

Electronic state of an organic molecular magnet: Soft x-ray spectroscopy study of α -TDAE-C₆₀ single crystal

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Soft x-ray photoelectron spectroscopy was performed for α -TDAE-C₆₀ single crystal. A C 1s spectrum with a shakeup satellite of TDAE-C₆₀ is very similar to that of C₆₀ when we shift the energy, indicating a charge transfer to the C₆₀ site. A comparison of a N 1s spectrum with theoretical calculations indicates that TDAE mainly consists of the TDAE⁺ state. The valence-band spectrum near the Fermi edge also suggests a charge transfer from the TDAE to the C₆₀ cage. Based on these results we propose a modified model for the charge transfer: the charge states of C₆₀⁻ and TDAE⁺, and the dimer formation along the *c* axis between the TDAE⁺ states.

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Heisenberg ferromagnetism is normally not expected in organic compounds, but a few pure organic ferromagnets have been discovered so far.^{1,2} The mechanism of organic magnetism and its electronic state are of general interest. TDAE-C₆₀ (TDAE: tetrakis-dimethylamino-ethylene) is a first fullerene ferromagnetic, which has a transition temperature of $T_C = 16$ K.³ The lowest-unoccupied molecular orbitals (LUMOs) of C₆₀ are triply degenerated. If the orbitals are partially occupied, the orbital level splitting known as the Jahn-Teller distortion is caused and a beltlike unpaired spin distribution is expected.^{4,5} TDAE-C₆₀ has an elongated monoclinic structure along the *c* axis.^{6,7} This asymmetry provides highly anisotropic bands, where electrons are delocalized. The origin of the ferromagnetism at T_C is believed to be the orientational ordering of these delocalized states of C₆₀ ions.^{5,8} An electron-spin resonance (ESR) study showed anisotropy of the magnetism: ferromagnetic behavior along the *a* and *b* axes and weak antiferromagnetic correlation in the *c* axis.⁹

The recent profound understanding of the detailed physical properties of TDAE-C₆₀ may be owing to two facts. One is the discovery of two polymorphs phases: ferromagnetic α and nonmagnetic α' phases. Thermal annealing changes the phase from α' to α .^{7,10} Another is the development of a large size single crystal of the order of 1 mm³ with high quality.^{7,11} A structural difference at low temperature in the two polymorphs was reported, as was the anisotropy of the ESR parameters. The saturated magnetization of an α -phase single crystal was found to be $\sim 0.9 \pm 0.1 \mu_B$ per C₆₀, which is significantly higher than that in powder sample, indicating a C₆₀⁻ state, where μ_B is the Bohr magneton.¹¹ Recently antiferromagnetic order at $T_C = 7$ K was found for an α' -phase single crystal.¹²

The charge transfer from TDAE to the carbon cage plays an essential role in the appearance of organic ferromagnetism because C₆₀ itself never shows a magnetic character.² The electronic state of TDAE-C₆₀ has been measured by several methods. The ESR showed only one line (ESR silent), although we expect two single lines if the chemical state is in TDAE⁺C₆₀⁻.¹³ Then the electronic states of C₆₀⁻ without spin in the TDAE site was assigned. Singlet-spin pairing

due to the dimerization of neighboring TDAE molecules was also suggested.¹⁴ Raman spectroscopies indicated a one-electron charge transfer.^{15,16} An infrared spectroscopy study was compared with the calculations and also concluded in TDAE⁺ cations.¹⁷ In the measurements of nuclear magnetic resonance (NMR)¹⁸ and the electron-spin echo modulation,¹⁹ however, they found little spin density in the TDAE nitrogen site. Two lines in the NMR spectra were also observed, leading to an assignment of two charge states of TDAE⁰ and TDAE²⁺.²⁰ Photoelectron spectroscopy (PES) could measure the electronic states directly. To the best of our knowledge, only one PES study was performed for TDAE-C₆₀ so far.²¹ They suggested that TDAE charge states are both 0 and 2+ with almost equivalent intensity from the N 1s spectrum.

