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Evidence for $S=0$-type spin pairing in the nonferromagnetic modification of TDAE-C_{60}

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The *X*-band electron spin resonance (ESR) spectra, the methyl-proton ^{1}H nuclear magnetic resonance spectra, and the proton spin-lattice relaxation rate T_1^{-1} of the nonferromagnetic modification of tetrakis-dimethylamino-ethilene (TDAE)-C_{60} have been studied between room temperature and 4 K. The results are compared with those previously obtained for the ferromagnetic modification of TDAE-C_{60}. The nonferromagnetic modification of TDAE-C_{60} shows only a single proton line and an *X*-band ESR intensity that vanishes below 10 K. The temperature dependencies of the proton spin-lattice relaxation rate and the ESR intensity are characteristic for a system with a $S=0$ ground state and a nonzero energy gap between the ground state and the first excited triplet state. The singlet-triplet energy gap is estimated to be of the order of 15 K at $T=5$ K. The nonferromagnetic modification seems to be metastable and spontaneously transforms to a ferromagnetic modification at room temperature or above. [S0163-1829(99)01507-6]

I. INTRODUCTION

It is by now well known[1,2,3] that TDAE-C_{60} (where TDAE is tetrakis-dimethylamino-ethilene) has the highest transition temperature $T_C=16\,\mathrm{K}$ of all purely organic ferromagnets. Here TDAE—which is known to be one of the strongest organic donors—transfers one electron to the lowest unoccupied (π type) molecular orbital of the C_{60} ion. Ferromagnetic resonance[4,5] data have shown that TDAE-C_{60} is a uniaxial Heisenberg ferromagnet with an extremely small anisotropy field $H_A=29\,\mathrm{G}$. The easy axis is parallel to the crystal *c* direction, which is the direction of closest contact of the $C_{60}{}^-$ ions. The magnetic structure of TDAE-C_{60} thus seems to consist of an arrangement of quasi-one-dimensional chains of $C_{60}{}^-$ ions, each of them carrying a spin $\frac{1}{2}$, running along the crystal *c* axis with the TDAE$^+$ mediated interchain coupling leading to a transition in three dimensions.

It is less known that TDAE-C_{60} exists in two different modifications[6,7] (I and II). Single crystals of the modification I, exhibiting a ferromagnetic transition at 16 K, are grown from the toluene solution at or above room temperature. If, however, the crystals are grown around 0 °C another modification (here designated as modification II) is obtained, which is as well paramagnetic at room temperature but does not show the ferromagnetic transition at low temperatures. If these crystals are kept for a prolonged time at or above room temperature they gradually transform to the modification I exhibiting the ferromagnetic transition. It is also possible that all TDAE-C_{60} single crystals grown from the solution are at first in the nonferromagnetic modification II but that those grown at room temperature or above rapidly transform to the modification I. In this case, crystals grown at room temperature or above should be in fact always a mixture of the two modifications, I and II. Here, we present an electron spin resonance (ESR) and nuclear magnetic resonance (NMR) study of the nonferromagnetic modification II of the TDAE-C_{60} single crystals and compare the obtained results with those for the ferromagnetic modification I.

II. EXPERIMENT

Experiments were performed on virgin TDAE-C_{60} single crystals grown at 0 °C by a standard diffusion method.[8] Crystals used in these experiments were sealed into a quartz tube under dynamic vacuum in order to avoid contact with oxygen. *X*-band ESR experiments were performed on a commercial Bruker ESP 300 spectrometer equipped with an Oxford liquid-helium cryostat. NMR measurements were performed at a 270-MHz (6.3 T) pulsed spectrometer. In addition a field swept superconducting spectrometer working at a proton frequency 100 MHz has been used to check for additional shifted proton lines at low temperatures.

