Antiferromagnetic Ordering Driven by the Molecular Orbital Order of C_{60} in α'-Tetra-*Kis*-(Dimethylamino)-Ethylene-C_{60}

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We have studied the ground state of a fullerene-based magnet, the α'-phase tetra-*kis*-(dimethylamino)-ethylene-C_{60} (α'-TDAE-C_{60}), by electron spin resonance and magnetic torque measurements. Below $T_N = 7$ K, nonparamagnetic field dependent resonances with a finite excitation gap (1.7 GHz) are observed along the a axis. Strong enhancement in their intensity as temperature is decreased is inconsistent with excitation from a singlet state, which had been proposed for the α'-phase ground state. Below T_N, nonquadratic field dependence of the magnetic torque signal is also observed in contrast to quadratic field dependence in the paramagnetic phase. The angle-dependent torque signals below T_N indicate the existence of an anisotropy of the bulk magnetization. From both experiments, we propose an antiferromagnetic ground state driven by the cooperative orientational ordering of C_{60} in the α'-TDAE-C_{60}.

Molecular orbital ordering plays a key role in generating coherent magnetic interactions among localized spins on a fullerene cage [1] . The lowest-unoccupied molecular orbital (LUMO) of the C_{60} cage is known to have a threefold orbital degeneracy. This degeneracy is partly removed by a distortion of the C_{60}^- cage due to Jahn-Teller (JT) coupling. The cooperative arrangement between the wave functions of JT-distorted cages should be responsible for the coherent intermolecular magnetic interactions. Namely, one expects that the *ferro(antiferro)-rotative* orbital ordering of neighboring cages leads *antiferro(ferro)* magnetic correlation between cages, respectively. This type of ferromagnetism in the fullerene system has been discussed by Kawamoto, and the quasidegeneracy on the t_{1u} orbitals is advantageous for a ferromagnetic interaction [2]. The close coupling between the spin and orbital degrees of freedom is a conspicuous characteristic of fullerene-based magnets in comparison with other molecular magnets. However, it is very interesting to find a striking resemblance to the case of orbitally ordered inorganics [3].

Tetra-kis-(dimethylamino)-ethylene (TDAE) C_{60} is one of the fullerene-based magnets [4]. It has two polymorphic crystal structures, the α and α' phases. The α-phase is a bulk ferromagnet with the highest transition temperature, $T_c = 16$ K, among organic ferromagnets [4,5]. Our structural study revealed that the ferromagnetic interaction of the α-phase is grounded on structural peculiarities [6,7]. Only the α-phase shows a structural phase transition, around $T_s = 170$ K. Below T_s, the low-temperature (LT) unit cell contains two crystallographically inequivalent C_{60} sites, whose orbitals alternately interact with each other in all nearest-neighbor directions. We proposed the LT *antiferrorotative* structure for these t_{1u} orbitals.

On the contrary, the α'-phase crystals show no evidence of a structural phase transition down to 25 K. The unit cell of the α'-phase contains one C_{60}, and the LT structure allows for the *ferrorotative* arrangement of t_{1u} orbitals within the ab plane and along the c axis. The concept of

molecular orbital ordering was first introduced for the antiferromagnetic (AF) ground state of the ammoniated alkali-metal C_{60} salt $NH_3K_3C_{60}$ [8–10]. It was proposed that the t_{1u} orbitals alternately order along the diagonal direction within the ab-plane, together with directional ordering of K-NH_3 molecular pairs, which have a dielectric moment. The α-phase takes a similar aspect so that the orientational ordering works in close cooperation with the cubical distortion of surrounding TDAE molecules. Accordingly, the magnetism in the fullerene-based system tightly correlates with the structural peculiarities, especially the orientational freedom of C_{60} cages.

