Ferromagnetic Resonance in TDAE-C_{60}

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A nonlinear variation of the electron resonance frequency with resonance field characteristic of ferromagnetic resonance has been observed in a TDAE-C_{60} in the radio-frequency region. The results not only definitely prove the existence of long range order below T_C but also show that well annealed TDAE-C_{60} behaves as an easy axis three dimensional Heisenberg ferromagnet with an exceptionally small anisotropy field $H_K = 29$ G. The easy axis coincides with the crystal c direction which is the direction of closest approach of the C_{60}^- ions. [S0031-9007(98)05369-1]

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The magnetic properties of the charge transfer compound TDAE-C_{60}, where TDAE stands for tetrakis-dimethylamino-ethylene, represent one of the most challenging physical phenomena discovered in the field of fullerenes [1]. The origin of the magnetic behavior has been shown to be due to an unpaired electronic spin localized on the C_{60}^- ion. The magnetic transition temperature $T_C = 16$ K is exceptionally high for a purely organic ferromagnet consisting only of light elements such as carbon, hydrogen, oxygen, and nitrogen [2]. While the origin of superconductivity in A_3C_{60} compounds ($A = \mathrm{K, Rb, Cs}$) seems to be by now well understood [3,4], the nature of the magnetic transition in TDAE-C_{60} still remains controversial [5]. Conflicting models such as itinerant ferromagnetism, superparamagnetism, spin glass behavior, and spin canted weak ferromagnetism have been proposed [1,6–8] to account for the magnetic ordering below T_C. The basic question is whether we deal with a magnetic field induced ordering of superparamagnetic clusters or with an intrinsic long range ordered state, and if the latter is true, what is the nature of this state. Whereas detailed conductivity measurements [9,10] have ruled out itinerant ferromagnetism, no experiment allowing for a definite discrimination between the various possible models has been carried out so far.

Electron and muon spin resonance in magnetically ordered phases represents one of the most direct ways to determine the microscopic nature of the magnetic ground state. In view of the presence of strong exchange fields electron spin resonance in ferromagnetic and antiferromagnetic systems, in particular, is completely different from ordinary paramagnetic spin resonance. It represents a coherent precession of the entire magnetization or sublattice magnetization around the effective fields and is in contrast to normal paramagnetic resonance characterized by a nonlinear dependence of the resonance frequency on the external field. The number of modes and the field dependence of the resonance frequencies allow for a discrimination between ferromagnets, antiferromagnets, or spin canted antiferromagnets [11].

Whereas muon spin rotation data [12] in powdered TDAE-C_{60} indicate the presence of intrinsic long range magnetic order below T_C, X-band and Q-band electron spin resonance (ESR) measurements [5,6,8] performed so far show only a single paramagneticlike ESR line near $g = 2$ which slightly shifts and broadens below T_C. Only a paramagneticlike ESR line near $g = 2$ has also been found in high field ESR at 94 and 245 GHz [13] between 0 and 10 T. Here, as well as in the X and Q bands, no sign of nonlinear ferromagnetic or antiferromagnetic resonance behavior, characteristic of magnetically long range ordered states, could be detected below T_C.

In this Letter we report on the first observation of ferromagnetic resonance in a TDAE-C_{60} single crystal. A nonlinear variation of the resonance frequency with resonance field characteristic of ferromagnetic resonance was observed via low field ESR in the 30 MHz–1.2 GHz range. The obtained results provide completely new insights on the magnetic order in this system and a better understanding of high field ESR experiments performed previously [5,6,8,13]. For $H \parallel a$ a zero magnetic field gap of 105 MHz has been detected below T_C as well as a dip in the Larmor frequency versus magnetic field relation at $H = 31$ G. For $H \parallel c$ the zero field gap is much smaller and the Larmor frequency increases linearly with increasing magnetic field. These results show that TDAE-C_{60} can be described as a three dimensional Heisenberg easy axis ferromagnet with an extremely small anisotropy field $H_K = 29$ G. Such a low anisotropy field and zero field gap has to our knowledge not yet been observed in any other ferromagnetic system. In other ferromagnetic systems the ferromagnetic modes and dips are typically observed in the far infrared or in the microwave range and not in the radio-frequency region as in TDAE-C_{60}. It should also be stressed that only one ferromagnetic resonance mode has been observed at any given orientation both for the radio-frequency (rf) field applied perpendicular to the external magnetic field ($H_1 \perp H$) as well as for the rf field parallel to the external magnetic field ($H_1 \parallel H$). The above results rule out superparamagnetism as well as an antiferromagnetic

or spin canted ground state where two resonance modes are expected. Using the parameters determined from low field ferromagnetic resonance one can also consistently describe the angular dependence of the Larmor frequency for a crystal rotation in X-band ESR.