Theoretically, the total energy takes the lowest value for the charge states of 1- or 2- of C₆₀ in the open-shell restricted Hartree-Fock calculation, including the configuration interaction.²² A band calculation within a tight-binding approximation showed neutral, singly, and doubly charged TDAE molecules,²³ while the local density approximation (LDA) calculation for α' -TDAE-C₆₀ showed a different result in the monovalent charge state.²⁴ They considered that the difference in these calculations originated from the different crystal structure.

Thus both experimental and theoretical works are still in contradiction. The exact electronic structure of the TDAE-C₆₀ remains an unresolved puzzle. Therefore, measuring the electronic states of both TDAE and C₆₀, especially for a single crystal, is crucial to understand the magnetism of TDAE-C₆₀. In this Rapid Communication we report on the soft x-ray PES for an α -TDAE-C₆₀ single crystal. We measured N 1s, C 1s, and valence-band spectra. The binding energy of N 1s was compared with the theoretical calculations to confirm the charge state of TDAE. Our results suggest a modified model for the charge transfer in TDAE-C₆₀.

Single crystals of TDAE-C₆₀ were prepared by the diffusion method with dimensions of $\sim 1.0 \times 0.5 \times 1.5$ mm³.^{7,11} Soft x-ray PES was performed at the BL17SU undulator beamline in SPring-8 with a hemispherical electron analyzer SCIENTA

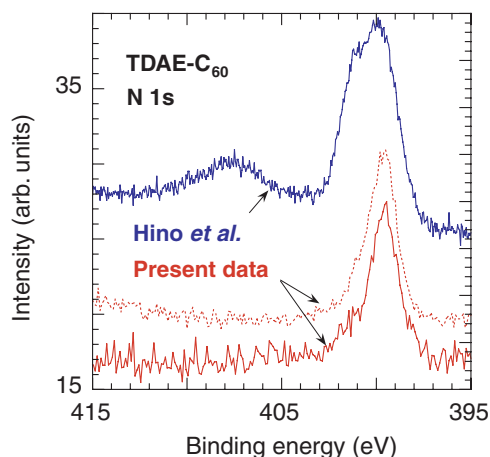


FIG. 1. (Color online) N 1s photoelectron spectra at $h\nu = 797$ eV for fractured (solid line) and nonfractured (dotted line) crystals. The data for the crushed powder sample by Hino *et al.* is also shown for comparison (Ref. 21).

SES 2002 at room temperature. The crystal was fractured before the measurement. The resolution (δE) was estimated to be ~ 0.12 – 0.3 eV from the Au Fermi edge, where E is the emitted electron energy. During the measurement the vacuum pressure was kept at less than 5×10^{-8} Pa. The incident photon energy ($h\nu$) was 797 eV throughout the measurements. We checked the x-ray irradiation effect after the above measurement by confirming the reproducibility of the C 1s spectrum.

Figure 1 shows N 1s photoelectron spectra ($\delta E \simeq 0.3$ eV) with the data by Hino *et al.* for comparison.²¹ There is a clear difference between the two spectra. Hino *et al.* showed that the N 1s spectrum consists of two intense peaks at $E_b = 399.8$ and 401.3 eV, and the intensity of the peak at $E_b = 401.3$ eV decreased with x-ray irradiation, where E_b is the electron binding energy. Based on the calculations of the chemical shifts for TDAE⁰, TDAE⁺, and TDAE²⁺ with the semiempirical complete neglect of differential overlap (CNDO/2) method, they considered the charge separation reaction of TDAE⁺ + TDAE⁺ \rightarrow TDAE⁰ + TDAE²⁺, suggesting that there are two charge states of TDAE; TDAE⁰ and TDAE²⁺ equivalently coexist rather than TDAE⁺ alone.

