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Theoretical Study of Pressure Effect on TDAE-C_{60}

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We have theoretically studied pressure effects on molecular ferromagnet C_{60} complexes with tetrakis (dimethylamino) ethylene (TDAE), particularly the pressure-induced depression of the Curie temperature. The observed behavior is well simulated by our model which is based on a charge transfer induced intramolecular Jahn-Teller distortion and an intermolecular cooperative Jahn-Teller interaction. We emphasize that the theoretical simulation is carried out with reasonable parameters known for C_{60}^- complexes. It is concluded that the enhancement of the crystal field at C_{60} sites due to increasing pressure causes the depression of Curie temperature.

KEYWORDS: TDAE-C_{60}, orbital ordering, ferromagnetism, pressure effect

In 1991, Allemand *et al.* reported the ferromagnetic behavior of tetrakis (dimethylamino) ethylene (TDAE)-C_{60} with $T_C = 16$ K.[1)] It has been attracting many scientists due to its having the highest Curie temperature among pure organic molecular ferromagnets and its unusual magnetism. Allemand *et al.* proposed 'soft ferromagnetism' with no hysteresis in the M–H curve.[1)] Tanaka *et al.*[2)] and Blinc *et al.*[3)] have observed behaviors like a 'superparamagnetism' of spin clusters consisting of hundreds of spins in the magnetization and the proton nuclear magnetic resonance (NMR) measurements below T_C, respectively. Venturini *et al.* suggested 'spin glass model' from analysis of the electron spin resonance (ESR) lineshape.[4)] In 1997, we proposed a model for clarifying the properties of this system.[5)] This model is introduced in order to clarify the origin of intermolecular ferromagnetic coupling between C_{60}'s, and it is based on the orbital ordering of unpaired electrons on C_{60}'s due to the adjacent alignment of the Jahn-Teller distorted C_{60}'s. The spin-glass-like behavior and superparamagnetism of the spin clusters may also be explained qualitatively in this framework.[6)]

Very recently, Mizoguchi *et al.* observed the pressure dependence of the Curie temperature (T_C) in TDAE-C_{60}, as shown in Fig. 1.[7)] It appears that T_C is parabolically depressed upon the application of pressure. The purpose of this paper is to provide a quantitative understanding of this behavior in the framework of the model mentioned above. It should be noted that the observed value is simulated quantitatively with the reasonable parameters known for the C_{60} molecule.

First, our orbital ordering model is briefly introduced. With respect to this model, the magnetic interaction between local spins on C_{60}'s are discussed. In TDAE-C_{60}, both TDAE and C_{60} are regarded to have an unpaired electron since one electron transfers from TDAE to C_{60}.

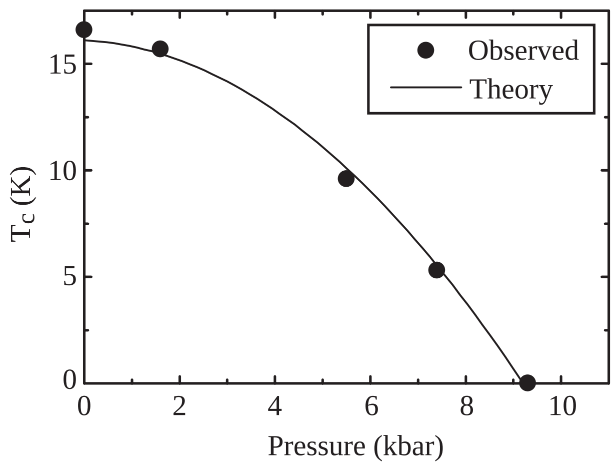

Fig. 1. Pressure dependence of Curie temperature in TDAE-C_{60}. Closed circles represent observed value. Solid line indicates the simulation result based on the orbital ordering model.

However, it has not yet been clarified whether or not bare spin moments exist on TDAE molecules. On the other hand, unpaired electrons on C_{60} molecules are considered to play a crucial role in bulk ferromagnetism. Figure 2 shows an example of a molecular arrangement which is likely to cause three-dimensional ferromagnetic order.

The lowest unoccupied orbitals (LUMO) of C_{60} in I_h are triply degenerated with t_{1u} symmetry. When degenerated orbitals are partially occupied, the molecule is distorted in order to stabilize one orbital, which is known as the Jahn-Teller (JT) effect. We assume the D_{2h} structure for the C_{60}^- anion in this study. We performed a geometrical optimization of single a C_{60}^- anion in a previous study. The optimized structure resembles a rugby ball whose elongated axis lies along one of the three symmetry axes in the D_{2h} structure. The atomic displacement from the ideal icosahedral is small, i.e., 0.01 Å at most.

