Antiferromagnetic Correlations and Weak Ferromagnetism in a TDAE$^+$-C$_{60}^-$ Single Crystal

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The ESR spectra of a TDAE$^+$-C$_{60}^-$ single crystal show the existence of antiferromagnetic (AFM) correlations between the unpaired spins on neighboring C$_{60}^-$ ions along the c axis and spin canting which leads, below T_c, to weak ferromagnetism along a direction perpendicular to the c axis. This suggests that a Dzyaloshinsky-Moriya type mechanism is responsible for ferromagnetic ordering rather than itinerant ferromagnetism. The incomplete orientational ordering of the C$_{60}^-$ ions leads to a distribution of exchange coupling constants resulting in spin-glass type behavior which coexists with long range ferromagnetic ordering below T_c. The observation of AFM correlations may help to understand why the same basic molecule C$_{60}$ can support such different phenomena as ferromagnetism (in TDAE-C$_{60}$) and superconductivity (in, e.g., K$_3$C$_{60}$).

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According to Heisenberg [1] ferromagnetism is not expected to be found in compounds consisting only of first row elements like carbon, hydrogen, oxygen, and nitrogen. In fact, only a few purely organic ferromagnets have been discovered so far, and the corresponding transition temperatures T_c are very low. In view of that, it is rather remarkable that the C$_{60}$ based purely organic 1:1 charge transfer compound TDAE$^+$-C$_{60}^-$ (TDAE = tetrakis dimethyl amino ethylene) exhibits a magnetic transition at $T_c = 16$ K [2]. The transition temperature is the highest of all known nonpolymeric purely organic ferromagnets. ^{13}C NMR measurements [3], and the ESR g values seem to show that the unpaired electron is mainly localized at the C$_{60}^-$ ion [4]. The absence of an analogous transition in TDAE-C$_{70}$ supports this observation [4].

Up until now all experiments on TDAE-C$_{60}$ have been performed on powder samples, and the microscopic nature of the transition is still rather controversial. Early investigations [2,5] showed a nonlinear magnetization versus magnetic field curve below T_c, but no divergent static susceptibility, no hysteresis, and no "remanent" magnetization. The linear susceptibility [4] was found to follow a Curie-Weiss law $\chi = C/(T - \theta)$ with a negative Curie temperature θ. The average internal field determined by powder ESR below T_c has been found to be surprisingly small, i.e., of the order of a few gauss only [6]. This is significantly smaller than the width of the ESR lines below T_c. The third-, fifth-, and seventh-harmonic ac susceptibilities show a divergent behavior at 10 K which seems to indicate a spin-glass type phase transition [7]. The broad heat capacity peak at 12.5 K [8] could also be associated with spin-glass freezing or the coexistence of ferromagnetic and spin-glass order. Recent muon spin rotation data [9], on the other hand, found an internal field of 68 G at the interstitial muon site. This value is larger than the width of the internal field distribution ≈48 G and indicates the presence of long range ferromagnetic order [9]. A small hysteresis loop and a small value of the saturation magnetization (0.84 emu G$/g$) have been recently reported below 10 K [10] as well. Whereas it has been generally assumed that the origin of the magnetic transition in TDAE-C$_{60}$ is itinerant ferromagnetism, conductivity studies [11] failed to show the expected metallic behavior. Single crystal studies are thus badly needed to clear up the microscopic nature of the magnetic transition in TDAE-C$_{60}$.

Here we report on the first study of the magnetic resonance properties of a TDAE$^+$-C$_{60}^-$ single crystal. The ESR results below T_c clearly show the presence of a large anisotropic internal field which is proportional to the spontaneous magnetization. The presence of long range spontaneous magnetic ordering in TDAE-C$_{60}$ is thus validated.

