

# $^{13}\text{C}$ NMR of the organic ferromagnet TDAE- $\text{C}_{60}$

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(Received 20 June 1995)

The temperature dependence of the  $^{13}\text{C}$  NMR spectra and  $^{13}\text{C}$  spin-lattice relaxation time  $T_1$  has been studied in powdered TDAE- $\text{C}_{60}$  (TDAE=tetrakis-dimethylaminoethylene). A motionally narrowed  $^{13}\text{C}$  NMR line has been observed at 188 ppm relative to tetramethylsilane (TMS) at room temperature which can be assigned to the  $\text{C}_{60}^-$  ion. A large line broadening has been observed on cooling below 150 K. The second moment of the line increases again below 50 K and reaches  $250 \text{ kHz}^2$ . This is rather close to the value of the second moment calculated for the static dipolar interaction between the  $^{13}\text{C}$  nuclei and the unpaired electron in the  $2p_z$  state smeared out over all carbon sites in the  $\text{C}_{60}^-$  ion. The freeze-out of the "isotropic" rotation between 150 and 100 K is connected with a high field shift of the  $^{13}\text{C}$  line by 160 ppm which changes into a low field shift of 87 ppm below 50 K. The change in the sign of the shift may indicate that antiferromagnetic correlations change into ferromagneticlike correlations at low temperatures.

## I. INTRODUCTION

The discovery<sup>1-3</sup> of the possibly ferromagnetic transition at  $T_c=16 \text{ K}$  in the  $\text{C}_{60}$  based charge transfer compound  $\text{TDAE}^+-\text{C}_{60}^-$  (TDAE=tetrakis-dimethylamino-ethylene) has recently stimulated a lot of research but the detailed microscopic nature of the transition is still not well understood. ESR studies have shown that the unpaired electron spin should be mainly localized at the  $\text{C}_{60}^-$  ion<sup>4-6</sup> as the  $g$  value is close to the one observed for the electrochemically prepared  $\text{C}_{60}^-$  ion. The fact that the magnetic transition is absent<sup>7</sup> in  $\text{TDAE}^+-\text{C}_{70}^-$  demonstrates the role of the spherical shape and high symmetry of the  $\text{C}_{60}^-$  ion for the existence of the long range ordered magnetic state below  $T_c$ .

It has been recently shown<sup>8</sup> that the magnetic susceptibility  $\chi$  and the ferromagnetic transition<sup>1,2</sup> temperature  $T_c \approx 16 \text{ K}$  of TDAE- $\text{C}_{60}$  depend on whether the sample is quenched or slowly cooled from room temperature down to 30 K, i.e., to a temperature well above  $T_c$ . In the quenched sample  $T_c$  is depressed and both the imaginary as well as the real part of the susceptibility are for  $T < T_c$  significantly smaller than in the slowly cooled sample. The above results were obtained<sup>8</sup> for the same cooling rate 0.3 K/min below 30 K.

In order to check whether the above effects are due to an orientational ordering transition of the  $\text{C}_{60}^-$  ions we decided to perform a  $^{13}\text{C}$  NMR study of powdered TDAE- $\text{C}_{60}$  between room temperature and 4 K. We also hoped to throw some additional light on the molecular dynamics of this system.

An additional motivation for the study of the  $^{13}\text{C}$  NMR spectra of TDAE- $\text{C}_{60}$  comes from the fact that a Dzyaloshinsky-Moriya mechanism,<sup>9</sup> based on superexchange, was recently proposed<sup>10</sup> as the microscopic origin of the weak ferromagnetism in TDAE- $\text{C}_{60}$ . Here the correlations between unpaired spins on neighboring  $\text{C}_{60}^-$  ions are of antiferromagnetic nature and weak ferromagnetism in a direction perpendicular to the  $c$  axis (i.e., the axis of the closest approach of the  $\text{C}_{60}^-$  ions) is the result of spin canting. In this connection it is worthwhile mentioning that some of the freshly grown crystals do not show a ferromagnetic transi-

tion at all but become antiferromagnetic at low temperatures. After some time or after some thermal cycling they do however show the ferromagnetic transition at 16 K.

