Macroscopic magnetic measurements on the nonferromagnetic modification of TDAE-C_{60}

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We present macroscopic magnetic measurements on single crystals of the nonferromagnetic α' modification of TDAE-C_{60} in a wide temperature ($2\ \mathrm{K} < T < 100\ \mathrm{K}$) and field ($0 < H < 50$ kOe) range. Results show that the low-temperature magnetic properties of α'-TDAE-C_{60} can be described in terms of simple paramagnetic model of noninteracting spins with the effective number of spins corresponding to one Bohr magneton μ_B per formula unit. The effective number of spins gradually increases from one to two μ_B per formula unit as the temperature rises towards 100 K. We propose a model of two independent magnetic subsystems with different spin interactions which could account for the observed magnetic behavior of α'-TDAE-C_{60}.

During the last few years it has been well established that the organic charge-transfer salt TDAE-C_{60} can crystallize in two crystal modifications with completely different low-temperature magnetic properties.[1–3] The usual modification α-TDAE-C_{60} exhibits a ferromagnetic transition at 16 K.[4] The magnetic ground state of this modification can be described in terms of the Heisenberg model with a very low anisotropy.[5] A residual orientational disorder of nearly spherical C_{60} molecules, which is always present in the real samples, gives this system some characteristics of a spin glass.[6–9] On the contrary, the newly discovered α'-TDAE-C_{60} modification shows no ferromagnetic transition down to 1.7 K.[3] Interestingly, both modifications crystallize in the same $C2/c$ space group with the same parameters of the unit crystal cell.[10,11] It is known that the α' modification is the metastable one. It irreversibly transforms into the α modification when thermally treated.[1] Proton NMR measurements[2] revealed two resonance lines: a narrow line which is almost temperature independent in the α' modification and a broader line which follows the Curie-Weiss law with a positive Curie-Weiss constant in the α modification. These measurements imply that some structural changes have to occur during the α' to α transformation that affect the methyl groups of TDAE molecule, but they have not been identified yet in the x-ray measurements.

The ESR measurements[1] have shown that the static spin susceptibility of α'-TDAE-C_{60} obeys the Curie-Weiss law in the temperature range 100–300 K. Below 100 K it starts to deviate from the Curie-Weiss law, gradually decreasing from the paramagnetic value. Eventually, at temperatures below 10 K, the ESR signal completely vanishes. The authors tried to explain this behavior of the spin suceptibility by introducing antiferromagnetic correlations between spins[1] or invoking spin singlets as a magnetic ground state for α'-TDAE-C_{60}.[2] To resolve these questions we have performed measurements of the ac magnetic susceptibility and the static magnetization on α'-TDAE-C_{60} single crystals.

The crystals of α'-TDAE-C_{60} were grown by the diffusion method as decribed in Ref. 11. Samples used in the experiments had typical masses between 1 and 4 mg. For magnetic measurements, single crystals were sealed into quartz tubes under helium. Special care was taken to reduce the time of exposure of the samples to ambient temperature to avoid a spontaneous transformation into the more stable α modification. The magnetic measurements were performed with quantum design MPMS superconducting quantum interference device (SQUID) magnetometer in the temperature range $2\ \mathrm{K} < T < 100\ \mathrm{K}$ and magnetic fields up to 50 kOe (5 T). For the ac susceptibility measurements we used the ac magnetic field with an amplitude of 1 Oe and a frequency of 1 kHz in a zero dc field. A diamagnetic contribution of the quartz tube and the sample holder were separately measured and subtracted from the experimental data.

The results for the real, χ', and the imaginary, χ'', parts of the ac suceptibility are shown in Fig. 1. The susceptibility is essentially Curie-like. A weak hump is also visible near 16 K, which we attribute to a small part of the sample that has been already transformed into the ferromagnetic α modification. From the value of this anomaly ($\sim 1.5\times 10^{-7}$ emu) we can estimate that the transformed part of the sample is less then 0.1% of the whole sample. This part is too small for a

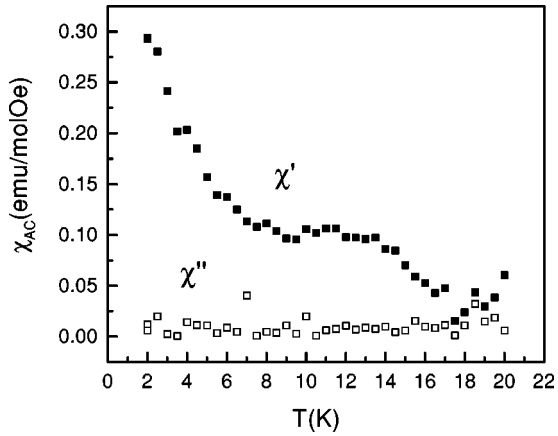

FIG. 1. The real part χ' (solid squares) and the imaginary part χ'' (open squares) of the ac susceptibility of α'-TDAE-C_{60} as a function of temperature.