Our spectrum consists of two peaks at 399.6 and 401.5 eV, but the fit shows that the intensity of the peak at 401.5 eV is much smaller than the main peak, only $\sim 12\%$ of that at 399.6 eV. Our result indicates that the TDAE consists of mainly one charge state with a small fraction of the satellite component. Furthermore, the peak at 408 eV observed by Hino *et al.* disappears in our spectrum. A similar N 1s spectrum in the fractured crystal sample is observed even in the nonfractured crystal, as shown in Fig. 1. The difference between our measurement and the result by Hino *et al.* may originate from the difference in the samples: Our sample is an α -phase single crystal, while the sample of Hino *et al.* was a crushed powder film on the Au substrate and the phase was unknown.

The C 1s spectrum is shown in Fig. 2(a). The spectrum of the C₆₀ film showed a peak at $E_b = 284.7$ eV. The spectrum for TDAE-C₆₀ shows a peak at 285.2 eV with a full width at half maximum of 1.1 eV. The enlargement for the shakeup satellite part ($\delta E \simeq 0.12$ eV) is shown in Fig. 2(b). Notably, the

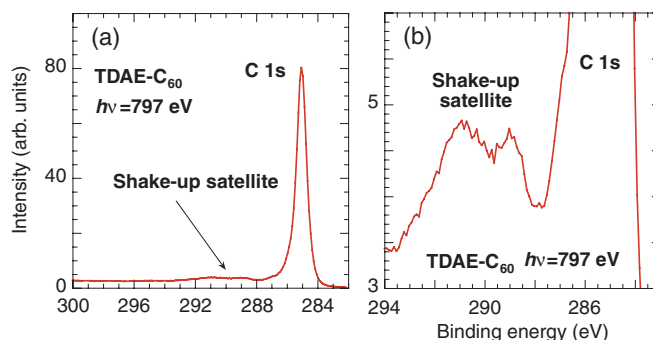


FIG. 2. (Color online) (a) C 1s photoelectron spectra. (b) Enlargement of the shakeup satellite part. Note that the spectrum of the C₆₀ film is shifted by 0.4 eV.

spectrum of the C₆₀ film is shifted by 0.4 eV to a higher binding energy, indicating a charge transfer from TDAE to C₆₀. Our shakeup satellite of TDAE-C₆₀ resembles that of the C₆₀ film, showing little effect of TDAE on the C 1s satellite structure of TDAE-C₆₀. The satellite structure does not correspond well to the LDA calculation for C₆₀.²⁵

Figure 3(a) shows the valence-band spectrum ($\delta E \simeq 0.12$ eV) of the TDAE-C₆₀ crystal. The solid line in Fig. 3(b) corresponds to a five-point smoothed curve. Hino *et al.*²¹ measured the ultraviolet photoelectron spectrum (UPS) by using a He I line ($h\nu = 21.2$ eV) with a resolution of 0.3 eV. In our case the incident photon energy of 797 eV is much higher, more bulk sensitive, and may cause an increase in the relative intensity of σ components at a higher binding energy due to the difference in the cross sections. Our result reproduces well the spectrum of Hino *et al.* overall, with better resolution in a wide energy range. The shift of each peak (A' – D') from the corresponding peak of C₆₀ seems to be small in our spectrum, although Hino *et al.* observed slight shift of the peaks of A – D .²¹ A detailed study of the valence spectrum in a narrow range around the Fermi edge was performed as shown in Fig. 3(b). We observe a small peak N' at $E_b \sim 1.2$ eV, corresponding to the peak N in the UPS. This peak may originate from a charge transfer from the TDAE to the carbon cage.

TDAE is a strong electron donor and the electrons in the highest-occupied molecular orbital of TDAE easily transfer to the acceptor of the LUMO of the C₆₀ carbon cage.

