. In that case, a spontaneous magnetization should appear when the concentration of the ferromagnetic configuration is high enough for the appearance of an infinite ferromagnetic cluster through a

percolation mechanism.<sup>23</sup> This scenario was recently supported by magnetization measurements.<sup>9</sup>

The orbital-ordering model of the ferromagnetism is recently supported by the work of Mizoguchi and co-workers,<sup>26,27</sup> where they reported the parabolic suppression of  $T_c$  with pressure. In addition, they reported the polymerization of TDAE-C<sub>60</sub> under a pressure of  $\sim 10$  kbar. The polymerized phase ( $\beta$  phase) remains stable even after releasing the pressure. The polymerization process occurs along the  $c$  axis, where the C<sub>60</sub>-C<sub>60</sub> center-to-center distances are the shortest in the monomer phase. They suggested that the linear polymers can be formed due to a [2+2] cycloaddition process.

In this paper, we report on the  $P$ - $T$  diagram of the stability of the polymeric TDAE-C<sub>60</sub> structure. The effects of the high-hydrostatic pressure on the physical properties of both monomeric and polymeric phases are investigated. We studied the physical properties of the  $\beta$ -phase at low and high temperatures and the effect of the temperature-induced depolymerization. The properties of the TDAE-C<sub>60</sub> polymer are compared with those of other bonded fullerene structures.

## II. EXPERIMENT

Single crystals of the TDAE-C<sub>60</sub> were prepared by the diffusion method reported in Ref. 8. The single crystals dimensions were, typically, of  $0.3 \times 0.3 \times 0.3$  mm<sup>3</sup>. The presence of the ferromagnetic phase was checked by the magnetization measurements.

Ambient pressure ESR measurements were performed in the temperature range of 5–600 K using a Bruker ESP300E X-band spectrometer. In the temperature range of 5–300 K the ESR spectra were acquired using a standard Bruker TE<sub>102</sub> cavity that was equipped with an Oxford Instrument, Model ESR900, gas-flow cooling system. In the upper temperature range (300–600 K) we used a Bruker ER4114HT high-temperature cavity system. The magnetic field and the microwave frequency were calibrated using a commercially available NMR Gauss meter and a frequency counter, respectively. The ESR line intensities were calibrated using a secondary standard sample, a small speck of DPPH (2,2-diphenyl-1-picrylhydrazyl from Sigma).

The high-pressure ESR measurements were performed using a high-pressure system that was recently developed at the École Polytechnique Fédérale de Lausanne. The high-pressure ESR probe was designed as an interface to our Bruker ESP300E X-band spectrometer. The probe consists of two subassemblies: (1) the microwave resonant structure containing the double-stacked dielectric resonator (DR), and (2) the miniature sapphire-anvil pressure cell (SAC). The SAC is ruby-calibrated; thus the hydrostatic pressure can be monitored *in situ* by detecting the pressure-induced shift of the red fluorescence of Cr<sup>3+</sup> ions in a small crystal of ruby. The commercially available “Daphne” oil was used as a pressure-transmitting medium. In this work, the maximum applied pressure was of 9 kbar. For performing low temperature measurements, the high-pressure probe was inserted into the CF-1200 Oxford Instrument gas-flow cryostat operating in the 5–290-K temperature range. The details of the DR-