TDAE-C_{60} single crystals were grown by a standard diffusion method and were characterized by x-ray diffraction [8]. Special care was taken to avoid twins. After the preparation the crystals used in these experiments were sealed into a quartz tube under the dynamic vacuum and then annealed at 70 °C for 12 h just before the experiment.

Measurements between 30 and 260 MHz and in the L band (1.2 GHz) were done on home built cw ESR spectrometers. X-band and Q-band ESR measurements were done on a commercial Bruker spectrometer. All the spectrometers were equipped with an Oxford He cryostat which allowed us to vary the temperature between 4.4 and 300 K.

The electron magnetic resonance spectra of a TDAE-C_{60} single crystal at $a \parallel H$ and $T = 5\ \mathrm{K} < T_C$ are shown in Fig. 1 in the magnetic field range between 0 and 100 G for fixed resonance frequencies between 40 and 200 MHz. The applied rf field H_1 was perpendicular to the external magnetic field H. In all these cases a single resonance line with no fine structure was found. With decreasing resonance frequency the resonance field at first monotonically decreases down to 110 MHz. Below that for a given resonance frequency two resonance fields were found. At 105 MHz the center of the high field resonance is at 59 G and the center of the low field resonance at 2 G. The higher resonance field decreases and the lower resonance field increases with decreasing resonance frequency until the two lines merge at 50 MHz. The resulting resonance frequency versus resonance field relation [Fig. 2(a)] shows a zero field gap at 105 MHz and a dip at 29 G. This nonlinear behavior is characteristic of ferromagnetic resonance. At frequencies higher than 200 MHz the resonance frequency versus resonance field relation is linear, thus explaining the failure of earlier attempts to observe ferromagnetic resonance in this system. The field-frequency relation is linear up to the L band (1.2 GHz) as well as in the X band (9.6 GHz) and Q band (34 GHz). This is also true for the high field ESR spectra at 94 GHz (Q band) and 245 GHz [13]. In this last case the magnetic field was swept between 0 and 10 T but only the paramagneticlike $g = 2$ line around 8.7 T was detected [13].

It should be stressed that no other resonance mode was detected in the low field frequency range between 30 and 200 MHz for $H_1 \parallel H$. As will be shown later this rules out the existence of antiferromagnetic resonance where two resonance modes—one detectable with $H_1 \perp H$ and another with $H_1 \parallel H$—should be seen.

Above T_C the zero field gap as well as the dip in the resonance frequency versus resonance field relation disappear [Fig. 2(b)]. The Larmor frequency now linearly increases with the magnetic field from zero as expected for a paramagnetic system with no long range magnetic order.

For $H \parallel c$ and $H_1 \perp H$ the low field ESR spectra below T_C show a single resonance line with a nearly linear relation between the Larmor frequency and the external field. There is, however, a zero field gap of about 27 MHz [Fig. 2(c)] which again disappears above $T_C = 16$ K.

The above ferromagnetic resonance data are characteristic for a three dimensional Heisenberg ferromagnet with a small positive ($K > 0$) uniaxial anisotropy field. The easy axis coincides with the crystal c axis which is the direction of the closest approach of the C_{60}^- ions. The center to