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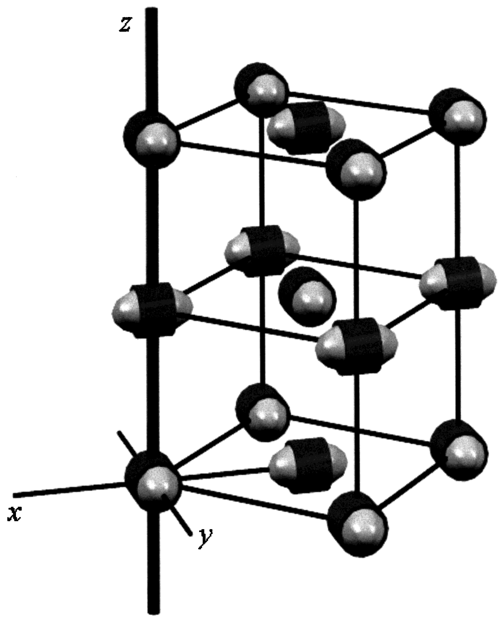

Fig. 2. An example of possible JT-distorted crystal structures which are likely to cause three-dimensional ferromagnetic ordering. Elongated spheres indicate JT-distorted C_{60}'s and thick lines express one-dimensional chains. Note that distortion is exaggerated. In this structure the elongated axes of C_{60}'s are perpendicular to each other for the interchain nearest neighbor C_{60}'s as well as for the intrachain nearest neighbor C_{60}'s. The gray belts around C_{60}'s schematically represent the distribution of a unpaired electron.

The three t_{1u} states, LUMO_x, LUMO_y, and LUMO_z, which are degenerate LUMO's of C_{60} with I_h symmetry before the charge-transfer, each split into three states. If the elongated axis is the x-axis, LUMO_x has the lowest energy, and the other two orbitals, LUMO_y and LUMO_z, with higher energies are almost degenerate. It should be noted that the charge density is not spherical but takes large values along a belt surrounding the elongated axis (see Fig. 2).

Magnetic interactions between distorted molecules depend on their alignment. We concluded that the ferromagnetism is realized in the structure illustrated in Fig. 2 due to periodic molecular distortion.[5] In a C_{60}^- array along the c-axis in this structure, the elongated axes of two nearest C_{60}^-'s are perpendicular to each other. In this case, the orbitals of unpaired electrons align in an alternating manner, for example, LUMO_x, LUMO_y, LUMO_x, ... Such a system is called an orbital ordering system and an interaction acting to favor an alternating alignment is called a cooperative JT interaction. It is known that the ferromagnetic coupling between neighbors is preferred in such a orbital ordering system. It should be noted that the intermolecular transfer occurs only between the same kind of orbitals if the crystal field at the C_{60}^-'s has perfectly orthorhombic symmetry. It is a key point in favoring the intermolecular ferromagnetic interaction.

It is expected that the magnetic interactions between C_{60}'s lying along the c-axis are the strongest among the intermolecular magnetic interactions, because their distance is shorter than that in the ab-plane by 0.3 Å. Electrical transport along the c-axis is also observed about 10 times larger than that along the a-axis.[8] In this paper, we assume that the system is quasi-one-dimensional along the c-axis. The extended Hubbard Hamiltonian for the one-dimensional chain with LUMO_x's and LUMO_y's as the basis functions is shown as follows:

$$\begin{aligned} H = {} & \frac{\Delta}{2}\sum_{i\mu\sigma}(-1)^i n_{ix\sigma} + (-1)^{i+1} n_{iy\sigma} \\ & + t_{\mathrm{g}}\sum_{i\sigma}(c^\dagger_{ix\sigma}c_{i+1y\sigma} + c^\dagger_{iy\sigma}c_{i+1x\sigma} + \mathrm{h.c.}) \\ & + t_\ell\sum_{i\sigma}(c^\dagger_{ix\sigma}c_{i+1x\sigma} + c^\dagger_{iy\sigma}c_{i+1y\sigma} + \mathrm{h.c.}) \\ & + \sum_{i\mu} U n_{i\mu\uparrow}n_{i\mu\downarrow} \\ & + \sum_{i\mu\neq\nu\sigma\sigma'}(U - J\delta_{\sigma\sigma'})n_{i\mu\sigma}n_{i\nu\sigma'} \\ & + \sum_{i\mu\nu\sigma} J c^\dagger_{i\mu\sigma}c^\dagger_{i\nu\bar{\sigma}}c_{i\mu\bar{\sigma}}c_{i\nu\sigma}, \end{aligned} \tag{1}$$

