The role of TDAE for the magnetism in [TDAE]C_{60}

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New Journal of Physics 1 (1999) 5.1–5.11 (http://www.njp.org/)
Received 19 October 1998; online 15 March 1999

Abstract. The mechanism leading to the outstanding magnetic property of the organic charge-transfer salt [TDAE]^{++}C_{60}^{-} is still a matter of discussion. The scope of this paper is to explore the role of TDAE^{++} for the magnetic ordering below \( T_C = 16 \text{ } K \) and to find a model which is in accordance with the experimental findings. Therefore besides [TDAE]^{++}C_{60}^{-} we synthesized slightly altered compounds by either perdeuterating TDAE or replacing C_{60} by C_{70} in various concentrations. The magnetic ordering and the electric transport properties in these systems are investigated between 4 and 300 K by ac-susceptibility, ESR, NMR and microwave conductivity. As a result, itinerant magnetic moments can be excluded in the whole temperature range and the TDAE^{++} radical ion is coupled with C_{60}^{-} by strong spin-exchange and has to be taken into account for a description of the magnetic ordering. Microscopic models assuming a second charge transfer seem to be an appropriate way to describe the experimental results.

1. Introduction

The magnetism in organic materials attracted rapidly increasing interest in 1991 when Wudl et al [1] discovered a magnetically ordered phase below \( T_C = 16 \text{ } K \) in [TDAE]^{++}C_{60}^{-}. This compound is a charge-transfer salt of the strong organic electron donor TDAE [2] with C_{60} in which one electron is transferred from TDAE to C_{60}. Many groups [3,4,5,6] directed activity towards unravelling the origin of this magnetism with a Curie temperature which is about an order of magnitude higher than for all other known organic compounds [7,8] consisting of elements with no d- and f-orbitals. One must bear in mind that in organic materials only s- and p-orbitals with small magnetic moments can overlap to give a macroscopic magnetic ordering.

Since many attempts to replace TDAE by other organic donors [9,10] failed to give a ferromagnetic compound, we will focus in this paper on the role of the TDAE radical ion for macroscopic magnetic ordering and we will apply ac-susceptibility, microwave-conductivity,
ESR and NMR to investigate \([\text{TDAE}]^\bullet \text{C}_{60}^\bullet\) and slightly altered compounds by replacing \(\text{C}_{60}\) in variable ratios by \(\text{C}_{70}\) or by perdeuterating TDAE.

2. Samples and methods

We used microcrystalline powder samples and, in addition, small crystals for ESR. The powder samples were precipitated from a benzene solution of \(\text{C}_{60}\) by adding a benzene TDAE solution (see figure 1) and dried afterwards under a dynamic vacuum. In order to reach a high sample quality the air-sensitive TDAE and TDAE-d_{24} was freshly synthesized [11] or at least distilled before precipitation. All steps of precipitation and sample production were performed in an inert atmosphere. Sample amounts between 1 mg and 30 mg were sealed in glass capillaries for the different methods of investigation. The sample quality was testified by x-ray diffraction (G Bendele, Brookhaven) at 295 K which showed no peaks from phases other than the reported lattice structure for \([\text{TDAE}]^\bullet \text{C}_{60}^\bullet\) (see figure 2) [12]. SQUID-magnetometry between 2 K and 295 K (M Kelemen, Karlsruhe) gave about 88% of the nominal spins when assuming two spin-\(1/2\) per formula unit of \([\text{TDAE}]\text{C}_{60}\).

We performed contactless conductivity measurements, ac-susceptibility, ESR and NMR \((^1\text{H} \text{and} ^2\text{H})\) in order to elucidate the role of TDAE for the magnetic order in \([\text{TDAE}]^\bullet \text{C}_{60}^\bullet\). Microwave conductivity at three frequencies 8.8, 11.8 and 15.5 GHz and ac-susceptibility at 10 kHz were measured using home-built apparatus [13]. ESR and NMR was done on commercial Bruker spectrometers for X-band-ESR (9 GHz), Q-band-ESR (34 GHz), \(^1\text{H}-\text{NMR}\) (46 MHz) and \(^2\text{H}-\text{NMR}\) (45 MHz) with home-built NMR-probeheads.
3. Microwave conductivity

Whereas conductivity data of $[\text{TDAE}]^{+}\text{C}_{60}^{-}$ for $T>120$ K were already known \cite{15,16,17} the temperature range below 120 K especially in the ferromagnetic ordered phase (i.e. below 16 K) had still not been examined. These data are very valuable to decide unambiguously about the existence of itinerant electrons in the magnetically ordered phase.