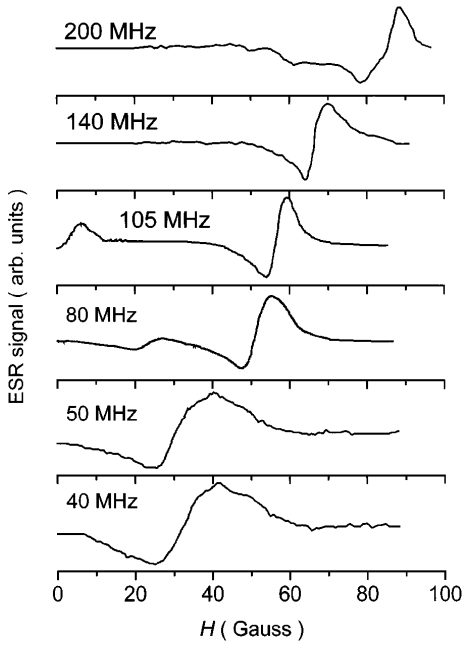

FIG. 1. Radio-frequency range electron magnetic resonance spectra of a TDAE-C_{60} single crystal for $a \parallel H$ and $T = 5\ \mathrm{K} < T_C$. The radio-frequency field was applied perpendicularly to the external magnetic field. The frequency was fixed and the magnetic field H was swept between 0 and 100 G.

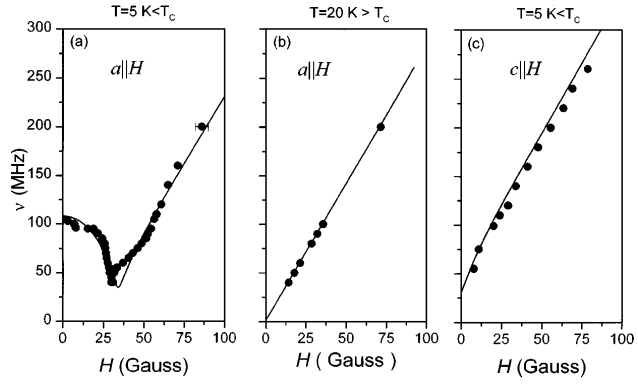

FIG. 2. Observed ferromagnetic resonance frequency versus resonance field relations for (a) $a \parallel H$, $T = 5\ \mathrm{K} < T_C$, (b) $a \parallel H$, $T = 20\ \mathrm{K} > T_C$, and (c) $c \parallel H$, $T = 5\ \mathrm{K} < T_C$. The solid lines are theoretical fits according to expressions (2a) and (2b).

center C_{60} ion distance is here 9.99 Å [8,14]. The difference in the zero field gaps for $H \parallel a$ and $H \parallel c$ can be explained by the presence of a small demagnetizing field. In order to fit the experimental data, we thus have to add to the magnetic free energy density in addition to the Zeeman term f_Z and anisotropy term f_K, also a demagnetizing field term f_{dem} which roughly reflects the shape of the thin plate of the TDAE-C_{60} single crystal used in this experiment,

$$\begin{aligned} f &= f_Z + f_K + F_{\mathrm{dem}} \\ &= -\vec{H}\cdot\vec{M} + K(M_x^2 + M_y^2) \\ &\quad + [N_{\parallel}(M_y^2 + M_z^2) + N_{\perp}M_x^2]. \end{aligned} \tag{1}$$

For $H \parallel a$, i.e., for a magnetic field applied perpendicularly to the easy axis ($\theta_H = \pi/2$), the ferromagnetic resonance frequency is for $K > 0$

$$\frac{\omega}{\gamma} = \sqrt{2H_K(2H_K + H_{\mathrm{dem}})\left[1 - \left(\frac{H}{2H_K + H_{\mathrm{dem}}}\right)^2\right]}\,,$$

$$H \le 2H_K + H_{\mathrm{dem}}\,, \tag{2a}$$

$$\frac{\omega}{\gamma} = \sqrt{(H - H_{\mathrm{dem}})[H - (2H_K + H_{\mathrm{dem}})]},$$

$$H \ge 2H_K + H_{\mathrm{dem}}\,. \tag{2b}$$

Here we introduced the demagnetizing magnetic field $H_{\mathrm{dem}} = (N_{\parallel} - N_{\perp})M$ and the anisotropy field $H_K = KM$, where M is the spontaneous magnetization. For other orientations of the magnetic field, the ferromagnetic resonance frequencies have to be calculated numerically. We were able to fit the dependence of the ferromagnetic resonance frequency on the resonance field using expressions (2a) and (2b) with the same set of parameters both for $a \parallel H$ and $c \parallel H$ (Fig. 2). The obtained value of the anisotropy field is $H_K = 29$ G and of the demagnetizing field is $H_{\mathrm{dem}} = -39$ G.