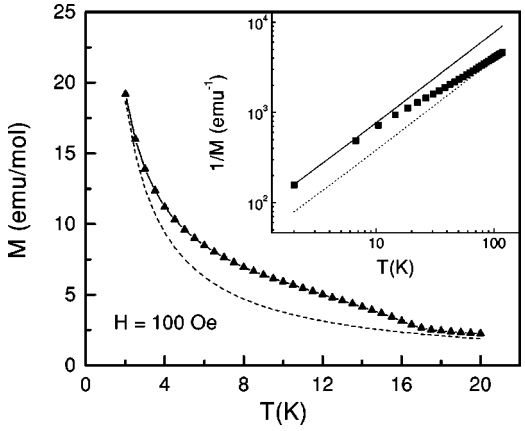

FIG. 2. Temperature dependence of the static magnetization M of α'-TDAE-C_{60} measured in a static magnetic field $H=100$ Oe. The magnetization follows the Curie law $M=(C/T)H$ (dashed curve). Inset: the temperature dependence of the magnetization in the high magnetic field 10 kOe between 2 and 100 K shown in a log-log plot of M^{-1} versus T. The upper (solid) and the lower (dotted) curves are the theoretical Brillouin functions $M=N\mu\tanh(\mu H/k_BT)$ for one and two spins per formula unit of TDAE-C_{60}, respectively.

divergence of χ'' at T_c to be observed.

The low-temperature paramagnetic nature of α'-TDAE-C_{60} is demonstrated by the measurement of the static magnetization in low magnetic field. In Fig. 2 we show the temperature dependence of the magnetization M measured with $H=100$ Oe. Also shown in Fig. 2 is the Curie law $M=\chi H=(C/T)H$, where $C=N\mu^2/k_B$ is the Curie constant with $N=1$/f.u. calculated from the measured mass of the sample where $N=m_{sample}/m_{molar}(TDAE\text{-}C_{60})$ and $\mu=\mu_B$. At low temperatures below 16 K a slight deviation from Curie behavior is observed, which we attribute to the presence of a minute amount of the FM α phase impurity, as already discussed in the previous paragraph. The comparison of the experimental and calculated curves for $M(T)$ yields *one s=1/2 spin per formula unit of TDAE-C_{60}* with an error of less than 2%. This is somehow surprising. One would expect that unpaired spins on both C_{60}^- and $TDAE^+$ should contribute to the macroscopic magnetization, but this is obviously not the case at low temperatures. Above 20 K the low inherent signal requires the mesurement of the temperature dependence of $M(T)$ with a higher magnetic field. For measurements up to 100 K we have used a field of 10 kOe (1 T). The measured curve $M(T,H=10$ kOe) up to 100 K is shown in the inset of Fig. 2. For reasons of clarity we show the results in a plot of M^{-1} versus T in a log-log plot.

For a system of noninteracting 1/2 spins in high magnetic fields we use the Brillouin function

$$M=N\mu\tanh(\mu H/k_BT) \tag{1}$$

to model the data. The upper (solid) and the lower (dotted) line are the theoretical predictions (1) with one and two spins per formula unit, respectively. A crossover from one to two spins per formula unit around 30 K is clearly apparent in the data.

To prove unambiguously the existence of a crossover from two to one spin per f.u. near 30 K we have performed

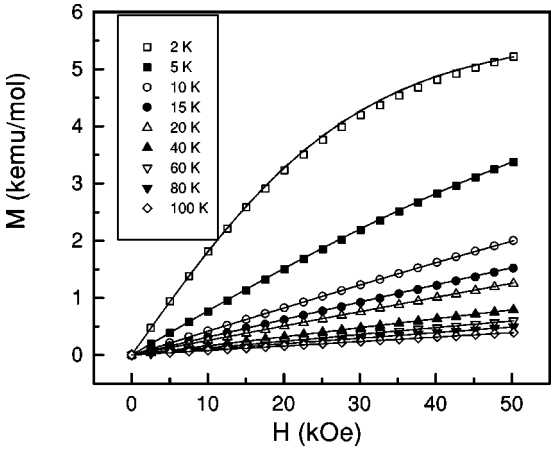

FIG. 3. The magnetization curves of α'-TDAE-C_{60} measured at several temperatures between 2 and 100 K up to the maximal magnetic field of 50 kOe (5 T). The solid lines represent the theoretical Brillouin function.

measurements of the field dependence of the magnetization from 0 to 50 kOe at several temperatures between 2 and 100 K. Those measurements enabled us to determine the number of spins from (1) with a higher accuracy, while providing *independent* measurement of the number of spins per unit cell. Results of those measurements are shown in Fig. 3. We fitted the $M(H)$ curves with the expresion (1) and obtained the number of spins in the sample, N, at different temperatures. We have found that the effective number of spins, N_{eff}, indeed changes with temperature (upper curve in Fig. 4). It gradually increases from 1 at 2 K with increasing temperature and reaches a value of 2 around 100 K.[12] For comparison, we also show the temperature dependence of the product MT measured in a 10 kOe field (the lower curve in Fig. 4). It obviously traces the same curve as N_{eff}.