where $c^\dagger_{i\mu\sigma}(c_{i\mu\sigma})$ represents the creation (annihilation) operator of μ-orbital with σ-spin at the i-th C_{60} molecule and $n_{i\mu\sigma}$ is its number operator. The lines represent the orbital energy, the intermolecular transfer energy between different orbitals, that between the same orbitals, the intra-orbital Coulomb energy, the inter-orbital Coulomb energy and the S_zS_z part of the exchange interaction, and the S_+S_- part of exchange interaction, respectively. The intra-orbital and inter-orbital Coulomb energies are assumed to be the same. LUMO_z's are not included because they are not occupied on any C_{60}'s in the molecular alignment shown in Fig 2. It should be noted that a small transfer energy exists even between different orbitals related to the third term because of a small deviation from the perfect orthorhombic symmetry of the crystal.

We suggest that the unpaired electron can be regarded to exist locally on each molecule since the Coulomb energy is sufficiently larger than the transfer energy. The energies t_ℓ and U are estimated to be about 0.05 eV and 0.6 eV, respectively.[9,10] Experimentally, the Curie-Weiss like behavior is also observed in the magnetic susceptibility even under the application of pressure.[7] For a localized system, the Hamiltonian (1) can be transformed into an extended Heisenberg Hamiltonian.

$$H = -J_1\sum_i \boldsymbol{S}_i\cdot\boldsymbol{S}_{i+1} - J_2\sum_i \boldsymbol{S}_i\cdot\boldsymbol{S}_{i+2}, \tag{2}$$

$$J_1 = -\frac{4}{U}t_g^2 + \frac{4t_\ell^2 J}{(U+\Delta)^2}, \tag{3}$$

$$J_2 = \frac{-4t_\ell^4}{U(U+\Delta)^2}, \tag{4}$$

where J_1 and J_2 represent intrachain exchange interactions between nearest neighbors and second nearest neighbors, respectively. The magnitude is calculated from a second order perturbation of the transfer energy and the maximum terms of a fourth order perturbation.

Details of the transformation are reported for another orbital ordering system, K_2CuF_4.[11] From this Hamiltonian, the Curie temperature T_C is derived with mean field theory as

$$T_C^{MF} = \frac{2}{3k} S(S+1) J(0) \tag{5}$$

$$= \frac{1}{k}(J_1 + J_2 + 2J_3), \tag{6}$$

where we assume the existence of interchain ferromagnetic couplings J_3, and k represents the Boltzmann factor. S $(= 1/2)$ and $J(0)$ $(\equiv 2J_1 + 2J_2 + 4J_3)$ indicate the value of a single spin and the $q = 0$ component of the Fourier transformation of exchange interactions $J(q)$, respectively. It should be noted that the mean field theory generally overestimates the Curie temperature T_C. Here we derive the pressure dependence of TDAE-C_{60} based on Hamiltonian (2). It is assumed that the transfer energy linearly depends on pressure as $t_a = t_a^0 + pt'_a$ $(a = \ell, g)$. To describe the difference of the Curie temperature derived by mean field theory T_C^{MF} from that observed experimentally T_C^{Ex} , a reduction parameter α is introduced as $T_C^{Ex} = \alpha T_C^{MF}$.

The solid line shown in Fig. 1 represents the simulation result of the pressure dependence of T_C with $t_\ell^0 = 0.065$ eV, $t_g^0 = 0.0035$ eV, $t'_\ell = 0.001$ eV/kbar, $t'_g = 0.00243$ eV/kbar, $U = 0.55$ eV, $J = 0.09$ eV, $\Delta = 0.15$ eV, $J_3 = 3$ K, and $\alpha = 0.75$. It is found that the theoretical result simulates the observation well. We emphasize that the parameters used in the simulation are reasonable. The intramolecular parameters U, J, and Δ are almost the same as the values estimated by Suzuki and Nakao.[10] The report of ab-initio calculations for fcc-C_{60} by Saito and Oshiyama is used for the determination of the intermolecular transfer t_ℓ^0.[9] The width of the LUMO band is calculated to be about 0.5 eV in fcc-C_{60} and the intermolecular transfer energy can be roughly estimated as 0.04 eV. It is in good agreement with our parameter t_ℓ^0. We have no quantitative information of the intermolecular interaction J_3. It is considered that 3 K may be appropriate for the value of J_3 because the interchain distance is also longer than the intrachain molecular distance by about 0.3 Å. In conclusion, the parameters used in our simulation is found to be quite reasonable for TDAE-C_{60}. Tanaka *et al.* calculated the dependence of the intermolecular magnetic coupling between C_{60}'s on their orientation with a semi-empirical approach without the JT distortion.[12] They reported that even the strongest ferromagnetic coupling is very small, about 0.03 K. Therefore, it is very important that the high T_C of this material can be explained by the JT distortion of C_{60}'s with the reasonable parameters.