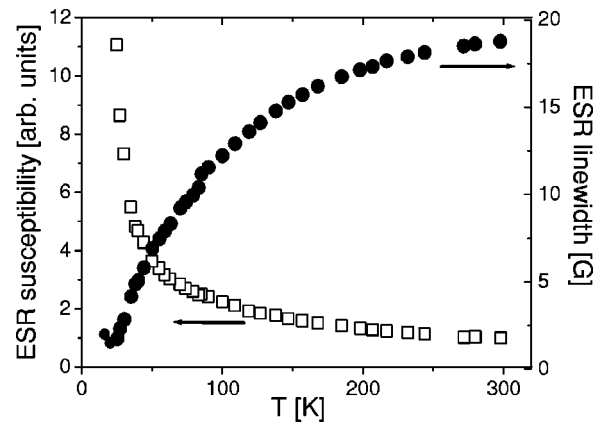


FIG. 1. Spin susceptibility (left scale, open squares) and ESR linewidth (right scale, filled circles) of the ferromagnetic TDAE-C<sub>60</sub> single crystal as a function of temperature. In the ferromagnetic region below  $T_c = 16$  K, the linewidth cannot be easily defined because the line shapes are strongly distorted due to the mosaicity of the crystal.

based high-pressure ESR probe will be published shortly elsewhere.<sup>28</sup> The ESR line intensities and the  $g$  factor were calibrated using an additional reference sample, a polycrystalline MnO/MgO, which was positioned in the active zone of the microwave resonant structure (close to the gasket of the SAC).

## III. RESULTS

### A. Pressure-induced polymerization

Figure 1 shows the temperature evolution of the ESR-probed spin susceptibility and the ESR linewidth of the ferromagnetic phase of TDAE-C<sub>60</sub> measured at ambient pressure. In the ferromagnetic region, below  $T_c = 16$  K, the linewidth cannot be determined precisely due to the strong distortion of the ESR line shape. The line shape distortion is probably due to the nonhomogeneity of the local internal fields in different ferromagnetic domains of the crystal.

The pressure dependence of the ESR linewidth (peak to peak,  $\Delta H_{pp}$ ) of TDAE-C<sub>60</sub> at ambient temperature is shown in Fig. 2(a), whereas Fig. 2(b) shows the pressure dependence of the  $g$  factor. The initial (ambient pressure) linewidth of  $\Delta H_{pp} \approx 20$  G slowly decreases with increasing pressure to 15 G at  $P = 6$  kbar. Then, at  $P_c = 7$  kbar, a transition to the polymeric phase is clearly seen as a sudden drop in the ESR linewidth [Fig. 2(a)]. This is also accompanied by an abrupt change (increase) in the  $g$  factor [Fig. 2(b)]. The phase transition is irreversible and the polymeric phase remains stable after releasing the pressure.

In the monomeric TDAE-C<sub>60</sub> the ESR linewidth is defined by dipolar interaction with additional narrowing introduced by the exchange interaction. Accordingly, as can be seen in Fig. 2(a), the monomer’s linewidth slowly narrows with pressure approaching 7 kbar. This is due to the larger overlap of the electronic wave functions, which leads to an enhanced exchange interaction. At ambient pressure, the  $g$ -factor value for the monomeric phase of TDAE-C<sub>60</sub> is 2.0006 and is distinctively closer to the  $g$  factor of the

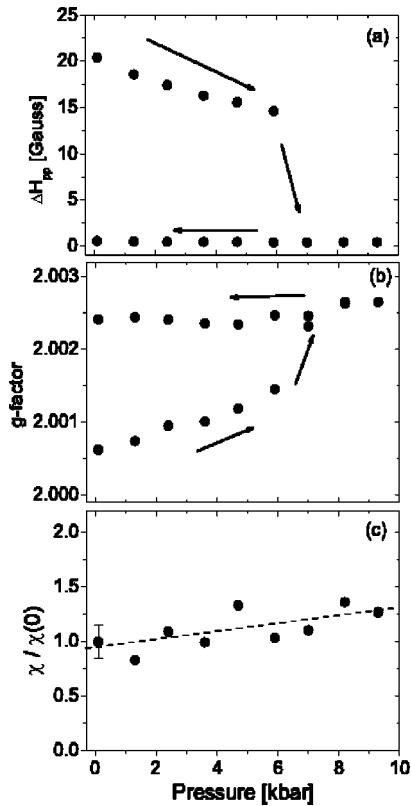


FIG. 2. Pressure dependence of the ESR parameters for single crystal TDAE-C<sub>60</sub> at room temperature: (a) linewidth, (b)  $g$  factor, (c) relative spin susceptibility. The phase transition to the polymerized phase is visible at  $P_C=7$  kbar.