## II. EXPERIMENT

The Fourier transform  $^{13}\text{C}$  NMR spectra of powdered TDAE- $\text{C}_{60}$  were measured in a field of 6.34 T at a Larmor frequency  $\omega_L/2\pi=67.925 \text{ MHz}$ . The cooling rate was 3 K/min. The  $^{13}\text{C}$  spin-lattice relaxation time has been measured by the  $180^\circ-\tau-90^\circ$  sequence. To check on the purity of the sample and the existence of the magnetic transition we as well performed X-band ESR measurements. The ESR intensity times temperature and the temperature dependence of the ESR linewidth are shown in Fig. 1. The existence of the magnetic transition is obvious. The shift of  $T_c$  from 16 K in zero field to 25 K in the  $^{13}\text{C}$  NMR experiment is due to the presence of a magnetic field of 6.34 T.

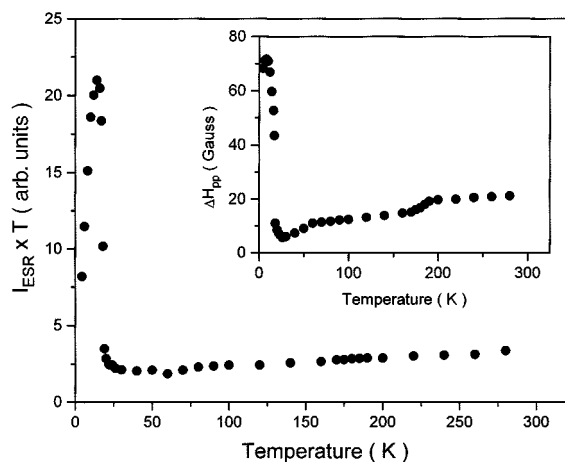


FIG. 1. The X-band ESR intensity times temperature in powdered TDAE- $\text{C}_{60}$ . Inset: Peak to peak linewidth of the X-band ESR line in the same sample.

### III. THEORY

#### A. Electron-nuclear coupling in paramagnetic systems

The electron-nuclear coupling in paramagnetic systems can be described by a coupling of the nuclear spin  $\mathbf{I}$  to a fictitious local magnetic field  $\mathbf{h}(t)$

$$H = \gamma \hbar \mathbf{I} \cdot \mathbf{h}(t), \quad (1)$$

where

$$\mathbf{h}(t) = -\gamma_e \hbar \left( \frac{\mathbf{S}}{R^3} - \frac{3(\mathbf{R} \cdot \mathbf{S})\mathbf{R}}{R^5} \right) - \frac{A}{\gamma} \mathbf{S} = \mathbf{h}_D(t) + \mathbf{h}_C(t) \quad (2)$$

takes into account electron-nuclear dipole-dipole,  $\mathbf{h}_D(t)$ , as well as contact,  $\mathbf{h}_C(t)$ , hyperfine ( $A \neq 0$ ) interactions. Here  $\mathbf{S}$  is the electronic spin and  $\mathbf{R}$  the electron-nuclear radius vector. The paramagnetic shift  $\delta\nu$  of the center of the line (i.e., the first moment  $M_1$ ) is determined by the time averaged values of the local field  $\langle \mathbf{h}(t) \rangle$ .

Above  $T_c$   $\delta\nu$  is proportional to the electronic susceptibility  $\chi(0)$  and the external magnetic field  $H_0$

$$\delta\nu \propto \langle \mathbf{h}(t) \rangle_{H \neq 0} \propto \langle \mathbf{S} \rangle_{H \neq 0} \propto \chi_{\text{static}}(0) H_0; \quad T > T_c, \quad (3a)$$

whereas below  $T_c$   $\delta\nu$  is proportional to the spontaneous magnetization  $M$ :

$$\delta\nu \propto \langle \mathbf{h}(t) \rangle_{H \neq 0} \propto M; \quad T < T_c. \quad (3b)$$

In a powdered sample  $\delta\nu$  has to be averaged also over all possible angles between the internuclear vector  $\mathbf{R}$  and the axis of quantization of  $\mathbf{S}$ , i.e., the direction of the external field  $\mathbf{H}_0$ . Thus we get

$$\delta\nu \propto \overline{\langle \mathbf{h}(t) \rangle} = \overline{\langle \mathbf{h}_C(t) \rangle} \quad (4)$$

as

$$\overline{\langle \mathbf{h}_D(t) \rangle} = 0.$$

#### B. Second moment of the $^{13}\text{C}$ NMR line

Let us now evaluate the second moment of the  $^{13}\text{C}$  NMR spectra in detail. The Hamiltonian of our problem is