Figure 3 shows the pressure dependence of the intermolecular exchange interactions J_1 and J_2 as well as their sum. It is found that the negative parabolic shape in the pressure dependence of T_C is almost determined by J_1 although its magnitude is weakened by the antiferromagnetic interaction J_2. The negative dependence of T_C on the application of pressure is formed by a coefficient of the parabolic term in the pressure dependence of J_1 shown in eq. (3). With the parameters used in the simulation, it is expected that T_C is decreased by applying pressure in the case of $t'_\ell < 12t'_g$. The parameters for the simulation satisfy this condition. The crystal structure of TDAE-C_{60} is slightly different from the orthorhombic one although the C_{60} molecule has complete orthorhombic symmetry. Therefore, the enhancement of the crystal field at C_{60}'s site due to the application of pressure makes t_g significantly larger. In fact, it is suggested from an ab initio calculation that t'_g and t'_ℓ have the same order in another orbital ordering system, K_2CuF_4, in which local crystal field at the Cu site also has a lower symmetry than that of JT distorted molecules.[11]

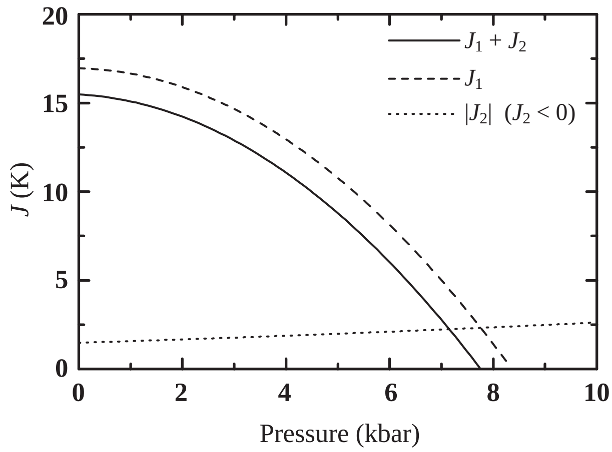

Fig. 3. Pressure dependence of exchange interaction between intrachain nearest neighbors J_1, between second nearest neighbors J_2, and their sum.

A helical magnetism can be realized if the second neighbor coupling J_2 is sufficiently large.[11] We examine the stability of ferromagnetism against the helical magnetism. According to the mean field theory, the magnetic order with the wave number Q is realized if the Q-component is the largest in the Fourier form of an exchange interaction $J(q)$. In the case of $J_1/|J_2| > 4$, a ferromagnetic ordering is the most stable. Otherwise a helical magnetism is realized. It is evident in Fig. 3 that helical ordering is expected above 6 kbar. It is not clarified at the present time whether the magnetic ordering at $p = 7.4$ kbar is ferromagnetic or helical ordering with a long wavelength.

Let us discuss the dimensionality of TDAE-C_{60} and the origin of the interchain ferromagnetic interaction. We assume the one-dimensionality of this system in our model. It is also indicated experimentally with the measurement of the electrical conductivity.[8] Although Blinc *et al.* reported that TDAE-C_{60} is the isotropic ferromagnet in the temperature dependence of the spin-wave resonance in ESR,[13] the temperature dependence of the magnetization of the quasi-one dimensional system with $J_1/J_3 \sim 6$ is not significantly different from that of an isotropic system. Therefore, the assumption of quasi-one-dimensionality does not conflict with the observations by Blinc *et al.* The origin of interchain ferromagnetic coupling can be explained with the orbital ordering structure shown in Fig. 2. In this structure, the ferromagnetic ordering is favored not only inside the chain but also interchain coupling.[5] The quasi-one dimensionality can be explained with this mechanism since the magnitude of magnetic interaction depends on intermolecular transfer energy. The interchain distance is about 0.3 Å longer than the intrachain molecular distance. Another model is the superexchange mechanism by way of TDAE molecules. The status of unpaired electrons on $TDAE^+$ cations is an open question but it is likely that their molecular spins form pairs.[14] The reason for electron pairing on TDAE should be clarified in order to discuss the interchain magnetic interaction.

