

## C<sub>60</sub> molecular configurations leading to ferromagnetic exchange interactions in TDAE-C<sub>60</sub>

Bakhyt Narymbetov,<sup>1</sup> Ales Omerzu,<sup>2,3</sup> Victor V. Kabanov,<sup>2</sup> Madoka Tokumoto,<sup>1,3</sup>  
Hayao Kobayashi,<sup>1</sup> and Dragan Mihailovic<sup>2</sup>

<sup>1</sup>Institute for Molecular Science, Okazaki 444-8585, Japan,

<sup>2</sup>Institute Josef Stefan, Jamova 39, 1000 Ljubljana, Slovenia

<sup>3</sup>Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan

Fax: 81-298-61-5447, e-mail: madoka@etl.go.jp

The charge-transfer salt tetrakis(dimethylamino)ethylene-fullerene [C<sub>60</sub>] or TDAE-C<sub>60</sub> 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<sub>60</sub> has remained mysterious. To resolve this problem we have performed a comparative structural study of two different magnetic forms of TDAE-C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> molecules. Thus we have resolved the apparent contradictions posed by different macroscopic measurements and have opened the way to a microscopic understanding of  $\pi$ -electron FM exchange interactions.

Keywords: fullerene, C<sub>60</sub>, ferromagnet, exchange interaction, spin-glass

### 1. INTRODUCTION

The room temperature structure of ferromagnetic TDAE-C<sub>60</sub> crystal has been determined to be monoclinic ( $C2/c$ )<sup>1</sup> with two formula units per unit cell and rapidly rotating C<sub>60</sub> molecules.<sup>2</sup> As the temperature is lowered, the rotation gradually slows down and, although NMR data suggest that the rotational motion freezes out below about 150K, the onset of the ferromagnetic (FM) state occurs at a significantly lower temperature, suggesting that stationary C<sub>60</sub> molecules may be a necessary but not sufficient condition for the occurrence of a FM state. Fortunately, from the point of view of understanding the low-temperature magnetic interactions, TDAE-C<sub>60</sub> exists in two modifications, one ferromagnetic and one paramagnetic (PM). We have identified the relative orientations of C<sub>60</sub> molecules along the c-axis 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<sub>60</sub> molecules.

### 2. EXPERIMENTAL

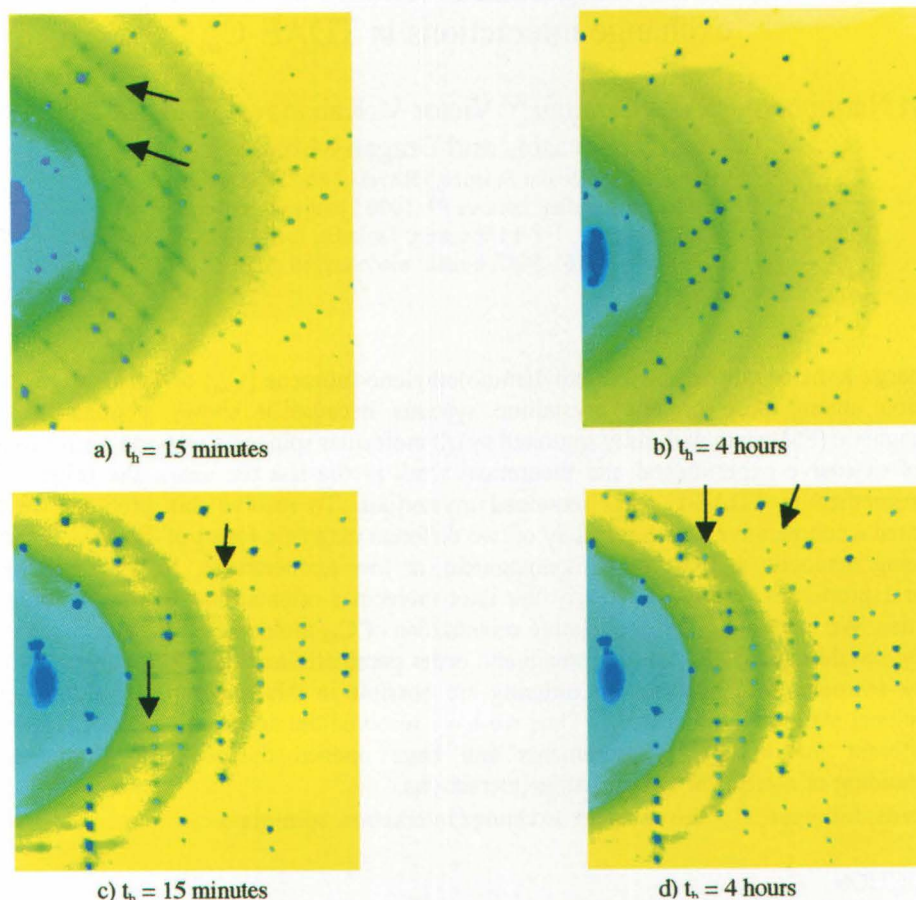
For crystal growth we have used the diffusion method. A solution of C<sub>60</sub> (2 mg ml<sup>-1</sup>, Hoechst gold grade) and a 3:1 mixture of toluene and TDAE (Aldrich, 95% pure) were poured into two compartments of a growth cell separated by fritted glass. The cell was carefully closed and thermostated at 8 °C for six months, whereupon crystals were extracted from it. The measurements were performed on a selected sample in the PM phase without annealing, and compared with

