

## Pressure effect in TDAE-C<sub>60</sub> ferromagnet: Mechanism and polymerization

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Effects of hydrostatic pressure on TDAE-C<sub>60</sub> are investigated by electron spin resonance to reveal a mechanism of the ferromagnetism, where TDAE is tetrakis-dimethylamino-ethylene.  $T_C$  decreases with increasing pressure, reaching zero around 9 kbar, following a relation of  $\approx T_C(0)(1 - aP^2)$ . The orbital-ordering model of Jahn-Teller distorted C<sub>60</sub> molecules reproduces such a dependence successfully. Furthermore, above  $\approx 10$  kbar at 300 K,  $\alpha$ -TDAE-C<sub>60</sub> transforms to the  $\beta$  phase with a [2+2] cycloadditive one-dimensional polymer, stable even after pressure release. Remarkably, a missing spin in TDAE<sup>+</sup> revives in the polymer with  $g = 2.0028$ .

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Since a discovery of ferromagnetic behavior in TDAE-C<sub>60</sub>, where TDAE is tetrakis-dimethylamino-ethylene, with a high-transition temperature of 16 K as a pure organic system,<sup>1</sup> a great number of investigations have been reported to unveil the nature of the ground state. However, two things are required to extract the intrinsic nature of this material. One is to anneal as-grown crystals around 350 K (Ref. 2) and the other is availability of a single crystal. The annealing promotes a meroheral ordering of the Jahn-Teller distorted C<sub>60</sub><sup>-</sup> balls, which makes the coupling between the balls ferromagnetic, as discussed experimentally<sup>3,4</sup> and theoretically.<sup>5-8</sup> A lack of the ordering results in antiferromagnetic coupling, as demonstrated by the susceptibility data showing a negative Weiss temperature above 150 K, where the balls are freely rotating, and changing to a positive ferromagnetic value below 50 K, where the meroheral order develops enough in the annealed samples.<sup>9,10</sup> Since the powder sample has a higher number of molecules in its surface, the meroheral disorder could be an origin of a variety of findings observed in powder samples,<sup>11</sup> such as itinerant ferromagnetism,<sup>9</sup> superparamagnetism,<sup>12</sup> spin glass,<sup>13</sup> weak ferromagnetism, and so on. A recent series of electron spin resonance (ESR) studies on single crystals in the wide frequency range have revealed a nature of ferromagnetic ground states; a nearly isotropic Heisenberg ferromagnet with the exchange field of  $H_E \approx 450$  kG and the exceptionally small anisotropy field of several tens of Gauss caused mainly by the electronic dipolar field,<sup>14</sup> consistent with the magnetization curve of single crystal.<sup>4,15</sup>

The number of  $S = \frac{1}{2}$  unpaired spins per TDAE-C<sub>60</sub> unit was determined to be approximately unity, not only from the Curie constant in the paramagnetic region by both the superconducting quantum interference device<sup>9,10,16</sup> (SQUID) and the ESR intensity,<sup>4,10</sup> but also from the saturation magnetization in the ferromagnetic state of the single crystal by SQUID,<sup>4,15</sup> namely, the number of unpaired spins is constant through the phase transition. This fact suggests that a localized moment picture holds, consistent with a semiconducting electrical property.<sup>17-20</sup> Furthermore, the above fact demonstrates that the ESR signal catches all the unpaired spins in TDAE-C<sub>60</sub>. The location of the unpaired spins was determined to be mainly on the C<sub>60</sub><sup>-</sup> anions from the single sym-

metrical ESR line with  $g \approx 2.0005$  close to 1.9998 for C<sub>60</sub><sup>-</sup>, but far from 2.0036 for TDAE<sup>+</sup>.

In this paper we demonstrate the effect of pressure on the physical properties of TDAE-C<sub>60</sub> studied by ESR. The transition temperature  $T_C$  is found to be less sensitive than the earlier report,<sup>9</sup> attributable to the quality of the samples. Instead, it was suppressed entirely around 9 kbar with a fashion reproducible by the theoretical model taking into account the effective interball exchange interaction in terms of the interball transfer energies. Above  $\approx 10$  kbar, one-dimensional (1D)-polymerization of C<sub>60</sub>-chain occurs along the  $c$  axis, stable even after pressure release.

