Interplay between antiferromagnetic and ferromagnetic phases of TDAE-C_{60}: An ESR study of high-temperature annealed samples

A. Mrzel, P. Cevc, A. Omerzu, and D. Mihailovic
Jozef Stefan Institute, Jamova 39, Ljubljana, Slovenia
(Received 24 October 1995)

The low-temperature magnetic properties of annealed TDAE-C_{60} single crystals are studied with electron spin resonance. Whereas freshly grown single crystals are found to order antiferromagnetically at low temperature, annealing at room temperature and above results in an enhanced ferromagnetic ordering and three separate magnetic phases can be identified below 25 K, below 16 K, and below 10 K. The orientational ordering transition temperature T_0 is found to be correlated with the annealing temperature T_a and the drop in susceptibility which is systematically observed below 100 K is interpreted as the onset of antiferromagnetic correlations.

The magnetic properties of organically doped [60]fullerene have attracted significant attention after the discovery of tetrakis(dimethylamino)ethylene doped C_{60} or TDAE-C_{60}.[1] However, in powder samples different groups often reported slightly different critical temperatures,[2] with the highest reported to date being 24 K.[3] The reason for this behavior was thought to be the different synthesis procedures, but the details were not understood. It was also found that samples of the material showed signs of aging when kept at room temperature, but this effect was thought to be related to the extreme sensitivity to oxygen contamination and the large surface-to-volume ratio of powder samples.

With the growth of single crystals of the material,[4,5] significant progress has now been possible in both enabling more systematic studies of these effects as well as in elucidating the microscopic origin of the magnetic behavior.[6] Because of the significantly smaller surface-to-volume ratio of the crystals, their sensitivity to oxygen is no longer a problem, especially when handled in an oxygen-free atmosphere. In this paper we report on an important hitherto unreported aspect of the properties of TDAE-C_{60}, namely, the effects of high-temperature annealing of single crystal samples of TDAE-C_{60} on the low-temperature magnetic properties and in particular on the spin susceptibility as measured by electron spin resonance (ESR).

The measurements were done on single crystals of TDAE-C_{60} grown by the diffusion method as described previously.[6] The crystals are typically 0.5–1 mm^3 and are of somewhat irregular shape, and the crystal edges have been found by x rays not to coincide with the crystallographic axes. Since the low-temperature spin susceptibility measurements showed that aging at room temperature is very rapid, the measurements were performed immediately after their extraction from the growth apparatus. The ESR measurements were performed in an Oxford Instruments flow cryostat in a Bruker ESR300 spectrometer. The samples were handled in an O-free atmosphere at all times and transferred to the ESR without exposure to elevated temperature. The annealing was done in the cryostat itself and always for a fixed time of 30 minutes.

In Fig. 1 we show the integrated ESR intensity as a function of temperature for the same sample after annealing successively at different elevated temperatures from 20 to 110 °C. The susceptibility first starts to increase in the range 10–20 K with T_a from 20 to 60 °C. With increasing T_a from 70 to 100 °C, we observe an increase in the susceptibility also below 10 K, indicating that there are clearly two phases present, one below 10 K and one in the range 10 K $< T <$ 20 K. For $T_a > 80$ °C, we also observe an increase in the ESR signal intensity at temperatures above 20 K. Thus the onset of the increase in susceptibility—which is usually taken as the critical temperature to a ferromagnetic state—is also strongly dependent on the annealing temperature, increasing from $T_c \sim 18$ K in the room-temperature annealed sample to 25 K after annealing at 100 °C. Finally the susceptibility starts to fall again until the signal eventually changes its width and disappears for $T_a >$ 110 °C. In Fig. 1(b) the peak ESR intensity at 4 K and at 12 K is plotted as a function of annealing temperature, showing the rapid change to a nonmagnetic state for $T_a >$ 110 °C.

The temperature dependence of the susceptibility above T_c is plotted in Fig. 1(c) as χT versus T, showing Curie-like behavior in the temperature range 100 K $<$ T $<$ 280 K for all T_a, (except for 110 °C). Below 100 K, there appears to be a systematic deviation from the Curie law with a drop in susceptibility, which is more pronounced for $T_a <$ 80 °C. Since we consider a transition from a Curie-like to a temperature-independent Pauli-like temperature-independent susceptibility unlikely to occur below 100 K (usually because of low-temperature spin localization the reverse is observed[7]), we interpret the drop in susceptibility below 100 K as the onset of antiferromagnetic spin correlations below this temperature.

The shape of the ESR signal is very much dependent on the annealing temperature, T_a and is shown in Fig. 2 for a number of temperatures above and below T_c. Whereas for the unannealed sample we observe essentially a single ESR line, whose intensity decreases below 16 K and disappears at 6 K, with increasing T_a the line shape above T_c is essentially unchanged, but below T_c it gets progressively distorted, giving very unusual multiple lines. This structure in the ESR line shape below T_c changes when the sample is rotated in magnetic field and also with cycling of the magnetic field from 0 to 10 kGauss, eventually settling to a fixed pattern where it no longer responds to a magnetic field perturbation.