We measured microwave conductivity from 5 to 300 K, which has the advantage of no need for contacts, therefore avoiding contact resistivities, and the possibility to seal the sample in a quartz capillary.

Working at frequencies between 8 and 18 GHz, this method is sensitive to the intrinsic conductivity of microcrystalline samples with negligible influence of contacts between microcrystallites. The results are shown in figure 3 and demonstrate clearly a non-metallic behaviour down to 5 K. The temperature dependence can be described by hopping- and tunneling-models for disordered systems \cite{13,14,18}. The disorder is a consequence of the rotational dynamic \cite{19} of the $\text{C}_{60}$-molecules above about 150 K and the merohedral disorder \cite{16} at lower temperatures. The slowing down of the rotational jumps is also seen in the real part of the dielectric constant (figure 3, inset) which is nearly constant below 150 K.

In conclusion, our conductivity measurements in the ferromagnetic region exclude together with investigations \cite{15,16,17} at temperatures above 16 K, models for itinerant ferromagnetism (bandferromagnetism). Thus we will focus on microscopic models for localized spins both on TDAE$^{++}$ and $\text{C}_{60}^{-}$. 

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4. ESR

It was surprising that a compound consisting of two radicals, TDAE$^+$• and C$_{60}$$^-$•, shows only one ESR-line [20, 21] even at frequencies as high as 240 GHz [22] or as low as 30 MHz [23]. Different mechanisms of spin-cancellation were discussed in order to understand the absence of one ESR-line.

We performed ESR on [TDAE]$^+$•C$_{60}$$^-$•, perdeuterated [TDAE]$^+$•C$_{60}$$^-$• and explained the data by comparison with ESR-spectra of model systems for C$_{60}$$^-$• and TDAE$^+$•, respectively. In our first samples of [TDAE]$^+$•C$_{60}$$^-$• the single line was asymmetric and not easy to analyse.

As the ESR-line shows a perfectly Lorentzian shape above 50 K (figure 4) we succeeded in increasing the sample quality as described in section 2. In addition the maximum value of the ac-susceptibility increases to 45 emu/mole (figure 7) which is equivalent to an improvement of a factor of three. Thus the shape of the room-temperature ESR can be utilized as an indicator of the sample quality and the size of the magnetic susceptibility below 16 K. Detailed investigations showed that the former asymmetric lineshapes can be explained by a superposition of the symmetric line of good samples with the narrow and weak lines of completely degraded samples. Carefully prepared samples are stable on a timescale of more than one year, provided they are stored in an inert atmosphere, as proved by ESR and ac-susceptibility measurements.

Below 50 K but above $T_C$ the ESR-spectrum already starts to become asymmetric due to a g-factor anisotropy, which is best seen in a Q-band rotation pattern of a single crystal for which the static field $B_0$ was rotated in the plane perpendicular to the c-axis (figure 5). Below 20 K the line broadens due to a field-induced increase of $T_C$ and assumes a Gaussian shape (figure 4).
Figure 4. Q-band ESR spectra on a [TDAE]+•C_60−• powder sample at four temperatures.

Figure 5. Maximum g-value anisotropy $\Delta g$ at 34 GHz for a [TDAE]+•C_60−• single crystal. The sample was rotated about the c-axis with the static magnetic field in the a-b-plane. The rotation patterns for two temperatures are shown in the inset.
The field anisotropy in the a-b-plane can be roughly estimated to about 33 G and is comparable with the value of 29 G found by Blinc et al [22].