Single crystals of TDAE-C<sub>60</sub> were prepared by a diffusion technique.<sup>11</sup> The crystals were successively annealed at 60 °C for 30 min., followed by SQUID measurements after each annealing, till magnetization below  $T_C$  saturates. ESR measurements of a single crystal were performed with home-built spectrometers for both low frequency and the  $K$  band. For the pressure experiment, a clamp-type cell made of a CuBe alloy is used with Daphne 7373 oil as a pressurizing medium. Pressure  $P_{50K}$  is a value valid below 50 K estimated by  $P_{rT} \times 1.096 - 2.215$ , obtained from a reported temperature variation.<sup>21</sup>

ESR linewidth measured at 100 MHz and the  $K$  band is shown in Fig. 1, together with the reported.<sup>2</sup> A single symmetrical ESR spectrum is obtained above  $T_C$ , consistent with the other single crystal ESR studies.<sup>4,14</sup> Furthermore, no frequency dependence was observed even in powder samples, suggesting an absence of sizable  $g$ -shift anisotropy assumed by Gotschy.<sup>22</sup> The observed linewidth would be dominated by the dipolar field of electron spins on C<sub>60</sub><sup>-</sup>s, amounting to 100 G or more, narrowed by an exchange interaction. A difference of temperature dependence between before (paramagnetic  $\alpha'$ -phase) and after (ferromagnetic  $\alpha$ -phase) annealing is remarkable as reported.<sup>2</sup> The steep narrowing below 170 K in the unannealed  $\alpha'$  phase was attributed to the exchange narrowing resulted from the overlapping between wave functions on the neighboring balls developed by quenching of rotational motion.<sup>11</sup> The slower decrease in the ferromagnetic  $\alpha$  phase than  $\alpha'$  might be related to the reduced overlapping of the wave functions than

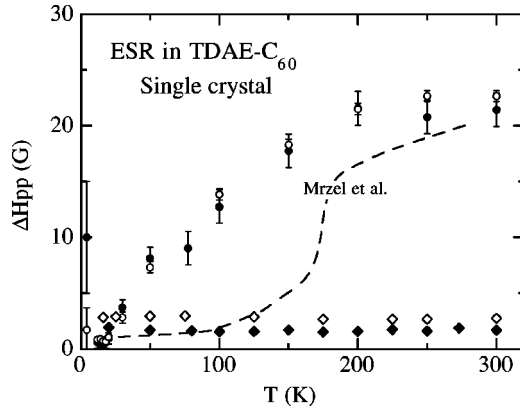


FIG. 1. Temperature dependence of ESR peak-to-peak linewidth in TDAE-C<sub>60</sub>. The open and closed circles were taken at 24 GHz and 100 MHz, respectively. The dashed curve shows the reported data measured at the X band for unannealed TDAE-C<sub>60</sub> by Mrzel *et al.* (Ref. 2). The closed diamonds were measured at the 9.2 kbar and the open diamonds at ambient pressure in the same sample restored from the 9.2 kbar measurement.

the random orientation in the unannealed  $\alpha'$  phase. A model for the ferromagnetism in TDAE-C<sub>60</sub> will be proposed later to interpret the present experimental data, based on the antiferro-orbital ordering of Jahn-Teller distorted balls,<sup>7</sup> where the Jahn-Teller orbitals on the neighboring balls are geometrically perpendicular to each other, which diminishes the transfer energy between the neighboring balls, consistent with the above requirement. It is worthy to note that the recent x-ray study reported a superlattice scattering, suggesting an antiferro-orbital-ordered phase below 180 K in the  $\alpha$ -TDAE-C<sub>60</sub>.<sup>4</sup>

The hydrostatic pressure was applied up to 12.2 kbar to investigate the interaction between electron spins, as shown in Fig. 2. Below  $T_C$  the resonance field moves rapidly by the demagnetization field that is proportional to the spontaneous magnetization  $M_s$  of the sample. Note that the magnitude and sign of the shift  $\Delta H$  depend on the parameters; sample morphology and orientation of the external magnetic field. At higher pressure than 5 kbar, the shifts extrapolated to absolute zero are nearly half of that at lower than 5 kbar, as

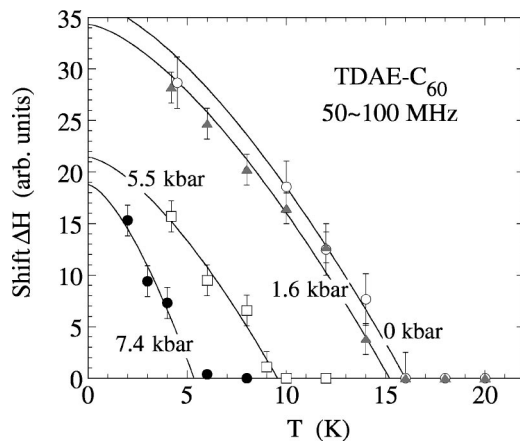


FIG. 2. Resonance shift versus temperature under several applied pressures  $P_{50K}$ . The solid curves represent Bloch's  $T^{3/2}$  law.