fullerene anion C<sub>60</sub><sup>-</sup> ( $g_{C_{60}^-}=1.9998$ ) than to the  $g$  factor value that is characteristic for the TDAE<sup>+</sup> cation ( $g_{TDAE^+}=2.0036$ ). This is due to the fact that the ESR signal originates from the electrons that are mainly localized on the C<sub>60</sub> balls. The spins on the TDAE<sup>+</sup> radicals are ESR silent, which is probably due to a slight dimerization of TDAE molecules, thus yielding a spin-singlet configuration. With increasing pressure, the  $g$  factor linearly increases towards the value of the TDAE<sup>+</sup> cation. This implies that the unpaired spin density is spreading towards the TDAE molecule with increasing pressure.

At  $P_C=7$  kbar, a sudden narrowing of the ESR line is visible due to polymerization. The linewidth drops by two orders of magnitude, reaching  $\Delta H_{pp}(\text{polymer})=0.5$  G. The narrow linewidth and the Currie type temperature dependence of the spin susceptibility at this pressure suggest that the polymeric phase is nonmetallic. Upon polymerization the  $g$ -factor value rises, reaching 2.0024 and becomes almost pressure independent.

Mizoguchi *et al.*<sup>26</sup> suggested that the polymerization process directly decouples the previously ESR-silent spins related to the TDAE<sup>+</sup>, which should lead to an effective doubling of the total number of spins. The observed pressure dependence of the ESR susceptibility at room temperature [Fig. 2(c)] does not support this suggestion. The ESR susceptibility increase of  $\sim 20\%$  upon polymerization can be

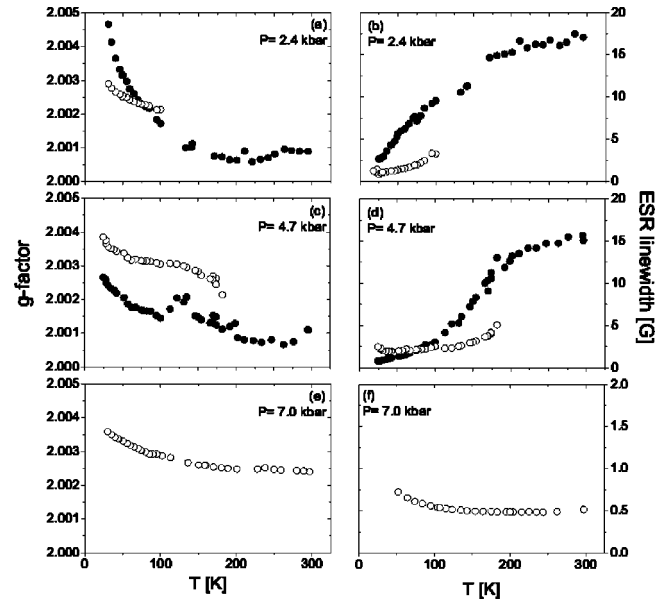


FIG. 3. Temperature dependence of the ESR linewidth and the  $g$  factor for pressures of 2.4 kbar (a) and (b), 4.7 kbar (c) and (d), and 7 kbar (e) and (f). Below the polymerization temperature, in addition to monomeric line (filled circles), a new line appears (open circles) which was assigned to the polymer. At 7 kbar the system is fully polymerized at room temperature.

explained by the difference in the Weiss temperatures between the two phases (see Sec. IV).