In contrast to the α-phase ferromagnet, very few studies have been reported on the LT magnetic ground state of the α'-phase. This may be due to the instability of α'-phase, crystals of which gradually degenerate to the stable α-phase at room temperature and begin to show ferromagnetic behavior. Annealing procedures hasten the irreversible degeneration toward the α-phase. We were unsuccessful in distinguishing the two polymorphs by the room-temperature structural studies, in spite of the distinct difference in the LT structures [11]. It was reported that the magnetic susceptibility of the α'-phase obeys a simple Curie-Weiss law at high temperature with a negative Weiss constant. No magnetic ordering was observed on powder sample down to 1.5 K. However, ESR measurements on single crystals suggested a nonmagnetic singlet ground state for this phase because of the strong decrease of electron paramagnetic resonance (EPR) intensity [12]. Thus, the ground state of the α'-phase is still open to debate. As mentioned above, LT structures for two polymorphs have remarkable differences in C_{60} orientation. For the α'-phase, we expect an AF long range ordering associated with the ferro-rotative alignment of t_{1u} orbitals. Therefore, we stress this system is eminently suitable for studying a correlation between the orbital freedom and the magnetism in the fullerene-based magnets.

Our aim is to search for a long range ordered phase in the α'-phase TDAE-C_{60} using highly sensitive magnetic torque and low-frequency ESR experiments. In this Letter, we show the appearance of AF spin ordering in α'-TDAE-C_{60} and discuss coherent magnetic interactions among the cages in relation to the LT molecular orbital ordering structure. Our findings signify the convertible magnetic interactions in two polymorphic TDAE-C_{60}, which basically have identical structures. We also strive to attain a unified understanding of the mechanism of magnetic interactions between C_{60}.

Single crystals were obtained by the usual diffusion method [6]. We selected crystals with no twinning (via x-ray diffraction) and also confirmed no ferromagnetic component by magnetization measurements down to 2 K using a Quantum Design superconducting quantum interference device (SQUID). For the usual frequency region, we used a Bruker ESP300e spectrometer. For the low-frequency (LF) region from 1 to 3 GHz, we used a home-built loop-gapped resonator. Magnetic torque of one single crystal was measured using a piezoresistive microcantilever (Seiko instruments. Ltd.). The detailed experimental set ups for torque and LF ESR experiments are described in Ref. [13].

First, we present the results of magnetic torque experiments. The inset of Fig. 1(a) shows the magnetic field dependence of torque signals at 1.5 and 7 K. The magnetic field is applied around $\theta = -45°$, where the angles are defined in the inset of Fig. 1(b). Above 7 K, the spin system is in a paramagnetic state because the torque signal is proportional to the square of the magnetic field strength. However, below 7 K, the torque signals showed remarkable temperature dependence and had nonquadratic field dependence. The torque signal at 1.5 K has a clear anomaly around $H_a \sim 500$ Oe. Previous ESR measurements pro-

posed a nonmagnetic ground state because of the disappearance of EPR signals. If the ground state is a spin-singlet, the torque signals should exactly vanish below a critical magnetic field, which corresponds to the spin-excitation gap. The observed large field dependence of torque signals in all field regions clearly deny the singlet ground state for the α'-phase. Figure 1(a) shows the angular dependence of torque signals at $T = 1.5$ K for $H \parallel ab$ plane. The magnetic torque signals depend on the applied magnetic field direction. The angular dependence of peaks in the torque signals are shown in the Fig. 1(b). The peak shifts toward the high field side when the magnetic field leans toward the a axis. The angle-dependent torque signals indicate the existence of anisotropy of the bulk magnetization and, around H_a, a spin rearrangement under the magnetic field, such as a spin-flop transition, takes place. The angular dependence of H_a indicates a spin-hard direction along the a axis.