$$H = H_Z + H_D(C-C) + H_D(C-H) + H_D(C-e) + H_{\text{hf}} + H_{\text{CS}}, \quad (5)$$

where  $H_Z = -\gamma B_0 \sum_k I_{Z,k}$  is the Zeeman interaction,  $H_D(C-C)$  is the dipolar interaction between  $^{13}\text{C}$  nuclei,  $H_D(C-H)$  is the dipolar interaction between the  $^{13}\text{C}$  nuclei and the methyl protons on the TDAE molecule,  $H_D(C-e)$  is the dipolar interaction between the  $^{13}\text{C}$  nuclei on the  $\text{C}_{60}$  molecule and the unpaired transferred electron,  $H_{\text{hf}} = \mathbf{S} \cdot \sum_k A_k \mathbf{I}_k$  is the Fermi contact interaction between the carbon nuclei and the unpaired electron, and finally  $H_{\text{CS}} = -\gamma \mathbf{B}_0 \cdot \mathbf{g} \cdot \mathbf{I}$  is the  $^{13}\text{C}$  chemical shift interaction.

For the calculation of the second moment of the  $^{13}\text{C}$  NMR line the only important terms are  $H_D(C-e)$  and  $H_{\text{CS}}$  since the natural abundance of  $^{13}\text{C}$  is only 1.108% and therefore  $H_D(C-C)$  as well as  $H_D(C-H)$  are negligible. In addition the Fermi contact interaction can be dropped if we assume

that the unpaired electron is in a  $\pi$ -type molecular orbital of the  $\text{C}_{60}^-$  ion, resulting in a hydrogenic  $2p_z$  orbital around a given  $^{13}\text{C}$  nucleus.

We would like to compare the experimentally observed second moment of the  $^{13}\text{C}$  NMR line

$$M_2 = \frac{\int_{-\infty}^{\infty} (\omega - M_1)^2 f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega} \quad (6)$$

with the one calculated from the known Hamiltonian of our problem

$$M_2 = -\frac{1}{2\hbar} \text{Tr}\{[H, I_x]^2\}. \quad (7)$$

Here  $f(\omega)$  is the observed  $^{13}\text{C}$  NMR line shape and  $M_1$  is the first moment defined as

$$M_1 = \frac{\int_{-\infty}^{\infty} \omega f(\omega) d\omega}{\int_{-\infty}^{\infty} f(\omega) d\omega}. \quad (8)$$

The second moment of our problem can be reduced to

$$M_2 = -\frac{1}{2\hbar} (\text{Tr}\{[H_D(C-e), I_x]^2\} + \text{Tr}\{[H_{\text{CS}}, I_x]^2\}), \quad (9)$$

since all the cross terms like  $\text{Tr}\{[H_D(C-e), I_x][H_{\text{CS}}, I_x]\}$  are proportional to  $\text{Tr}\{I_{Z,k}\} = 0$ .

The second moment of the chemical shift anisotropy term is given by

$$\langle \omega^2 \rangle_{\sigma} = \frac{1}{15} (\omega_0 \delta)^2 (3 + \eta^2), \quad (10)$$

where  $\delta = \sigma_{ZZ} - \frac{1}{3} \text{Tr} \underline{\sigma}$  and  $\eta = \sigma_{YY} - \sigma_{XX} / \delta$ . Using for sake of simplicity the values for the chemical shift anisotropy of pure  $\text{C}_{60}$ ,<sup>11</sup>  $\sigma_{XX} = 199$  ppm,  $\sigma_{YY} = 188$  ppm,  $\sigma_{ZZ} = 40$  ppm, one find that

$$\left\langle \left( \frac{\omega}{2\pi} \right)^2 \right\rangle_{\sigma} = 10.11 \text{ kHz}^2. \quad (11)$$

We can estimate the magnitude of the second moment of the dipolar interaction between the  $^{13}\text{C}$  nuclei and the unpaired electron by assuming that each  $^{13}\text{C}$  nucleus is coupled to 1/60 of an electron in a hydrogenic  $2p_z$  orbital centered at that nucleus. The second moment is given by the expression

$$\langle \omega^2 \rangle_{H_D(C-e)} = 0.011 \times \frac{1}{3} \left( \frac{\mu_0}{4\pi} \right)^2 \gamma_C^2 \gamma_e^2 \hbar^2 S \times (S+1) \frac{1}{N} \sum_{i=1}^{60} \frac{(1 - 3 \cos^2 \theta_{i,e})^2}{r_{i,e}^6}, \quad (12)$$

where  $\theta_{i,e}$  is the angle between the axis of quantization (e.g., the axis of the external magnetic field) and the radius vector between the  $i$ th carbon nuclei on the  $\text{C}_{60}$  sphere and the unpaired electron,  $r_{i,e}$  is the distance between  $i$ th carbon nuclei and the unpaired electron,  $1.1 \times 10^{-2}$  is the natural abundance of the  $^{13}\text{C}$ , and  $N = 60$ .