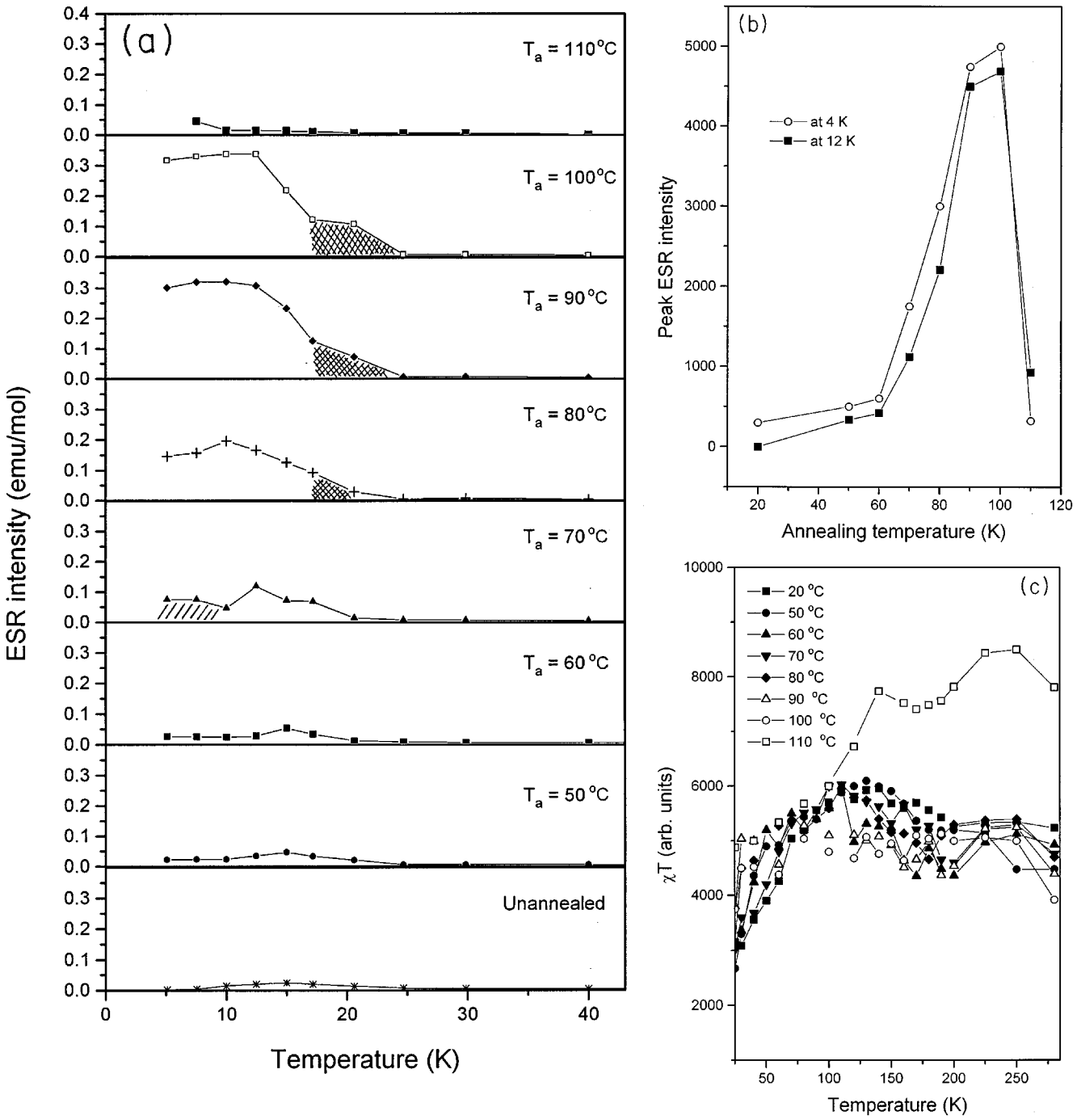

FIG. 1. (a) Temperature dependence of the low-temperature spin susceptibility (ESR integrated intensity) for different annealing temperatures. Whereas the fresh sample shows no sign of a low-temperature phase change, a clear increase of the susceptibility is seen upon annealing, together with a shift of T_c to higher temperatures. (b) The peak ESR intensity as a function of annealing temperature T_a measured at 4 K and at 12 K. (c) χT versus T above T_c. Below 100 K there is a drop in susceptibility and a departure from the Curie-like behavior seen above this temperature.

