Ab initio study on geometrical structures of the TTTA molecular crystal

Miou Furuya\textsuperscript{a}, Yoshiyuki Kawazoe\textsuperscript{b}, Kaoru Ohno\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a}Department of Physics, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
\textsuperscript{b}Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8501, Japan

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Abstract

The crystal made of organic radical, 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA), exhibits a large first-order magnetic and structural phase transition between a paramagnetic high-temperature (HT) phase and a diamagnetic low-temperature (LT) phase, with a surprisingly wide thermal hysteresis loop over room temperature. We investigate theoretically the crystal structures for the two phases by means of the ab initio structural optimization method based on the local density approximation. We present necessary and sufficient atomic coordinates in this paper. The resulting structures are in good agreement with the recent X-ray diffraction experiment. In the HT phase, uniform one-dimensional stacking of the radical molecule appears, while, in the LT phase, strong dimerization along the stacking direction appears.

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1. Introduction

Recently, magnetic and optical properties of molecule-based materials have been studied extensively. In particular, crystals composed of organic radical molecules have attracted great attention due to their potential in future molecular magnetic and optical devices. They are also expected to play a major role in novel materials research. An organic radical TTTA (1,3,5-trithia-2,4,6-triazapentalenyl) molecule consists of three sulfur, three nitrogen and two carbon atoms. It has a flat heterocyclic triazayl structure, and its crystal has two structurally stable phases in both high temperature (HT) and low temperature (LT) regions. The crystal structure of the HT phase was originally reported by Wolmershauser [1]. More recently, Fujita and Awaga [2,3] found that the TTTA crystal exhibits a first-order phase transition between a paramagnetic HT phase and a diamagnetic LT phase, with a surprisingly wide thermal hysteresis loop over the room temperature. They also determined the crystal structures for the both phases by means of the X-ray diffraction experiment. Recently, Matsuzaki et al. [4] and Takeda et al. [5] reported that a photo-induced magnetic phase transition takes place in this system and its magnetic properties may be optically controlled by light irradiation.

In the present paper, to confirm all atomic coordinates obtained previously by the X-ray diffraction experiment [3], we perform the ab initio structural optimization for both phases of TTTA crystal. We present necessary and sufficient atomic coordinates determined by the present theory. Next, to study the mechanism of this phase transition between the HT and LT phases, we carry out the electronic structure calculations for the both phases of the TTTA crystal. We argue that the phase transition can be regarded as a kind of Peierls transition.

2. Calculation and results

In order to check the crystallography data determined experimentally [3], we have carried out the structural optimization for the both phases of the TTTA crystal in the following way. Assuming the crystal symmetries, lattice constants and angles of the unit cell (Tables 1 and 2), we optimized all atomic positions inside the unit cell (four molecules exist in the unit cell) by means of the standard
ab initio ultrasoft-pseudopotential approach (Vienna ab initio simulation package, VASP [7]) using 36 special k points and the 26 Ry cutoff energy for the plane waves (PW’s), whereas a conjugate-gradient algorithm is used for geometrical relaxation into a local energy minimum. The resulting structures are shown in Figs. 1 and 2, respectively, for the HT and LT phases. Several interatomic distances are given in Tables 3 and 4. Calculated atomic coordinates are also listed in Tables 1 and 2, respectively, for the HT and LT phases. From these data, we confirmed that the position data determined experimentally [3] are reproduced within the error of 0.09 Å.

Here we briefly summarize the characteristics of the crystal structures for the HT and LT phases. There is a crucial difference in molecular packing in the two phases: the molecular planes are all parallel in the HT phase (Fig. 1), whereas the unit cell of the LT phase includes two

**Table 1**

| Crystal system | Monoclinic |
|----------------|------------|
| Space group    | P2_1/c     |
| a (Å)          | 9.4420 a   |
| b (Å)          | 3.7110 a   |
| c (Å)          | 15.062 a   |
| α (°)          | 90         |
| β (°)          | 104.630 a  |
| γ (°)          | 90         |
| V (Å³)         | 510.6 a    |
| Z              | 4          |

| Atom | x | y | z |
|------|---|---|---|
| C1   | 0.31224 | 0.75325 | 0.40480 |
| C2   | 0.17140 | 0.89798 | 0.36027 |
| N1   | 0.30915 | 0.82671 | 0.23616 |
| N2   | 0.08479 | 0.95223 | 0.41582 |
| N3   | 0.33152 | 0.69811 | 0.49419 |
| S1   | 0.14689 | 0.96843 | 0.24456 |
| S2   | 0.42365 | 0.68444 | 0.33208 |
| S3   | 0.17859 | 0.82505 | 0.51904 |

Ref. [3].