When the external magnetic field becomes much larger than H_K and H_{dem}, the direction of the magnetization coincides with the direction of the magnetic field. The resonance frequency now becomes

$$\begin{aligned} \frac{\omega}{\gamma} &\approx H + H_K \cos 2\theta_H \\ &\quad + \frac{1}{2} H_{\mathrm{dem}}(\cos^2\phi_H \cos 2\theta_H - \cos 2\phi_H)\,. \end{aligned} \tag{3}$$

It linearly increases with increasing magnetic field thus explaining the previously obtained high field ESR data. Here θ_H is the angle between the magnetic field and the easy (c) axis while ϕ_H is the angle between the projection of the magnetization on the a-b plane and the a axis. As can be seen in Fig. 3, expression (3) describes well the measured angular dependence of the X-band ESR frequency both for a rotation around the crystal c axis as well as for a rotation around the crystal a axis. The parameters used in fitting the observed angular dependence are the ones obtained from the low field ferromagnetic resonance data.

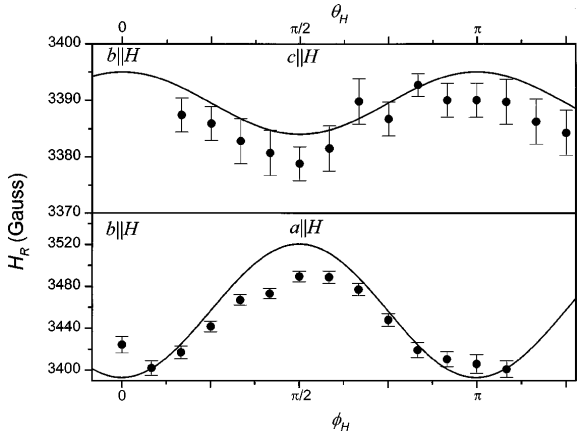

FIG. 3. Angular dependence of the X-band resonance field in TDAE-C_{60} at $T = 5$ K for crystal rotations around the a and c crystal axes. The solid lines are the fits according to expression (3) with the parameters obtained from the low field ferromagnetic resonance data.

It should be stressed that the observed ferromagnetic resonance data exclude the existence of either an easy plane ferromagnetic state, an antiferromagnetic state or a spin canted weakly ferromagnetic state in TDAE-C_{60}. In case of an easy plane ($K < 0$) ferromagnet no dip in the resonance frequency versus resonance field relation should be found. In the case of an antiferromagnet two antiferromagnetic resonance modes ω_1 and ω_2 should exist for all orientations of the crystal in the magnetic field as long as the external magnetic field is smaller than the spin flop field, i.e., for $H < \sqrt{2H_E H_K}$ (Fig. 4). Here H_E is the exchange field $H_E = JM$ and J is the exchange coupling constant. This has not been observed. For fields higher than the spin flop field no dip in the resonance frequency-field relation should exist. On the same grounds spin canted weak ferromagnetism can be excluded. Two resonance modes, one of which should show a dip around the spin flop field should be observed in this case for $K > 0$ and H perpendicular to the easy axis. This was not found. In addition, the observed anisotropy in the angular dependence of the resonance frequency (Fig. 3) is much too small to be consistent with this model. The observed data are also not consistent with a spin glass ground state without long range order. It should, however, be pointed out that our data do not exclude the existence of a mixed ferromagnetic state with nonzero random fields as long as they are smaller than the mean exchange field, i.e., as long as long range magnetic order characteristic of an easy axis Heisenberg ferromagnet does exist.

In summary, we have observed ferromagnetic resonance in well annealed TDAE-C_{60} single crystals below T_C in the radio-frequency range. The results not only definitely prove the existence of long range order below