Another important observation is that the electronic susceptibilities determined from the intensities of the X-band ESR lines are strongly anisotropic and exhibit a ferromagneticlike behavior along the crystal a and b axes and an antiferromagneticlike behavior along the crystal c axis. A weak antiferromagneticlike hysteresis loop in the c direction was also observed by SQUID measurements at 4 K. These results show that the microscopic mechanism leading to magnetic ordering in TDAE-C$_{60}$ is quite different from the one assumed so far. They indicate the existence of antiferromagnetic correlations along the c axis where the C$_{60}$-C$_{60}$ distance (9.99 Å) is the shortest and spin canting [12] in a plane perpendicular

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to the c axis that leads to weak ferromagnetism. The spin-glass features which coexist with the ferromagnetic ordering seem to be related to the incomplete orientational ordering of the Jahn-Teller distorted C_{60}^- ions—which rotate rapidly at room temperature and freeze out below 150 K—leading to a distribution of exchange coupling constants.

The TDAE-C_{60} single crystals were grown in our laboratory by the diffusion method designed earlier for low dimensional organic conductors [13]. The crystals were oriented and characterized by x-ray diffraction, and special care was taken to eliminate twins. The crystals were found at room temperature to be monoclinic with unit cell dimensions $a = 15.858(2)$ Å, $b = 12.998(1)$ Å, $c = 19.987(2)$ Å, and $\beta = 93.37(1)$ Å, and four chemically equivalent formula units per unit cell. The unit cell size in the c direction is twice as large as reported previously [14], and the space group is $C2/c$ and not $C2/m$ as deduced from previous powder diffraction data [14]. In fact, the unit cell consists of the two subcells that were deduced from powder diffraction data [14]. They are stacked along the c direction. In one of them the TDAE ions are shifted along the b axis for about 0.02 Å and in the other for the same distance in the opposite direction. The TDAE coordinates are $(0.5, 0.502, 0.75)$, $(0.5, 0.498, 0.25)$, $(0, 0.002, 0.75)$, and $(0, -0.002, 0.25)$ with C=C double bond parallel to the c axis, whereas the C_{60} coordinates are $(0, 0.5, 0)$, $(0, 0.5, 0.5)$, $(0.5, 0, 0)$, and $(0.5, 0, 0.5)$. The C_{60} center to center distance along the c axis decreases at 80 K to 9.87 Å.

A single ESR line is observed in the TDAE-C_{60} single crystal at room temperature (Fig. 1). The g factors for the X-band ESR lines at room temperature are $g_a = 2.0001$, $g_b = 1.9999$, and $g_c = 2.0005$. They do not change on cooling down to 50 K. The line shape at room temperature is not a simple Lorentzian suggesting that the dipole-dipole interactions are not completely averaged out by the C_{60}^- rotations. The linewidths are 20.8, 23.1, and 19.7 G for $\mathbf{a} \parallel \mathbf{H}_0$, $\mathbf{b} \parallel \mathbf{H}_0$, and $\mathbf{c} \parallel \mathbf{H}_0$, respectively. On cooling an ESR linewidth transition occurs below 150 K [Fig. 2(a)]. The abrupt narrowing of the ESR line is shown in Fig. 2(a). At 50 K the linewidths do not exceed 2 G for all three orientations. It is interesting to note that in the same temperature range an orientational ordering transition of the C_{60}^- ions takes place [Fig. 2(b)]. Below this transition the second moment [15] of the C_{60}^- ^{13}C NMR line (which is shifted by 188 ppm with respect to TMS) changes from its room temperature value ≈ 1 kHz^2, characteristic of fast and nearly isotropic rotation of the C_{60}^- ions, to the static value ≈ 250 kHz^2. This value is characteristic for frozen out C_{60}^- icosahedra where the ^{13}C NMR line is broadened due to dipolar interactions with the unpaired electron in the $2p_z$ state smeared out over all carbon sites in the C_{60}^- ion.

