PHYSICAL REVIEW B, VOLUME 63, 140417(R)

Pressure effect in TDAE-C_{60} ferromagnet: Mechanism and polymerization

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(Received 27 December 2000; published 23 March 2001)

Effects of hydrostatic pressure on TDAE-C_{60} 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_{60} molecules reproduces such a dependence successfully. Furthermore, above ≈ 10 kbar at 300 K, α-TDAE-C_{60} transforms to the β phase with a $[2+2]$ cycloadditive one-dimensional polymer, stable even after pressure release. Remarkably, a missing spin in TDAE$^+$ revives in the polymer with $g=2.0028$.

DOI: 10.1103/PhysRevB.63.140417 PACS number(s): 75.50.Dd, 76.50.+g, 71.20.Tx

Since a discovery of ferromagnetic behavior in TDAE-C_{60}, where TDAE is tetrakis-dimethylamino-ethylene, with a high-transition temperature of 16 K as a pure organic system,[1] 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 merohedral ordering of the Jahn-Teller distorted C_{60}^- balls, which makes the coupling between the balls ferromagnetic, as discussed experimentally[3,4] and theoretically.[5–8] 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 merohedral order develops enough in the annealed samples.[9,10] Since the powder sample has a higher number of molecules in its surface, the merohedral disorder could be an origin of a variety of findings observed in powder samples,[11] such as itinerant ferromagnetism,[9] superparamagnetism,[12] spin glass,[13] 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,[14] consistent with the magnetization curve of single crystal.[4,15]

The number of $S=\frac{1}{2}$ unpaired spins per TDAE-C_{60} unit was determined to be approximately unity, not only from the Curie constant in the paramagnetic region by both the superconducting quantum interference device[9,10,16] (SQUID) and the ESR intensity,[4,10] but also from the saturation magnetization in the ferromagnetic state of the single crystal by SQUID,[4,15] 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.[17–20] Furthermore, the above fact demonstrates that the ESR signal catches all the unpaired spins in TDAE-C_{60}. The location of the unpaired spins was determined to be mainly on the C_{60}^- anions from the single symmetrical ESR line with $g \cong 2.0005$ close to 1.9998 for C_{60}^-, but far from 2.0036 for TDAE$^+$.

In this paper we demonstrate the effect of pressure on the physical properties of TDAE-C_{60} studied by ESR. The transition temperature T_C is found to be less sensitive than the earlier report,[9] 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 ≈ 10 kbar, one-dimensional (1D)-polymerization of C_{60}-chain occurs along the *c* axis, stable even after pressure release.

Single crystals of TDAE-C_{60} were prepared by a diffusion technique.[11] 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.[21]

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

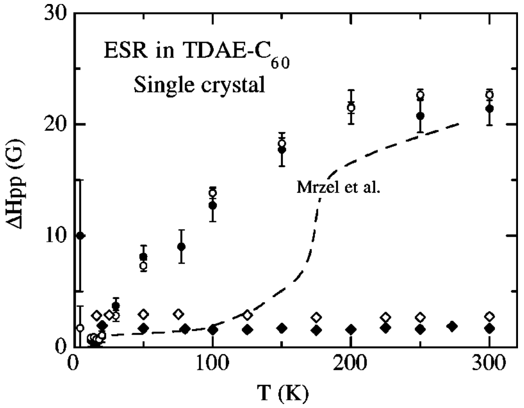

FIG. 1. Temperature dependence of ESR peak-to-peak linewidth in TDAE-C_{60}. The open and closed circles were taken at 24 GHz and 100 MHz, respectively. The dashed curve shows the reported data measured at the *X* band for unannealed TDAE-C_{60} by Mrzel *et al.* (Ref. 2). The closed diamonds were measured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

