Microwave Conductivity of the Soft Ferromagnet (TDAE)-C_{60}

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(Received 6 June 1994)

(Tetrakisdimethylaminoethylene)-C_{60} was the first fullerene charge transfer complex with a transition into a soft ferromagnetic low temperature phase at 16 K. The origin of the low temperature phase in (TDAE)-C_{60} is still a subject of discussion. To unravel the real nature of the ferromagnetic ground state we will present measurements of the conductivity in (TDAE)-C_{60} for the first time. The conductivity is of the order of 10^{-4} S/cm at room temperature and the temperature dependence is clearly nonmetallic. This contradicts the assumption that (TDAE)-C_{60} is a ferromagnetic metal.

The magnetic susceptibility of the fullerene charge transfer (CT) complex (tetrakisdimethylaminoethylene)-C_{60}, abbreviated as (TDAE)-C_{60}, exhibits a strong increase below 16 K [1] but showing no hysteresis. This was claimed to be the sign of a soft ferromagnetic ground state. The Curie temperature T_C of about 16 K is the highest transition temperature of a pure organic material reported. The magnetic properties of (TDAE)-C_{60} were interpreted on the basis of itinerant ferromagnetism (IFM) [1–3] which is unusual for organic ferromagnets. Common concepts [4] are based on localized strongly exchange interacting spins. Even though the presence of ferromagnetic spin correlations was further confirmed by electron paramagnetic resonance (EPR) [5,6] and NMR [7] the real nature of the low temperature phase is still a subject of controversial discussion. Especially no experimental evidence for the presence of itinerant moments was given so far. In EPR measurements a simple Curie-Weiss susceptibility is found [8]. In contrast some authors report a temperature independent Pauli-like contribution in the static susceptibility besides a dominating Curie-Weiss part [1,2]. In static susceptibility measurements the temperature independent diamagnetic part of the susceptibility has to be calculated from Pascals constants [9]. If this contribution is overestimated or the sample-holder contribution is not correctly subtracted, an artificial positive temperature independent Pauli-like offset is easily introduced. EPR is free of such artifacts unless very adverse experimental conditions, but a small Pauli-like contribution to the total susceptibility can be beyond the resolution of an EPR experiment. A stoichiometry of 1:1 and a complete charge transfer [10] for (TDAE)-C_{60} was reported, i.e., (TDAE)-C_{60} is a truly ionic charge transfer complex. The Coulomb interaction in fullerene salts was estimated to be of the order of 1 eV and about 0.5 eV for the bandwidth [11,12]. Thus, these systems are close to a Mott-Hubbard localization in a real stoichiometric system. The proton NMR in (TDAE)-C_{60} exhibits a pure paramagnetic shift $\Delta\nu[\Delta\nu \propto 1/(T - T_C)]$ [13]. The ^{1}H-relaxation probes the static susceptibility χ above T_C and no Korringa behavior was found [7,13]. Anyhow,

both results are not in contradiction with a metallic behavior. The temperature dependence of the relaxation rate is in agreement with predictions from spin fluctuation theory for a weakly itinerant ferromagnetic system [14]. For a strongly correlated metallic system a Curie-Weiss susceptibility is found instead of a Pauli-like susceptibility [15]. Extensive magnetic resonance investigations so far could not clarify the origin of the huge moment below 16 K. Though the interpretation on the basis of itinerant ferromagnetism is quite attractive, since the lack of hystereses effects in the magnetization below 16 K and the pressure dependence of T_C [2] can be explained, no studies of the conductivity in (TDAE)-C_{60} were reported. Only one room temperature value for the conductivity of a pressed pellet of 0.01 S/cm [1] was stretched to confirm the existence of IFM. In this Letter we will present for the first time conductivity data in (TDAE)-C_{60} between 80 and 420 K.

C_{60} (99.4%, Hoechst), TDAE, and solvents (Aldrich and Fluka Corporation, p.a. purity) were purchased. TDAE and all solvents were first dried with a molar sieve, then vacuum distilled with a column containing Raschig rings. After the distillation TDAE is a colorless liquid with a weak green fluorescence. Benzene was dried under reflux in a N_2 atmosphere over P_2O_5 and a second time over KOH and finally distilled in an Ar atmosphere in a column containing Raschig rings. Careful purification and drying of the solvents is necessary, since all amine based C_{60} CT complexes are very moisture sensitive. The salts were prepared under Ar atmosphere with conventional Schlenk technique. To a saturated dark violet C_{60}/benzene solution a 40 eq. excess of TDAE was added under stirring. (TDAE)-C_{60} precipitates almost instantaneously. The remaining clear light grey liquid was decanted and the precipitate washed 3 times with fresh benzene. Finally the precipitate was dried under vacuum for 2 h. All samples were handled only in a glove box. The sample quality was controlled with ac susceptibility. A typical susceptibility curve is shown in Fig. 1. The ferromagnetic ground state below 16 K clearly emerges.
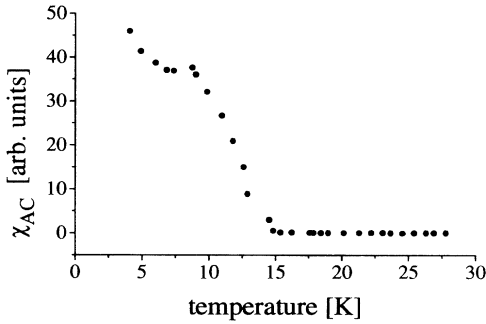
FIG. 1. Typical ac-susceptibility curve in (TDAE)-C_{60} at 10 kHz ac-field frequency in arbitrary units. The ferromagnetic ground state below 16 K clearly emerges.