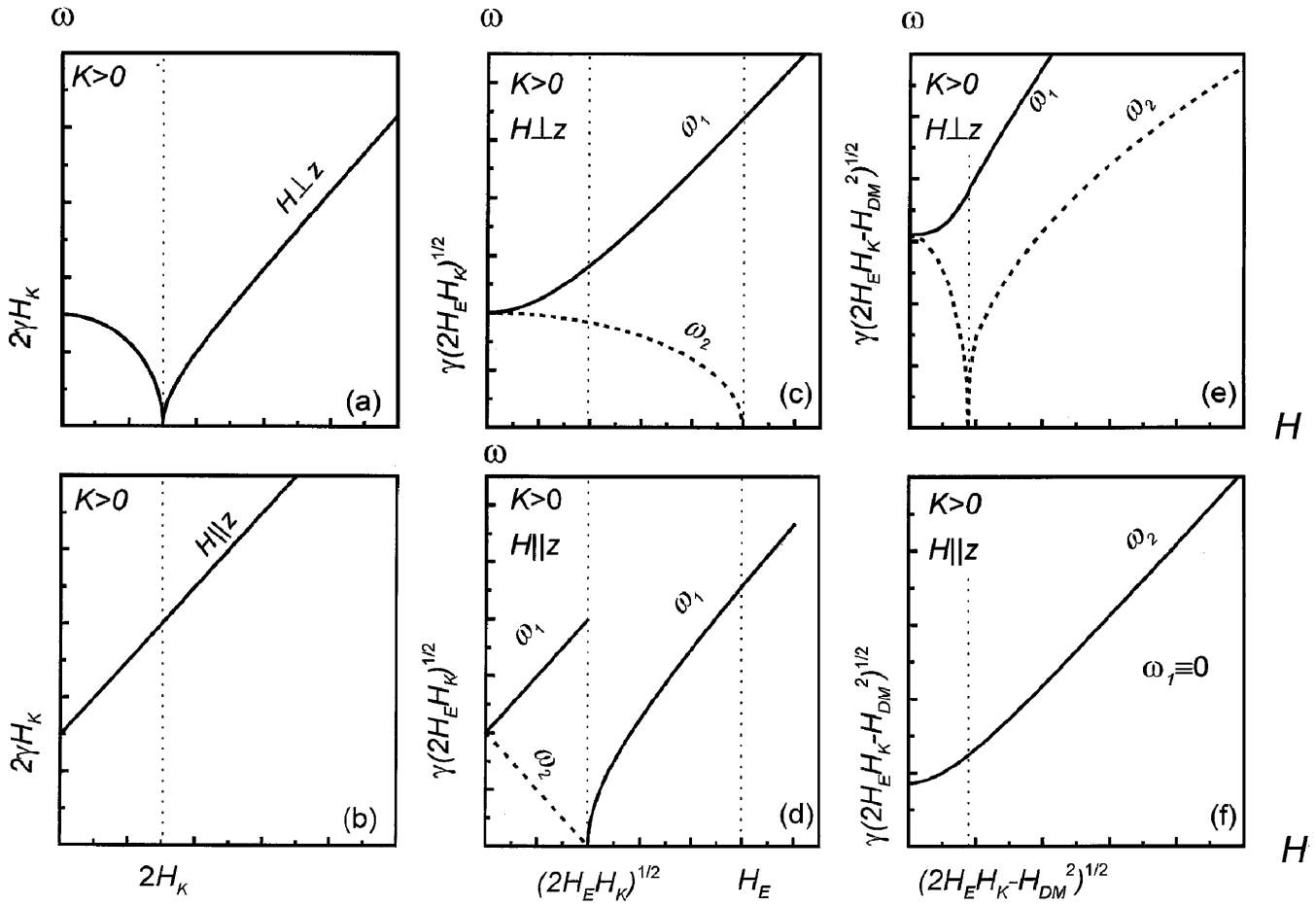

FIG. 4. Resonance field versus resonance frequency relations for (a) an easy axis ferromagnet with $K > 0$ and $\theta_H = \pi/2$; (b) the same as (a) but for $\theta_H = 0$; (c) an antiferromagnet with $K > 0$ and $\theta_H = \pi/2$; (d) same as (c) but for $\theta_H = 0$; (e) a spin canted weak ferromagnet with $K > 0$ and $\theta_H = \pi/2$; and (f) the same as (e) but for $\theta_H = 0$. For the sake of simplicity the effect of the demagnetizing field was neglected. the full lines represent modes which can be excited with $H_1 \perp H$, whereas the dotted lines represent modes excitable with $H_1 \parallel H$.

T_C but also show that TDAE-C_{60} behaves as a simple easy axis Heisenberg ferromagnet with an extremely small anisotropy field of only 29 G. Such small anisotropy fields have not been found in other ferromagnets so far. The direction of the easy axis coincides with the direction of the closest approach of the C_{60} ions.

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