III. RESULTS

A. EPR spectra

The temperature dependence of the *X*-band electron paramagnetic resonance (EPR) spectra of the nonferromagnetic modification II of a TDAE-C_{60} single crystal is shown in Fig. 1(a) whereas Fig. 1(b) shows the temperature dependence of the EPR spectra of the ferromagnetic modification I. The room-temperature spectra are clearly the same and the *g*-factor values of both modifications coincide. Whereas the *X*-band ESR intensity of the ferromagnetic modification increases with decreasing temperature by a factor of 1000, the intensity of the EPR spectrum of the nonferromagnetic modification at first shows a paramagneticlike increase with decreasing temperature but then starts to decrease with decreasing temperature below 20 K. The EPR signal practically vanishes at 6 K (Fig. 2). Whereas a nonlinear variation[4,5] of the electron resonance frequency with magnetic field characteristic of ferromagnetic resonance has been observed in the modification I below 16 K in the radio-frequency region, no analogous spectrum could be detected for modification II. Only a rather weak line has been seen at the ESR Larmor frequency and the intensity of this line vanishes below 10 K.

The temperature dependence of the widths of the *X*-band ESR spectra of the two modifications is shown in Fig. 3. Until 170 K the width and shape of the EPR spectra of the

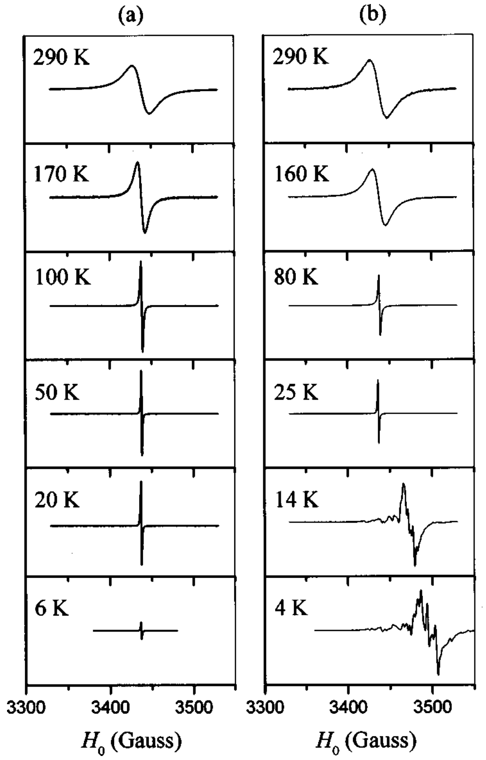

FIG. 1. The temperature dependence of the *X*-band ESR spectra of the (a) nonferromagnetic modification II and (b) ferromagnetic modification I. Here the crystal orientation was such that $a \| H_0$.

two modifications are practically identical. Between room temperature and 170 K—where the C_{60} rotation freezes out[9]—the width is nearly temperature independent and amounts to around 20 G. Below 170 K the width decreases to about 2 G as a result of exchange narrowing due to the increase of the overlap of the electronic wave function on the neighboring C_{60}^{-} ions. Below 20 K the width of the EPR line of the modification I, undergoing the ferromagnetic transition, strongly increases with decreasing temperature. The width of the modification II, which does not show the ferromagnetic transition, is nearly temperature independent until the EPR intensity vanishes below 6 K. The position of the *X*-band EPR resonance signal of the ferromagnetic modification I shifts at T_C for about 60 G. No such shift is seen in the position of the EPR signal of nonferromagnetic modification II.

