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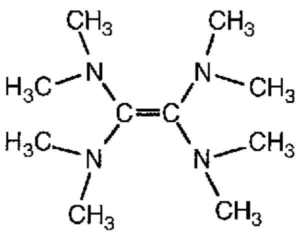
Magnetically Modulated Microwave Absorption (MMMA) Measurements at Low Magnetic Fields on the Ferromagnetic State of [TDAE]C_{60}**

By *Petra Bele,* Hermann Brunner, Andreas Schilder, Jürgen Gmeiner,* and *Markus Schwoerer**

The discovery of a ferromagnetic state in the charge-transfer compound [TDAE]C_{60}, with an ordering temperature of about 16 K,[1] initialized much interest and research on the synthesis of various C_{60}-compounds, with the aim of finding other complexes with similar magnetic properties. Tetrakis(dimethylamino)ethylene (TDAE) (Scheme 1)—



Scheme 1.

one of the strongest organic donors—was replaced by molecules with similar electrochemical properties, but all efforts were unsuccessful. [TDAE]C_{60} is still the only known C_{60}-charge-transfer complex exhibiting that strange ferromagnetic behavior.[2]

The ferromagnetism in [TDAE]C_{60} has become an object of investigation, using different physical measurement techniques to extract more detailed information about the magnetic ordering within this system. The C_{60}-complex behaves like a non-metal, as confirmed by microwave and optical conductivity,[3,4] and also by DC- and AC-conductivity measurements on [TDAE]C_{60} single crystals.[5] All recent EPR, NMR, and magnetization experiments[6–8] led to the conclusion that [TDAE]C_{60} shows antiferromagnetic ordering above $T_c \approx 16$ K and weak ferromagnetic behavior through spin canting below T_c.

Since superconductivity was even reported for this charge transfer complex,[9] we decided to perform magnetically modulated microwave absorption (MMMA) experiments, which are very sensitive to superconductivity, but can also be applied successfully to the detection of weak ferromagnetism.[10]

In Figure 1 the temperature-dependent data of the EPR linewidth of a powder sample of [TDAE]C_{60} are presented. As mentioned in the experimental section, this measurement was taken to ensure the quality of our sample. A single Lorentzian-shaped EPR line between room temperature and 20 K is seen. Below the ordering temperature of 16 K the received data could be described better by a Gaussian line due to internal fields in the sample. There was no superpositioned small line visible, which would have originated from a non-ordered phase in [TDAE]C_{60}. After a decrease of the linewidth with decreasing temperature down to 20 K, the transition into the ferromagnetic state is clearly indicated by an abrupt increase in linewidth. This experimental result is consistent with that expected theoretically for a ferromagnet and was also recently published in more detail by Mihailovic et al.[11]

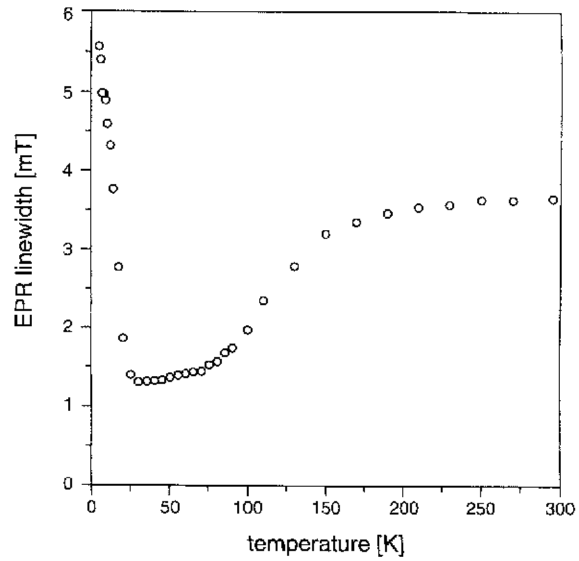


Fig. 1. Q-band EPR linewidth of a powder sample of [TDAE]C_{60} as a function of temperature.

Figure 2 presents the measurement of the in-phase component of the AC-susceptibility in the temperature range 30 K to 4 K (the out-of-phase magnetic response was below the detection limit). The plot of the data clearly shows that the susceptibility is higher below 15 K. This behavior is a further indication that, below the transition temperature, spin ordering takes place. The spin-glass-like cusp at about 10 K is remarkable, as is the second increase in susceptibility below ~5 K. A more detailed discussion of the frequency-dependent investigations carried out on [TDAE]C_{60} are given by Scheinast et al.[12]

In Figure 3 we present the temperature-dependent MMMA signal for a [TDAE]C_{60} powder sample. These MMMA measurements, which we performed for the first time on the charge-transfer complex [TDAE]C_{60}, are in good agreement with the above discussed low temperature

