

C_{60} molecular configurations leading to ferromagnetic exchange interactions in TDAE* C_{60}

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The charge-transfer salt tetrakis(demethylamino)ethylene-fullerene (C_{60}) or TDAE* C_{60} is a rare exception among pure organic crystalline systems because it shows a transition to a ferromagnetic (FM) state with fully saturated $s = 1/2$ molecular spins at a respectable $T_c = 16$ K. In spite of extensive experimental and theoretical work in the last ten years, the origin of the ferromagnetism in TDAE* C_{60} has remained mysterious. To resolve this problem we have performed a comparative structural study of two different magnetic forms of TDAE* C_{60} crystals, one being magnetic and the other nonmagnetic, at low temperatures, fully correlating the structural properties — and particularly the inter-molecular orientations — with the magnetic properties. We have identified the relative orientations of C_{60} molecules along the c -axis as the primary variable controlling the ferromagnetic order parameter and have shown that both FM and low-temperature spin-glass-like ordering are possible in this material, depending on the orientational state of C_{60} molecules. Thus we have resolved the apparent contradictions posed by different macroscopic measurements and have opened the way to a microscopic understanding of p -electron FM exchange interactions.

A lot of effort have been made by many research groups to investigate the low-temperature state of crystals of purely organic molecular ferromagnet TDAE* C_{60} . However until recently, despite numerous studies of physical properties, the structural features of TDAE* C_{60} compound were not characterized by single crystal diffraction methods at low temperatures. The room temperature structure of TDAE* C_{60} has been determined on single crystal X -ray diffraction data. It was shown that the space group of symmetry is $C2/c$ with the c -parameter 19.992 Å and with four formula units per unit cell [1]. The low lattice symmetry suggests anisotropic interactions between constituent molecules, which might be subject to a variety of instabilities that lead to solid-state phase transitions. On the other hand, ^{13}C NMR studies have shown that in TDAE* C_{60} crystals, C_{60} molecules rotate rapidly at room temperature [2]. At lowering the temperature, rotation of C_{60} molecules gradually slows down and, although NMR data suggest that the rotational motion freezes out below about 150 K [2], the onset of the ferromagnetic (FM) state occurs at a significantly lower temperature, suggesting that stationary C_{60} molecules may be a necessary but not sufficient condition for the realization of a FM state.

It is well established that TDAE* C_{60} exists in two modifications, one being ferromagnetic and another paramagnetic (PM). Fresh single crystals show no FM behavior and are PM down to 2 K. On annealing at high temperature they transform into FM phase [3]. We have performed a comparative diffraction and structural studies of the two different forms of TDAE* C_{60} crystals, and have shown that both FM and low temperature spin-glass-like ordering are possible in this material, depending on the orientational state of C_{60} molecules.

1. Experimental

The diffusion method was used for crystal growth. The measurements were performed on a selected sample in the PM phase without annealing, and the results were compared with the data obtained on the same sample after transformation to the FM phase by annealing for 6 h at 70°C.

Single crystal X -ray diffraction studies were carried out using the Imaging Plate (IP) system (DIP 320S, MAC Science Co., Inc., monochromatized MoK_{α} radiation, $\lambda = 0.7107$ Å) equipped with a liquid helium cooling device. The standard oscillation and Weissenberg-type diffraction patterns were used to control the crystal structures of both samples (unannealed PM and annealed FM) at different temperatures. The crystal structure of TDAE* C_{60} was solved by direct method on data obtained from the unannealed crystal at 7 K and refined by least-squares method in $C2/c$ space group. The averaged structure of the annealed sample at 7 K was firstly refined by using the structural model of the unannealed crystal and then refined further by taking into account the presence of two orientations of the C_{60} molecules with half-occupation of the positions.

2. Results and discussion

All diffraction spots observed on X -ray oscillation patterns are indexed in $C2/c$ space group. The diffraction patterns have not revealed any essential changes of the structures in the temperature range 250–70 K, except that with decreasing temperature, some redistribution of reflection intensities occurred, and the total number of reflections on diffraction images decreased. Remarkable changes of the diffraction patterns are observed for both samples below 50 K. In Fig. 1 the temperature dependences of the lattice constants are presented which testify to the presence of noticeable changes