When the C_{60}^- ions freeze out and the lattice contracts, the overlap of the electronic wave functions increases and the ESR line becomes Lorentzian and strongly exchange narrowed [16]. It should be noted that the exact value of T_c as well as the amount of the ESR line broadening below T_c depend [17] on the rate of cooling through the C_{60}^- ion orientational ordering transition around 150 K. This demonstrates that the electronic overlap and the C_{60}^--C_{60}^- exchange interaction depend on the degree of orientational ordering of the Jahn-Teller distorted C_{60}^- ions.

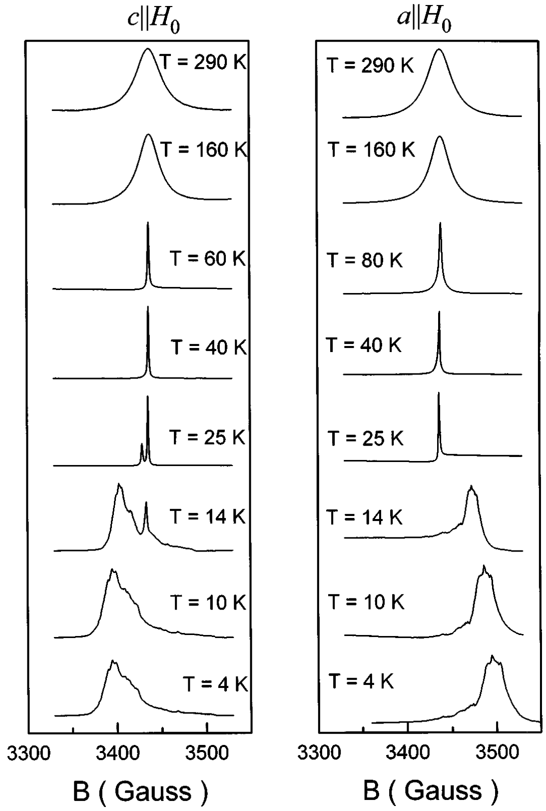

FIG. 1. X-band ESR spectra of TDAE$^+$-C_{60}^- for $\mathbf{c} \parallel \mathbf{H}_0$ and $\mathbf{a} \parallel \mathbf{H}_0$ at various temperatures.

Below 45 K a line splitting occurs (Fig. 1) when $\mathbf{H}_0$ is not parallel to the $\mathbf{a}$ axis. A strongly anisotropic "ferromagneticlike" line appears in addition to the nearly isotropic "paramagnetic" line. At 25 K we have two well separated X-band ESR lines for $\mathbf{c} \parallel \mathbf{H}_0$ and $\mathbf{b} \parallel \mathbf{H}_0$ and only one line for $\mathbf{a} \parallel \mathbf{H}_0$. Below $T_c \approx 16$ K the "paramagneticlike" ESR line disappears, and the "ferromagneticlike" ESR line becomes strongly inhomogeneously broadened. The center of this line strongly shifts with decreasing temperature (Fig. 3). For $\mathbf{b} \parallel \mathbf{H}_0$ the center of the line shifts to lower fields. The shifts saturate below 10 K and amount to 43 G at 5 K while the linewidth is about 10 G at this temperature. For $\mathbf{a} \parallel \mathbf{H}_0$ the shift is in the opposite direction, i.e., to higher fields and amounts to 61 G at 4 K. The shift is again significantly larger than the linewidth which here is of the order of 14 G.

The question whether the shifts are due to internal fields or due to a temperature dependent change in the g factor can be answered by comparing the shifts in the Q band