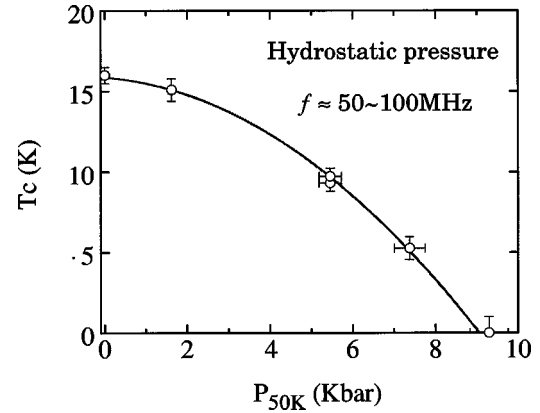


FIG. 3.  $T_C$  versus  $P_{50K}$  in TDAE-C<sub>60</sub>. The solid curve indicates the theoretical prediction with the data up to 7.4 kbar.

shown in Fig. 2. This is due to the frequency-dependent shift that follows a magnetization curve; the shift taken at  $\approx 100$  MHz and 1.6 kbar should be nearly twice that at  $\approx 50$  MHz and higher pressure than 5 kbar. Only at 7.4 kbar, a paramagnetic signal was observed together with the ferromagnetic one even at 2 K, probably due to a coexistence of the  $\beta$  phase that will be discussed later. To determine  $T_C$ , the data with definite shift were analyzed with a relation  $\Delta H(T) \propto M_s(0)(1 - \alpha T^{3/2})$  that approximately holds below  $T_C$  in the present system,<sup>14,23</sup> although it is expected for the Heisenberg ferromagnet with magnon excitations at temperatures enough below  $T_C$ . Using this relation, we obtain  $T_C$  as a function of pressure in Fig. 3, which is less affected by the external magnetic field by virtue of the low enough resonance field around 20~30 G at  $T_C$ . This result remarkably differs from the earlier report studied by induction method with powder sample.<sup>9</sup> Their conclusion of preferable itinerant ferromagnetism deduced from the rapid suppression of  $T_C$  around 1 kbar has already been excluded by semiconducting behavior of TDAE-C<sub>60</sub>.<sup>17-20</sup> This issue might be resulted from the lower sample quality of powder than the single crystals.

We can simulate the observed pressure dependence of  $T_C$  in the framework of orbital ordering model.<sup>7,8</sup> It was suggested that the interball coupling should be ferromagnetic between neighboring C<sub>60</sub><sup>-</sup>'s if the elongated axes of C<sub>60</sub><sup>-</sup>'s distorted into D<sub>2h</sub> symmetry are perpendicular to each other, and perpendicular or parallel to the  $c$  axis. Recently, an observation of such a distortion of C<sub>60</sub><sup>-</sup>'s was reported in the

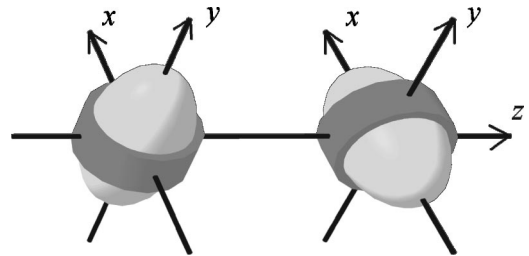


FIG. 4. Schematic view of the pair of distorted C<sub>60</sub> anions whose elongated axes are perpendicular to each other. In this alignment, the interball coupling is ferromagnetic. The belt around the balls represents the density of the unpaired electron.

model monoanion-fullerene compound by ESR.<sup>24</sup> Further, an x-ray analysis on a similar compound suggested that the orientational ordering transition around 120 K, which lowers the crystal symmetry, might relate to the stabilization of the static Jahn-Teller effect.<sup>25</sup> Such a symmetry lowering only in the ferromagnetic  $\alpha$ -TDAE-C<sub>60</sub>, but not in the unannealed paramagnetic  $\alpha'$  phase, was reported below 50 K by a precise x-ray structural determination.<sup>4,26</sup> Figure 4 shows the example of the pair of two distorted C<sub>60</sub><sup>-</sup>'s which favors to be triplet. Existence of the nearly orthogonal configurations of the twofold axes in the neighboring C<sub>60</sub><sup>-</sup>'s along the  $c$  axis was confirmed with the refined structure.<sup>26</sup> The interball magnetic coupling  $J_1$  is approximately calculated with a second order perturbation for the interball transfer,