The fact that the electronic probability density is given by the absolute value of the square of the  $2p_z$  orbital wave function averages the  $^{13}\text{C}$ -electron dipolar interaction. Fur-

ther averaging comes from the fact that we are dealing with a powder sample. Therefore we replace the dipolar interaction term in the above expression with

$$\frac{(1-3\cos^2\theta_{i,e})^2}{r_{i,e}^6} \Rightarrow \left\langle \left\langle \frac{(1-3\cos^2\theta_{i,e})}{r_{i,e}^3} \right\rangle^2 \right\rangle, \quad (13)$$

where the bracket means averaging over the electron density  $P(r_{i,e}, \theta_{i,e}, \varphi_{i,e})$  of the  $2p_z$  orbital centered around a given  $^{13}\text{C}$  nuclei

$$\begin{aligned} \left\langle \frac{(1-3\cos^2\theta_{i,e})}{r_{i,e}^3} \right\rangle &= \int_0^\infty r_{i,e}^2 dr_{i,e} \int_0^\pi \sin\theta_{i,e} d\theta_{i,e} \int_0^{2\pi} d\varphi \\ &\times \frac{(1-3\cos^2\theta_{i,e})}{r_{i,e}^3} P(r_{i,e}, \theta_{i,e}, \varphi_{i,e}). \end{aligned} \quad (14)$$

Here  $P(r_{i,e}, \theta_{i,e}, \varphi_{i,e})$  is given by

$$\begin{aligned} P(r_{i,e}, \theta_{i,e}, \varphi_{i,e}) &= |\Psi_{2p_z}|^2 = \left| \sqrt{\frac{1}{60}} \sqrt{\left(\frac{Z}{a_B}\right)^3} \frac{1}{4\sqrt{2\pi}} \left(\frac{r_{i,e}}{a_B}\right) Z \right. \\ &\left. \times \exp\left(-\frac{r_{i,e}}{a_B} \frac{Z}{2}\right) \cos\theta_{i,e} \right|^2, \end{aligned} \quad (15)$$

where  $Z$  is the effective  $^{13}\text{C}$  nuclear charge<sup>12</sup> and  $a_B$  is the Bohr radius. The bar indicates the powder average.

The calculated contribution of the dipolar interaction between the  $^{13}\text{C}$  nuclei of the  $\text{C}_{60}^-$  ion and the unpaired electron in  $2p_z$  state uniformly distributed over the  $\text{C}_{60}^-$  ion is

$$\left\langle \left\langle \frac{\omega}{2\pi} \right\rangle^2 \right\rangle_{H_D(\text{C}^-e)} = 223.24 \text{ kHz}^2. \quad (16)$$

Thus the total second moment is

$$\left\langle \left\langle \frac{\omega}{2\pi} \right\rangle^2 \right\rangle = \left\langle \left\langle \frac{\omega}{2\pi} \right\rangle^2 \right\rangle_\sigma + \left\langle \left\langle \frac{\omega}{2\pi} \right\rangle^2 \right\rangle_{H_D(\text{C}^-e)} = 233.35 \text{ kHz}^2 \quad (17)$$

which is—as we shall see—in excellent agreement with the experiment where the second moment is  $250 \pm 20 \text{ kHz}^2$ .

#### IV. RESULTS AND DISCUSSION

The  $^{13}\text{C}$  NMR powder spectra at 290, 100, and 7 K are shown in Fig. 2. The temperature dependences of the second and first moments of the  $^{13}\text{C}$  spectra are shown in Fig. 3. In view of the low natural abundance of the  $^{13}\text{C}$  nuclei and the fact that there are nearly ten times less TDAE than  $\text{C}_{60}$  carbons, the observed  $^{13}\text{C}$  spectra can be safely assigned to the  $\text{C}_{60}^-$  ions. This is also confirmed by the observed  $^{13}\text{C}$  NMR lineshift with respect to tetramethylsilane (TMS) which amounts at room temperature 188 ppm. This agrees rather well with the value of 185 ppm observed for the electrochemically prepared  $\text{C}_{60}^-$  in solution. The shift for pure  $\text{C}_{60}$  at room temperature, on the other hand, is 143 ppm.