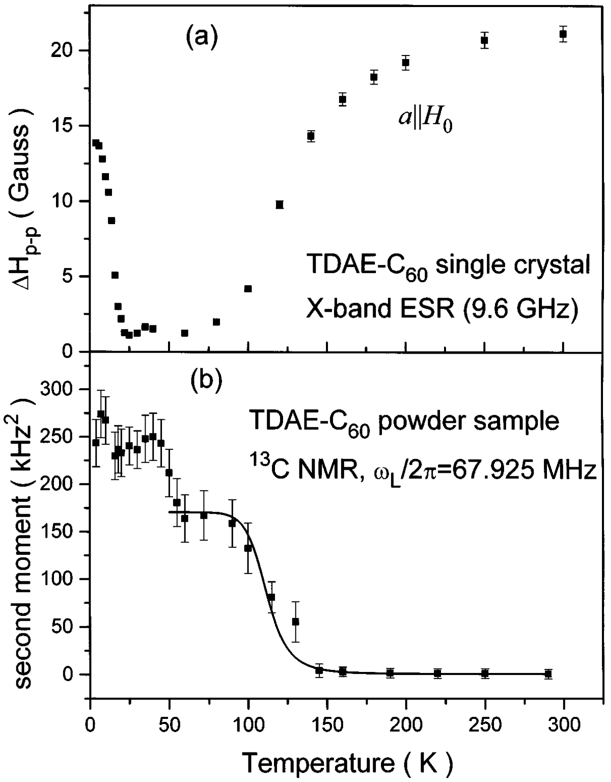

FIG. 2. (a) Temperature dependence of the half-width of the X-band ESR line of TDAE$^+$-C$_{60}^-$ for **a** || **H**$_0$. (b) Temperature dependence of the second moment of the ^{13}C NMR spectra of TDAE-C$_{60}$.

(35 GHz), X band (9 GHz), and in the radiofrequency region (100 MHz). We found that the magnitude of the shifts below T_c is the same in all three bands (inset to Fig. 3). This demonstrates that we deal below T_c with internal fields which are due to long range magnetic ordering. If the ESR line shifts were due to changes in the g factor they would be 350 times larger in the Q band than at 100 MHz. This is obviously not the case.

It should be noted (inset to Fig. 3) that the transition—as shown by the line shift versus temperature plots—is rather sharp at 100 MHz, whereas it is smeared out in the X and Q bands where the applied magnetic fields are much larger. This is indeed expected if the order parameter of the transition couples bilinearly to the external magnetic field. Such a behavior is characteristic for a ferromagnetic transition where the order parameter is the spontaneous magnetization and not for a pure spin-glass transition.

At T_c there is also a huge anisotropic increase in the integrated intensity of the ESR lines. The integrated intensity of the X-band ESR line times temperature—which is proportional to the electronic susceptibility times temperature—is temperature independent between 300 and 25 K and exhibits a sharp peak at T_c for **a**||**H**$_0$ and **b**||**H**$_0$, whereas it shows only a rounded cusp for **c**||**H**$_0$ (Fig. 4). This shows that the electronic correlations between the unpaired spins on the C$_{60}^-$ ions are of an antiferromagnetic nature along the c axis, whereas they are of a ferromagnetic nature along the a and b axes. The fact that the a and c axes are magnetically inequivalent below T_c is also shown by the different angular dependences of the ESR lines. At 7 K the position of the center of the ESR line shows a strong angular dependence upon rotation around the c axis, whereas the angular dependence is for an order of magnitude smaller for the rotation around the a axis.

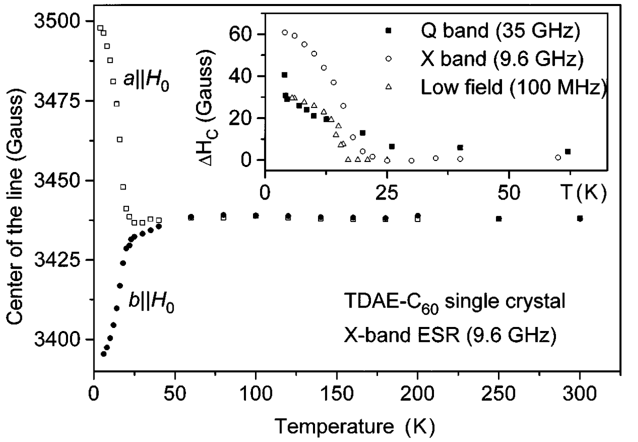

FIG. 3. Temperature dependence of the position of the center of the X-band ESR line for **a** || **H**$_0$ and **b** || **H**$_0$. The inset shows the temperature dependence of the ESR line shifts for the Q band (35 GHz), the X band (9 GHz), and at 100 MHz on cooling through T_c taken at slightly different crystal orientations.