$$J_1 = -\frac{4}{U}t_g^2 + \frac{4t_l^2 J_m}{(U + \Delta)^2}, \quad (1)$$

where  $t_l$ ,  $t_g$ ,  $U$ ,  $J_m$ , and  $\Delta$  represent the interball transfer energy between lowest unoccupied molecular orbitals (LUMO's) with same symmetry, that with different symmetry, the onball Coulomb interaction, the onball exchange interaction, and the energy splitting due to the Jahn-Teller distortion between LUMO's on C<sub>60</sub><sup>-</sup>, respectively. The increase of  $t_g$  due to the adding pressure mainly makes a contribution to the parabolic dependence of  $T_C$ . The parameter  $t_g$  should be zero in the case of crystal field at C<sub>60</sub> is perfectly orthorhombic. The crystal structure of TDAE-C<sub>60</sub> is different from orthorhombic one a little bit although C<sub>60</sub> molecule has complete orthorhombic symmetry. Therefore, the enhancement of crystal field at C<sub>60</sub>'s site due to applying pressure makes  $t_g$  larger. To simulate Fig. 3,  $U=0.55$  eV,  $J_m=0.09$  eV, and  $\Delta=0.15$  eV are used, which are almost the same as that estimated by Suzuki *et al.*<sup>27</sup> The transfer energies are assumed to depend linearly on the pressure  $P$  as  $t_a = t_a^0 + Pt'_a$  ( $a=l, g$ ).  $t_l^0 = 65$  meV and  $t'_l = 1.0$  meV/kbar are used. The above parameters dominate the maximum  $T_C$ . Since  $t_g^0$  (4.3 meV) and  $t'_g$  (2.2 meV/kbar) predominate the pressure dependence, these parameters, along with a reduction factor  $\delta$  (0.75) for the mean-field approximation, are used as fitting parameters. The parentheses show the values for the solid curve in Fig. 3, where the 2nd nearest coupling along the chain,  $J_2$  was taken into account. More theoretical details will appear elsewhere.

As shown in Fig. 1, the ESR linewidth at 9.2 kbar is  $\approx 2$  G in the whole temperature range. This figure also shows a curious irreversible feature of the ESR linewidth in the sample restored to ambient from 9.2 kbar. Namely, it does not come back to 20 G after pressure release, but it is still narrow, less than 3 G in the whole temperature range. The sample treated under 9.2 kbar shows a weak trace of ferromagnetism below 10 K at ambient pressure, but that treated at 12.2 kbar shows Curie-like susceptibility down to 2 K.

In such a pressure released sample (named as the  $\beta$  phase), x-ray diffraction data at 89 K yielded us  $a = 15.70$ ,  $b = 13.69$ , and  $c = 9.17 \pm 0.07$  Å with  $P$  symmetry, suggesting a disappearance of the dimerizing shift of TDAE molecules along the  $b$  axis in the ferromagnetic TDAE-C<sub>60</sub>.<sup>11</sup> The shortest distance between balls dramatically reduced by

TABLE I. The distances between C<sub>60</sub>'s or neighboring chains at 89 K for the 1D polymer of TDAE-C<sub>60</sub>, together with these at 300 K for the ferromagnetic phase,  $o$ -Rb<sub>1</sub>C<sub>60</sub> (Ref. 28) and dimer-Rb<sub>1</sub>C<sub>60</sub> (Ref. 29) for comparison.  $r_n$  represents the  $n$ th shortest distance.  $N_S$ , the number of  $S = \frac{1}{2}$  unpaired spins per (cation + C<sub>60</sub><sup>-</sup>) unit and  $g$  values are also listed.