Because we do not expect any chemical or structural phase changes to occur as a result of a magnetic field at low temperatures, we deduce that the multiple line structure is due to the effect of magnetic domains in the sample having different local fields and hence different resonant transition frequencies in ESR. The pattern which is eventually fixed is determined by pinning of the ferromagnetic domain walls.

The ESR linewidth also shows rather significant changes in its temperature dependence for different T_a. In the single crystals we find a clear drop in linewidth at T_0, which was seen previously in powder samples as a small anomaly in ΔH_{pp}.[8] A major change in behavior occurs for the two highest temperatures, where the linewidth increases first below the ordering temperature T_0 (T_a = 100 °C) and then also above T_0 for T_a = 110 °C [Fig. 3(a)].

For $T_a < 100$ °C, the effects of T_a are less pronounced, but more systematic and we observe a clear shift to lower T_0 with increasing T_a. In Fig. 3(b) we plot the ESR line-

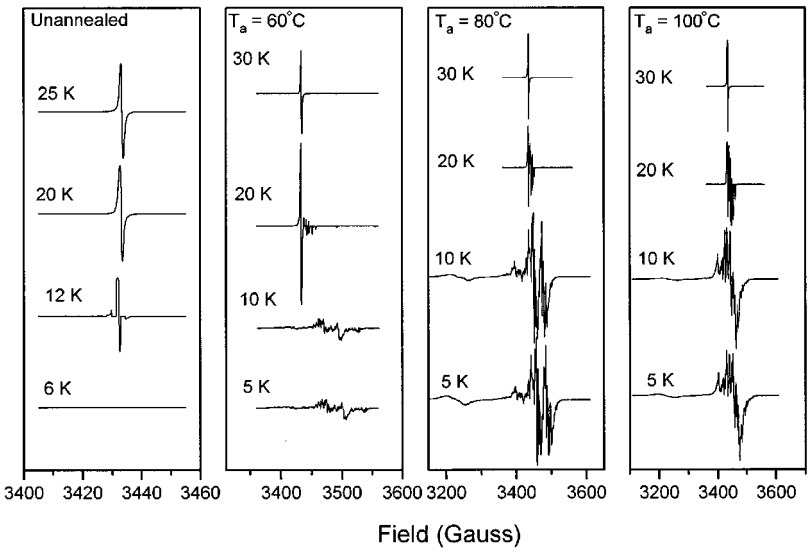

FIG. 2. The ESR spectra are shown measured at different temperatures shown for different T_a. The line shapes are strongly distorted below T_c most probably because of the different internal fields in different domains in the ferromagnetic state.

width ΔH_{pp} as a function of temperature near T_0 for different T_a. The shift in the ordering temperature T_0 with increasing T_a indicates that in the annealed samples rotational freezing occurs at a lower temperature than in unannealed samples. Having already established a link between the degree of ordering and the transition temperature,[8] it follows that the correlation between the magnetic critical temperature T_c and T_0 is probably not accidental.

In the unannealed single crystal samples of TDAE-C_{60} antiferromagnetic spin ordering is seen below 10 K and the ESR signal disappears completely at 6 K. Annealing at room temperature and above gives rise to a modified phase which results in an increase of the low-temperature phase spin susceptibility, suggesting that the heat treatment induces a structural phase transformation which favors a net ferromagnetic spin ordering at low temperatures with the appearance of three distinct phases: (1) a spin-glass phase, judging by the divergence in $\chi^{(3)}$ (Ref. 9) and the slow relaxation dynamics below this temperature[10] for $T<10$ K, (2) a ferromagnetic phase for $10<T<16$ K and, which was originally identified,