The  $^{13}\text{C}$  spectra at room temperature are clearly motionally averaged by nearly isotropic rotation of the  $\text{C}_{60}^-$  ion. The motion probably consists of uniaxial rotation combined with a flipping of the axis of rotation as in pure  $\text{C}_{60}$ .<sup>11</sup> The

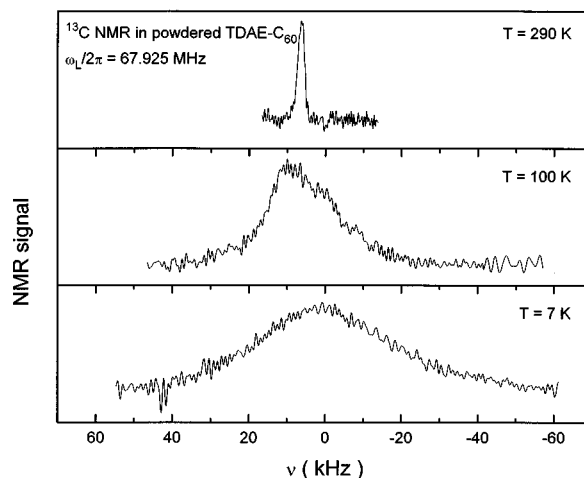


FIG. 2.  $^{13}\text{C}$  NMR spectra of powdered TDAE- $\text{C}_{60}$  at 290, 100, and 7 K. The intensities are plotted in arbitrary units.

second moment  $M_2$  amounts here to less than  $1 \text{ kHz}^2$ . The spectral shape does not change between room temperature and 170 K. Between 150 and 70 K a  $^{13}\text{C}$  linewidth transition takes place indicating a freeze-out of the  $\text{C}_{60}^-$  “isotropic” rotation on the NMR time scale. It is possible that—in analogy to pure  $\text{C}_{60}$ —the flipping of the rotational axes freezes out while uniaxial rotation still persists. The second moment  $M_2$  increases to  $160 \text{ kHz}^2$ . The activation energy for the motion of the  $\text{C}_{60}^-$  ions which freezes out in this temperature

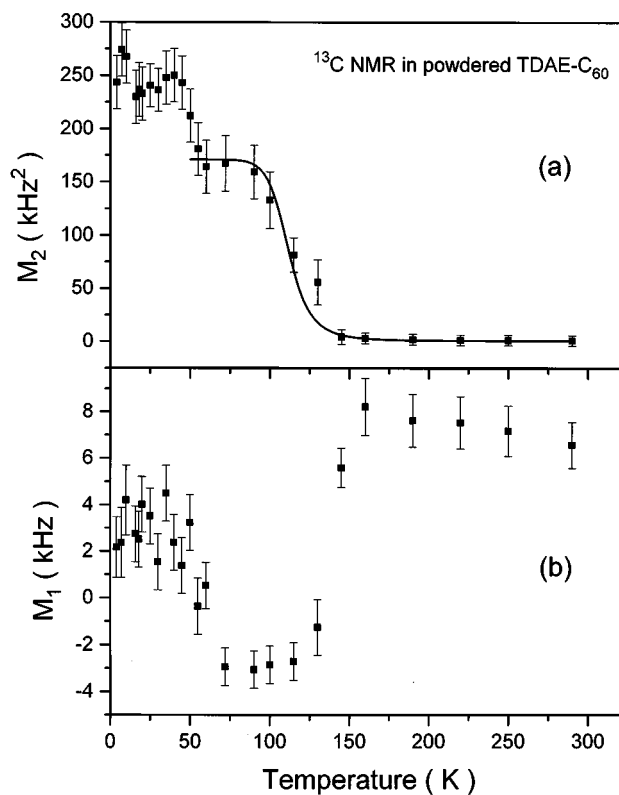


FIG. 3. Temperature dependences of (a) the second moment and (b) the first moment of the  $^{13}\text{C}$  NMR spectra in powdered TDAE- $\text{C}_{60}$ . The reference compound corresponding to  $M_1=0$  is tetramethylsilane.

range amounts to  $E_a \approx 130$  meV. The occurrence of a  $^{13}\text{C}$  linewidth transition around 170 K has been already seen by Ricco *et al.*<sup>13</sup> It should be stressed that the  $^{13}\text{C}$  linewidth transition cannot be due to a change in the state of the motion of the TDAE methyl protons. The proton- $^{13}\text{C}$  contribution is not large enough to account for the observed increase in the  $^{13}\text{C}$   $M_2$ .