As model systems for C\textsubscript{60} and TDAE\textsuperscript{+} we chose a deoxygenated solution of TDAE in water and single crystals of [P(C\textsubscript{6}H\textsubscript{5})\textsubscript{12}]C\textsubscript{60}. The latter is a charge-transfer salt with only C\textsubscript{60} as radical because the positively charged counterion has a closed-shell configuration [24, 25]. We measured the g-values for TDAE\textsuperscript{+} (2.0035 at 295 K) and for C\textsubscript{60} (1.9998 at 295 K). We were also able to determine the hyperfine coupling constants of the \textsuperscript{1}H-nuclei in TDAE\textsuperscript{+} to \(|a_\text{H}|=3.2\) G. This value will be compared with results from NMR investigations in the next section.

We now turn to the interpretation of the ESR-spectra of [TDAE]\textsuperscript{+}C\textsubscript{60}. An estimation of the dipolar electronic interaction for [TDAE]\textsuperscript{+}C\textsubscript{60} by van Vleck’s formula [26] including spins on TDAE- and C\textsubscript{60}-sites in a lattice of 10 \(\times\) 10 \(\times\) 10 lattice constants yields a theoretical linewidth of about 100 G while the observed experimental values vary between 4 G at 30 K and 20 G at 295 K (figure 4). The g-value (2.0008 at 295 K) can be identified neither with C\textsubscript{60} (1.9998 at 295 K) nor with TDAE\textsuperscript{+} (2.0035 at 295 K) and leads, together with the aforementioned results of ESR, to the following conclusion.

The localized spins on C\textsubscript{60} and TDAE\textsuperscript{+} are strongly coupled by spin-exchange interaction as described by Anderson [27]. This mechanism explains all the experimental findings such as Lorentzian lineshape, averaged g-factor between \(g(\text{C}_{60}^*)\) and \(g(\text{TDAE}^+)\) and narrowed linewidth. The averaged g-value of [TDAE]\textsuperscript{+}C\textsubscript{60} is slightly nearer to \(g(\text{C}_{60}^*)\) than to \(g(\text{TDAE}^+)\), indicating the presence of less radicalic TDAE\textsuperscript{+} than C\textsubscript{60}-molecules, which will be discussed later. However, the influence of TDAE is crucial for the magnetic properties. To underline this last point we modified [TDAE]\textsuperscript{+}C\textsubscript{60} with regard to both C\textsubscript{60} and TDAE.

In [TDAE]C\textsubscript{70} no magnetic order is observed above 4.2 K but the ESR linewidth is still exchange-narrowed to values of 6 G at 295 K and 3.5 G at 5 K. For [P(C\textsubscript{6}H\textsubscript{5})\textsubscript{12}]C\textsubscript{70} it is known from investigations by ourselves and other groups [28] that exchange interaction between C\textsubscript{70} is inefficient and leads to ESR linewidths of more than 100 G in this compound at room temperature. Therefore strong narrowing in [TDAE]C\textsubscript{70} is mediated by the TDAE molecules which is again in accordance with the g-factor of 2.0027 lying between the g-factors of TDAE\textsuperscript{+} (2.0035) and C\textsubscript{70} (2.0023).

This is further supported by our microwave conductivity studies on mixed systems such as [TDAE]C\textsubscript{60,0.5}C\textsubscript{70,0.5} which show a strongly reduced conductivity which might be due to less molecular overlap between the C\textsubscript{70} -HOMOs (figure 6).

As the smallest possible change of TDAE we chose perdeuteration. The motivation was to disturb the system [TDAE]\textsuperscript{+}C\textsubscript{60} slightly in order to induce a change in the magnetic transition temperature. Such phenomena are reported for other radical ion salts [29]. A further aim was to perform \textsuperscript{2}H-NMR which will be the topic of the next section.

Figure 7 demonstrates that perdeuteration has no significant effect on either the onset temperature of the magnetic ordering or the maximum value of the ac-susceptibility. The slightly weaker signal of [TDAE-d\textsubscript{24}]\textsuperscript{+}C\textsubscript{60} could also be due to errors in determining the sample mass as only small samples of [TDAE-d\textsubscript{24}]\textsuperscript{+}C\textsubscript{60} were available. The temperature-dependent ESR linewidth of [TDAE-d\textsubscript{24}]\textsuperscript{+}C\textsubscript{60} (figure 7) is narrower below 120 K, which is interpreted as a reduced hyperfine interaction due to the smaller magnetic moment of deuterons in comparison to protons. The g-factor shows no difference between [TDAE]\textsuperscript{+}C\textsubscript{60} and [TDAE-d\textsubscript{24}]\textsuperscript{+}C\textsubscript{60}.