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 by using an Imaging Plate (IP) system (DIP 320S, MAC Science Co., Inc.) 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. Monochromated Mo K $\alpha$  radiation ( $\lambda=0.7107$  Å) was used in the X-ray experiments. The intensity data for structure analyses were collected by the Weissenberg type IP system. The crystal structure of TDAE-C<sub>60</sub> 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.<sup>3</sup> 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<sub>60</sub> molecules with half-occupation of the positions.

### 3. RESULTS AND DISCUSSION

On cooling below 50 K, remarkable changes are found in the X-ray diffraction patterns of both PM and FM samples with the appearance of new diffuse lines. Those lines gradually, in a period of a few hours, disappear for PM sample, while they transform into additional sharp diffraction spots for FM one, as the samples are kept at low temperature. The X-ray oscillation patterns are shown in Figs. 1a-d, where the

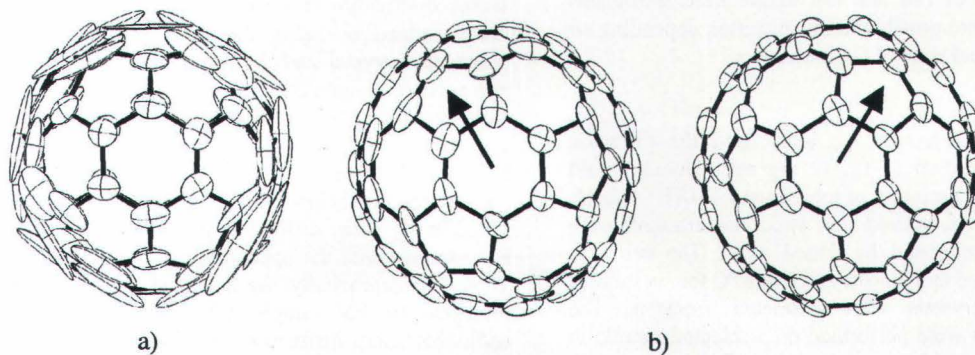


**Fig. 1.** The fragments of X-ray oscillation patterns of TDAE-C<sub>60</sub> single crystal: (a) and (b) – from the unannealed sample at 7 K; (c) and (d) – from the annealed sample at 20 K;  $t_h$  is a time of holding the samples at low temperatures before starting the measurements.

diffuse lines are indicated by arrows. (The data used here were obtained at 11 K and 7 K, on PM and FM samples, respectively, after a 4-hour cooling period.)

The X-ray structure analysis of PM sample has revealed the presence of some degree of molecular orientational disorder of the C<sub>60</sub> molecules due to their rotations along the threefold molecular axis.<sup>3</sup> 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 to be satisfactorily and resulted in high values of R-factor ( $\sim 0.16$ ) 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 ( $\sim 0.20$ ) but with the reasonable thermal ellipsoids of individual atoms of C<sub>60</sub> which testified to the presence of a high degree of orientational disorder of C<sub>60</sub> molecules (Fig. 2a).



**Fig. 2.** Molecular structures of C<sub>60</sub> in the annealed crystal of TDAE-C<sub>60</sub> in C<sub>2/c</sub> space group (ORTEPIII, 50% probability): a) averaged structure; b) obtained by refinement with taking into account two orientations of C<sub>60</sub> related by  $\pm 60^\circ$  rotations. The arrows denote relative orientations of C<sub>60</sub>.

Further analysis of the obtained  $C_{60}$  molecular structure has shown that in the FM sample the molecules are statistically distributed in two orientations related to each other by  $60^\circ$  rotation about their threefold axis. Use 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. The experimentally obtained molecular structures of  $C_{60}$ s in two orientations are shown in Fig. 2b).

Thus, in the FM phase, in addition to the conventional  $120^\circ$  rotations found in other  $C_{60}$ -based crystal structures, we find evidence of additional positions with  $C_{60}$  rotated by  $\pm 60^\circ$  about its threefold molecular axis. This leads to a set of new interfullerene contact configurations not previously observed in  $C_{60}$ -based solids.