## B. Coexistence of phases

Figure 3 shows the temperature dependence of the ESR linewidth and the  $g$  factor for three different pressures. The temperature dependence of the linewidth and the  $g$  factor at an applied pressure of  $P=2.4$  kbar is shown in Figs. 3(a) and 3(b), respectively. As can be seen in Fig. 3(a), below the characteristic temperature  $T_P=100$  K, in addition to the ESR line of TDAE-C<sub>60</sub> monomer (full circles), a new line appears (open circles). This new ESR line can be assigned to the polymeric phase while taking into account the  $g$  factor and the ESR linewidth evolution with pressure. The intensity of the polymeric line does not exceed 15% of the intensity of the monomeric line. The temperature dependence of the  $g$  factor and ESR linewidth at  $P=4.7$  kbar is shown in Figs. 3(c) and 3(d), respectively. At this pressure, a partial polymerization starts at higher temperatures, around  $T_P \approx 180$  K. The intensity of the polymeric line is now much more pronounced. For both applied pressures, the monomeric phase undergoes a ferromagnetic phase transition, whereas the polymeric phase does not. At a pressure of  $P=7.0$  kbar, the sample is already fully polymerized at room temperature [Figs. 3(e) and 3(f)]. No ferromagnetic phase transition is visible down to 5 K. At this applied pressure, the ESR susceptibility follows a simple Currie law, without a detectable Weiss constant. The ESR linewidth is very narrow (0.5 G) and is almost independent of temperature, whereas the  $g$  factor changes slightly with temperature.

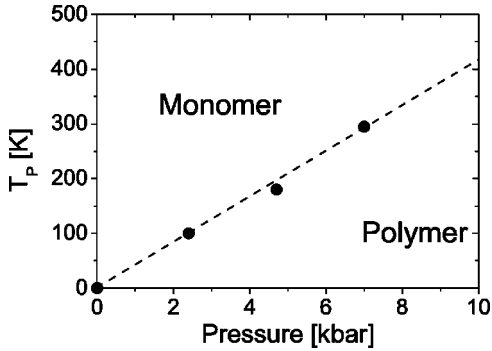


FIG. 4. Polymerization temperature ( $T_p$ ) as a function of applied pressure. The polymerization temperature has a linear dependence on the applied pressure, with a constant of proportionality of  $|dT_p/dP=41\pm 2$  K/kbar.

The stability of the polymer phase in the  $P$ - $T$  parameter space is depicted in Fig. 4. The polymerization temperature ( $T_p$ ) has a linear dependence with applied pressure, where the proportionality constant is  $|dT_p/dP=41\pm 2$  K/kbar. The ratio of the polymeric and monomeric ESR line intensities depends not only on pressure, but also on temperature. To deduce the exact structural dynamics of the polymer formation an additional structural study is needed.

The pressure dependence of the ferromagnetic transition temperature ( $T_C$ ) of the monomeric phase is depicted in Fig. 5. To determine  $T_C$ , we cannot compare the resonance field shift with the conventional Bloch's law, because the resonance field has a pronounced temperature dependence even above  $T_C$  (see Fig. 3). This shift is due to demagnetization effects, which depend on the sample shape.<sup>29</sup> Concomitantly, we define  $T_C$  as the onset temperature of the broadening of a linewidth distribution of the monomer-related ESR features (see the inset to Fig. 5). This linewidth distribution broadening is due to the growth of an internal field below  $T_C$  and the mosaicity of the crystal. The observed pressure dependence of  $T_C$  is similar to the parabolic dependence reported in Ref. 26, but quantitatively different. In contrast to their ESR data

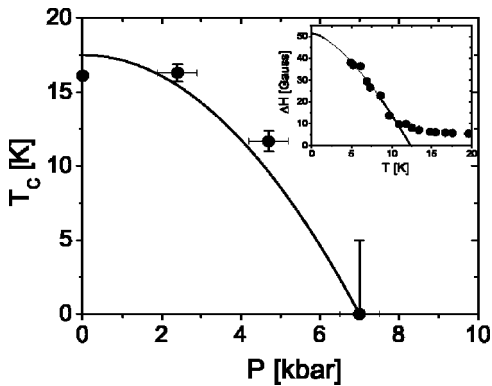


FIG. 5. Pressure dependence of the ferromagnetic transition temperature  $T_C$  for single crystal TDAE- $C_{60}$ .  $T_C$  at each pressure is determined by the onset temperature of the broadening of the linewidth distribution of the monomeric signal. The lines are guides for the eye. Inset: line distribution broadening for the pressure of 4.6 kbar.