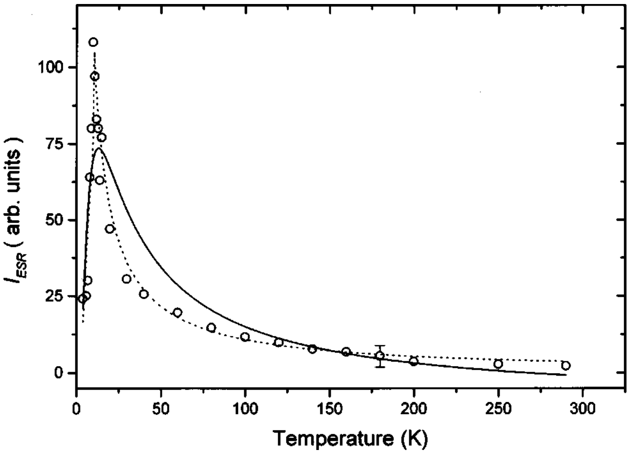

FIG. 2. The temperature dependence of the *X*-band ESR intensity of the nonferromagnetic modification II. The solid line represents the fit to the expression (3) with a constant singlet-triplet gap while the dotted line is evaluated for the case that the singlet-triplet gap is zero above 11 K and nonzero below that temperature. The constants used in a fit with a constant singlet-triplet gap were $C_T = 9315.8$ and $C = 0.112$ while in fit evaluated for the case of a temperature dependent gap the constants were $C_T = 4307.5$ and $C = 1.745$.

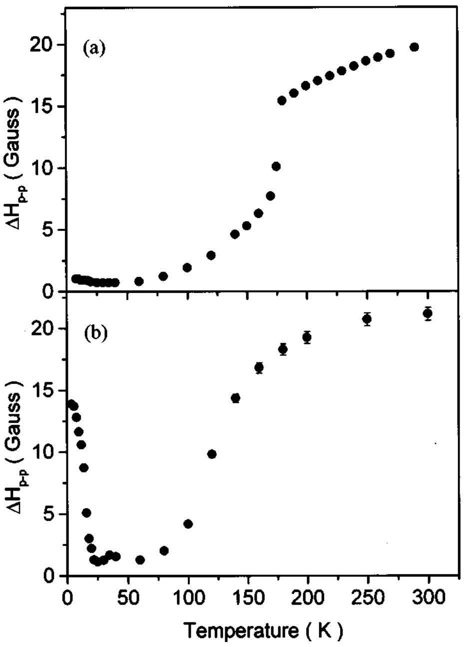

FIG. 3. The temperature dependence of the widths of the *X*-band ESR spectra of (a) nonferromagnetic modification II and (b) ferromagnetic modification I.

B. Proton NMR spectra

The methyl proton ^{1}H NMR spectra of crystals of the modification I, which exhibit a ferromagnetic transition at 16 K, are shown in Fig. 4. Two proton lines, called *A* and *B*, are seen[10,11] at room temperature. The intensities of these two lines were about the equal. It should be however noted that in different crystals the ratio of the intensities of these two lines is not constant but seems to depend on the crystal growth and annealing condition. With decreasing temperature the position of the line *A* shifts to lower fields with decreasing temperature exhibiting a Curie-Weiss law (Fig. 5)

$$\Delta v \propto \langle \vec{S} \rangle \propto \chi_0 H = \frac{C}{T-\theta} H, \quad T > T_C . \tag{1}$$

At low temperatures the shifts are as large as 1 MHz whereas they amount to only 40 kHz at room temperature. The shift still increases below T_C where Δv should be proportional to the spontaneous magnetization.

The resonance frequency of the line *B* is rather close to the Larmor frequency. Its position does not change with decreasing temperature. In particular it is not affected by the transition to the ferromagnetic phase. The proton spin-lattice relaxation time of this line is nevertheless rather short (~1