**Table 2**

| Crystal system | Triclinic |
|----------------|-----------|
| Space group    | P1        |
| a (Å)          | 7.5310 a  |
| b (Å)          | 10.0230 a |
| c (Å)          | 7.0240 a  |
| α (°)          | 100.598 a |
| β (°)          | 96.978 a  |
| γ (°)          | 77.638 a  |
| V (Å³)         | 507.2 a   |
| Z              | 4         |

| Atom | x | y | z |
|------|---|---|---|
| C1   | 0.86186 | 0.14149 | 0.71448 |
| C2   | 0.78264 | 0.28220 | 0.69369 |
| C3   | 0.80274 | 0.20930 | 0.19967 |
| C4   | 0.72314 | 0.35081 | 0.18193 |
| N1   | 0.51699 | 0.15397 | 0.64867 |
| N2   | 0.90145 | 0.36535 | 0.71811 |
| N3   | 0.04194 | 0.11889 | 0.75371 |
| N4   | 0.46126 | 0.21857 | 0.10826 |
| N5   | 0.84229 | 0.43455 | 0.21163 |
| N6   | 0.98147 | 0.18861 | 0.24407 |
| S1   | 0.70272 | 0.03643 | 0.68878 |
| S2   | 0.54798 | 0.31156 | 0.64602 |
| S3   | 0.10410 | 0.26917 | 0.76548 |
| S4   | 0.48984 | 0.37933 | 0.12193 |
| S5   | 0.64539 | 0.10160 | 0.15128 |
| S6   | 0.04493 | 0.33728 | 0.25719 |

Ref. [3].

Fig. 1. Geometrical structure of the HT phase of the TTTA crystal in which the regular packing of molecules appear along the stacking direction, i.e. along the b axis. Selected bond lengths (in units of Å) are listed in Table 3.

Fig. 2. Geometrical structure in the LT phase of the TTTA molecules in which the Peierls distortion along the stacking direction appears. Selected bond lengths (in units of Å) are listed in Table 4.
molecular-plane orientations (Fig. 2). In addition, uniform one-dimensional (1D) stacking of the radical molecules appear in the HT phase, while, in the LT phase, strong dimerization along the stacking direction appears. The existence of the volume and symmetry changes guarantee that the phase transition between HT and LT phases is first order.

For the electronic structure calculations [8], we used the all-electron mixed basis approach [9,10] using both PW’s and atomic orbitals (AO’s) as a basis set. Here all the core and valence AO’s are determined numerically within the non-overlapping atomic spheres by a standard atomic program in Herman–Slillman’s framework [11] with the logarithmic radial mesh. For the LDA exchange-correlation functional, we adopt the Ceperley–Alder fitting form [12]. For the present system, we use 208 numerical AO’s and 2135 (in the HT phase) or 2401 (in the LT phase) PW’s corresponding to a 12 Ry cutoff energy using 33 special $k$ points. The resulting valence band structures are shown in Figs. 4 and 5, respectively, for the HT and LT phases. Fermi surface (FS) exists in the HT phase (Fig. 4), although nearly 0.8 eV band gap appear in the LT phase (Fig. 5).

3. Discussions

In view of Figs. 1 and 2, one can recognize that the structural phase transition from the $P2_1/c$ (in the HT phase) to the $P1$ (in the LT phase) symmetries takes place due to the Jahn–Teller effect, because the static Jahn–Teller effect occurs when the highest occupied level is degenerate and occupied partially by electrons. In such cases, the crystal is distorted spontaneously in order to gain the energy by removing the degeneracy. In the present case, a TTTA molecule is radical and its highest occupied molecular orbital (shown in Fig. 3) is half filled. Therefore, FS exists in the HT phase (Fig. 4), although nearly 0.8 eV band gap appear in the LT phase (Fig. 5).

Table 3

| Distance       | Value 1 | Value 2 |
|----------------|---------|---------|
| N5–S2          | 3.089   |         |
| N2–N5          | 3.089   |         |
| N5′–S2         | 4.891   |         |
| N1–N6          | 5.570   |         |

The labels correspond to those indicated in Fig. 1.

Table 4

| Distance       | Value 1 | Value 2 |
|----------------|---------|---------|
| N1–N4          | 3.925   |         |
| N2–S12         | 3.062   |         |
| S1–S4          | 3.906   |         |
| S2–S4          | 3.784   |         |
| S2–S5′         | 3.349   |         |
| S9–S12         | 3.714   |         |

The labels correspond to those indicated in Fig. 2.