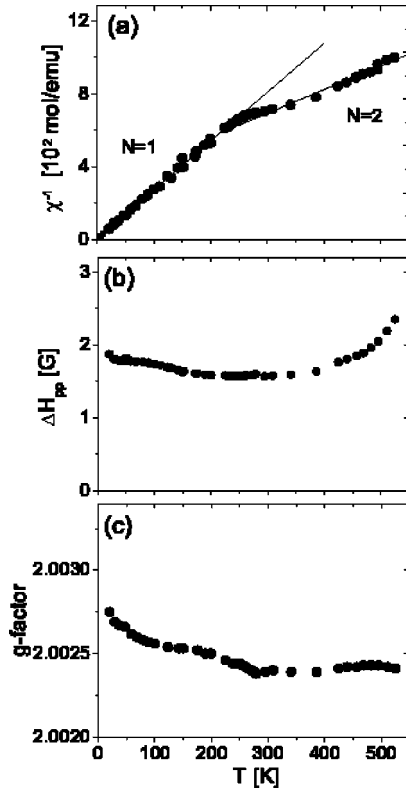


FIG. 6. Temperature dependence of ESR parameters for the polymeric  $\beta$ -TDAE- $C_{60}$  phase at ambient pressures: (a) inverse susceptibility, (b) linewidth, (c)  $g$  factor. In susceptibility, the onset from a simple Curie law is seen above 250 K, but the full appearance of previously silent TDAE<sup>+</sup> spins is seen at 320 K, a leading to a doubling of the number of spins and the appearance of the Weiss constant. The effect is probably connected to structural dynamics of the TDAE dopant.

acquired at low microwave frequencies and fields, the critical pressure of the suppression of the ferromagnetic transition in our measurements is rather lower (7 kbar vs 9 kbar) and coincides with the pressure of the complete polymerization. The onset of polymerization should prevent the antiferro-orbital-ordering of the JT distorted fullerene molecules, therefore hinder the ferromagnetism in the framework of the theory proposed by Kawamoto.<sup>16</sup>

### C. Polymer phase at ambient pressure

The polymeric phase remains stable even after the pressure is released. For the polymeric phase, the temperature dependences of the ESR parameters are shown in Fig. 6. As can be seen from comparison of the results presented in Fig. 6 and in Figs. 3(a) and 3(b), the low-temperature properties of the polymeric phase at ambient pressure are very similar to those observed at  $P=7$  kbar. The temperature dependence of the inverse ESR susceptibility,  $\chi^{-1}$ , of the polymeric phase is shown in Fig. 6(a). Since we are dealing with localized spins, this type of plot ( $\chi^{-1}$  vs  $T$ ) is the most informative, directly yielding information on the Curie constant and the Weiss temperature of the system. The spin sus-

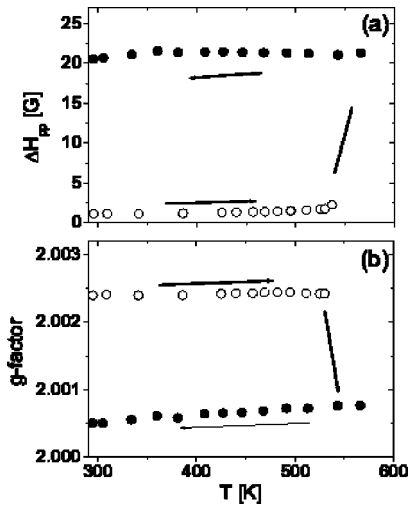


FIG. 7. Temperature dependence of the linewidth and the  $g$  factor of the polymerized crystal in the high-temperature region. The polymeric phase is marked with open circles and the monomeric phase with closed circles. Full depolymerization is observed above 520 K. At the transition temperature, signals of both phases are detected, suggesting the coexistence of the phases similar to the case of partial polymerization.

ceptibility below the room temperature reveals one spin  $S = 1/2$  per chemical formula unit ( $N = 1$ ) and a simple Curie behavior.