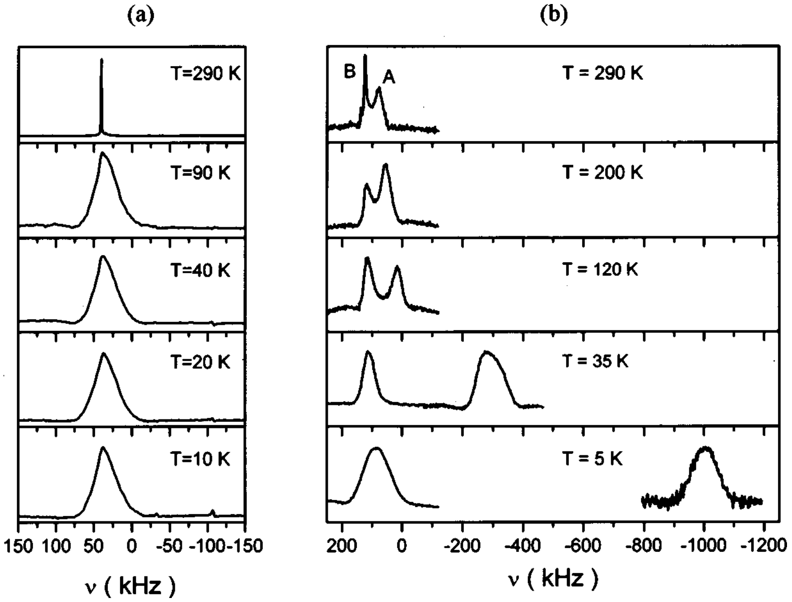

FIG. 4. The temperature dependence of the methyl-proton ^{1}H NMR spectra of (a) the modification II and (b) the modification I. Here, $\nu_L = 270\,\mathrm{MHz}$ ($H_0 = 6.3\,\mathrm{T}$).

sec) and weakly temperature dependent between 300 and 10 K.[10] It is clearly of paramagnetic origin. It should be mentioned that the proton T_1 of the line A is by three orders of magnitude shorter and is of the order of 1–2 msec between 300 and 16 K.[10] The fact that the proton spin-lattice relaxation rates of the two proton lines A and B are so different seems to show that they originate from spatially separated parts of the sample.

The TDAE proton NMR spectra of the modification II, on the other hand, exhibit just one proton line. The position of this line is close to the proton Larmor frequency and thus coincides with the position of the B line of the modification I. Its position does not change with decreasing temperature even down to 4 K.

In spite of an extensive search with a field swept (±1000 G) superconducting magnet we were unable to find any other, more shifted proton line in the modification II.

C. Proton spin-lattice relaxation and EPR intensity of modification II

The temperature dependence of the proton spin-lattice relaxation time T_1 of the methyl protons of TDAE-C_{60} crystals of modification II is shown in Fig. 6. The proton spin-lattice relaxation rate is practically temperature independent between room temperature and 20 K. Between 20 and 10 K the relaxation rate slowly increases with decreasing temperature whereas a dramatic decrease of the relaxation rate occurs below 10 K. This is completely different from the behavior of the proton relaxation rate of the ferromagnetic line A (modification I) but somewhat analogous to the behavior of the line B protons. The temperature dependence of the proton T_1 in modification II is somewhat similar to the temperature dependence of the T_1 in mesoscopic size magnetic systems like iron clusters[12] Fe_8 with a $S=0$ ground state, which is separated with a gap from the $S=1$ triplet state.

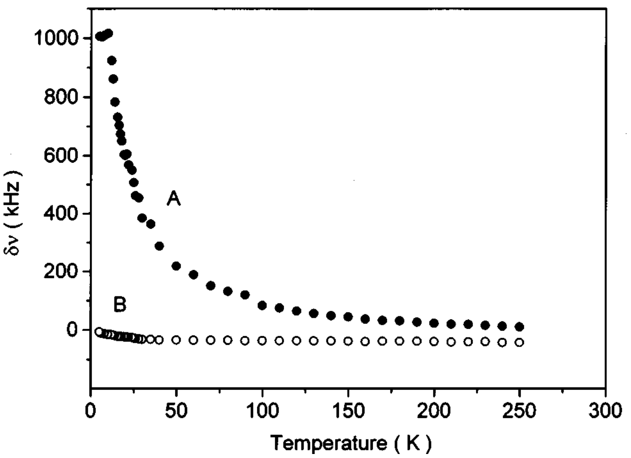

FIG. 5. The temperature dependence of the methyl-proton ^{1}H NMR shift of the line A of the modification I.