In this letter, we assumed that one two-fold axis is parallel to the *c*-axis. However, the constraint for realizing the ferromagnetic interaction along the *c*-axis is looser in reality. The suppression of the electronic transfer interaction between singly occupied molecular orbitals of neighboring C_{60} anions is the most important. Consequently, our model requires that the elongated axes of neighboring C_{60}'s be oriented perpendicular or parallel to the *c*-axis and also perpendicular to each other. A structure proposed with X-ray analysis[15] is feasible with this constraint.

Recently, additional collateral evidence has been reported. Kambe *et al.* also observed a structural phase transition at 180 K with X-ray diffraction measurements and they have reported the possibility of cooperative JT ordering in the low-temperature phase.[16] Clear experimental evidence of D_{2h} JT distortion in monoanion-C_{60} was also reported on a single crystal of a model compound of monoanion-C_{60}, $[As(C_6H_5)_4]_2C_{60}Cl$.[17] Furthermore, in another C_{60}^- compound, an X-ray analysis also suggests the stabilization of the static JT distortion by symmetry lowering of the crystal caused by rotational ordering.[18] For complete confirmation of our model, we urge to perform the neutron scattering observation. In neutron scattering measurements, we can obtain information on the spin density. The spin distribution on C_{60}^-'s is not spherical but takes large values along the belt around the elongated axis, as shown in Fig. 2. It has a much larger spatial difference than the lattice distortion.

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1) P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Grüner and J. D. Thompson: Science **253** (1991) 301.
2) K. Tanaka, A. A. Zakhidov, K. Yoshizawa, K. Okahara, T. Yamabe, K. Yakushi, K. Kikuchi, S. Suzuki, I. Ikemoto and Y. Achiba: Phys. Rev. B **47** (1993) 7554.
3) R. Blinc, J. Dolinšek, D. Arčon, D. Mihailovič and P. Venturini: Solid State Commun. **89** (1994) 487.
4) P. Venturini, D. Mihailovič, R. Blinc, P. Cevc, J. Dolinšek, D. Abramic, B. Zalar, H. Oshio, P.-M. Allemand, A. Hirsch and F. Wudl: Int. J. Mod. Phys. B **6** (1992) 3947.
5) T. Kawamoto: Solid State Commun. **101** (1997) 231.
6) T. Kawamoto and N. Suzuki: Synth. Met. **86** (1997) 2387.
7) K. Mizoguchi, M Machino, H. Sakamoto, T. Kawamoto, M. Tokumoto, A. Omerzu and D. Mihailovič: Phys. Rev. B **63** (2001) 140417.
8) A. Omerzu, D. Mihailovič, N. Biskup, O. Milat and S. Tomic: Synth. Met. **85** (1997) 1723.
9) S. Saito and A. Oshiyama: Phys. Rev. Lett. **66** (1991) 2637.
10) S. Suzuki and K. Nakao: Phys. Rev. B **52** (1995) 14206.
11) T. Kawamoto and N. Suzuki: J. Phys. Soc. Jpn. **66** (1997) 2487.
12) K. Tanaka, Y. Asai, T. Sato, T. Kuga, T. Yamabe and M. Tokumoto: Chem. Phys. Lett. **259** (1996) 574.
13) R. Blinc, P. Cevc, D. Arčon, A. Omerzu, M. Mehring, S. Knorr, A. Grupp, A.-L. Barra and G. Chouteau: Phys. Rev. B **58** (1998) 14416.
14) K. I. Pokhodnia, J. Papavassiliou, P. Umek, A. Omerzu and D. Mihailovič: J. Chem. Phys. **110** (1999) 3606.
15) B. Narymbetov, A. Omerzu, V. V. Kabanov, M. Tokumoto, H. Kobayashi and D. Mihailovič: Nature **407** (2000) 883.
16) T. Kambe, Y. Nogami and K. Oshima: Phys. Rev. B **61** (2000) 862.
17) W. Bietsch, J. Bao, J. Lüdecke and S. van Smaalen: Chem. Phys. Lett. **324** (2000) 37.
18) P. Launois, R. Moret, N.-R. de Souza, J. A. Azamar-Barrios and A. Pénicaud: Eur. Phys. J. B **15** (2000) 445.