Thus, both the magnetic field dependence of $M(T,H)$ at different temperature and the T dependence in fixed field

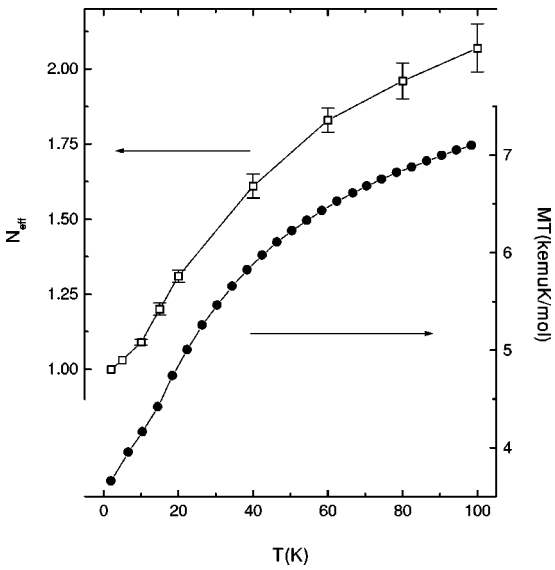

FIG. 4. The effective number of spins per formula unit of α'-TDAE-C_{60} as a function of temperature (upper curve) and the temperature dependence of the product of magnetization and temperature MT measured with a 10 kOe field (lower curve).

give a consistent picture of the crossover from one spin per unit cell to two occuring near 30 K. The low-temperature magnetic properties of α'-TDAE-C_{60} can be very well described with a simple classical model for a paramagnet. Both the temperature and the field dependence of the magnetization exactly follow the Curie and the Brillouin theoretical formulas (the Curie formula being only the low-field limit of the Brillouin formula). The number of spins at low temperatures corresponds to one spin per pair of ions $TDAE^{+}$-C_{60}^{-} but this number is not constant. It changes with temperature and reaches a value of 2 at temperatures around 100 K. This can be compared with the ESR measurements[1] which also show a net decrease of the static spin susceptibility with decreasing temperature. In view of these results, it seems plausible to propose a model of two independent spin subsystems with different magnetic ground states which are simultaneously present in α'-TDAE-C_{60}: one is the subsystem of noninteracting spins that shows paramagnetic behavior down to the lowest temperatures and another is the subsystem of strongly antiferromagnetically coupled spins that gradually cancel out with decreasing temperature. Since the value of the saturation magnetization for the ferromagnetic modification α-TDAE-C_{60} at low temperatures also corresponds to one Bohr magneton μ_B per formula unit,[3] we find that the same mechanism of the spin cancellation may take place also in the ferromagnetic α modification. From low-temperature structural measurements[13] we know that the transformation from α' to α modification affects only the orientations of C_{60} molecules, while structural and electronic properties of TDAE molecules remain unchanged. This enables us to identify the subsystem of spins on C_{60} as the one responsible for the ferromagnetic (paramagnetic) behavior of α-TDAE-C_{60} (α'-TDAE-C_{60}). The subsystem of $TDAE^{+}$ spins has a nonmagnetic ground state and does not influence the low-temperature magnetic properties of TDAE-C_{60} complex.

In conclusion, from measurements of macroscopic magnetic properties of α'-TDAE-C_{60} in low and high magnetic fields at different temperatures between 2 and 100 K we have found that spins in α'-TDAE-C_{60} could be divided into two subsystems. The subsystem of spins localized on C_{60} molecules behaves as a system of noniteracting magnetic moments and gives a paramagnetic contribution to the macroscopic magnetic quantities, i.e., magnetization and magnetic susceptibility. The subsystem of $TDAE^{+}$ spins appears to be effectively decoupled from the C_{60}- spin subsystem. Its contribution to the macroscopic magnetic quantities gradually diminishes with decreasing temperature indicating the presence of some mechanism for spin cancellation in this subsystem. The presence of two spins per formula unit evident from the magnetization measurements at high temperatures is consistent with quantitative measurements of the ESR susceptibility at 300 K.[14] The nature of the spin cancellation mechanism at lower temperatures is not yet known.

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