Next, we show ESR results. Figure 2(a) shows the temperature dependence of ESR spectra at the usual X-band frequency for the $H \parallel a$ axis. Three well-separated peaks were observed in different temperature windows. P
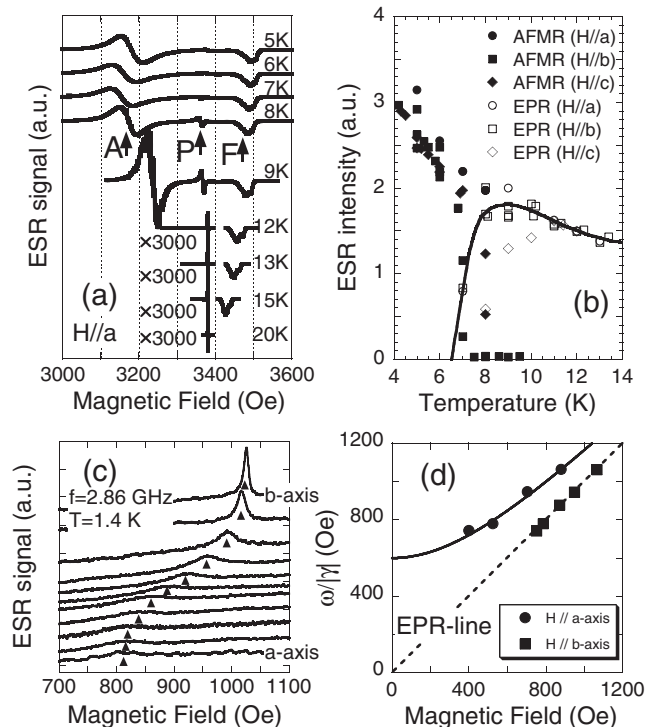
FIG. 2.   (a) Temperature dependence of ESR spectra for $H \parallel a$ at 9 GHz region. Three peaks (P, A, and F) are observed, which correspond to the EPR, AFMR, and (extrinsic) FMR signals, respectively. (b) Temperature dependence of EPR and AFMR intensity for three crystallographic axes. (c) Angular dependence of AFMR signals within the ab plane at 2.86 GHz. Each spectrum was taken every 10°. (d) Frequency ($\omega/|\gamma|$)-field relation at $T = 1.5$ K. Solid line is the calculation with the easy-plane anisotropy along the a axis.
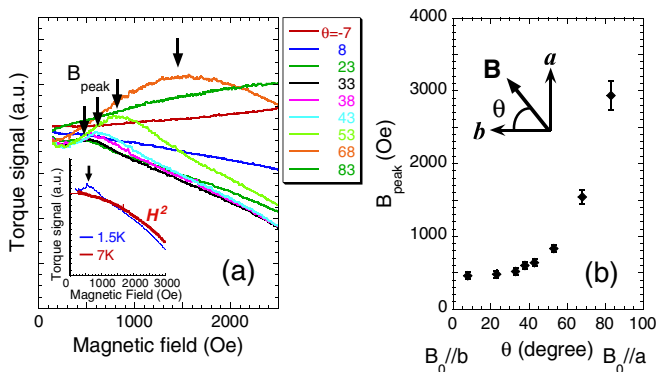

FIG. 1 (color online).   (a) Angular dependence of magnetic torque signals at $T = 1.5$ K. The inset shows the torque at 7 K (paramagnetic) and 1.5 K for $\theta = -45°$. The torque curve at 7 K is proportional to the square of magnetic field strength. (b) Angular dependence of peak in the torque signal as a function of θ. The inset shows the angles between the magnetic field and the crystal axis.

peaks correspond to the EPR signals with linewidths of about 20 Oe. Their intensities obey a simple Curie law down to 9 K. Below 9 K, however, the intensity rapidly decreased with decreasing temperature [see Fig. 2(b)] and the EPR signals completely disappeared below 6 K. This result is consistent with the previous ESR measurements [12]. Contrary to this agreement, however, we found new absorption signals (*A*), following the disappearance of the EPR signals. Note that the resonance field of *A* peaks are different from the corresponding EPR position. Their resonance fields markedly depend not only on the magnetic field direction but also on the temperature. In Fig. 2(b), the temperature dependence of the absorption intensity for the *A* signals is also shown. The *A* intensity at 9 K is about 70 times stronger than the EPR intensity. Strong enhancement in intensity as temperature decreases is inconsistent with a singlet ground state because the excitation from the singlet state is normally forbidden by the ESR selection-rules. Notice that nonquadratic torque curves are also observed below 7 K. As mentioned later, we attribute the *A* signals to antiferromagnetic resonance (AFMR) from the frequency-field relation of the *A* excitation. Both magnetic torque and ESR experiments indicate that the ground state of the α'-phase is not nonmagnetic, but rather magnetic with a finite magnetic ordering temperature. Contrary to these intrinsic signals, *F* peaks, which have large angular dependence, were observed below 16 K. This temperature corresponds to the onset temperature of ferromagnetic ordering in the α-phase. The *F* intensity increased with decreasing temperature, but was 2 orders of magnitude weaker than that of the EPR as well as the *A* signals. Thus, we assign the *F* peaks as originating from a degeneration of the α'-phase on part of crystal, such as the surface. We emphasize that this crystal shows no trace of ferromagnetic component using the SQUID measurements.