	$r_1$ (Å)	$r_2$ (Å)	$r_3$ (Å)	$N_S$	$g$
TDAE-C <sub>60</sub>					
· 1D polymer	9.17 ± .07	13.69	15.70	2	2.0028
· Ferromagnet	9.99	13.00	15.86	1	2.0005
[2+2] polymer					
$o$ -Rb <sub>1</sub> C <sub>60</sub>	9.138	10.107	14.173	1	2.0012
Single bond					
Rb <sub>1</sub> C <sub>60</sub> dimer	9.34	9.92	14.15	0	

0.7 from 9.87 Å at 80 K in  $\alpha$ -TDAE-C<sub>60</sub>.<sup>11</sup> While the  $b$  axis expanded by 0.6 Å, which is reasonable to account for the TDAE molecules sandwiched by the balls along this direction. The  $c$  axis distance is comparable to 9.138 Å in  $o$ -RbC<sub>60</sub>,<sup>28</sup> as listed in Table I, together with magnetic properties. In case of a single-bonded dimer the shortest distance is 9.34 Å,<sup>29</sup> rather longer than the present case. Therefore we conclude that  $\alpha$ -TDAE-C<sub>60</sub> transforms to a 1D-polymer  $\beta$  phase with [2+2] cyclo-addition under the pressure of more than 10 kbar at room temperature, which is stable even after pressure release.

Magnetic properties of the polymer phase are interesting in the meaning that the missing spin of TDAE<sup>+</sup> in  $\alpha$ -TDAE-C<sub>60</sub> revives. That is, two  $S = \frac{1}{2}$  spins, twice of the ferromagnetic case, contributed to the paramagnetic susceptibility with the negative Weiss temperature  $\Theta$  of 4 K. Accompanying this change, the  $g$  factor moved from 2.0005 to 2.0028 in between 2.0012 for the polymer phase of  $o$ -RbC<sub>60</sub> and 2.0036 for TDAE<sup>+</sup> cation radical.<sup>22</sup> Recently, in the  $\alpha$  phase, the spin density on <sup>14</sup>N in TDAE<sup>+</sup> has been confirmed to be extremely small even in the ferromagnetic state by the electron spin echo envelope modulation technique.<sup>30</sup> Furthermore, it was unambiguously revealed by a detailed analysis of the infrared spectra on TDAE neutral, monocation, and dication molecules that TDAE in TDAE-C<sub>60</sub> is monocation,<sup>31</sup> consistent with the recent structural analysis of both  $\alpha'$ - and  $\alpha$ -TDAE-C<sub>60</sub>.<sup>26,32</sup> Therefore, the spins on TDAE<sup>+</sup>'s are likely to form dimers with spin singlet ground states in the  $\alpha$  phase,<sup>31</sup> which is unstable in the polymerized  $\beta$  phase.

The paramagnetic ground state of the polymer phase with the small  $\Theta \approx -4$  K would provide us with some insights on the interaction between the spins; it is very small compared with larger  $\Theta$  than  $-200$  K in  $o$ -A<sub>1</sub>C<sub>60</sub>, where  $A$  is Rb or Cs. Differences between these systems are in chain separation of 10.4 Å for the  $\beta$  phase and 10.1 Å for A<sub>1</sub>C<sub>60</sub>, and spin-spin interactions via cations; radical TDAE<sup>+</sup> and spin-silent A<sup>+</sup>. Since the interchain exchange in the  $\beta$  phase is weak,  $\Theta$  would be dominated by the intrachain exchange, which could still be the order of magnitude larger than 4 K.<sup>33</sup> Therefore, such a small  $\Theta$  in  $\beta$ -TDAE-C<sub>60</sub> implies a revival of possible magnetic interaction in *positive* exchange cou-



pling via radical TDAE<sup>+</sup>,<sup>6</sup> which fortuitously compensates the remained intrachain *negative* exchange. Then, further investigations not only experimental but also theoretical aspects on the polymer phase could promote further understanding of the electronic state in the monoanion C<sub>60</sub> compounds.

The present model to elucidate Fig. 3 suggests several interesting features. First is that a role of spin-silent TDAE<sup>+</sup> is a simple electron donor in this model. Then, a simple volume tuning to enhance  $T_C$  is not fruitful, because  $T_C$  of  $\alpha$ -TDAE-C<sub>60</sub> locates approximately peak position of the parabolic dependence in Fig. 3. It will be a better way to prevent TDAE to dimerize, which provides us the possibility to have additional *positive* exchange interaction between the spins via TDAE<sup>+</sup>. Second is a possibility of ferromagnetism

in C<sub>60</sub> compounds doped by spin-silent alkali ions. Since the orbital-ordering mechanism requires Jahn-Teller stabilized orbitals, C<sub>60</sub> monoanion compounds could be a candidate for the ferromagnetism. Unfortunately, even if one can avoid polymerization, A<sub>1</sub>C<sub>60</sub> composes a face-centered cubic structure, equivalent to a triangle network. Since the antiferro-orbital ordering will be easily destroyed by a frustrating nature of the triangle network, the possibility of ferromagnetism with the present model is pretty low in the alkali-doped fullerenes, consistent with the experimental findings.

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