(TDAE)-C_{60} is formed by precipitation from solution and is an amorphous or microcrystalline powder. Efforts to produce single crystals of (TDAE)-C_{60} have failed so far. Doping of C_{60} films by diffusion of TDAE into the film is less promising, since TDAE is a bulky molecule. Because of the air and moisture sensitivity of the material contacting of a pressed pellet will probably cause a lasting damage of the contact region. Inclusion of solid contacts into pellets, which are very fragile and brittle, will result in a hard to estimate resistance between the contact and the (TDAE)-C_{60} bulk. In contrast microwave conductivity is a contactless method.

For all measurements we used a homebuilt apparatus operating in transmission geometry. Microwaves generated by a YIG oscillator (8–12.5 GHz) are attenuated and coupled to a cylindrical cavity which contains the sample. The transmitted power is detected and rectified by a square-law detector (Schottky diode, incident microwave power less than 5 nW). Temperature is controlled by a N_2-gas-flow cryostat for temperatures between 80 and 450 K. The microwave cavity can be excited either in the TM_{010} or the TE_{111} mode. It is made of copper. The inner surface is polished and gold plated and has a quality factor of 3000 without sample holder. Weak coupling is done by loops. The sample was mounted in a sealed glass tube with an inner diameter of 1.8 mm and held in position by small pieces of styrofoam (Grace/Eccofoam PP-2) which has a dielectric constant close to unity (1.04 from 60 to 10^{10} Hz at temperatures lower than 360 K) and a very low loss factor (10^{-4}). The sample tube was exposed to argon; this protects the sample during sealing and ensures a good thermal coupling of the sample. When the sample is inserted in the cavity at a maximum of the electrical and a minimum of the magnetic field the complex dielectric constant of the sample causes a decrease of the resonance frequency and of the cavity quality factor Q (resonance frequency and Q factor f_s, Q_s with and f_e, Q_e without sample). For each temperature all four quantities were measured several times and averaged. The sample

was positioned by a lift. We now can calculate a complex frequency shift Δf:

$$\Delta f = \Delta f' + i \Delta f'' = \frac{f_s - f_0}{f_s} + \frac{i}{2}\left(\frac{1}{Q_s} - \frac{1}{Q_0}\right).$$

Since conductivity and sample volume (compared to the wavelength) were small, the field penetrates the sample homogeneously and no skin effect has to be taken into account. In this quasistatic regime perturbation theory relates Δf to the imaginary part of the dielectric constant ε [16]:

$$\varepsilon'' = \frac{1}{N}\frac{\frac{N}{\alpha}\Delta f''}{\left(1 + \frac{N}{\alpha}\Delta f'\right)^2 + \left(\frac{N}{\alpha}\Delta f''\right)^2}.$$

The geometry dependent filling factor α is determined by numerical integration of the electric field over the sample volume and the depolarization factor N by formulas given by Osborn [17] under the assumption of ellipsoidal shaped samples. This finally gives the conductivity

$$\sigma = 2\pi f_S(T)\varepsilon_0\varepsilon''(T).$$

The most critical point of the evaluation of σ is the calculation of α. Though we used pressed pellets the density of the sample can be overestimated and the absolute value of the conductivity can be underestimated under worse circumstances by an order of magnitude. Anyhow, the temperature dependence of σ is much less affected by an error in α and is absolutely reliable.

Figure 2 shows a typical conductivity plot of (TDAE)-C_{60} between 100 and 320 K. The temperature dependence and the absolute value of the conductivity are reproducible in various batches. The conductivity is exceptionally low. With 10^{-4} to 10^{-5} S/cm it is near the limit of resolution of the microwave conductivity technique (about 10^{-6} S/cm). Thus, only a very limited temperature interval was accessible and we want to anticipate that in
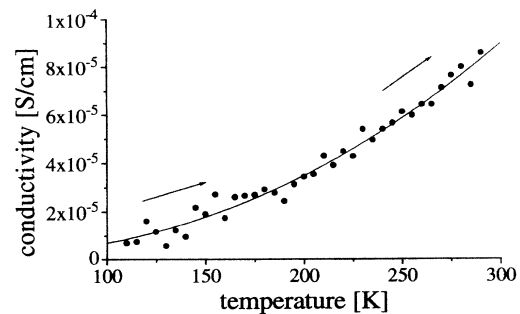