Figures 2(c) and 2(d) show the angular dependence of the AFMR signals in the low-frequency region and the frequency-field (ω/γ-H) diagram at 1.5 K, respectively. Only the resonance fields of AFMR are plotted. The nonparamagnetic field dependence of excitations along the *a* axis indicates the existence of finite excitation energy in the spin-wave dispersion. The LF ESR is profitable to observe such low-energy excitation. As mentioned previously, because of the strong enhancement in their intensities at lower temperature, these excitations can not be identified as excitations from the singlet ground state to the triplet states. Accordingly, the frequency dependence of the excitation confirms the AF ordering below T_N for α'-TDAE-C$_{60}$. Large zero-field excitation energy exists along the *a* axis, while there is very weak anisotropy on the resonance field in the *bc* plane. In order to investigate these resonance field relations, we neglect the in-plane anisotropy within the *bc* plane, but introduce the AF configuration with out-of-plane anisotropy along the *a* axis. The angle-dependent torque experiments support

this anisotropy. The solid line in Fig. 2(c) is a calculation with the easy-plane anisotropy: $\omega_2/\gamma = \sqrt{2H_A H_E} = 612$ Oe, where H_A and H_E are the out-of-plane anisotropy and the exchange molecular field, respectively [14]. This is the first experimental evidence of a spin-wave excitation in the AF fullerene magnets.

The AF interactions among the spins on the cage should be controlled by the molecular orbital configuration and must dominate the dispersion relation of the magnetic excitation. We propose the AF spin structure driven by the cooperative ordering of t_{1u} orbitals. Figure 3 shows the LT structure of the α'-phase, which includes one crystallographically independent C$_{60}$ in the unit cell. This LT structure allows ferrorotative ordering of the t_{1u} orbital due to its symmetry. Thus, the elongated axes of the distorted cages should align parallel to each other (see the balls in the right panel, which represent one of the t_{1u} orbitals of the cage). This panel shows a possible molecular orbital configuration, where the elongated axis of the cages aligns parallel to the *c* axis. This configuration is completely different from that of the α-phase. The LT symmetry of the α-phase permits an alternate configuration of t_{1u} orbitals along all neighboring directions (Fig. 5 in Ref. [7]), which should be responsible for the ferromagnetic interactions.

It should be necessary to introduce orientational disorder if the symmetry of the cage is lower than that of the lattice
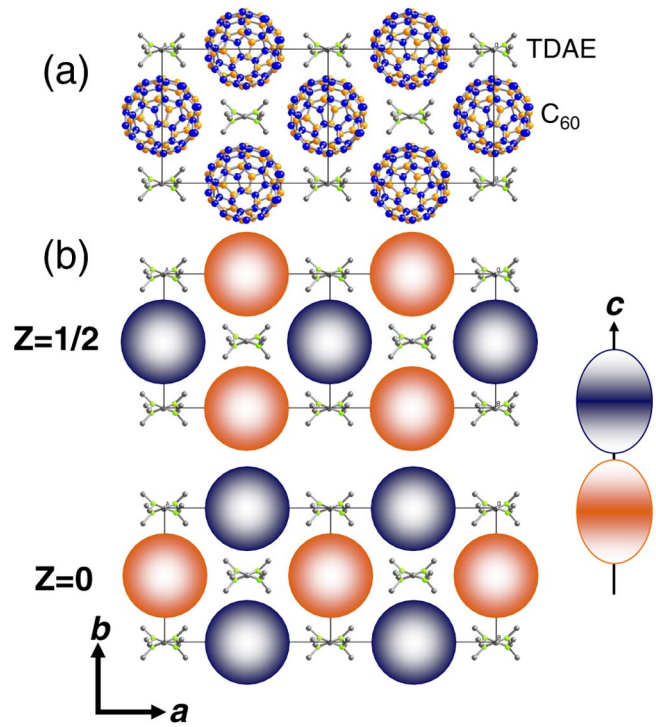