We made an attempt to describe the observed proton spin-lattice relaxation rate T_1^{-1} quantitatively. We assumed that the ground state is a singlet state with $S=0$. We further assumed that T_1^{-1} has contributions proportional to the probability of occupation of the different excited spin energy lev-

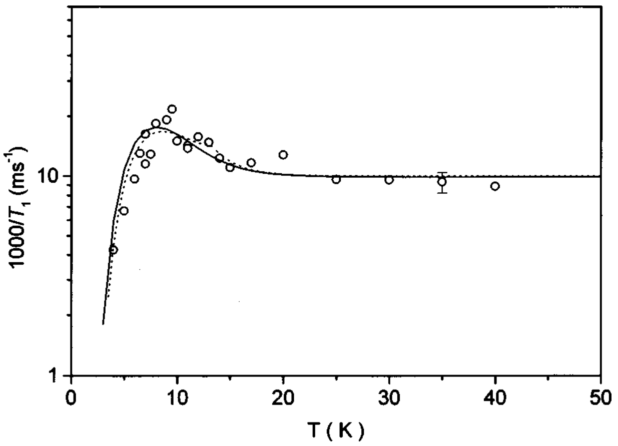

FIG. 6. The temperature dependence of the methyl-proton spin-lattice relaxation rate T_1^{-1} of the modification II measured at a proton Larmor frequency $\nu_L = 270\,\mathrm{MHz}$. The solid line represents the fit using the expression (2) with a constant singlet-triplet gap. The dotted line represents the fit with a temperature dependent gap as determined from the ESR data.

els. The dominant contribution comes from the first excited triplet state (total spin $S=1$). The remaining states are approximated by a continuum. Within this model we end up with the following expression for the temperature dependence of the proton spin-lattice relaxation rate:

$$T_1^{-1}=\left\{A\exp(-E_T/kT)+B\int_d^{\infty}D(E)\times\exp(-E/kT)dE\right\}\Bigg/\int_0^{\infty}D(E)\exp(-E/kT)dE. \tag{2}$$

Here A,B are adjustable parameters, E_T is the energy for the singlet-triplet excitation and $D(E)$ is a function representing the continuous distribution of the remaining excited states. It is noted that the lower limit d of the integral is also treated as an adjustable parameter since it represents the minimum energy above which the distribution of spin energy levels can be approximated by a continuous function. In the first approximation we assumed that $D(E)$ takes the form of a Gaussian. The fit between the experimental data and calculated $1/T_1$ is reasonable. The obtained value for the singlet-triplet gap is $E_T=19.1\,\mathrm{K}$ (Fig. 6). The other parameters of the fit are $A=1.6\times10^{-8}\,\mathrm{msec}^{-1}$ and $B=9.9\times10^{-3}\,\mathrm{msec}^{-1}$.

The presence of a gap between the $S=0$ ground state and the $S=1$ excited state—necessary to describe the temperature dependence of the proton T_1^{-1}—should be also clearly seen in the static electronic susceptibility determining the ESR intensity. If one assumes that the observed ESR signal is the result of the excited triplet state, then one finds the temperature dependence of the ESR intensity as

$$I_{\mathrm{ESR}}=C_T/T(1+3\exp[E_T/kT])+C/kT. \tag{3}$$

Here, E_T is the singlet-triplet energy gap determined from the proton T_1^{-1} measurements. The parameter C measures the small contribution of paramagnetic impurities present in the sample. The only free parameters are the prefactors C_T and C. The resulting fit is reasonable but not perfect (Fig. 2, solid line). One possible reason for the observed discrepancy between the theory and experiment is that the gap between the singlet and the triplet is not constant but rather temperature dependent as expected in the case of a spin-Peierls transition like in $\mathrm{CuGeO_3}$. If one assumes a temperature dependent gap and uses the ESR intensity data for a determination of the gap we get the results shown in Fig. 7. The fit of the temperature dependence of the intensity of the ESR is now nearly perfect (Fig. 2, dotted line) and the observed temperature dependence of the proton T_1^{-1} is as well reasonably reproduced (Fig. 6, dotted line). The singlet-triplet gap E_T is zero above 11 K and starts to increase with decreasing temperature below 10 K. At 5 K the value of the gap is of the order of 14 K.