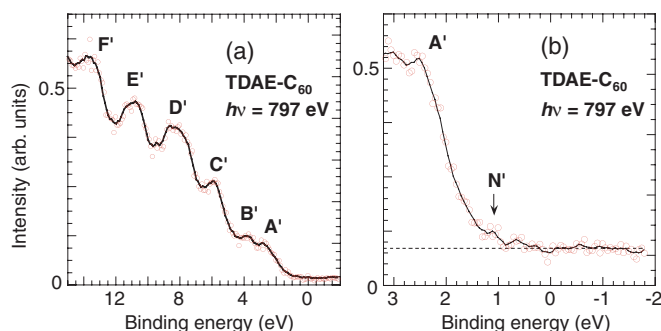


FIG. 3. (Color online) (a) Valence spectra of a TDAE-C₆₀ crystal. (b) Enlargement of the spectra around the Fermi edge. The open circles are experimental data. The solid line for the present data corresponds to five-point smoothed curve. The dashed line corresponds to the mean value of the background above the Fermi edge.

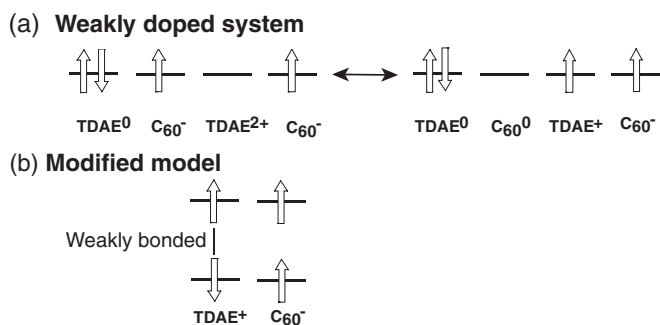


FIG. 4. Models of the charge transfer. (a) Mixing of configurations of a weakly doped system (Ref. 26). (b) Our proposed model. TDAE⁺ ions are weakly bonded, forming a dimer.

Here we consider the previously proposed model for the charge transfer. Theoretically, Sato *et al.*²⁶ considered the model of charge transfer corresponding to a weakly doped system, as shown in Fig. 4(a): $\text{TDAE}^0\text{-C}_{60}^- \leftrightarrow \text{TDAE}^{2+}\text{-C}_{60}^- \leftrightarrow \text{TDAE}^0\text{-C}_{60}^0 \leftrightarrow \text{TDAE}^+\text{-C}_{60}^-$. They concluded that the electronic state of the TDAE-C₆₀ was in a weakly doped system of $\text{TDAE}^{+\delta}\text{-C}_{60}^- \leftrightarrow \text{TDAE}^{2+\delta}\text{-C}_{60}^-$ ($0 \leq \delta \leq 1$). However, this model was based on previous PES results.

We perform the Δ self-consistent field method calculations of N 1s and C 1s binding energies of TDAE and its ionized states by using the Amsterdam density functional program (2008.01),²⁷ with the combination of the Perdew-Wang functional (1986) for exchange and the Perdew-Wang functional (1991) for correlation under relativistic correction.²⁸ Thus the binding energies of N 1s and C 1s of TDAE are calculated for each TDAE charge state. It is noted that this method is more reliable compared to the semiempirical method of CNDO/2. We used the Slater-type orbital basis set of TZ2P. The molecular structure is optimized using the GAUSSIAN03 code²⁹ at the level of HF/6-31G(d). The band calculation of TDAE-C₆₀ of Ref. 26 indicates an extremely flat band of the TDAE. It signifies that the electronic structure of the TDAE in the crystal is almost the same as that of the isolated molecule. This indicates that the calculations of E_b for the isolated TDAE molecule are also valid for those for the TDAE in the crystal. First we confirm the reliability of these calculations for molecules such as NH₃, N₂O, and NF₃, with the result that the differences of E_b with experimental values³⁰ are within 0.4 eV. The binding energies of TDAE⁰, TDAE⁺, and TDAE²⁺ are estimated to be 404.14, 408.72, and 413.92 eV, respectively. The relative difference in the binding energies (δE_b) of TDAE⁺ to C 1s is 113.89 eV. We also made a similar calculation for the structure obtained by x-ray diffraction.⁷ The above binding energies are estimated to be 403.96, 408.69, and 413.85 eV, respectively, and δE_b of TDAE⁺ is 113.47 eV. These values agree well with the ones above. The δE_b of the main N 1s peak in our measurement is 114.9 eV. Thus the main N 1s peak in our measurement could be assigned to the TDAE⁺ state. The δE_b of the weak satellite N 1s peak is ~ 116.8 eV, and we cannot assign the satellite peak to TDAE²⁺.