FIG. 3 (color online). (a) Low-temperature structure and (b) possible antiferromagnetic (AF) structure with molecular orbital order. Balls represent one of the C$_{60}$ t_{1u} orbitals. Blue and orange balls correspond to opposite spins.

site. The static orientational ordering of C_{60} takes place in the LT structures of both phases. Thus, we expect that the distortion of the cage fits the local symmetry of the lattice site. Only inversion symmetry remains at the cage site in the LT structure of α'-phase. Recent molecular orbital calculations suggested that the C_i distorted cage is slightly stable, but neither C_i and C_{2h} distortion can be determined [15,16]. In fact, in $[Ph_4As]_2ClC_{60}$, the anisotropy of the ESR g-factor and vibrational analysis suggest the stability of C_{2h} or C_i distortion [15,17]. In the α'-phase, on the contrary, angular variations of the ESR g factor indicate that, below 150K, an axial g factor changes to three different components ($g_c \sim 2.0012$, $g_b \sim 2.0003$ and $g_a \sim 2.0006$) [18]. This anisotropy is 3 times lower than that of $[Ph_4As]_2ClC_{60}$. The largest g factor was obtained along the c axis, which corresponds to the vertical axis of the $C = C$ double bond between the six-membered rings of the cage. On the contrary, the elongated axis for the C_i distorted cage should align with the axis through the five-membered rings on the cage [15,16]. For the α'-phase, this direction may correspond to the b-axis for all cages [7]. Although the distortion (elongation) of the cage has not been experimentally determined in this TDAE-C_{60} system (not only the α-phase but also α'-phase) by x-ray measurements, in either case of C_i or C_{2h}, on-site symmetry possibly requires the most stable structure of the cage and the elongated axes of cages align parallel to each other. Accordingly, *ferrorotative* molecular orbital ordering plays a key role to establish the antiferromagnetic interactions between the cages in the α'-TDAE-C_{60}. Possible AF spin structure under this molecular orbital ordering is shown in Fig. 3(b), where the opposite spins are represented by ball colors. The spin-hard direction is parallel to the a axis, which is perpendicular to the elongated axes of the cages. This magnetic anisotropy should be mainly dominated by a dipole-dipole interaction between the spins. In the LT structure, the nearest-neighbor distance between the cages is along the c axis, and the next-nearest-neighbor distance is along the b axis. The close packing configuration along the c axis may yield a vertical anisotropy against the c axis due to dipole-dipole interactions. This may be consistent with the AF structure with the spin-hard anisotropy along the a axis.

In summary, we have measured the magnetic torque and LF ESR on the α'-phase of TDAE-C_{60} in order to search for a magnetic ground state. From both experiments, we conclude the ground state of α'-TDAE-C_{60} is AF with $T_N \sim 7$ K and also propose the AF ordering structure associated with the *ferrorotative* orbital ordering of the JT-distorted C_{60}, which agrees well with the molecular ordering scenario. Our results insist that the JT-distorted C_{60} functions as the magnetic constituent element at low-temperatures, though the distortion of C_{60} has not been

verified by LT x-ray measurements [11]. The TDAE-C_{60} system provides a good example to obtain a unified understanding of the mechanism of magnetic interactions between C_{60}. We emphasize that this system shows convertible magnetic interactions due to the relative molecular orbital ordering of the JT-distorted C_{60}.

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