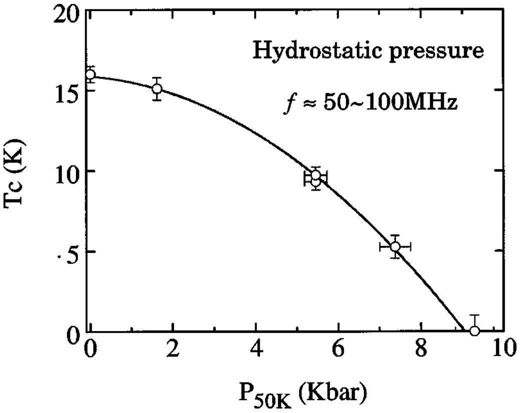

FIG. 3. T_C versus P_{50K} in TDAE-C_{60}. The solid curve indicates the theoretical prediction with the data up to 7.4 kbar.

the random orientation in the unannealed α' phase. A model for the ferromagnetism in TDAE-C_{60} will be proposed later to interpret the present experimental data, based on the antiferro-orbital ordering of Jahn-Teller distorted balls,[7] 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 α-TDAE-C_{60}.[4]

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 ΔH 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 shown in Fig. 2. This is due to the frequency-dependent shift that follows a magnetization curve; the shift taken at ≈ 100 MHz and 1.6 kbar should be nearly twice that at ≈ 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 β 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,[14,23] 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.[9] 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_{60}.[17–20] This issue might be resulted from the lower sample quality of powder than the single crystals.

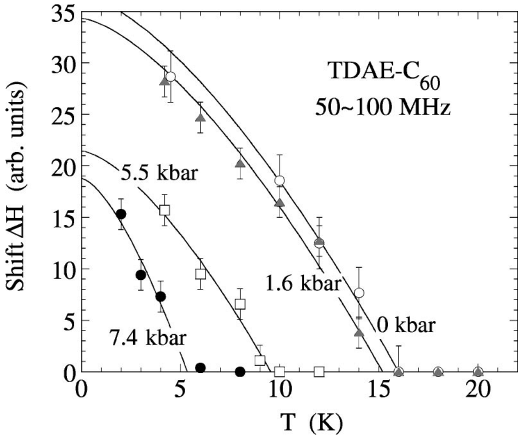

FIG. 2. Resonance shift versus temperature under several applied pressures P_{50K}. The solid curves represent Bloch's $T^{3/2}$ law.

We can simulate the observed pressure dependence of T_C in the framework of orbital ordering model.[7,8] It was suggested that the interball coupling should be ferromagnetic between neighboring C_{60}^-'s if the elongated axes of C_{60}^-'s distorted into D_{2h} symmetry are perpendicular to each other, and perpendicular or parallel to the *c* axis. Recently, an observation of such a distortion of C_{60}^-'s was reported in the

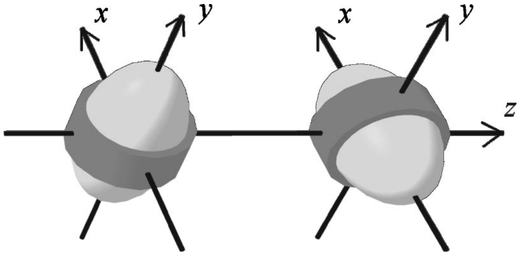

FIG. 4. Schematic view of the pair of distorted C_{60} anions whose elongated axes are perpendicular to each other. In this alignment, the interball coupling is ferromagnetic. The belt around the balls represents the density of the unpaired electron.

model monoanion-fullerene compound by ESR.[24] 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.[25] Such a symmetry lowering only in the ferromagnetic α-TDAE-C_{60}, but not in the unannealed paramagnetic α' phase, was reported below 50 K by a precise x-ray structural determination.[4,26] Figure 4 shows the example of the pair of two distorted C_{60}^{-}'s which favors to be triplet. Existence of the nearly orthogonal configurations of the twofold axes in the neighboring C_{60}^{-}'s along the c axis was confirmed with the refined structure.[26] The interball magnetic coupling J_1 is approximately calculated with a second order perturbation for the interball transfer,

