# Beltlike $C_{60}^-$ Electron Spin Density Distribution in the Organic Ferromagnet TDAE-$C_{60}$

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The observed huge increase in the width of the $^{13}$C NMR spectra of TDAE-$C_{60}$ in the middle of the ferromagnetic phase at 10 K is due to a Jahn-Teller distortion of the $C_{60}^-$ ions which becomes visible in view of the resulting changes in the Fermi contact electron-$^{13}$C NMR shifts. The shape of the $^{13}$C spectra allows for a direct determination of the beltlike redistribution of the unpaired electron spin density on the $C_{60}^-$ ions, which is responsible for the relatively high ferromagnetic transition temperature in this purely organic system.

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Jahn-Teller effects [1] have been proposed to play a key role in the extraordinary electronic properties of doped fullerenes such as high $T_C$ superconductivity [2] and ferromagnetism [3]. The fact that TDAE$^+$-$C_{60}^-$ (where TDAE stands for tetrakis dimethylamino ethylene) has the highest transition temperature of all purely organic nonpolymeric ferromagnets has been specifically ascribed [4] to a possible Jahn-Teller distortion and a resulting redistribution of the unpaired electronic spin density into a beltlike form. No experimental observation of this effect has been, however, reported so far. Ionic fullerenes $C_{60}^-$ and $C_{60}^+$ are expected to undergo a Jahn-Teller distortion resulting in the deformation of the spherical $C_{60}^{\pm}$ into a rugby-ball–like form. The distortion should be accompanied by a resulting redistribution of the unpaired electron spin density [4]. For symmetry reasons the distortions may occur in a number of different directions and the system may move through the different distorted configurations, thus effectively restoring the original symmetry before the distortion [5]. The expected Jahn-Teller distortions are rather small (~0.01 Å) since the perturbation caused by the added or subtracted electron in this huge molecule is tiny. Direct structural observations of these distortions and the resulting redistribution of the electron spin densities are therefore rather difficult [6].

Here we report on the first direct observation of a Jahn-Teller induced beltlike redistribution of the unpaired electron spin density on the $C_{60}^-$ ions in any fullerene exhibiting superconducting [7] or ferromagnetic [3,8,9] transitions. The observation of this effect in TDAE$^+$-$C_{60}^-$ is made possible by the changes in the Fermi contact electron-nuclear coupling shifts of the $^{13}$C NMR lines which accompany the Jahn-Teller distortion and act as a magnifying glass, making the minute Jahn-Teller distortions and the resulting redistribution of the unpaired electron density visible in the $^{13}$C NMR spectra. The Fermi contact coupling is nonzero in view of the $s$-wave admixture into the $p$-type unpaired electron spin wave function. The obtained results allow for a quantitative determination of the beltlike unpaired electron spin density distribution around the elongated $C_{60}^-$ ions, which is responsible for the relatively high ferromagnetic transition temperature in this purely organic ferromagnet.

The positions of the $^{13}$C NMR lines in $C_{60}^-$ ions are mainly determined by the Fermi contact electron-$^{13}$C nuclear coupling

$$\mathcal{H}_{hf} = \sum_{i,j} \vec{I}_j \cdot \mathbf{A}_{i,j} \cdot \vec{S}_i \,. \tag{1}$$

Here $\vec{I}_j$ is the $^{13}$C nuclear spin, $\vec{S}_i$ is the unpaired electronic spin, and $\mathbf{A}_{i,j}$ is the Fermi contact hyperfine coupling tensor. This coupling is identical for all $^{13}$C nuclei as long as the $C_{60}^-$ ion is spherical but becomes different for different nuclei after the Jahn-Teller distortion. The width of the $^{13}$C NMR lines is, on the other hand, mainly determined by the electron-nuclear dipolar interaction

$$\mathcal{H}_{dd} = \sum_{j,k} \frac{\hbar^2 \gamma_e^2 \gamma_C^2}{r_{i,j}^3} \left( \vec{I}_j \cdot \vec{S}_i - 3\, \frac{(\vec{I}_j \cdot \vec{r}_{i,j})(\vec{S}_i \cdot \vec{r}_{i,j})}{r_{i,j}^2} \right), \tag{2}$$

where $\gamma_e$ and $\gamma_C$ are the electronic and $^{13}$C nuclear gyromagnetic ratios, respectively, and $\vec{r}_{i,j}$ is the vector connecting the $^{13}$C site and the unpaired electronic position. In view of the small magnitude of the Jahn-Teller distortions the electron-$^{13}$C dipolar interaction is not significantly affected by the Jahn-Teller effect. The same is true for the contribution to the $^{13}$C NMR linewidth of the anisotropic $^{13}$C chemical shift tensor $\mathcal{H}_{CS} = \sum_j \vec{I}_j \cdot \boldsymbol{\sigma}_j \cdot \vec{B}_0$ which is minor when compared to the electron-nuclear contact coupling.