As seen in Fig. 6(a), the inverse susceptibility departs from the simple Curie behavior at 260 K. This transition region is relatively broad and extends up to circa 320 K. Above 320 K, the ESR susceptibility reveals the doubling of the number of spins per chemical formula. This phenomenon can be understood in terms of the reappearance of the previously hidden spins of the TDAE<sup>+</sup> radicals. The Weiss temperature does not vanish anymore, having the value of  $\Theta = 230 \pm 20$  K. This change of behavior at high temperatures is also seen in the temperature dependence of the linewidth [Fig. 6(b)]. At lower temperatures the  $\Delta H_{pp}$  is almost constant, with a slight tendency to decrease with increasing temperature, whereas above the room temperature it changes its slope and starts to increase more rapidly. The temperature dependence of the  $g$  factor [Fig. 6(c)] reveals a similar, distinctive change of behavior above the room temperature.

The polymeric phase remains stable up to the depolymerization temperature,  $T_{DP} = 520$  K. Above this temperature, both the  $\Delta H_{pp}$  and the  $g$  factor recover their characteristic values for the ferromagnetic phase (Fig. 7). The depolymerization process is an irreversible transition. At the depolymerization temperature, both polymeric and ferromagnetic ESR features are present, thus pointing to the coexistence of the two phases. It also suggests that this phase transition does not seem to be an abrupt one. As in the case of ferromagnetism, the polymerization process might be influenced by percolation mechanism, as the samples of apparently lesser quality exhibit a bit lower depolymerization temperature.

At low temperatures, the depolymerized crystals reveal the same temperature dependences of the ESR parameters as those observed for the ferromagnetic crystals. The  $g$  factor

shifts remarkably below 15 K, which indicates that the depolymerized crystal undergoes the ferromagnetic phase transition.

#### IV. DISCUSSION

In the intermediate pressure range, below  $P_C = 7$  kbar, the TDAE-C<sub>60</sub> monomer partially polymerizes on cooling. Both the polymerization temperature ( $T_P$ ) and the relative ratio of the polymeric to the monomeric fractions depend on pressure (Fig. 4). Preliminary analysis<sup>26</sup> has suggested that the polymer would have a linear [2+2] cycloadduct bonding structure with a similar intrachain ball distance as in the case of Rb<sub>1</sub>C<sub>60</sub> (Ref. 30). The most prominent difference between the systems is a much larger interchain distance in the case of TDAE-C<sub>60</sub>, which is due to the large size and anisotropic (steric) properties of the TDAE interstitials.

Rich phase diagrams have already been reported for several C<sub>60</sub>-related compounds. In particular, interesting phase transitions were found for Rb<sub>1</sub>C<sub>60</sub>. Depending on the cooling rate and quenching, it can form either monomeric, dimeric<sup>31</sup> or polymeric phases.<sup>30,32</sup> Nevertheless, the coexistence of the two phases has never been observed for Rb<sub>1</sub>C<sub>60</sub>. In contrast, the coexistence of two phases at low temperatures was observed in the case of single-bonded linear polymers of Na<sub>2</sub>RbC<sub>60</sub> system.<sup>33</sup> In that case, the partial polymerization can be explained by steric effects and by disorder resulting from different possible directions of the bond formation. In contrast, TDAE-C<sub>60</sub> is a strongly anisotropic structure with only one possible direction of the bond formation ( $c$  axis). Hence, the partial polymerization is probably governed by the orientation disorder of JTD-C<sub>60</sub> molecules. The polymerization temperature  $T_P$  is much lower than the freezing temperature of the C<sub>60</sub> molecule rotation for a given pressure. This suggests that the freezing of molecular orientations is not sufficient for initiating the polymerization process, and that there exists a kinetic barrier for this phase transition. It seems to be natural that different kinetic barriers can characterize various relative orientations of the JTD-C<sub>60</sub> molecules. As the remaining monomeric phase still shows a pronounced ferromagnetic order, most probably the FM molecular configuration has the highest energetic barrier.