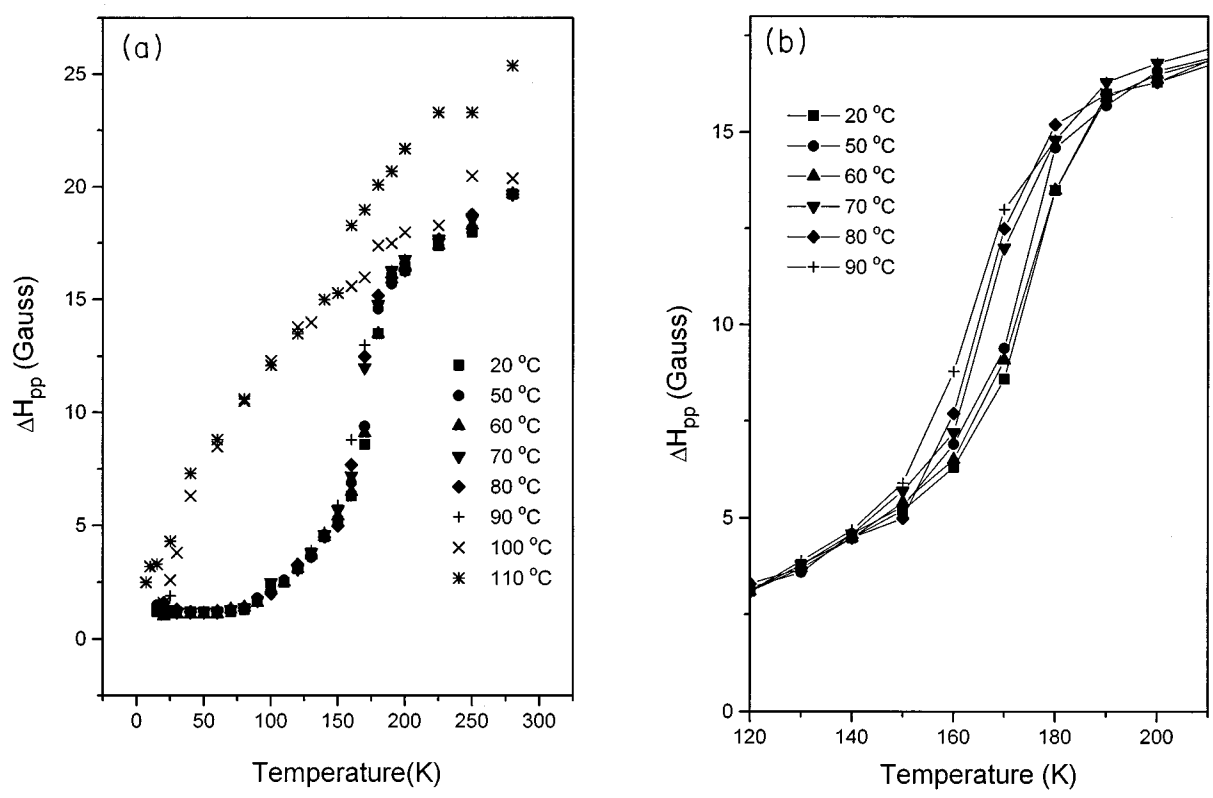

FIG. 3. (a) The ESR linewidth as a function of temperature for different annealing temperatures T_a. The expanded scale near the C_{60} ordering temperature is shown in (b) showing that T_0 systematically shifts downwards as T_a increases.

and (3) for increased annealing a phase, which is evident for $16 < T < 25$ K.

All three phases show enhanced susceptibility with respect to $\chi_{30\,\mathrm{K}}$. The fact that the ESR signal *intensity* above T_c is not affected by the annealing process means that the same number of spins are observed for all T_a and that it is unlikely that the signal is related to defects of any kind. The experiments show clearly that the ferromagnetic properties of TDAE-C_{60} are due to a phase which forms only upon either extended room-temperature annealing (typically for a few days or more) or after heating to temperatures in the range 50–100 C. The origin of the higher T_c's in some samples[3] has now been clarified by the presence of a new phase for $T < 24$ K.

The link between T_c and the C_{60} rotational ordering previously studied in powder quenching experiments[8] is confirmed in the crystals as a correlation between T_0 and the magnetic T_c. The drop in susceptibility below 100 K, which is interpreted as the onset of AFM correlations further lends support to the hypothesis of canted spin ferromagnetic ordering at low temperatures[6] which is enhanced by the structural deformations caused by annealing. Detailed structural studies of the material are underway and we hope that they will elucidate the interplay between the crystal structure and the magnetic properties in TDAE-[60]fullerene.

We wish to acknowledge valuable discussions with A. Zakhidov. This work was funded in part by the EC through the SELMAT Network.

[1] P.-M. Allemand *et al.*, Science **253**, 301 (1991).
[2] K. Tanaka *et al.*, Phys. Rev. B **47**, 7554 (1993).
[3] D. Mihailovic, K. Lutar, A. Hassanien, P. Cevc, and P. Venturini, Solid State Commun. **89**, 209 (1994).
[4] D. Mihailovic *et al.*, *Physics and Chemistry of Fullerenes and Derivatives*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (World Scientific, Singapore, 1995); R. Blinc *et al.*, *ibid.* p. 485.
[5] A. Suzuki, T. Suzuki, and Y. Maruyama, Solid State Commun. **96**, 253 (1995).
[6] R. Blinc *et al.*, Phys. Rev. Lett. **76**, 523 (1996).
[7] H. Kamimura, Philos. Mag. B **42**, 763 (1980).
[8] D. Mihailovic, D. Arcon, P. Venturini, R. Blinc, A. Omerzu, and P. Cevc, Science **268**, 400 (1995).
[9] K. Tanaka, T. Sato, K. Yoshizawa, K. Okahara, T. Tamabe, and M. Tokumoto, Chem. Phys. Lett. **237**, 123 (1995).
[10] R. Blinc, P. Cevc, D. Arcon, D. Mihailovic, and P. Venturini, Phys. Rev. B **50**, 13 051 (1994).