Distortion is characterized by the dimerization of molecules and the corresponding phase transition can be regarded as a kind of Peierls transition (due to the quasi-1D response of the three-dimensional electronic system) between the HT phase having the uniform 1D stacking and the dimerized LT phase. This explanation is the analogy of the well-known 1D organic radical conductor, TTF–TCNQ [13]. In general, the Peierls instability in 1D electron systems is induced by the electron–phonon interaction, which can develop due to the characteristic topology of the FS with a perfect nesting. A 1D metal is unstable towards static periodic lattice distortions below the Peierls temperature because of
the nesting property of the FS. Such a distortion opens an energy gap at the new zone boundary, and thus the total energy decreases. In the LT phase, because of the dimerization of TTTA molecules, all two-fold degenerated levels including core levels split into two separate levels and band gap appears (Fig. 5). This is the origin of the closed-shell diamagnetism (for an insulator) in the LT phase. The HT phase is, however, not optically a metal in experiments. To solve this discrepancy, it is necessary to perform at least a calculation based on the local spin density approximation instead of the LDA. Such a calculation is, however, beyond the scope of the present paper and will be reported elsewhere.

4. Summary

In this paper, we have investigated the recently found TTTA molecular crystal by means of the ab initio methods. First, we have performed the structural optimization of the crystal and found good agreement with the experimental data for the atomic positions inside the unit cell. Secondly, we have demonstrated theoretically that the phase transition from the HT phase to the LT phase can be regarded as a kind of Peierls transition of the quasi-1D system that has a half-filled conduction band.

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References

[1] G. Wolmershauser, R. Johann, 1,3,5-Trithia-2,4,6-triazapentalenyl—a stable sulfur–nitrogen radical, Angew. Chem., Int. Ed. Engl. 28 (1989) 920–921.
[2] W. Fujita, K. Awaga, Room-temperature magnetic bistability in organic radical crystals, Science 286 (1999) 261–262.
[3] W. Fujita, A. Awaga, H. Matsuzaki, H. Okamoto, Room-temperature magnetic bistability in organic radical crystals: paramagnetic–diamagnetic phase transition in 1,3,5-trithia-2,4,6-triazapentalenyl, Phys. Rev. B 65 (2002) 064434.
[4] H. Matsuzaki, W. Fujita, K. Awaga, H. Okamoto, Photoinduced phase transition in an organic radical crystal with room-temperature optical and magnetic bistability, Phys. Rev. Lett. 91 (2003) 017403.
[5] J. Takeda, M. Imae, O. Hanado, S. Kurita, M. Furuya, K. Ohno, T. Kodaia, Photoinduced magnetic phase transition in an organic radical 1,3,5-trithia-2,4,6-triazapentalenyl crystal at room temperature, Chem. Phys. Lett. 378 (2003) 456–462.
[6] G.D. McManus, J.M. Rawson, N. Feeder, J. van Duijn, E.J.L. McInnes, J.J. Novoa, R. Burriel, F. Palacio, P. Oliete, Synthesis, crystal structures, electronic structure and magnetic behaviour of the trithiatrazapentalenyl radical, C_{3}S_{3}N_{3}, J. Mater. Chem. 11 (2001) 1992–2003.
[7] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1996) 15–50; G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169–11186.
[8] M. Furuya, K. Ohno, T. Morisato, Y. Kawazoe, J. Takeda, Band structure calculation of TTTA crystal, Trans. MRSJ 28 (3) (2003) 911–914.
[9] K. Ohno, Y. Maruyama, Y. Esfarjani, N. Kawazoe, R. Sato, T. Hatakeyama, M. Hirata, Ab initio molecular dynamics simulations for collision between C_{60} and alkali-metal ions: a possibility of Li@C_{60}, Phys. Rev. Lett. 76 (1996) 3590–3593.
[10] K. Ohno, F. Marui, S.G. Louie, Magnetic susceptibility of semiconductors by an all-electron first-principles approach, Phys. Rev. B 56 (1997) 1009–1012.
[11] F. Herman, S. Skillman, Atomic Structure Calculations, Prentice-Hall, New Jersey, 1963.
[12] D.M. Ceperley, B.J. Alder, Ground state of the electron gas by a stochastic method, Phys. Rev. Lett. 45 (1980) 566–569.
[13] J. Ferraris, D.O. Cowan, W. Walatka, J.H. Perlstein, Electron transfer in a new highly conducting donor-acceptor complex, J. Am. Chem. Soc. 95 (1973) 948–949.

Fig. 5. Calculated valence band structure in the LT phase. The symmetry points are represented as \( \Gamma: (0, 0, 0) \), X: \((1/2, 0, 0)\), M: \((1/2, 1/2, 0)\), R: \((1/2, 1/2, 1/2)\) in the components of the primitive reciprocal lattice vectors, \( b_1, b_2, b_3 \).