In Ref. 8 it was found that the rate of cooling the TDAE- $\text{C}_{60}$  sample through the temperature range around 150 K significantly influences the magnetic susceptibility and ferromagnetic transition temperature  $T_c$ . Below 150 K the rate of cooling has no effect on the magnetic properties of TDAE- $\text{C}_{60}$ . The present results clearly show that an orientational ordering transition of the  $\text{C}_{60}$  ions takes place below 150 K. It is thus natural to conclude that the depression of  $T_c$  and the decrease in the magnetic susceptibility in the rapidly quenched sample is connected with the incomplete orientational ordering of the  $\text{C}_{60}$  ions when the sample is rapidly taken through the region of the orientational transition.

It should be noted that whereas the reorientational motion of the  $\text{C}_{60}$  ions significantly affects the  $^{13}\text{C}$  NMR line shapes the  $^{13}\text{C}$  NMR powder spectra are not sensitive to static orientational disorder. The remaining static orientational disorder of the  $\text{C}_{60}$  ions can be thus seen in the  $^{13}\text{C}$  line shapes only in single crystal experiments. In fact no correlation between the cooling rate and the  $^{13}\text{C}$  NMR powder line shapes has been observed below the motional transition. Evidence for the static disorder of the  $\text{C}_{60}$  ions has been however obtained from the stretched exponential character of the  $^{13}\text{C}$  magnetization recovery in the  $^{13}\text{C}$  spin-lattice relaxation measurements. The reason for the sensitivity of the  $^{13}\text{C}$  magnetization recovery measurements to the static  $\text{C}_{60}$  disorder is the fact that the  $^{13}\text{C}$  spins are relaxed via electronic spin fluctuations.

In this connection it is interesting to note that in the temperature range where the  $\text{C}_{60}^-$  pseudoisotropic rotation freezes out we also see a break in the ESR linewidth versus temperature relation (Fig. 1). The ESR linewidth decreases from 21 at room temperature to  $\approx 12$  G in a powder and to 2 G in a single crystal at 150 K indicating that the exchange narrowing is enhanced by orientational ordering of the  $\text{C}_{60}^-$  ions.

Between 90 and 50 K the  $^{13}\text{C}$   $M_2$  is nearly constant. Below 50 K there is another increase in  $M_2$ . It reaches a value of  $\approx 250$  kHz<sup>2</sup> around 20 K. Below  $T_c$   $M_2$  increases again. The observed value of  $M_2$  at 20 K is dominated by the static broadening of the  $^{13}\text{C}$  line due to dipolar interactions of the  $^{13}\text{C}$  nucleus with the unpaired electron in the  $2p_z$  state smeared out over all carbon sites in the  $\text{C}_{60}^-$  ion as shown by the close agreement of the experimental and theoretical  $M_2$  values. The chemical shift anisotropy contribution which has been for sake of simplicity assumed to be the same as in pure  $\text{C}_{60}$  is less than 5% of the experimentally observed  $M_2$ . The fact that the observed value of  $M_2$  is dominated by the dipolar electron-nuclear interactions and not by the hyperfine-contact field demonstrates the predominant  $2p_z$  character of the unpaired electron wave function. The unpaired electron spin density at the carbon sites in the  $\text{C}_{60}$  ion, which is due to the  $s$  component in the electronic wave function, is thus rather small.