To a rather good approximation we can assume that all three above-mentioned electron-$^{13}$C coupling tensors are axially symmetric and that the sum of their contributions determine the components of the shift tensor $\mathbf{K}$. In this case the shape of the $^{13}$C NMR spectrum depends on the values of the $^{13}$C shift tensor $K_{\parallel}$ and $K_{\perp}$. $K_{\parallel}$ is the component of the $^{13}$C shift tensor normal, while the component $K_{\perp}$ is tangential to the $C_{60}$ surface. When the Jahn-Teller distortion of the $C_{60}^-$ ions is significant the dominant contribution to the $^{13}$C shift tensor comes from the Fermi contact interaction, resulting in an inhomogeneously broadened $^{13}$C NMR spectrum. The change of the $^{13}$C shift tensor components with the Jahn-Teller distortion $\delta K_{\parallel}$ and $\delta K_{\perp}$ is directly related to the electron spin density redistribution on the $C_{60}^{-}$ sphere and can be thus positive or negative. Because of the dynamic Jahn-Teller distortions the components of the $^{13}$C shift tensor and the NMR frequencies $\omega_j(t)$ will fluctuate in time

$$K_{\parallel} = K_{\parallel}^{0} + \delta K_{\parallel}(\theta_j, \varphi_j, t), \quad K_{\perp} = K_{\perp}^{0} + \delta K_{\perp}(\theta_j, \varphi_j, t). \tag{3}$$

The $^{13}$C NMR line shape is then obtained by the Fourier transform of

$$G(t) = \langle G_j(t) \rangle = \left\langle \exp\left[ i \int_0^t \omega_j(t')\, dt' \right] \right\rangle. \tag{4}$$

One can immediately notice that, when the fluctuations of the Jahn-Teller distortion are fast on the $^{13}$C NMR time scale, the components of the $^{13}$C shift tensor are simply given by $K_{\parallel} = K_{\parallel}^{0}$ and $K_{\perp} = K_{\perp}^{0}$. The expected line shape is in this case powderlike. On the other hand, when the Jahn-Teller fluctuations become slow on the $^{13}$C NMR time scale the components of the $^{13}$C shift tensor become site dependent and proportional to the charge density at a given $^{13}$C site. The $^{13}$C NMR lineshape in this case directly reflects the charge density distribution on the $C_{60}^{-}$ sphere.

We have observed a huge increase in the $^{13}$C NMR linewidth of the charge transfer compound TDAE$^{+}$-$C_{60}^{-}$ at 10 K in the middle of the ferromagnetic phase (Fig. 1). The full width of the inhomogeneously broadened $^{13}$C NMR spectrum increases between 10 and 5 K from ~110 to ~500 kHz. This sharp increase in the width below 10 K is striking since the $C_{60}$ rotational motions are frozen out at much higher temperatures [10]. The width of the $^{13}$C spectrum in the ferromagnetic phase between 25 and 10 K varies only weakly with temperature and the $^{13}$C linewidth even slightly decreases with decreasing temperature in the ferromagnetic phase down to 10 K. The mean resonance frequency, on the other hand, slightly increases with decreasing temperature in the ferromagnetic phase. Even more striking than the change in the width at 10 K is the accompanying change in the $^{13}$C NMR line shape (inset of Fig. 1). Whereas the line shape in the ferromagnetic phase approaches the typical asymmetric form expected for a static powder pattern, it suddenly becomes again nearly symmetric below 10 K.