At room temperature the sample is fully polymerized upon applying a pressure of  $P_C = 7$  kbar. These results are in quantitative disagreement with the ESR measurements performed at lower microwave frequencies by Mizoguchi *et al.*,<sup>26</sup> reporting polymerization at higher pressures, above 10 kbar. To investigate this discrepancy, we recently performed independent measurements with different experimental techniques, namely, electrical resistivity and thermoelectric power measurements on single crystals under pressure. The preliminary results are fully consistent with our ESR measurements, demonstrating the polymerization at  $P_C = 6.9 \pm 0.1$  kbars.<sup>34</sup> Our ESR and electrical transport measurements are performed on different samples coming from different laboratories, the transport measurements being performed on the samples coming from the same source as the ones used by Mizoguchi *et al.* However, we keep a possibility open that the discrepancy in the polymerization pressures

reported by Mizoguchi *et al.* and ourselves could arise from different qualities of the samples. It was illustrated in Sec. I paragraph that many properties critically depend on minute structural changes and the thermal history of the sample. We demonstrated that the polymerization might be influenced by the orientational disorder of the  $C_{60}$  molecules; therefore, the difference in the polymerization pressure might arise from different degrees of order in the crystals.

It follows from our measurements that the depolymerization of TDAE- $C_{60}$  occurs at the higher temperature than in the case of one-dimensional  $A_1C_{60}$  polymers ( $A = K, Rb, Cs$ ), where, depending on the compound,  $T_{DP}$  varies in the range of 300–400 K (Ref. 12). It seems that  $T_{DP}$  of TDAE- $C_{60}$  is rather comparable to that found for the two-dimensional polymer  $Na_4C_{60}$  ( $T_{DP} \approx 500$  K).<sup>35</sup> Therefore, the polymeric chains of TDAE- $C_{60}$  seem to form much more stable structures than the double-bonded polymeric chains of the  $Rb_1C_{60}$  system. If the intrachain bonds of both TDAE- $C_{60}$  and  $Rb_1C_{60}$  were of the same nature (isostructural), one would expect similar temperature stabilities for them. The observed discrepancy in the temperature stability can be ascribed to a potential structural difference in the two polymeric structures. Alternatively, the previously uninvestigated effects of dopant molecule and the interchain coupling can be important for the polymeric chain stability. A precise structural analysis is needed to answer these questions.

Below 260 K, the ESR spin susceptibility of the polymerized  $\beta$  phase at ambient pressure follows a simple Curie law with one spin  $S = 1/2$  per chemical formula, as calculated from the calibrated ESR intensity [Fig. 6(c)]. This indicates that spins probed by ESR are localized. Moreover, in this temperature range, the ESR linewidth for the polymerized  $\beta$  phase is very narrow (0.5 G) and almost temperature independent, which suggests strong exchange interactions between the spins. The theoretical band calculations, however, predict that in the absence of electron correlations, the isolated single-charged, double-bonded linear polymer should be metallic with a half-filled band.<sup>36</sup> Also, the same property holds well for single-bonded linear polymers encountered in  $Na_2AC_{60}$  systems.<sup>37</sup> Indeed, all the other charged linear polymers of the  $C_{60}$  compounds, discovered to date, are metallic in a wide temperature range, with possible ground-state instabilities, such as the spin-density wave.<sup>38</sup> Therefore, the TDAE- $C_{60}$  polymeric phase seems to be unique.

The inter-chain coupling is very important in alkali fullerenes  $A_1C_{60}$ , influencing their dimensionality. However, according to Erwin *et al.*,<sup>36</sup> a direct interchain coupling interaction can be neglected in TDAE- $C_{60}$  based on the large interchain separation found in these systems.