In conclusion we can state that perdeuteration of TDAE does not suppress the magnetic behaviour in [TDAE]\textsuperscript{+}C\textsubscript{60} which has to be compared with all our experiments where we...
Figure 6. Comparison of conductivity measured on [TDAE]+•C₆₀⁻•, [P(C₆H₅)₄]₂C₆₀I and [TDAE]C₆₀₋₀.₅C₇₀₋₀.₅ at 11.7 GHz. A model including hopping- and tunneling-processes is fitted to each dataset.

Figure 7. ESR-linewidth at 34 GHz of [TDAE]+•C₆₀⁻• and [TDAE-d₂₄]+•C₆₀⁻•. Inset: ac-susceptibility of [TDAE]+•C₆₀⁻• and [TDAE-d₂₄]+•C₆₀⁻• at 10 kHz.
Figure 8. $^2$H-NMR spectrum of a [TDAE-d_{24}]^{+\ast}C_{60}^{-\ast}$ powder sample at 114 K. The line can be described by two paramagnetic shifted powder spectra of single transitions (tensor$_1$) and a non-shifted Pake-spectrum.

replaced TDAE by other donors [9, 10]. All of them gave at most paramagnetic compounds above 4.2 K.

5. NMR

In NMR the situation is somehow inverse to that of ESR. While in ESR only one line could be observed in $^1$H-NMR there are two lines where we expected only one line. This was also reported by Arčon et al [30]. We wanted to clarify this point by perdeuteration of TDAE which allows structured $^2$H-NMR spectra. In addition to the motivation we gave in the preceding section, the $^2$H-spectra should give more information about the nature of this second line and a better insight of the charge transfer.

Figure 8 shows as an example the $^2$H-NMR spectrum at 114 K together with an analysis of the lineshape consisting of two powder spectra for single transitions (tensor$_1$) and one Pake-spectrum [31]. Similar to the $^1$H-NMR spectra there are two components visible: one part of the spectrum shifts in dependence of temperature (abbreviated as I) and the other (II) remains at the same position. The temperature dependent shift of I can be described by a Curie–Weiss law following from the isotropic Fermi-contact interaction of the nuclei with the unpaired electron on TDAE$^{+\ast}$. The isotropic coupling constant $a_D = 0.44$ G is in good agreement with the value found in $^1$H-NMR ($a_H = 3.0$ G) when the different magnetic moments of protons and deuterons ($a_H/a_D = 6.5$) are taken into account [32]. The accordance with the proton hyperfine coupling constant from ESR on TDAE$^{+\ast}$ in solution ($a_H=3.2$ G) shows that the isotropic hyperfine interaction is an intramolecular property of the TDAE$^{+\ast}$-molecule. Intermolecular
Figure 9. Dipolar and quadrupolar coupling frequency as determined from a temperature dependent analysis of $^2$H-spectra. Below 40 K the dipolar interaction overwhelms the quadrupolar interaction and broadens the spectra dramatically, as can be seen in the inset.

spin-polarization between $^{1}C_{60}^{-}\cdot$ and TDAE$^{+}\cdot$ is of minor importance, at least above 40 K.

The shape of spectrum I can be understood when, in addition to the quadrupolar interaction, a dipolar electron–nucleus interaction is also considered (beneath the Zeeman interaction). The latter can be due to the interaction of the nuclei either with the unpaired electron on the $^{1}C_{60}^{-}\cdot$ or on the TDAE$^{+}\cdot$. This causes a distortion of the symmetric Pake-spectrum to an overlay of two different powder spectra for the $\Delta m = -1 \leftrightarrow 0$ and $\Delta m = 0 \leftrightarrow 1$ transitions with the same position [13,33]. After fitting the temperature dependent spectra the strength of the dipolar interaction $\nu_D$ can be calculated. In figure 9 $\nu_D$ is shown between 40 and 300 K and compared with the quadrupolar interaction ($\nu_Q = \frac{3}{4} \delta_Q$), which is typical for rotating CH$_3$-groups.