The observed $^{13}$C linewidth transition and change in the line shape of TDAE$^{+}$-$C_{60}^{-}$ below 10 K can be both accounted for by a charge transfer induced dynamic Jahn-Teller distortion of the $C_{60}^{-}$ ions which gradually becomes static on the NMR time scale below 10 K. As discussed above the distortions produce a nonequivalency of the $^{13}$C sites on the $C_{60}^{-}$ ion and a redistribution [4] of the previously homogeneous unpaired electron spin density. Whereas the Fermi contact-coupling constants for all $^{13}$C nuclei were identical on the undistorted $C_{60}^{-}$ ion, this is not the case for the deformed ion. The Fermi contact couplings and the $^{13}$C NMR resonance frequencies become a function of the position of the $^{13}$C nuclei on the deformed $C_{60}^{-}$ sphere, resulting in a sizable inhomogeneous broadening of the $^{13}$C spectra. This broadening mechanism is absent as long as the $C_{60}^{-}$ ion is spherical on the NMR time scale ($10^{-4}$–$10^{-6}$ s) and the unpaired electron spin distribution on the $C_{60}^{-}$ ion is homogeneous and constant. It is also absent in the case of a dynamic Jahn-Teller distortion as long as we are in the fast motion limit. In this case the distortion induced shifts are motionally averaged out so that all $^{13}$C nuclei experience the same effective Fermi contact coupling. This results only in a shift of the center of the $^{13}$C NMR spectrum but not in line broadening.

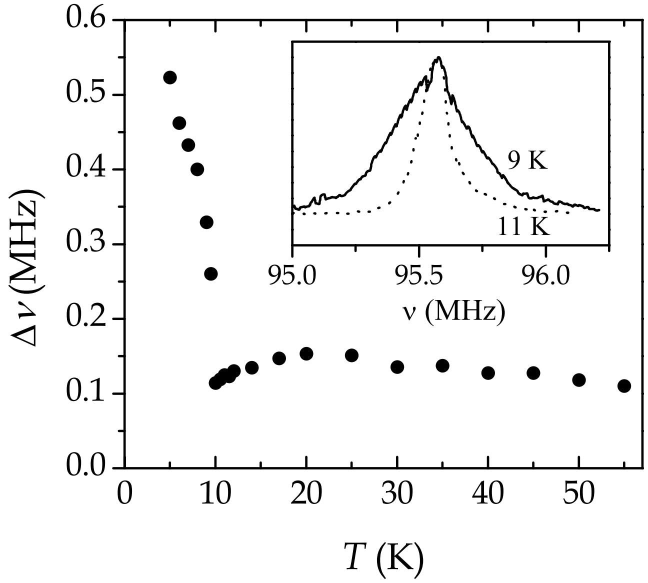

FIG. 1. Temperature dependence of the $C_{60}^{-}$ $^{13}$C NMR linewidth of TDAE-$C_{60}$ between 55 and 4 K. The ferromagnetic transition takes place at 16 K in the absence of the magnetic field and at about 25 K in the applied magnetic field of 9 T. Inset: a comparison of the $^{13}$C NMR spectra at $T = 11$ K and $T = 9$ K showing a dramatic broadening and the accompanying change in the $^{13}$C NMR line shape at $T = 10$ K.

The temperature dependence of the $^{13}$C NMR linewidth at a half height of TDAE-$C_{60}$ at 95.6 MHz is shown in Fig. 1 for the temperature interval between 55 and 5 K. Because of the huge linewidth, the spectra had to be measured with the frequency sweep technique. Above 10 K the width can be accounted for by the $^{13}$C chemical shift anisotropy and electron- $^{13}$C dipolar interactions. The comparison between the experimental and calculated $^{13}$C NMR line shapes of TDAE-$C_{60}$ at 250, 55, and 5 K is shown in Fig. 2. The lineshape at 250 K, which is Lorentzian and very narrow (5 kHz), is evidently motionally averaged due to fast uniaxial rotations and flipping of the rotational axes of the $C_{60}^{-}$ ions. At 55 K the flipping has effectively stopped and the uniaxial rotations become slow so that the spectral shape approaches the asymmetric powder pattern form expected in the static