Assuming a simple model, one would expect the TDAE- $C_{60}$  polymer should be a strongly anisotropic metal. The effective strong localization observed in the  $\beta$  phase of TDAE- $C_{60}$  might suggest that its actual polymer topology essentially differs from that of  $Rb_1C_{60}$ . Alternatively, the localization effect might originate from the possible enhancement of the effective Coulomb repulsion at  $C_{60}$  sites, due to the influence of the TDAE<sup>+</sup> radicals. In such a Mott-Hubbard localization scheme, one would expect a nonvanishing Weiss constant. In contrast, the presence of the Weiss

constant has not been detected in the low-temperature  $\beta$  phase. Mizoguchi *et al.*<sup>26</sup> suggested that the absence of the Weiss parameter could be explained by re-activation of the positive exchange coupling with the spins of TDAE<sup>+</sup> radicals. This, in turn, would fortuitously cancel the negative inter- $C_{60}$  spin coupling leading to a diminishing Weiss constant. Nevertheless, in this work, we did not observe the complete recovery of the TDAE<sup>+</sup> spins in the polymeric phase at the room temperature, as claimed by Mizoguchi *et al.* Indeed, the appearance of TDAE spins at elevated temperatures is accompanied by the development of the antiferromagnetic Weiss constant.

Assuming that polymeric chains in the  $\beta$ -TDAE- $C_{60}$  have rather small sizes and are disordered, one can apply a model of the random-exchange AFM Heisenberg 1D chains. In this case, the Weiss temperature would be absent, whereas the ESR susceptibility should be proportional to  $T^{-\alpha}$ , where  $\alpha \approx 0.7-0.8$ . Fitting this model to our data yields  $\alpha = 0.96 \pm 0.1$ . Clearly, this result does not support the above-mentioned model. For right now, a plausible reason for non-appearance of the Weiss temperature in the polymer phase remains unclear.

As can be seen in Fig. 6(a), in the polymeric  $\beta$  phase, a complete recovery of the TDAE<sup>+</sup>-related spins is not observed at ambient temperature. The recovery of the spins occurs rather at higher temperatures, with full development at 320 K. The dynamics of the TDAE<sup>+</sup>-related spins is probably connected to small movements of the TDAE<sup>+</sup> molecules leading to the dimerization shift.<sup>5</sup>

## V. CONCLUSION

In conclusion, we have investigated the polymerization mechanism in TDAE- $C_{60}$  ferromagnetic system and the physical properties of the polymeric  $\beta$  phase. The complete polymerization at room temperature is observed at a pressure of 7 kbar. At the same pressure, the ferromagnetic transition is suppressed. Partial polymerization is observed at lower pressures and temperatures, and the stability of the polymeric phase was established in the  $P$ - $T$  parameter space. The high depolymerization temperature suggests that the polymeric chains are much more stable than in the case of double-bonded linear polymers of the  $Rb_1C_{60}$  systems. To deduce the exact structural properties of the polymer, an additional high-resolution x-ray diffraction study is needed.

Moreover, the observed strong localization of spins in the polymeric TDAE- $C_{60}$  is in contradiction with conclusions from a simple theoretical reasoning and it is not comparable to any other charged linear polymer of the  $C_{60}$ . Therefore, an investigation of TDAE- $C_{60}$  polymer can shed new light towards our general understanding of the ground state electronic properties of the linear fullerenes polymers. Above 320 K, the previously silent spins on the TDAE- $C_{60}$  are revealed. The observed decoupling of the TDAE<sup>+</sup> spins is accompanied by the appearance of the Weiss constant. This recovery of previously hidden spins at higher temperature, while the  $C_{60}$  molecules are still closely locked in the chain structure, implies that the miniscule reorientation of TDAE molecules can profoundly affect the magnetic properties of the system.

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