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

where t_l, t_g, U, J_m, and Δ 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_{60}^{-}, 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_{60} is perfectly orthorhombic. The crystal structure of TDAE-C_{60} is different from orthorhombic one a little bit although C_{60} molecule has complete orthorhombic symmetry. Therefore, the enhancement of crystal field at C_{60}'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.*[27] The transfer energies are assumed to depend linearly on the pressure P as $t_a = t_a^0 + P t_a'$ $(a=l,g)$. $t_l^0=65$ 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 δ (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 ≈ 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 β phase), x-ray diffraction data at 89 K yielded us $a=15.70$, $b=13.69$, and $c=9.17\pm0.07$ Å with P symmetry, suggesting a disappearance of the dimerizing shift of TDAE molecules along the b axis in the ferromagnetic TDAE-C_{60}.[11] The shortest distance between balls dramatically reduced by 0.7 from 9.87 Å at 80 K in α-TDAE-C_{60}.[11] 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_{60},[28] as listed in Table I, together with magnetic properties. In case of a single-bonded dimer the shortest distance is 9.34 Å,[29] rather longer than the present case. Therefore we conclude that α-TDAE-C_{60} transforms to a 1D-polymer β phase with [2+2] cyclo-addition under the pressure of more than 10 kbar at room temperature, which is stable even after pressure release.

TABLE I. The distances between C_{60}'s or neighboring chains at 89 K for the 1D polymer of TDAE-C_{60}, together with these at 300 K for the ferromagnetic phase, o-Rb_1C_{60} (Ref. 28) and dimer-Rb_1C_{60} (Ref. 29) for comparison. r_n represents the nth shortest distance. N_S, the number of $S=\frac{1}{2}$ unpaired spins per (cation $+C_{60}^{-}$) unit and g values are also listed.

	r_1 (Å)	r_2 (Å)	r_3 (Å)	N_S	g
TDAE-C_{60}					
· 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_1C_{60}	9.138	10.107	14.173	1	2.0012
Single bond					
Rb_1C_{60} dimer	9.34	9.92	14.15	0	

Magnetic properties of the polymer phase are interesting in the meaning that the missing spin of $TDAE^+$ in α-TDAE-C_{60} revives. That is, two $S=\frac{1}{2}$ spins, twice of the ferromagnetic case, contributed to the paramagnetic susceptibility with the negative Weiss temperature Θ 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_{60} and 2.0036 for $TDAE^+$ cation radical.[22] Recently, in the α phase, the spin density on ^{14}N in $TDAE^+$ has been confirmed to be extremely small even in the ferromagnetic state by the electron spin echo envelope modulation technique.[30] 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_{60} is monocation,[31] consistent with the recent structural analysis of both α'- and α-TDAE-C_{60}.[26,32] Therefore, the spins on $TDAE^+$'s are likely to form dimers with spin singlet ground states in the α phase,[31] which is unstable in the polymerized β 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 Θ than -200 K in o-A_1C_{60}, where A is Rb or Cs. Differences between these systems are in chain separation of 10.4 Å for the β phase and 10.1 Å for A_1C_{60}, and spin-spin interactions via cations; radical $TDAE^+$ and spin-silent A^+. Since the interchain exchange in the β phase is weak, Θ would be dominated by the intrachain exchange, which could still be the order of magnitude larger than 4 K.[33] Therefore, such a small Θ in β-TDAE-C_{60} implies a revival of possible magnetic interaction in *positive* exchange coupling via radical TDAE$^+$,[6] 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_{60} compounds.

The present model to elucidate Fig. 3 suggests several interesting features. First is that a role of spin-silent TDAE$^+$ is a simple electron donor in this model. Then, a simple volume tuning to enhance T_C is not fruitful, because T_C of α-TDAE-C_{60} 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$^+$. Second is a possibility of ferromagnetism in C_{60} compounds doped by spin-silent alkali ions. Since the orbital-ordering mechanism requires Jahn-Teller stabilized orbitals, C_{60} monoanion compounds could be a candidate for the ferromagnetism. Unfortunately, even if one can avoid polymerization, A_1C_{60} 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 fullerides, consistent with the experimental findings.

K.M. gratefully thanks to Professor M. Yamashita and Dr. T. Ishii for utilization of an x-ray apparatus. This work is supported by Grant-in-Aid for Scientific Research on the Priority Area ''Fullerenes and Nanotubes'' by the Ministry of Education, Science, Sports and Culture of Japan.

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