Uniaxial Strain Study in Purely Organic Ferromagnet α -TDAE-C_{60} - Mechanism and Structure -

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Abstract

ESR has been carried out in ferromagnetic α -TDAE-C_{60} under uniaxial strain to study the mechanism and structure of ferromagnetism. Pressure is applied to a single crystal embedded in epoxy resin with a clamp type pressure cell. A preliminary study demonstrates that the uniaxial strain induces a change of the Curie temperature T_C, which depends on the crystal axis where the uniaxial strain applied. It is suggested that these preliminary results seem to be consistent with the Kawamoto's model (T. Kawamoto et al., J. Phys. Soc. Jpn. 70, 1892 (2001).) based on an intermolecular cooperative Jahn-Teller distortion. Further systematic studies will make clear the mechanism of the ferromagnetism.

Key words: Organic ferromagnetism, uniaxial strain, ESR, Curie temperature, TDAE-C60

1 Introduction

C_{60} mono-anion complexes with tetrakis(dimethylamino)ethylene (TDAE) are interesting system with the high Curie temperature of 16 K as a purely organic

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complex. An α-phase of TDAE-C_{60} has originally been synthesized as a ferromagnet in 1991 by Allemand et al. [1]. A peculiar feature of the α-phase is that the spins of $TDAE^{+}$ are not active because of dimerization. The second is a nonmagnetic complex, α'-phase with almost the same structure as the α-phase, which has been found in the course of study on the mechanism of the ferromagnetism [2]. The third is a β-phase reported more recently as a one dimensinally polymerized phase with [2+2] cycloadduct reaction from the α-phase under pressure $P \geq 10$ kbar, stable even after release of pressure [3]. An interesting feature of this phase is the revival of missing spins of $TDAE^{+}$ in the α-phase.

Understanding of the nature in these materials has remarkably progressed with single crystal samples [4] and an appropriate annealing procedure [5]. A lot of possible mechanisms proposed by the reports on powder samples are finally converged into the conclusion based on the single crystals that the nature is of Heisenberg-type ferromagnet with a very weak anisotropy field caused by the electronic dipolar interaction [6]. Recent models for the ferromagnetic interaction were developed mainly in terms of the orientational ordering of the Jahn-Teller orbitals of C_{60}^{-}. Sato and co-workers [7] have stressed that the positive direct exchange interaction dominates the ferromagnetism in α-TDAE-C_{60} and that the transition temperature could be governed by the Hubbard-type negative exchange interaction $\propto -t^2/U$ which depends on the orientation and partially cancels out the direct one. Here, t is the transfer integral and U the on-site Coulomb repulsion energy. This model requires special orientational ordering between the neighboring C_{60} molecules in one-dimensional chain along *c*-axis [8]. On the other hand, Kawamoto and co-workers [9,10] proposed the importance of the higher order exchange interaction between the neighboring Jahn-Teller orbitals perpendicular to each other, which is successful to reproduce the hydrostatic pressure dependence of the critical temperature [3].

In this report, the uniaxial strain was applied along *b*- and *c*-axis to investigate what kind of interaction dominates the ferromagnetism in α-TDAE-C_{60}, which helps to select the models applicable to this system. Since the present study is limited only to a single example for each applied direction, a full report will appear elsewhere.

2 Experimental

Single crystals are prepared with a diffusion technique [4]. Crystallographic axes are determined with X-ray analysis. An epoxy cylinder containing an aligned single crystal put in a coil is set in the Cu-Be clamp-type pressure cell. Magnitude of uniaxial strain is represented by a corresponding pressure applied to a zirconia piston with 6 mm ϕ. A resonance shift of ESR signal is measured at frequencies

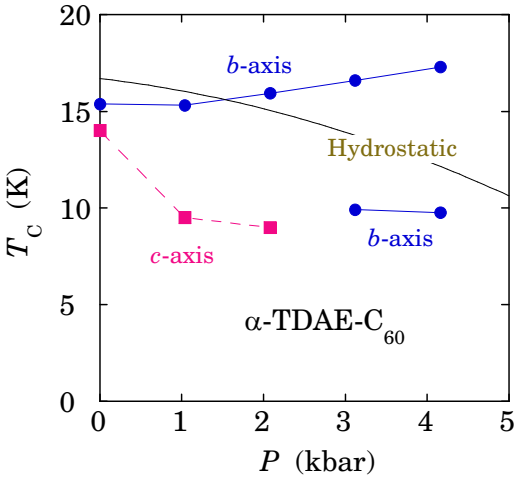

Fig. 1. T_C variations caused by uniaxial strain along *b*-axis [12] and *c*-axis, together with by hydrostatic pressure [3].

around 100 MHz [11], which is caused by a demagnetization field due to spontaneous magnetization. It is important to use the low resonance field of several tens of gauss, which does not produce a significant influence on the ferromagnetic transition.