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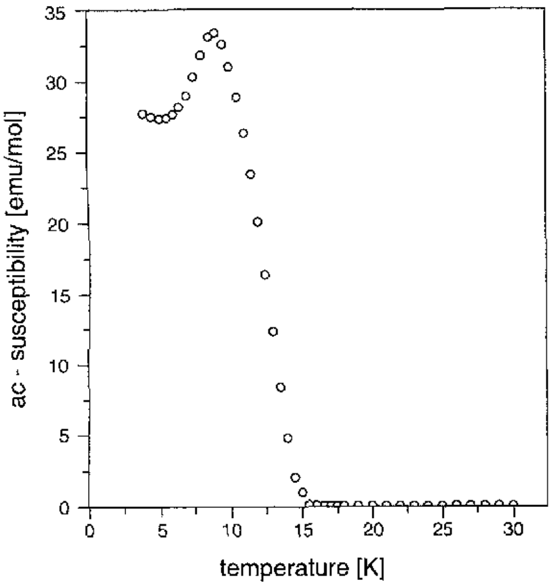

Fig. 2. Temperature dependence of the in-phase AC-susceptibility of $[TDAE]C_{60}$ measured at 10 kHz.

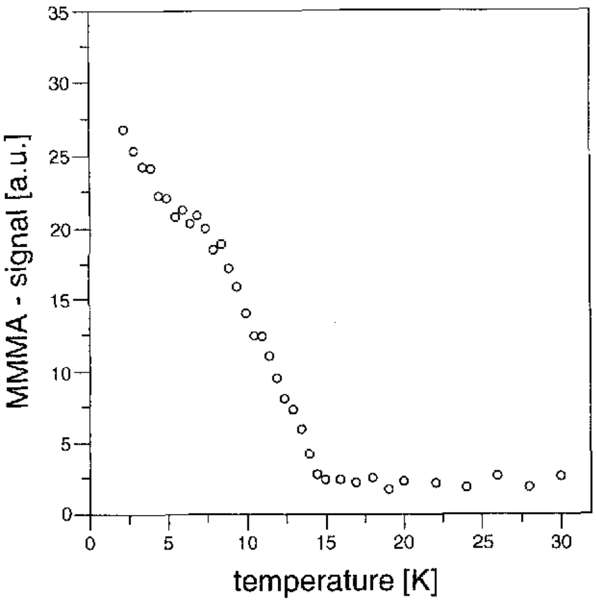

Fig. 3. Magnetically modulated microwave absorption signal of a powder sample of $[TDAE]C_{60}$ as a function of temperature.

behavior of this compound. A sudden onset of an even, though weak, MMMA signal at 15 K, which increases by a factor of 20 (with reference to the noise level) between 15 K and 8 K was observed. Between 8 K and 5 K the temperature-dependent plot of the MMMA signal shows a shoulder and increases again below 5 K.

The dependence of the MMMA signal on an externally applied magnetic field is presented in Figure 4 . The signal increases continuously in the field range between –5 mT and +5 mT. By reversing the field scan direction a very small hysteresis effect can be observed.

Ricco et al. reported the observation of superconductivity in $[TDAE]C_{60}$,[9] but, upon analysis of our MMMA signal, no indication of superconductivity in the powder sample used could be found. From our experimental experience with superconducting charge-transfer complexes based on the organic donor bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), the MMMA signal of a superconducting sample the same size as our measured $[TDAE]C_{60}$ samples would be at least two or three orders of magnitude higher in amplitude, and in addition the signal would show a much sharper dependence on temperature.[13] The result that $[TDAE]C_{60}$ shows no superconducting properties is confirmed by the AC-susceptibility measurement presented in Figure 2, where no evidence for superconductivity was detected either. Instead, the behavior of the MMMA signal of $[TDAE]C_{60}$ is comparable to the observed MMMA signal of the organic free radical 1,3,5-triphenyl-6-oxoverdazyl,[10] which becomes a weak ferromagnet below 4 K. Also, a similar MMMA signal, related to weak ferromagnetism, has been observed at a temperature ≈ 25 K for the organic charge-transfer complex κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$.[14]

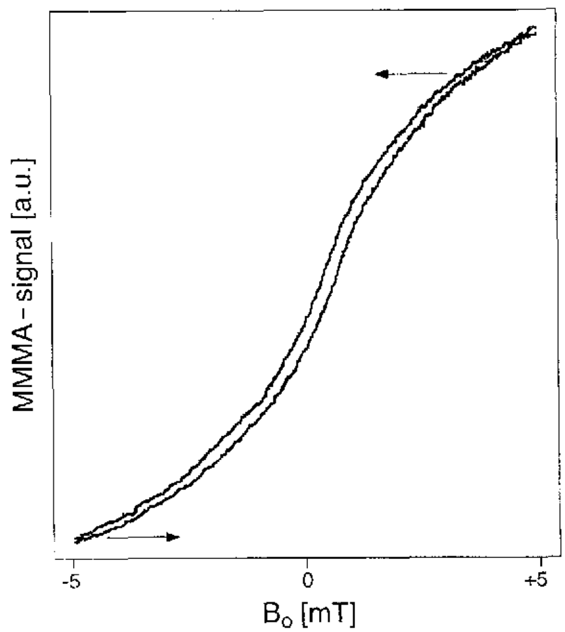

Fig. 4. Magnetic field dependence of the MMMA signal for a $[TDAE]C_{60}$ sample measured at a temperature of 4 K. The field cycle range of the external magnetic field $\boldsymbol{B}_0$ varies from –5 mT to +5 mT. The arrows indicate scan direction.