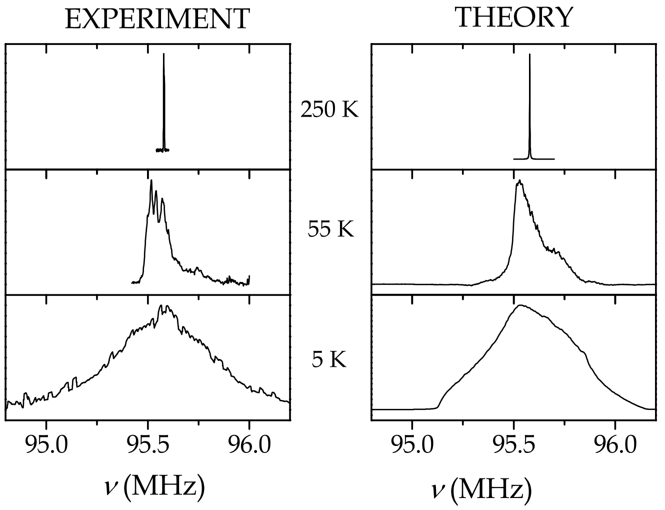

FIG. 2. Comparison between the experimental and calculated $^{13}$C NMR spectra of TDAE-$C_{60}$ at 250, 55, and 5 K.

case. The comparison between the experimental and calculated line shape allows for the determination of the electron-nuclear coupling tensor which is—similar to the $^{13}$C chemical shift tensor—approximately uniaxial and characterized by $K_{\parallel}^{0} = -2200$ ppm and $K_{\perp}^{0} = 900$ ppm. The rotational correlation time is here about 2 $\mu$s so that we are indeed in the slow motion limit. The occurrence of the linewidth transition at 10 K and the nearly symmetric but extremely broad inhomogeneous line shape at 5 K requires the presence of another interaction, which does not affect the line shapes at high temperatures in view of its fast fluctuations. A transition from the fast to the slow motion regime takes place at about 10 K. We believe that this interaction is a dynamic Jahn-Teller induced distortion of the $C_{60}^{-}$ ion which makes the electron spin distribution inhomogeneous thus resulting in different Fermi contact-coupling shifts for different $^{13}$C nuclei on the $C_{60}^{-}$ ion.

The observed $^{13}$C NMR line shape at 5 K, which is, as shown by spin-spin relaxation time ($T_2$) measurements, an inhomogeneous frequency distribution, can be accounted for by a beltlike distribution of the unpaired electron spin density $p(\theta)$ (Fig. 3). This distribution is more concentrated on the equator of the distorted elongated $C_{60}^{-}$ ion than on the poles. The electron distribution shown in Fig. 3 can be fitted to the Gaussian form $p(\theta) = \exp(-\frac{(\theta - \frac{\pi}{2})^2}{\Delta^2})$, where $\Delta = 0.85$ rad. Here $\theta$ is the angle between the elongated $C_{60}^{-}$ axis and the given $^{13}$C position. It should be noted that there is nothing unique about the Gaussian form shown in Fig. 3 and that the data can be also fitted to other functional expressions. As long as the Jahn-Teller distortions are dynamic and the axes of elongation are fluctuating between three mutually perpendicular directions (Fig. 4), the components of the electron-nuclear coupling tensor at the various $^{13}$C nuclear sites fluctuate between $-Bp(\theta) < \delta K < Bp(\theta)$, where $B = 3800$ ppm as a result of the changes in the unpaired electron spin density distribution. The Jahn-Teller distortions thus do not affect the line shape at higher temperatures. They become visible only at low temperatures when the inverse fluctuation frequency becomes slower than the NMR time scale.

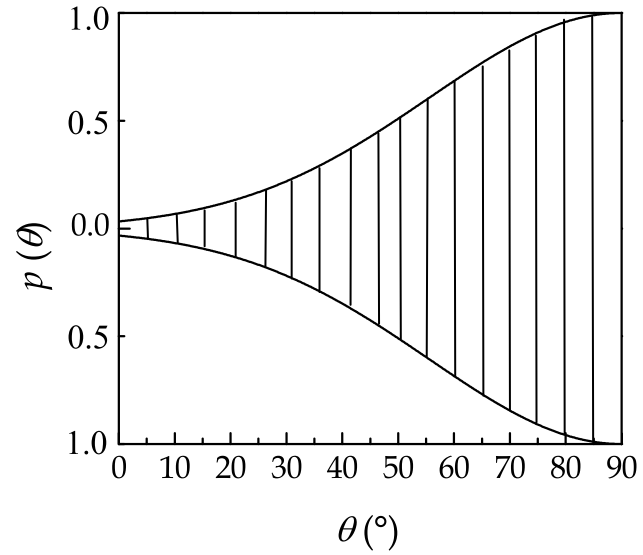

FIG. 3. Beltlike unpaired electron spin density distribution on the distorted $C_{60}^{-}$ ions in ferromagnetic TDAE-$C_{60}$ obtained from the $^{13}$C NMR spectra at $T = 5$ K. The electron charge density is largest at the equator and smallest at the poles.