3 Results and discussion

The transition temperature T_C is shown as functions of pressure applied along *b*- and *c*-axis together with hydrostatic pressure in Fig. 1, demonstrating anisotropic magnetic interactions. Characteristic features are summarized as follows. (1) The hydrostatic pressure suppresses T_C quadratically, $\propto 1\text{-}P^2$, which can be reproduced well with the orbital ordering model based on the intermolecular cooperative Jahn-Teller distortion (ICJT model) [3,9]. (2) The *b*-axis strain enhances T_C up to 17.5 K under 4 kbar of the applied pressure. (3) The c-axis strain strongly suppresses the ferromagnetism; 12 K in the minor part and 10 K for the main part of the sample under 1 kbar of the pressure. Interestingly, the *b*-axis strain also produces a fraction of the sample with the low T_C of about 10 K. The presence of the sub-phase with $T_C \approx 10$ K would relate to a freezing of the flipping between the Jahn-Teller distortion axes around 10 K [13].

To unveil the origin of these pressure dependences of T_C, let me discuss the ICJT mechanism of the high transition temperature. The main reason why the hydrostatic pressure suppresses T_C is a rapid increase of the negative exchange interaction $J \propto -t^2/U$ with pressure, which has been suppressed at ambient pressure because of the cancellation caused by the antiferro-orbital ordered structure with the Jahn-Teller orbitals of the *p*-like symmetry [3,9]. The important point of this

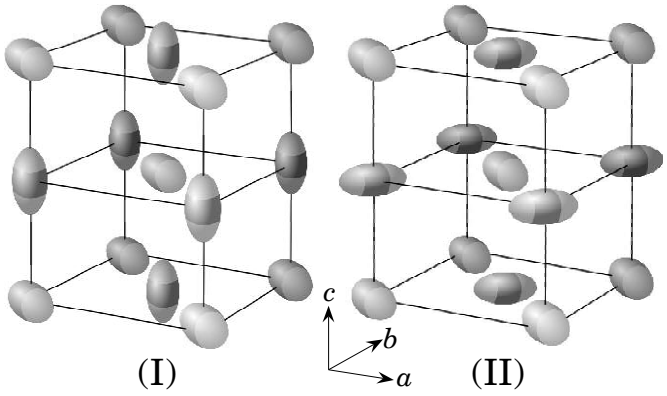

Fig. 2. Two possible antiferro-orbital ordered structures fulfill the requirement by the intermolecular Cooperative Jahn-Teller distortion model for the ferromagnetism of TDAE-C_{60}. For simplicity TDAE's are omitted. The angle β of the monoclinic structure is 93.4deg.

model is such a cancellation of the antiferromagnetic interaction, giving rise to the much less antiferromagnetic than the ferromagnetic interactions coming from the fourth-order perturbation of *t*. The pressure deteriorates the cancellation, resulting in the suppression of T_C.

The *b*-axis strain dependence in Fig. 1 requires not only to preserve the cancellation, but also to enhance the ferromagnetic interaction, which can be expected from the increased transfer integrals between neighboring orbitals by pressure. In contrast, the result of the *c*-axis strain suggests its critical role in strongly disturbing the growth of the cooperative Jahn-Teller distortion, giving rise to the rapid suppression of T_C demonstrated in Fig. 1.

What a structural model do these results meet? There are at least two ways to realize the antiferro-orbital ordered structure, as demonstrated in Fig. 2; (I) the axes of rugby ball structure for the Jahn-Teller distorted C_{60}'s are alternately arranged (parallel and perpendicular) along the *c*-axis, 1D chain of C_{60}'s, and (II) it aligns always perpendicular to the *c*-axis and partially fulfills the antiferro-orbital structure in the *a*-*b* plane with different *a* and *b* lattice constants. The former structure, (I) is preferred from the reasons that the *b*-axis strain never disturbs the antiferro-orbital ordering in the case (I) and that in the case (II) the *b*-axis strain directly spoils the symmetry required for the cancellation of the antiferromagnetic interaction. This should be consistent with the *c*-axis strain case, too. By virtue of the soft van der Waals coupling, the pressure as small as 1 kbar can easily produce the strain of the order of 0.01 Å between C_{60}'s along *c*-axis, comparable with the expected Jahn-Teller distortion [9]. This suggests that the *c*-axis strain prevents from forming the structure (I) with T_C=16 K, but forces to attain the structure (II) with the lower T_C than the structure (I). Note the possibility of the structure (II) to have $T_C \approx 10$ K corresponding to the second phase in Fig. 1. Therefore, if it were

confirmed that the result with the *c*-axis strain was reproducible, and not an artifact caused by a sample degradation suspected because of the somewhat lower T_C than 16 K, the ICJT model would be well consistent with the present uniaxial strain results. Further study and analysis will appear elsewhere.

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