IV. DISCUSSION

From the above data we may conclude the following.

(a) The existence of two proton lines A and B in TDAE-$\mathrm{C_{60}}$ crystals of modification I shows that crystals of this modification are generally not pure but in fact a mixture of a part exhibiting the ferromagnetic transition at 16 K and giving rise to proton line A (pure modification I), and another part showing no such transition and giving rise to proton line B (modification II). This is supported by the fact that the intensity of the nonferromagnetic proton NMR line B in modification I depends on the annealing condition.

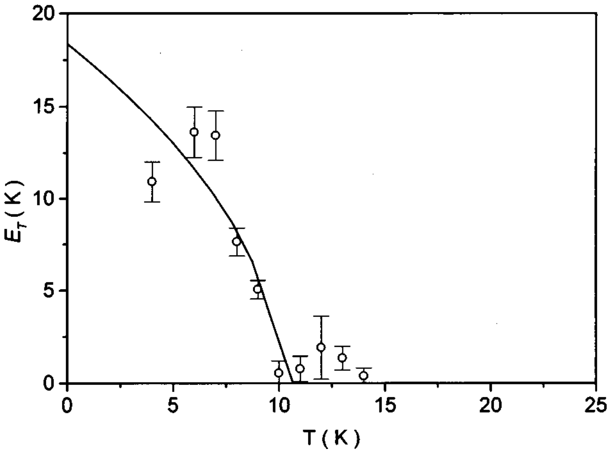

FIG. 7. The temperature dependence of the singlet-triplet gap as calculated from the temperature dependence of the ESR intensity using expression (3).

(b) The existence of only one proton line in virgin crystals of modification II, on the other hand, demonstrates that this nonferromagnetic modification is a pure state. It may be however metastable as it spontaneously starts to transform to the ferromagnetic modification II at room or higher temperatures.

(c) The above conclusions have to be contrasted with the EPR results for modifications I and II. As described above there is only one EPR line in modification I, which coincides with the line observed in modification II between room temperature and $T_C=16\,\mathrm{K}$. Below T_C the EPR line of modification I broadens and shifts whereas the EPR line of the nonferromagnetic modification II loses its intensity below 20 K. The EPR signal of the nonferromagnetic modification II present in nominally pure crystals of modification I cannot be seen in the presence of the EPR signal of the ferromagnetic part of the system, which is several orders of magnitude stronger.

(d) The fact that no paramagnetic shift is seen for the proton line B in the ferromagnetic modification I or for the corresponding proton line in the modification II demonstrates that there is no unpaired electron spin density at the position of the methyl protons in the nonferromagnetic modification II. On the other hand, the unpaired spin density is clearly nonzero at the position of the A line methyl protons in the ferromagnetic modification I.

This could have important consequences for the magnetic coupling between the $\mathrm{C_{60}}$ chains in the two systems. Whereas in modification I the unpaired spin density is not only localized at the $\mathrm{C_{60}}^-$ ions but is also spread out to the TDAE^+ ions (as demonstrated by the hyperfine contact shift of line A protons) this is not the case for the modification II. Here, the unpaired spin density is localized at the $\mathrm{C_{60}}^-$

chains decreasing the super-exchange through the TDAE$^+$ ions between the C_{60} chains. Therefore modification II is much more pseudo-one-dimensional than the modification I. The low dimensionality of this modification increases the possibility for the existence of ground-state instabilities such as the formation of spin-density wave, charge-density wave, or a spin-Peierls transition leading to a nonmagnetic ground state.

