Antiferromagnetic order 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 (ESR) and magnetic torque measurements. Below $T_N = 7$ K, non–paramagnetic field dependent resonances with a finite excitation gap (1.7 GHz) are observed along the α–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 $T_N$, non–quadratic field dependence of 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$_{60}$.

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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 quasi–degeneracy 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 [4, 6]. 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 antiferro–rotative 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 ferro–rotative 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 C$_{60}$ salt NH$_3$K$_3$C$_{60}$ [8, 9, 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 non–magnetic 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\textsubscript{60} orientation. For the \( \alpha' \)-phase, we expect an AF long range ordering associated with the ferro–rotative alignment of \( t_{2u} \) orbitals. Therefore, we stress this system is eminently suitable for study 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 \( \alpha' \)-phase TDAE–C\textsubscript{60} using high–sensitive magnetic torque and low–frequency ESR experiments. In this Letter, we show the appearance of AF spin ordering in \( \alpha' \)-TDAE–C\textsubscript{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\textsubscript{60}, which basically have identical structures. We also strive to attain a unified understanding of the mechanism of magnetic interactions between C\textsubscript{60}.

Single crystals were obtained by the usual diffusion method \cite{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 GHz to 3 GHz, we used a homebuilt loop–gapped resonator. Magnetic torque of one single crystal was measured using a piezo–resistive microcantilever (Seiko instruments.Ltd.). The detailed experimental set–ups for torque and LF–ESR experiments are described in ref. \cite{13}.

Firstly, we present the results of magnetic torque experiments. The inset of figure 1(a) shows the magnetic field dependence of torque signals at 1.5 K and 7 K. The magnetic field is applied around \( \theta = -45^\circ \), where the angles are defined in the inset of figure 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 non–quadratic field dependence. The torque signal at 1.5 K has a clear anomaly around \( H_a \sim 500 \) Oe. Previous ESR measurements proposed a non–magnetic ground state because of the disappearance of EPR signals. If the ground state is a spin–singlet, the torque ground state because of the disappearance of 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 figure 1(b), the temperature dependence of the absorption intensity for the \( A \) signals is also shown. The \( A \)–intensity at 9 K is about seventy 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 non–quadratic 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 \( \alpha' \)–phase is not non–magnetic, 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
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 degrees. (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.

K. This temperature corresponds to the onset temperature of ferromagnetic ordering in the \( \alpha \)–phase. The \( F \) intensity increased with decreasing temperature, but was two order 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 \( \alpha' \)–phase on part of crystal, such as the surface. We emphasize that this crystal shows no trace of ferromagnetic component using the SQUID measurements.

Figure 2 (c) and (d) show the angular dependence of the AFMR signals in the low frequency region and the frequency–field (\( \omega/\gamma \)–\( H \)) diagram at 1.5 K, respectively. Only the resonance fields of AFMR are plotted. The non–paramagnetic 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 \( \alpha' \)–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 figure 2 (c) is a calculation with the easy–plane anisotropy : \( \omega_2/\gamma = \sqrt{2}H_AH_E = 612 \) 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 \( \alpha' \)–phase, which includes one crystallographically independent C\(_{60}\) in the unit cell. This LT structure allows ferro–rotative 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 \( \alpha \)–phase. The LT symmetry of the \( \alpha \)–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 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 \( \alpha' \)–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 \cite{12,16}. In fact, in \([\text{Ph}_4\text{As}]_2\text{ClC}_60\), the anisotropy of the ESR \( g \)-factor and vibrational analysis suggest the stability of \( C_{2h} \) or \( C_i \) distortion \cite{13,17}. In the \( \alpha' \)–phase, on the contrary, angular variations of the ESR \( g \)-factor indicate that, below 150K, an axial \( g \)-factor changes to three different components \((g_c \sim 2.0012, \ g_b \sim 2.0003 \text{ and } g_a \sim 2.0006)\) \cite{18}. This anisotropy is three times lower than that of \([\text{Ph}_4\text{As}]_2\text{ClC}_60\). The largest \( g \)-factor was obtained along the \( c \)–axis, which corresponds to the vertical axis of the \( C=\text{C} \) double bond between the 6–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 \cite{15,16}. For the \( \alpha' \)–phase, this direction may correspond to the \( b \)–axis for all cages \cite{5}. Although the distortion (elongation) of the cage has not been experimentally determined in this TDAE–C\(_{60}\) system (not only the \( \alpha \)–phase but also \( \alpha' \)–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, ferro–rotative molecular orbital ordering plays a key role to establish the antiferromagnetic interactions between the cages in the \( \alpha' \)–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 \( \alpha' \)–phase of TDAE–C\(_{60}\) in order to search for a magnetic ground state. From both experiments, we conclude the ground state of \( \alpha' \)–TDAE–C\(_{60}\) is AF with \( T_N \sim 7 \text{ K} \) and also propose the AF ordering structure associated with the ferro–rotative 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 \cite{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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