It is clearly seen that at about 40 K the dipolar interaction reaches the size of the quadrupolar coupling explaining the experimental result of structurless broadened lines below 40 K (inset figure 9).

In contrast to I, component II can be fitted by a Pake-spectrum with a quadrupolar coupling constant $\delta_Q$ of about 43 kHz, which also indicates the presence of rotating CH$_3$-groups. From the temperature-independent position of the Pake-spectrum we conclude that these molecules are not radicals but probably neutral or doubly charged TDAE-molecules. They cannot be ascribed to decomposed parts of the sample, because the existence of such amounts of degraded material is not compatible with the perfect Lorentzian lineshape in ESR and the high stability of our samples.
6. Conclusion

Our results gained with the application of different methods on [TDAE]$^+\cdot\text{C}_{60}^-$ and related compounds can be summarized as follows. Conductivity investigations between 4.2 and 300 K, especially in the magnetic ordered phase, on the air sensitive [TDAE]$^+\cdot\text{C}_{60}^-$ exclude definitely all models based on itinerant moments (bandferromagnetism). The remaining microscopic models for localized moments must take into account the TDAE$^+\cdot$-radical to the same extent as the C$_{60}^-$-radical. This statement is based on both the combination of ESR and conductivity studies on [TDAE]$^+\cdot\text{C}_{60}^-$, model systems and specifically altered compounds. All ESR parameters such as g-value, lineshape and linewidth can be understood within the theory of spin-exchange as given by Anderson [27]. Intermolecular dynamic spin-polarization [34] between C$_{60}^-$ and TDAE$^+\cdot$ is of minor importance above 40 K as can be seen by comparing proton hyperfine coupling constants gained with ESR on TDAE$^+\cdot$ in solution and NMR on [TDAE]$^+\cdot\text{C}_{60}^-$.

Theoretical models for the macroscopic ordering thus must consider all possible exchange paths between C$_{60}^-$ and TDAE$^+\cdot$ and not omit one of the two components. Compatible with all our experimental results, especially the measured spin-concentration of less than two radicals per formula unit of [TDAE]$^+\cdot\text{C}_{60}^-$ (88%) and the existence of a second NMR-line, is the formation of a second charge transfer as discussed by Sato et al [35] leading to neutral, singly and doubly charged TDAE-molecules. TDAE$^0$ and TDAE$^{2+}$ should have no unpaired spin and should therefore give the unshifted NMR-line, assuming that TDAE$^{2+}$ has no triplet ground state. This interpretation is further supported by the g-value of [TDAE]$^+\cdot\text{C}_{60}^-$ which is nearer to the g-value of C$_{60}^-$ indicating a higher concentration of C$_{60}^-$ than of TDAE$^+\cdot$. Unfortunately Sato et al could not include the exchange integral between C$_{60}^-$ and TDAE-molecules quantitatively. However, this path is important as shown by our ESR and microwave-conductivity investigations and the proposed model should be extended in this way.

Perdeuteration of TDAE did not suppress the magnetic order in [TDAE]$^+\cdot\text{C}_{60}^-$, showing that the system is at least stable against minimal distortions of the lattice. This is not obvious, as can be seen from other radical ion salts [29]. Perdeuteration opens the door to neutron diffraction, the final experiment to probe the magnetic ordering directly. Therefore, the synthesis of TDAE-d$_{24}$ will be optimized in order to get higher amounts of [TDAE-d$_{24}$]$^+\cdot\text{C}_{60}^-$. 

Acknowledgments

We wish to thank J Gmeiner and I Bauer for help with the sample preparation, J Bao for creating the pictures of TDAE, Dr B Gotschy for initializing this work, Professor Dr E Rößler for critical and fruitful discussions of the NMR results, G Bendele (New York) for x-ray measurements and M Kelemen (Karlsruhe) for SQUID-magnetometry. Financial support by Sonderforschungsbereich SFB 279 and Fonds der Chemischen Industrie is acknowledged.

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