(e) The absence of super-exchange through TDAE$^+$ ions and the resulting larger pseudo-one-dimensionality of the modification II may explain the absence of a ferromagnetic transition at $T_C=16\,\mathrm{K}$ in the modification II as compared to the more three-dimensional coupled modification I. It can however not explain by itself the observed decrease of the EPR intensity to zero. A purely antiferromagnetic ground state can be excluded as there is no corresponding shift in the proton NMR lines and no antiferromagnetic resonance is observed. The proton NMR spectra are similarly not compatible with the existence of a spin-density wave state as no characteristic line-broadening has been observed.[13,14] The EPR spectra can be only understood if a $S=0$ type spin pairing takes place leading to a nonmagnetic ground state, which is separated from the magnetic excited state by a nonzero gap. One cannot exclude the possibility that we have a dimerized spin-Peierls ground state though there is no additional evidence for that.

(f) The temperature dependence of the proton spin-lattice relaxation rate and the ESR intensity of the nonferromagnetic modification II can be indeed qualitatively described by a model, which assumes the existence of spin pairing below 10 K leading to a $S=0$ ground state and the opening of a gap in the electron spin excitation spectrum. The value of the gap is zero above 10 K and reaches a value of $E_T=14\,\mathrm{K}$ at $T=5\,\mathrm{K}$.

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[1] P. M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, and J. D. Thompson, Science **253**, 301 (1991).

[2] P. Venturini, D. Mihailovič, R. Blinc, P. Cevc, J. Dolinšek, D. Abramič, B. Zalar, H. Oshio, P. M. Allemand, A. Hirsch, and F. Wudl, Int. J. Mod. Phys. B **6**, 3947 (1992).

[3] Tanaka, A. A. Zakhidov, K. Yoshizawa, K. Okahara, T. Yamabe, and K. Yasushi, Phys. Rev. B **47**, 7554 (1993).

[4] D. Arčon, P. Cevc, A. Omerzu, and R. Blinc, Phys. Rev. Lett. **80**, 1529 (1998).

[5] R. Blinc, P. Cevc, D. Arčon, A. Omerzu, M. Mehring, S. Knorr, A. Grupp, A.-L. Barra, and G. Chouteau, Phys. Rev. B **58**, 14 416 (1998).

[6] A. Mrzel, P. Cevc, A. Omerzu, and D. Mihailović, Phys. Rev. B **53**, R2922 (1996).

[7] D. Arčon, R. Blinc, P. Cevc, and T. Jesenko, Europhys. Lett. **35**, 469 (1996).

[8] R. Blinc, K. Pokhodnia, P. Cevc, D. Arčon, A. Omerzu, D. Mihailović, P. Venturini, L. Golič, Z. Trontelj, J. Lužnik, and J. Pirnat, Phys. Rev. Lett. **76**, 523 (1996).

[9] D. Arčon, J. Dolinšek, and R. Blinc, Phys. Rev. B **53**, 9137 (1996).

[10] R. Blinc, J. Dolinšek, D. Arčon, D. Mihailović, and P. Venturini, Solid State Commun. **89**, 487 (1994).

[11] D. Arčon, J. Dolinšek, R. Blinc, K. Pokhodnia, A. Omerzu, D. Mihailović, and P. Venturini, Phys. Rev. B **53**, 14 028 (1996).

[12] A. Lascialfari, D. Gatteschi, F. Borsa, and A. Cornia, Phys. Rev. B **55**, 14 341 (1997).

[13] H. Alloul, V. Brouet, E. Lafontaine, L. Malier, and L. Forro, Phys. Rev. Lett. **76**, 3638 (1996).

[14] K.-F. Thier, G. Zimmer, M. Mehring, and F. Rashdi, Phys. Rev. B **53**, R496 (1996).