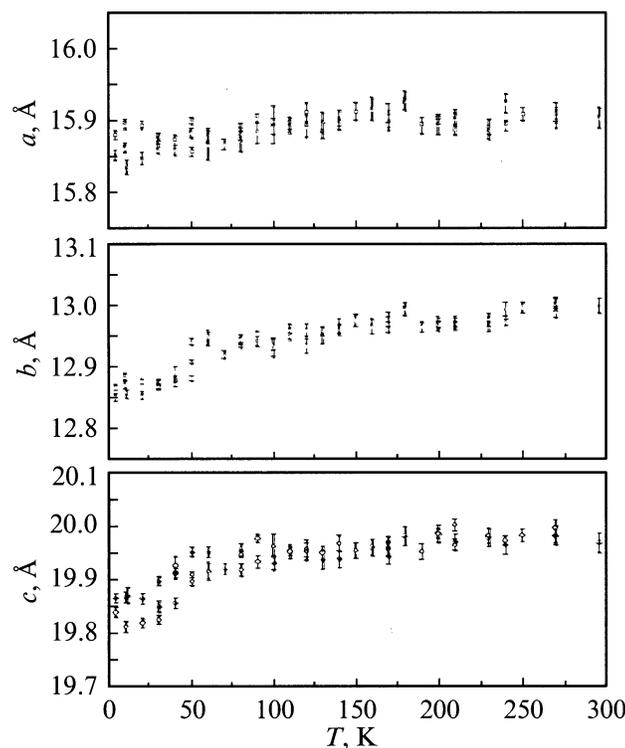


Figure 1. Temperature dependence of lattice constants for unannealed TDAE*C₆₀ crystal (open symbols) and after first cycle of annealing (filled symbols).

of the *b*- and the *c*-parameters of both crystals around 50 K. At this temperature the reflection intensities become higher, which results in essential increase of the total number of observed reflections. Characteristic for both crystals are the appearance of additional diffuse scatterings on X-ray oscillation patterns located between structural reflections and their transformations in a period of a few hours. Diffuse scatterings from the unannealed sample disappear as the sample is kept at low temperatures for 3–4 hrs. A distinctive feature of the annealed sample is that the diffuse lines on the diffraction patterns are transformed into additional diffraction spots whose positions coincide with those for a primitive lattice, i.e., testify to a violation of *C*-centricity of the lattice. These observations testify to the existence of some structural changes in both unannealed and annealed TDAE*C₆₀ crystals around 50 K and of crystal lattice tendency to transform from the *C*-centered to primitive one in the case of annealed samples. It should be noted that these changes are reversible, i.e., on heating the samples from low temperatures, the diffraction patterns of the high-temperature state are restored above 50 K.

The X-ray structure analysis of PM sample has revealed the presence of some degree of molecular orientational disorder of C₆₀ molecules due to their rotations along the threefold molecular axis. In the FM phase, the positions of the additional diffraction spots coincide with those of a primitive unit cell suggesting that the crystal transforms from

the *C*-centered structure to a primitive one. Our attempts to solve the structure in primitive unit cell failed and resulted in high values of *R*-factor (~ 0.16) and large divergence of temperature factors of individual atoms. Refinement of the structure in *C*-centered unit cell has also resulted in high *R*-factors (~ 0.20) but with the reasonable thermal ellipsoids of individual atoms of C₆₀ which testified to the presence of a high degree of orientational disorder of C₆₀ molecules. Further analysis of the obtained C₆₀ molecular structure has shown that in the FM sample the molecules are statistically distributed in two orientations related to each other by 60° rotation about their threefold axis. Using of this model, taking into account two molecules at the same positions with half occupation, in refinement procedure allowed us to essentially improve the *R*-factor and its final value was 0.066. Thus, in the FM phase, in addition to the conventional 120° rotations found in other C₆₀-based crystal structures, we find evidence of additional positions with C₆₀ rotated by $\pm 60^\circ$ about its threefold molecular axis, and in Figs. 2, *a, b* we show the crystal transformation mechanism from *C*-centered lattice (PM) to primitive type (FM). This leads to a set of new inter-fullerene contact configurations which are shown in Figs. 3, *a–d*. In the PM sample, the relative C₆₀ orientations are similar to those encountered in other C₆₀ solids, namely the 6–6 double bond (nearly) faces the center of the hexagon on the neighbouring molecule (Fig. 3, *a*), minimising the electronic overlap [4]. In the FM samples, on the other hand, a new orientation appears (II), which leads to three different possible relative orientations of the C₆₀s as shown in Figs. 3, *b–d*. In the first configuration, two C₆₀s of orientation I face each other, with the molecules slightly rotated about the *c*-axis, as shown in Fig. 3, *b*. In the second possible configuration, two C₆₀s with type II orientations are in contact as shown in Fig. 3, *c*. This orientation essentially corresponds to a slightly displaced PM configuration (Fig. 3, *a*), with the double bond displaced to the side. The third configuration involves two C₆₀s, with orientations I and II. In this case the double bond on one molecule approximately faces the center of the pentagon of its neighbour (Fig. 3, *d*). The II–II configuration can be eliminated from further considerations of the possible low-temperature equilibrium

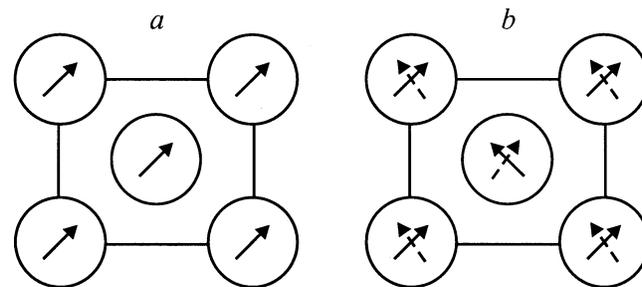


Figure 2. A schematic diagram of the C₆₀ molecular orientations in the *a, b* plain for: (a) the unannealed sample (PM phase); (b) the annealed sample (FM phase). Corresponding *C*-centered and primitive unit cells are shown.