The relative  $C_{60}$  contact configurations corresponding to the new low-temperature orientations, projected along the  $c$  axis (which is also the direction of closest contact between the  $C_{60}$ s) are shown in Figs. 3a-

d. In the PM sample, the relative  $C_{60}$  orientations are similar to those encountered in other  $C_{60}$  solids, namely the 6-6 double bond (nearly) faces the center of the hexagon on the neighbouring molecule (Fig. 3a), minimizing the electronic overlap<sup>4</sup>. In the FM samples on the other hand, a new orientation appears (II), which leads to three different possible relative orientations of the  $C_{60}$ s as shown in Figs. 3b-d. In the first configuration, two  $C_{60}$ s of orientation I face each other, with the molecules slightly rotated about the  $c$ -axis as shown in Fig. 3b. In the second possible configuration, two  $C_{60}$ s with type II orientations are in contact as shown in Fig. 3c. This orientation essentially corresponds to a slightly displaced PM configuration (Fig. 3a), with the double bond displaced to the side. The third configuration involves two  $C_{60}$ s, 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. 3d).

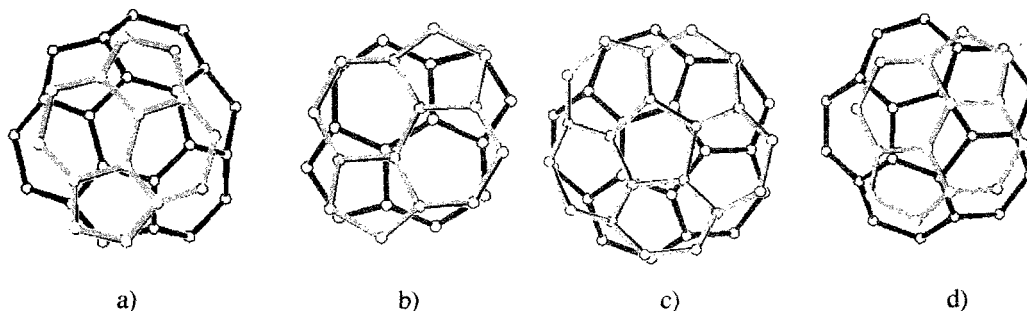


Fig. 3. Near-neighbour molecular environments of  $C_{60}$  viewed along the [001] direction. (a) for unannealed crystal; (b) for annealed crystal, the I-I configuration of  $C_{60}$  molecules; (c) for annealed crystal, the II-II configuration; (d) for annealed crystal, mixed, I-II configuration.

The II-II configuration can be eliminated from further considerations of the possible low-temperature equilibrium 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. 3d).

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  $J_{eff}$ <sup>6</sup>, which also shows a minimum corresponding to the I-II configuration in Fig. 3d, corresponding to the  $c$ -axis Euler angle  $\gamma \approx 30^\circ$ .

With two equilibrium configurations for the  $C_{60}$  molecules, we can describe the magnetic behaviour 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 because the exchange interaction  $J$  depends on the overlap between adjacent molecules along the  $c$  axis:

Here  $\Delta$  describes the energy difference between the two

$$H = - \sum_{i,j} J_{i,j}(x) \vec{S}_i \vec{S}_j + \Delta \sum_i \left( \sigma_i^z + \frac{1}{2} \right)$$

configurations (I-I and I-II in Fig. 3) and  $x$  is the relative concentration of configuration favouring a FM exchange interaction and in general  $J_{ij}$  is a function of  $\sigma^z$ . We assume that a spontaneous magnetization appears if the concentration  $x = \langle \sigma_i^z + \frac{1}{2} \rangle$  is larger than a certain critical value  $x_c$ . (This can be understood as a percolative threshold for the appearance of an infinite magnetic cluster.) Thus  $J_{ij}(x) = J$  if  $x > x_c$  and  $J_{ij}(x) = 0$  if  $x < x_c$ . We can write the free energy of the system as the sum of the magnetic energy, the configurational energy and an entropy term as:

$$F = -kT_c(x)M^2 / 2 + \Delta x + T[x \ln(x) + (1-x) \ln(1-x)]$$

where  $M$  is the magnetization and  $T_c$  depends on  $x$  via  $J$ . If the configurational energy  $\Delta$  is small (corresponding to the FM phase of TDAE-C<sub>60</sub>),  $T_c > -\Delta / \ln[x_c/(1-x_c)]$ , and the magnetic energy exceeds the configurational energy and a FM magnetic phase is stable below  $T_c$ . In the opposite case, (corresponding to the PM phase), the configurational energy is always greater than the magnetic energy, and a ferromagnetically ordered phase is unfavourable. Here it should be pointed out that a situation can arise whereby as  $T$  is lowered (below  $T_c$ ),  $x$  can fall below  $x_c$  which means that the magnetic energy can no longer overcome the configurational energy and a first order transition to a non-magnetic phase can take place at  $T < T_c$ . When this occurs, we expect that phase separation will take place and non-magnetic clusters will appear. The manifestation of this behaviour is a glass-like or superparamagnetic-like response, (depending on the size of the magnetic clusters) and would explain both the spin-glass-like behaviour and fall in the magnetisation (or susceptibility) observed in some experiments well below  $T_c$ .<sup>5</sup>

#### SUMMARY

We have identified the relative orientations of C<sub>60</sub> molecules in TDAE-C<sub>60</sub> 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<sub>60</sub> molecules.

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