This also agrees with the observed shifts of the center of

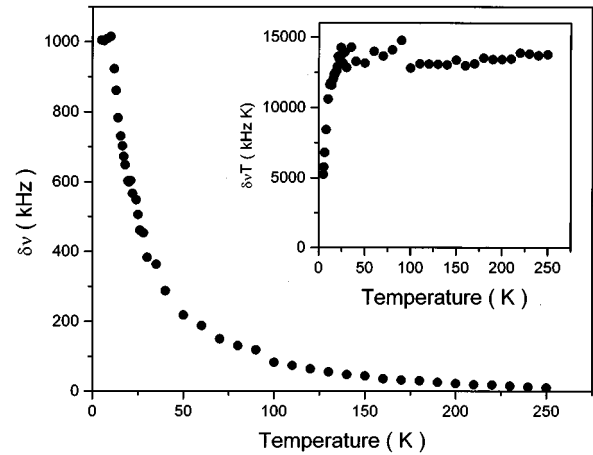


FIG. 4. Temperature dependence of the paramagnetic proton shift in powdered TDAE- $\text{C}_{60}$ . Inset: the product of the shift times the temperature.

the  $^{13}\text{C}$  line (Fig. 3) which are small as compared to the observed paramagnetic proton shifts<sup>14</sup> (Fig. 4). The TDAE methyl protons evidently feel a sizable hyperfine Fermi contact interaction with the unpaired electron spin density and the shifts reach 3700 ppm whereas the observed  $^{13}\text{C}$  shifts are less than 100 ppm. The existence of these  $^{13}\text{C}$  shifts nevertheless demonstrates a small but finite  $s$ -wave character of the transferred unpaired electron spin density of the  $\text{C}_{60}^-$  ion.

The temperature dependence of the  $^{13}\text{C}$  NMR lineshift is also rather interesting. In the temperature range where motional narrowing takes place due to fast rotation of the  $\text{C}_{60}^-$  ion, i.e., between room temperature and 150 K, the  $^{13}\text{C}$  NMR lineshift is almost temperature independent and amounts to 188 ppm at room temperature. The freeze-out of the “isotropic” rotation between 150 and 100 K is connected with a high field shift of the center of the  $^{13}\text{C}$  line by about 160 ppm. Below 50 K, on the other hand, we have a low field paramagnetic shift of about 87 ppm. In contrast to the  $^{13}\text{C}$  line the proton NMR line exhibits a continuous low field shift which follows above  $T_c$  a Curie-Weiss law. The fact that the internal field seen by the  $^{13}\text{C}$  nucleus changes its sign may indicate that antiferromagneticlike correlations exist which change into ferromagneticlike correlations at lower temperatures.

The above data thus clearly demonstrates the nearly isotropic rotation of the  $\text{C}_{60}^-$  ions above 150 K and the existence of the orientational ordering transition between 150 and 100 K. The question whether the resulting orientational order of the  $\text{C}_{60}^-$  ions is perfect or whether there is some residual orientational disorder at low temperatures cannot be answered by the  $^{13}\text{C}$  powder line shape data.

$^{13}\text{C}$  spin-lattice relaxation data, on the other hand, seem to demonstrate the existence of residual disorder. The recovery of the  $^{13}\text{C}$  spin magnetization after  $180^\circ$ - $\tau$ - $90^\circ$  pulse sequence is definitely nonexponential. It is clear that we deal with a distribution of spin-lattice relaxation times

$$\frac{M(t) - M_0}{M_0} = \int \rho(T_1) \exp\left(-\frac{t}{T_1}\right) dT_1, \quad (18a)$$