It should be mentioned that the MMMA signal of our $[TDAE]C_{60}$ samples increased about 10 % in amplitude during the first few temperature cycles (cooling down–warming up). After several days, the amplitude became almost stable and showed a weak decrease during the observation period of several weeks.

The sudden appearance of an MMMA signal at T_c = 15 K is not really understood. The change in the microwave absorption means that the imaginary part of the microwave susceptibility becomes dependent on the external magnetic field, i.e., the modulation field. This phenomenon can be

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explained as a ferromagnetic resonance of spins in strong internal magnetic fields, which are causally related to ferromagnetically ordered spins in small domains of the [TDAE]C_{60} sample. The existance of internal fields below T_c has been proven by NMR measurements[7] and by the EPR experiment, which shows a shift in and line broadening of the EPR signal. Nevertheless, these internal fields are not strong enough for spin resonance in zero field. Other possible reasons for the microwave absorption can be sought in non-resonant energy absorption and dissipation of ferromagnetic domain walls, or in a spin-flip-like reorientation of the sublattice magnetization in the microwave field due to weak crystal anisotropy. In any case, the prerequisite for the MMMA in [TDAE]C_{60} is the partial ferromagnetic ordering of the electronic spins.

Therefore we also favor the assumption of Blinc et al.[6] that [TDAE]C_{60} undergoes a phase transition from an antiferromagnetic state into a state of weak ferromagnetism through spin canting due to a Dzyaloshinsky–Moriya-type interaction.[15,16] As a consequence of this interaction, one would expect an anisotropy of the magnetic ordering along the different crystal axes. So it would be very interesting to look at the orientational dependence of the MMMA in a sufficient large single crystal of [TDAE]C_{60}.

Experimental

The sample was prepared by dissolving C_{60} (Hoechst, gold grade 99.4) in benzene after removing the oxygen by dynamic vacuum. A TDAE-benzene solution was added stepwise, the solvent decanted, and the powder residue dried under vacuum (10^{-2} mbar). These steps were all performed under inert atmosphere below room temperature in order to yield a good microcrystalline powder. The powder was filled into a Suprasil sample tube in a glove box, sealed with a Teflon cap, coated with Parafilm and, finally, covered with silicon rubber to avoid oxygen contamination.

To ensure the quality of the sample, we measured the temperature-dependent electron paramagnetic resonance using a conventional Bruker ESP300 spectrometer, working at Q-band conditions (34 GHz and $B_0 \approx 1.2$ T). An Oxford Instruments ESR900 helium cryostat was used to vary the temperature between 300 K and 4.2 K.

A homemade AC-susceptometer, which allows measurements between 300 K and 4.2 K at frequencies from 1 mHz to 20 kHz, was used for the measurement of AC-susceptibility. The samples were sealed in a quartz tube with an outer diameter of 4 mm and moved to the center of a pickup coil. Excitation within the above mentioned frequency range with a second coil induces a voltage in the pickup coil that depends on the susceptibility of the sample. A setup of two pickup coils and a stepper, to move the sample between them, allowed us to correct for the signal due to the empty coil.

The MMMA experiments were carried out on powder samples of [TDAE]C_{60}, using a slightly modified Varian E-line EPR spectrometer, working at the X-band ($\approx$ 10 GHz). Instead of the iron magnet, we used a system of two pairs of concentric coils, approximately fullfilling the Helmholtz conditions, to scan the external magnetic field, $\boldsymbol{B}_0$, from −5 mT, through 0, to +5 mT. This equipment also allowed us to look for hysteresis effects. The sample was cooled down in an Oxford Instruments ESR910 helium cryostat (range 300 to 2 K). For the detection of the MMMA signal, we used the usual 100 kHz field modulation and phase sensitive detection. The signal was registered either by recording 25 sweeps in a digital storage oscilloscope followed by computer treatment, as for the temperature- dependent measurements, or directly on an *X–Y* recorder, as for the field-dependent experiments. In contrast to most of the MMMA measurements on superconductors, the signal amplitude for ferromagnetic samples is quite weak. For this reason, it was necessary for us to apply a comparably strong microwave power of about 5 mW and higher modulation amplitudes of the order of 3 mT [13]. For sensitivity reasons, we could not work with single crystallites, so we had to use aproximately 15 mg of a polycrystalline sample.

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Formation of Metal-Laden Ultrafine Semiconductor Particles by Solid-State Diffusion

By *Min-Jin Ko,** *Meyer Birnboim,* and *Joel Plawsky*

There is increasing interest in the design and synthesis of nanometer-size materials because of their novel electronic, optic, and magnetic materials properties.[1–3] The materials, often referred to as clusters or quantum dots, are intermediate in size between molecular and bulk species and have a number of unique properties, for example, size quantization,[4,5] nonlinear optical behavior,[6] and unusual fluorescence.[7] The quantum confinement effects exhibited by these materials can lead to increased electron binding and enhanced oscillator strengths. In particular, materials with a relatively small exciton Bohr radius, such as CuCl,

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