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Charge ordering in δ_o-(BEDT-TTF)$_2$TaF$_6$

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1 Introduction

The δ-type organic conductor (BEDT-TTF)$_2M$F$_6$ (M = P, As, and Sb) shows a phase transition at approximately room temperature (260 – 300 K) [1-4]. The PF$_6$ salt has been investigated using x-ray diffraction, and the two-fold superlattice reflections corresponding to $2k_F$ have been observed [4]. However, the low temperature crystal structure shows that the phase transition is not a $2k_F$ charge-density-wave (CDW) but a charge order [5]. Recently, two δ-type polymorphs, monoclinic (δ_m) and orthorhombic (δ_o) phases have been found in (BEDT-TTF)$_2$TaF$_6$ [6]. Both phases show a semiconductor-insulator phase transition at 276 K and 300 K for the δ_m and δ_o phases, respectively. The two-fold superlattice reflections are observed at around the phase transition temperatures for both phases. However, the wave vector of the superlattice reflections, $\boldsymbol{q} = (\boldsymbol{b}^* + \boldsymbol{c}^*)/2$, of the δ_o-TaF$_6$ salt differs from that of the δ_o-PF$_6$ salt ($\boldsymbol{q} = \boldsymbol{c}^*/2$) despite the same crystal structure [6]. The present paper reports the low-temperature crystal structure of δ_o-(BEDT-TTF)$_2$TaF$_6$.

2 Experiment

X-ray oscillaiton photographs were taken using an imaging plate at BL-8B of PF, KEK. The sample was cooled down to 39 K by a helium gas stream cooling method. The structure was solved by the direct method (SHELXT) and refined by the full-matrix least-squares procedure (SHELXL) [7,8].

3 Results and Discussion

Although some reflections with $l \neq 2n$, where n is an integer, are observed in $h0l$ reflections, we have chosen $P2/c$ as suggested by SHELXT in order to clarify the average strucure in the low-temperature insulating phase [9]. This space group is a sub-group of the high temperature space group $Pnna$, where the superlattice is given by $\boldsymbol{a'} = 2\boldsymbol{c}$, $\boldsymbol{b'} = \boldsymbol{a}$, and $\boldsymbol{c'} = -\boldsymbol{c}$-$\boldsymbol{b}$ based on the superlattice wave vector. Therefore, the crystallographic independent molecules are four donors and two anions. Although two donors A and C are flat, B and D molecules are bent (Fig.1); the bent TTF skeleton is characteristic of the neutral BEDT-TTF. This indicates that the low tempertaure phase is a charge ordered state. Moreover, the charges of the donors estimated from the bond lengths are Q_A = +0.8(2), Q_B = +0.5(2), Q_C = +0.7(2), and Q_D = +0.2(2). These are in agreement with the molecular shape; the flat molecules are hole rich. The charge ordered pattern obtained shows that the hole rich donors are dimerized by the largest transfer integral; the spin singlet state observed in the electron spin resonance spectra can be realized.

In summary, the phase transition of the present compound is not a $2k_F$ CDW but a charge ordering transition originated from the intersite Coulomb repulsion.

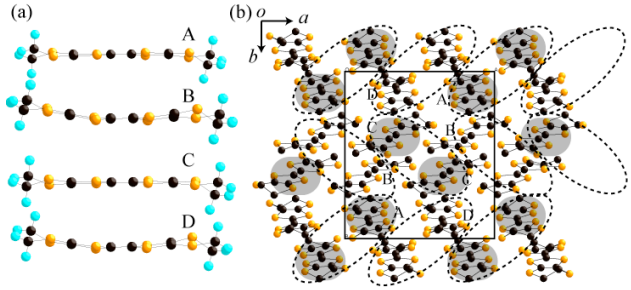

Fig. 1: Molecular shape projected along the molecular short axis (a) and the donor layer projected onto the *ab* plane (b) of δ_o-(BEDT-TTF)$_2$TaF$_6$ at 39 K. In (b), black rounded rectangles denote hole rich molecules A and C, and dashed ellipses represent dimers.

References

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[9] Crystal data of δ_o-(BEDT-TTF)$_2$TaF$_6$ at 39 K: monoclinic, space group $P2/c$, a = 13.2594(5) Å, b = 14.5036(4) Å, c = 33.8724(7) Å, β = 101.206(2)°, V = 6389.8(3)Å^3, and Z = 8. The final $R1$ value is 0.1387 for observed 20909 reflections ($F^2 > 2\sigma(F^2)$).

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