The magnetic inequivalence of the a and c directions was also confirmed by SQUID magnetization measurements. They showed a weak antiferromagnetic loop along

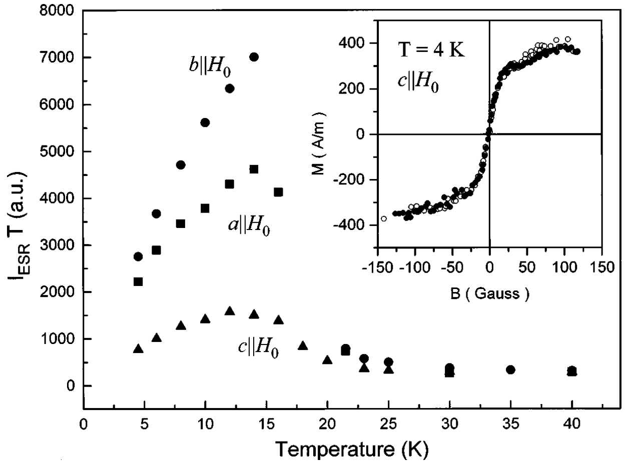

FIG. 4. Temperature dependence of the integrated intensity of the X-band ESR lines times temperature for **c** || **H**$_0$, **b** || **H**$_0$, and **a** || **H**$_0$. The inset shows the antiferromagneticlike magnetization versus magnetic field curve for **c** || **H**$_0$ obtained by SQUID measurements at 4 K. The data designed by full circles are taken with increasing **H**$_0$ and the empty circles with decreasing **H**$_0$.

the *c* axis (inset to Fig. 4) and a small ferromagnetic loop along the *a* axis.

The above results seem to demonstrate the presence of an antisymmetric term of the Dzyaloshinsky-Moriya type [12] (DM) $\mathbf{d}_{i,j} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ in the spin Hamiltonian in addition to the symmetric $J_{i,j}\mathbf{S}_i \cdot \mathbf{S}_j$ term. The Dzyaloshinsky-Moriya term is known to be the result of anisotropic superexchange interactions and is always present if the crystal symmetry is sufficiently low as in the case of TDAE-C_{60}. Thus the DM term leads to spin canting and weak ferromagnetism. In TDAE-C_{60} the spins on neighboring C_{60}^- ions seem to be canted away from the *c* axis so that we have weak ferromagnetic order in a direction perpendicular to the *c* axis and antiferromagneticlike order along the *c* direction.

Some of the freshly grown crystals do not show a ferromagnetic transition but exhibit an antiferromagnetic transition below 10 K leading to the disappearance of the ESR signal intensity. On annealing they transform to the phase described in this paper which exhibits a weak ferromagnetic transition at 16 K. The small structural differences between the ferromagnetic and antiferromagnetic phases and the effects of the annealing process are being investigated at present.

In conclusion, we have shown the presence of an anisotropic internal field in TDAE-C_{60} below T_c which is due to long range magnetic ordering. The anisotropy of the ESR susceptibility further demonstrates that the existence of weak ferromagnetism in a single crystal of TDAE-C_{60} is due to spin canting away from antiferromagnetic like spin ordering. The existence of long range ferromagnetic order in this C_{60} based charge transfer system is thus definitely validated. Weak ferromagnetism coexists with spin-glass type ordering resulting from a distribution of C_{60}^--C_{60}^- coupling constants due to the incomplete orientational ordering of the Jahn-Teller distorted C_{60}^- ions. The observation of antiferromagneticlike correlations in TDAE$^+$-C_{60}^- may help to understand why the same basic molecule—i.e., C_{60}—supports two such different phenomena as ferromagnetism (in TDAE-C_{60}) and superconductivity (e.g., in K_3C_{60}).

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