As described above, the magnetization measurement for the crystal¹¹ indicates that most of the C₆₀ of TDAE-C₆₀ is in the singly charged C₆₀⁻ state. Our observation of the valence-band spectrum and the shift of the C 1s peak from that in C₆₀ indicates the occurrence of a charge transfer from TDAE to

C₆₀. The N 1s spectrum shows a nearly singly charged state of TDAE⁺. These results suggest that TDAE-C₆₀ mainly consists of TDAE⁺ and C₆₀⁻ states. The above theoretical estimations seem to also support these results for the single crystal. Here we note that in TDAE-C₇₀ toluene, ESR shows a g factor of 2.0028, which is comparable to that of TDAE⁺, indicating the dimer formation of C₇₀⁻ ions, and the ESR signal is obtained mainly from TDAE⁺ ions.³¹ In TDAE-C₆₀ the g factor is nearly 2.000, which is also near the value of C₆₀⁻.⁷ Thus from the analogy to TDAE-C₇₀ toluene, we propose a modified model that the TDAE may be in the TDAE⁺ state and the TDAE⁺ ions are weakly bonded along the c axis, as shown in Fig. 4(b).^{9,14} A possible explanation for the ESR signal of only one line is a singlet spin formation of the TDAE⁺ dimer—one is in an up-spin state and another is in the down-spin state—resulting in a cancelling out of the TDAE spins. In an α -TDAE-C₆₀ single crystal the structural transition occurs at 170 K, the TDAE molecules shift along the b and c axes, and the TDAE molecules stack alternatively along the c axis. The inter-TDAE spacings along the c axis are $0.5c$ at $T \geq 170$ K and $0.508c$ at $T \leq 170$ K, where c is the lattice constant.⁷ We consider that the TDAE dimers are formed at room temperature and the dimer formation may be strengthened at low temperature.⁷

Finally we note that the existence of a weak satellite in the N 1s spectrum indicates another electronic state of TDAE-C₆₀. The E_b of the satellite of N 1s spectrum is higher than that of TDAE⁺, and thus it should correspond to a higher charge state of TDAE. However, the TDAE²⁺ state is ruled out as discussed above. These facts may suggest a possible mixed valence state, TDAE^{1+\delta} ($0 < \delta < 1$), of class III in the Robin-Day classification, as observed in the Creutz-Taube complex. As an example, the E_b of N 1s in TDAE^{1.5+} is estimated to be 411.22 eV. The δE_b between TDAE^{1.5+} and TDAE⁺ is ~ 2.5 eV, which is comparable to the experimental value of 1.9 eV, assuming the weak satellite originated by the TDAE^{1.5+} state. Note that in class III, TDAE⁺ and TDAE²⁺ do not coexist. We assume a superposition of the states between TDAE⁺ and TDAE²⁺, resulting in a state of TDAE^{1.5+}. But further theoretical studies are required to clarify whether such a superposed configuration is stable.

In summary, we successfully measured the photoelectron spectra for the pure organic magnet TDAE-C₆₀ crystal. The measurements for the single crystal shows a difference in the N 1s spectrum compared to the results for the powder sample measured previously. In TDAE-C₆₀ the crystal structure affects the physical properties and thus we believe that it is essential to measure the electronic state for the single crystal. We clarify that the main charge transfer process is one electron transfer from TDAE to C₆₀, resulting in a state of TDAE⁺ and C₆₀⁻. The TDAE⁺ charge state is also supported by the theoretical calculations. In this Rapid Communication we propose a modified charge transfer model for the origin of molecular magnetism in TDAE-C₆₀. The TDAE⁺ ions may be weakly bonded along the c axis, forming a TDAE⁺ dimer.

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