FIG. 2. Typical conductivity plot of (TDAE)-C_{60} between 100 and 320 K. With 10^{-4} to 10^{-5} S/cm the conductivity is near the limit of resolution of the microwave conductivity technique (about 10^{-6} S/cm). The solid line is a fit of the experimental data with a power law dependence: $\sigma_{\mu w} = (1.5 \pm 0.1) \times 10^{-10}T^{2.3\pm0.1}$ S/cm.

this case predictions about conductivity mechanisms will be elusive. Anyhow, the conductivity clearly decreases with decreasing temperature contradicting a metallic behavior. We want to emphasize that ac techniques usually even overestimate conductivities in very inhomogeneous or amorphous systems because they make a weighted average over the whole volume of the sample whereby regions with higher conductivities have a higher weight than regions with lower conductivities. Internal boundaries or grain contacts will affect mainly the absolute value of σ but not the temperature dependence. Thus, microwave conductivity ($\sigma_{\mu w}$) will elucidate an internal property of (TDAE)-C_{60}.

Presuming an activated behavior we deduce an activation energy of 55 meV for a pressed pellet of (TDAE)-C_{60}. Better reconciliation of our experimental data is found by a power law dependence: $\sigma_{\mu w} = (1.5 \pm 0.1) \times 10^{-10} T^{2.3 \pm 0.1}$ S/cm. The temperature dependence between 100 and 300 K is reproducible and reversible in pristine samples. Anyhow, if the samples are heated above 350 K, we find a strong increase of the conductivity. Between 350 and 420 K no static equilibrium at a constant temperature could be achieved. Figure 3 shows a temperature cycle where heating was stopped at 420 K and then the sample was cooled down again. Obviously the conductivity had increased by 2 orders of magnitude and $\sigma_{\mu w}$ is now comparable to the value of $\sigma = 10^{-2}$ S/cm at room temperature reported previously [1]. However, for such samples no ferromagnetic ground state was found above 3.5 K in EPR or ac-susceptibility measurements. Above 350 K either the onset of a sample decomposition is observed or an oxygen layer (even though the sample container and the styrofoam were stored for several days in a glove box) was degassed from the inner walls of the sample container. The reported [1] σ value could have been measured on an oxygen contaminated sample, but no details of the measurement were given.
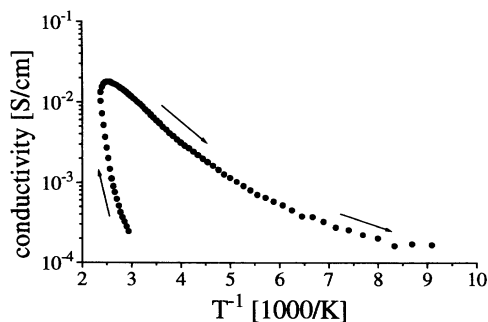

FIG. 3. If the samples are heated above 350 K, a strong increase of the conductivity is found. Between 350 and 420 K no static equilibrium at a constant temperature could be achieved. A temperature cycle is shown where heating was stopped at 420 K and then the sample was cooled down again. The conductivity had increased by 2 orders of magnitude compared to the value of pristine samples.

The threefold degeneracy of the C_{60} lowest unoccupied molecular orbital [18] is lifted in C_{60}-monoanions by a Jahn-Teller distortion of the C_{60} molecule [19]. The energy of one of the three levels is lowered by 50 to 100 meV [20]. According to the stoichiometry (TDAE)-C_{60} would be metallic [1]. However, huge correlation effects are expected for C_{60} CT complexes [21] and (TDAE)-C_{60} could be subjected to a Mott-Hubbard localization. Blinc and co-workers have proposed that (TDAE)-C_{60} could be a spin glass at low temperatures [22,23]. In this case of a disordered material even if Mott-Hubbard localization is prevented by nonstoichiometry the electronic states near the Fermi level are no longer extended but localized up to the mobility edge [24]. In this case a hopping conductivity prevails. A further possibility is the excitation of electrons into extended states above the mobility edge causing a thermally activated conductivity. If the vertical disorder of the energy levels which causes local potential fluctuations is comparable to the bandwidth, all electronic states are localized (Anderson localization) even in the absence of Mott-Hubbard splitting [24]. Transport in such a Fermi glass can be described by next-neighbor hopping in the high-temperature limit, having a simple exponential dependence [24].

The nature of the samples and the above statements suggest to consider (TDAE)-C_{60} as a semiconducting organic system without long range structural order. Electrons are localized at the band edges and can contribute via hopping processes to the electrical transport. One mechanism which predicts at least a quadratic temperature dependence of σ is the correlated barrier hopping. A pair of localized levels is separated by a potential well. If the two levels are separated in energy by more than kT the conductivity would be proportional [25] to T^n with $n \geq 2$. Our experimental data imply such a behavior. The conclusions [26] that the small band width expected in fullerene CT complexes rules out a traditional Stoner model (i.e., itinerant ferromagnetism as suggested by the absence of hysteresis effects [1] and the close C_{60}-C_{60} separation along the c axes [10]) are in good agreement with the exceptionally low, nonmetallic conductivity found by microwave conductivity in (TDAE)-C_{60} and AC_{60} [27].

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