It is interesting to note that recent theoretical calculations [4,11–15] have emphasized the necessity of a Jahn-Teller distortion and an accompanying redistribution of the electron cloud in TDAE-$C_{60}$ in order to account for the relatively high ferromagnetic transition temperature $T_C = 16$ K. Without the $C_{60}^{-}$ distortion the coupling between the $C_{60}^{-}$ ions in TDAE-$C_{60}$ would result in a ferromagnetic interaction yielding a $T_C$ of only 0.03 K instead of the observed 16 K.

On the basis of the above NMR results we cannot distinguish between cooperative or random orbital ordering and different spatial arrangements of the elongated axes of the distorted $C_{60}^{-}$ ions. It should be, however, stressed that, if the observed Jahn-Teller distortions are cooperative, they could lead to the alternating arrangements and mutually perpendicular orientations of the long axes of neighboring distorted $C_{60}^{-}$ ions in the unit cell favoring the ferromagnetic state [4,12,15].

The explanation of the observed $^{13}$C line width transition as reflecting a dynamic Jahn-Teller distortion becoming static on the NMR time scale also agrees with the fact that no significant shift of the center of gravity of the NMR spectrum is seen below 10 K. This results from the fact that after the Jahn-Teller distortion of the $C_{60}^{-}$ ion from the spherical to a rugby-ball–type shape the decrease in the Fermi contact constant in regions of smaller electronic

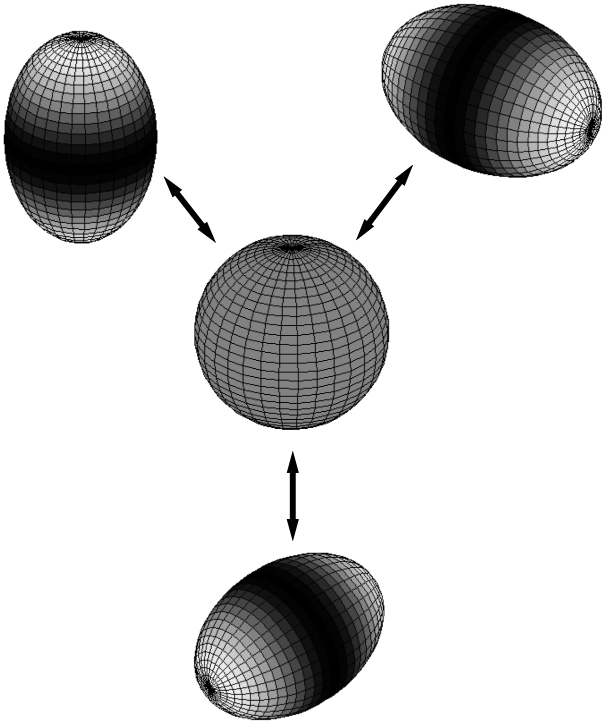

FIG. 4. Jahn-Teller distortions of the spherical $C_{60}^{-}$ ion along three mutually perpendicular directions.

density is compensated by the increase in the coupling constant in the regions where the electron density is larger so that the position of the center of gravity of the spectrum is unchanged. The fact that the $^{13}$C spin-lattice relaxation time starts to increase with decreasing temperature below 10 K [10] as well reflects the gradual freeze-out of the dynamic Jahn-Teller effect and strongly supports the above explanation.

In conclusion, we have observed the freeze-out of the dynamic Jahn-Teller distortion of the $C_{60}^{-}$ ion at 10 K via $^{13}$C NMR in the middle of the ferromagnetic phase of TDAE-$C_{60}$. The shape of the $^{13}$C spectrum allowed for a quantitative determination of the beltlike redistribution of the unpaired electron spin density on the distorted $C_{60}^{-}$ ion. It is this beltlike electron distribution which was predicted to be responsible for the fact that TDAE-$C_{60}$ has the highest transition temperature of all purely organic nonpolymeric ferromagnets. It should be stressed that similar Jahn-Teller distortions and redistributions of the unpaired electron spin density are expected to occur not only in other charge transfer fullerenes but in general for systems possessing in addition to spin also orbital degrees of freedom [16–18].

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