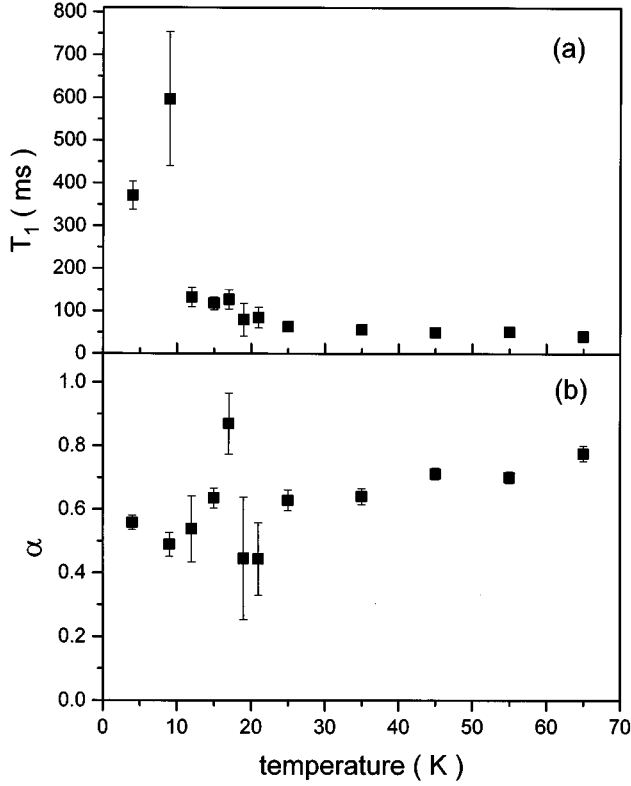


FIG. 5. Temperature dependence of (a) the <sup>13</sup>C spin-lattice relaxation time parameter  $T_1$  and (b) the stretched exponent  $\alpha$  in TDAE-C<sub>60</sub>.

which can be simulated by a stretched exponential function

$$\frac{M(t) - M_0}{M_0} \propto e^{-(t/T_1)^\alpha}. \quad (18b)$$

The distribution of  $T_1$  values  $\rho(T_1)$  can be related to a local magnetization distribution

$$W(m) = \frac{1}{N} \sum_i \delta(m - \langle S_i^Z \rangle), \quad (19)$$

which is characteristic for inhomogeneous ferromagnets or spin glasses

$$\begin{aligned} \frac{M(t) - M_0}{M_0} &= \int \exp\left(-\frac{t}{T_1(m)}\right) W(m) dm \\ &= \int \rho(T_1) \exp\left(-\frac{t}{T_1}\right) dT_1. \end{aligned} \quad (20)$$

The temperature dependence of the parameters  $T_1$  and  $\alpha$  is shown in Fig. 5. The parameter  $T_1$  is nearly temperature

independent down to  $T_c$  and amounts to  $\approx 100$  msec. Around  $T_c$  it increases demonstrating a slowing down of the electron spin fluctuations. The temperature dependence of  $T_1$  can be in the simplest case described by

$$\left(\frac{1}{T_1}\right)_{13C} = K \int_{-\infty}^{\infty} \langle (S^Z(0)S^Z(t)) e^{i\omega_L t} \rangle dt, \quad (21a)$$

where  $S^Z$  is the electronic spin and  $K$  measures the fluctuating part of the electron-dipolar interaction. A rough estimation of the constant  $K$  is given by

$$K = \left(\frac{\mu_0}{4\pi}\right)^2 (\gamma_C \gamma_e)^2 \hbar^2 \left\langle \frac{1}{r^3} \right\rangle^2, \quad (21b)$$

where

$$\left\langle \frac{1}{r^3} \right\rangle = \int \frac{1}{r^3} |\psi_{2p_z}|^2 dV = \frac{Z^3}{2880\pi a_B^3}. \quad (21c)$$

If the electron spin autocorrelation function

$$\langle S^Z(0)S^Z(t) \rangle \cong e^{-t/T_{1,e}} \quad (22)$$

decays exponentially with the electron spin-lattice relaxation time  $T_{1,e}$  one finds

$$(T_1)_{13C}^{-1} \approx K \frac{T_{1,e}}{1 + \omega_L^2 T_{1,e}^2}. \quad (23)$$

The temperature dependence of  $T_{1,e}$  in TDAE-C<sub>60</sub> has been already measured<sup>15</sup> by pulsed ESR. The electronic spin lattice relaxation time is in fact exceptionally long and is of the order of 100 ns at 4 K. As  $\omega_L T_{1,e} > 1$  one gets in the single correlation time approximation

$$(T_1)_{13C} = T_{1,e} \omega_L^2 / K. \quad (24)$$

Both the temperature dependence and the order of magnitude of the predicted  $(T_1)_{13C}$  qualitatively agree with the experiment.

The observed <sup>13</sup>C  $T_1$  stretched exponent  $\alpha$  has a value of  $\alpha \approx 0.6$  indicating the presence of a relatively broad  $T_1$  distribution reflecting a local polarization function  $W(m)$  characteristic for inhomogeneous ferromagnets and spin glasses. This in turn indicates the presence of residual orientational disorder of the C<sub>60</sub><sup>-</sup> ions. A similar conclusion has been obtained from the stretched exponential character of the remanent magnetization decay.<sup>16</sup> The temperature dependence of the second moment of the ESR line which shows a behavior reminiscent of spin glasses rather than of a homogeneous ferromagnet also supports the existence of residual orientational disorder at low temperatures in TDAE-C<sub>60</sub>.

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