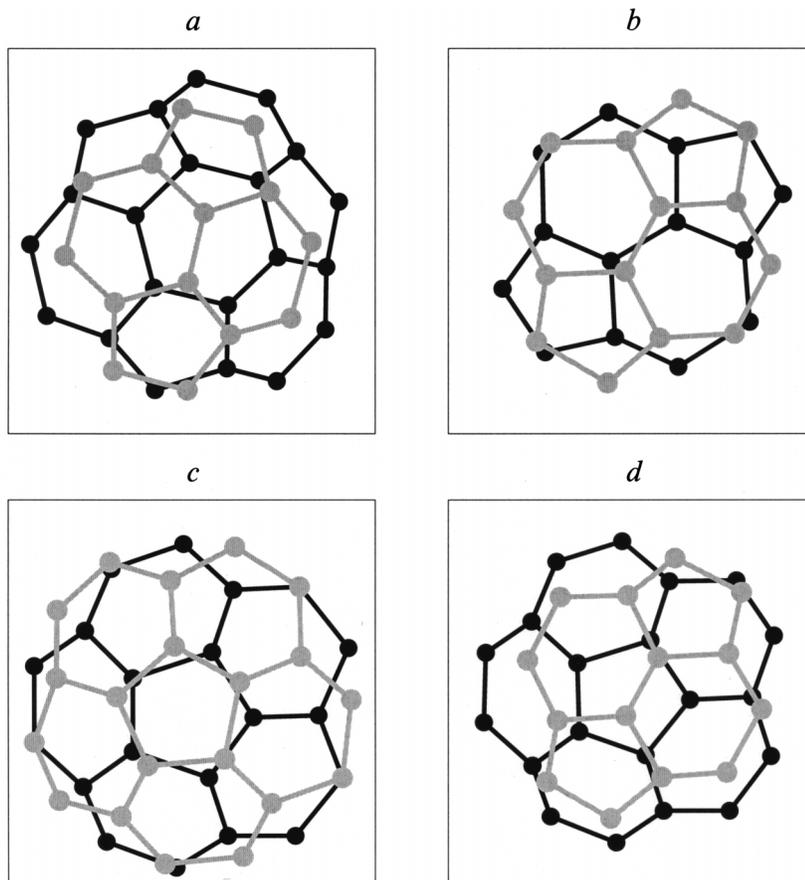


Figure 3. Projections of two neighboring C_{60} molecules of $TDAE \cdot C_{60}$ along the $[001]$ direction. (a) unannealed crystal (PM phase); (b) the I-I configuration of C_{60} molecules (annealed sample, FM phase); (c) the II-II configuration in FM phase; (d) mixed, I-II configuration in FM phase.

positions since the occurrence of two 6-6 double bonds in close proximity is clearly energetically very unfavourable. We can conclude therefore with reasonable confidence that only one of these configurations is compatible with the near 50% occupancy of configurations I and II and primitive unit cell determined from the structural refinement (Fig. 3, *d*).

We note that the observed arrangement associated with the FM state is in excellent agreement with calculations of the angular dependence of the effective FM exchange coupling strength J_{eff} [5], which also shows a minimum corresponding to the I-II configuration in Fig. 3, *d*, corresponding to the c -axis Euler angle $\gamma \approx 30^\circ$. Our consideration of the magnetic behavior of the system in terms of a hamiltonian for a non-interacting two-level system, in which the coupling between the configurational and magnetic degrees of freedom appears, shows [6] that both ferromagnetism and spin-glass-like ordering are possible in $TDAE \cdot C_{60}$ crystals, depending on the orientational state of C_{60} molecules.

In summary, low-temperature X-ray diffraction studies of $TDAE \cdot C_{60}$ single crystals show that some molecular reorientations and ordering take place in the structure below 50 K. We have determined low temperature crystal

structures for both unannealed and annealed samples, and have identified the relative orientations of C_{60} molecules in these structures along the c -axis of the crystals as the primary variable controlling the ferromagnetic order parameter. Analysis of the relative orientations shows that both FM and low-temperature spin-glass-like ordering are possible in $TDAE \cdot C_{60}$ compound, depending on the orientational state of C_{60} molecules.

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