

Structural Study of Relaxor-Like Behavior in the Organic Two-Dimensional Metal λ -(BETS)₂FeCl₄

The two-dimensional conductor λ -(BETS)₂FeCl₄ has attracted wide interests because it exhibits unique π -d interaction effects[1]. This compound has a layered structure consisting of bis(ethylenedithio) tetraselenafulvalene [abbreviated as BETS] organic donor layers and FeCl₄⁻ acceptor layers as shown in Fig. 1(a). Accordingly, from the simple band calculation disregarding interactions between electrons, the nature of a two-dimensional metal is expected. In fact, its dc conductivity shows a metallic behavior below 100 K to 8 K. However, this compound undergoes a metal-insulator transition at 8 K (T_{MI}) as shown in Fig. 2(a). The ground state below T_{MI} is an antiferromagnetic insulator. It is in contrast with a superconducting state of the isostructural λ -(BETS)₂ GaCl₄ salt without any metal-insulator transition. This difference indicates the importance of the strong interactions between π electron on BETS and 3d electron ($S = 5/2$) on FeCl₄⁻. Furthermore, by a microwave response experiment, a peculiar ferroelectric-relaxor-like behavior of the real part of dielectric function ϵ_1^c was recently found below T_{FM} ($= 70$ K) above T_{MI} for λ -(BETS)₂FeCl₄ despite of the metallic behavior of dc conductivity as shown in

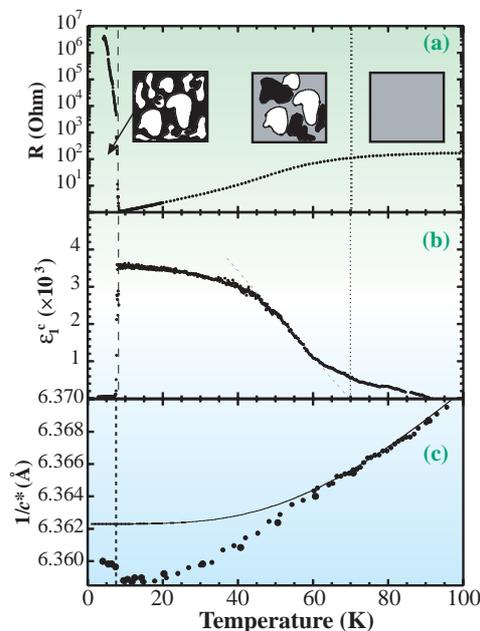


Fig. 2. (a) Temperature dependence of resistivity. Inset: Schematic figures of the domain structure. (b) Dielectric function ϵ_1^c [2]. (c) Temperature dependence of the lattice parameter $1/c^*$ measured with an ordinal resolution [3].

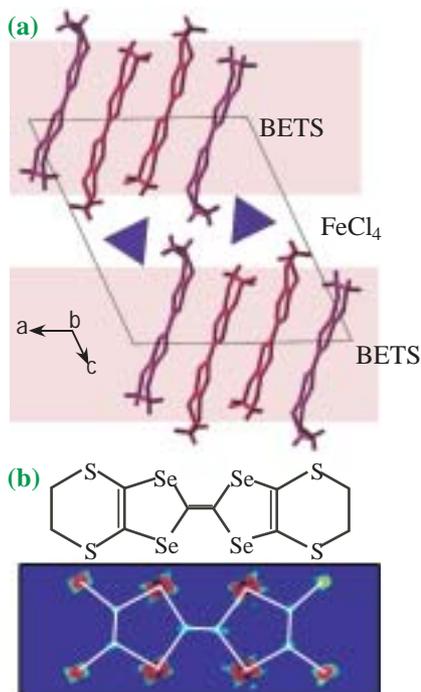


Fig. 1. (a) Crystal structure of λ -(BETS)FeCl₄. (b) Electron density map of the molecular plane of BETS at 20 K. Terminal ethylenes are not on this plane.

Fig. 2(b) [2]. Then, ϵ_1^c decreases steeply at T_{MI} . These anomalies seem to indicate a possible structural change at low temperature. However, no evidence of such structural change has been observed, partly because of the difficulty of experiments, in particular, high-resolution diffraction at very low temperature. Thus, the possibility of structural change at low temperature has been ignored so far. The aim of this work is to examine the possible structural change of λ -(BETS)₂FeCl₄ at low temperature, and to clarify the peculiar behavior of the anomalous metallic phase.

All measurements were performed at beamline BL02B1. The X-ray beam was tuned to 12.5 keV to avoid the absorption edge of Se atoms in the BETS molecule. First, to perform crystal structure analysis, we obtained oscillation photographs at 20 K (the lowest temperature limit of the instrument) using a vacuum camera with an imaging plate system [3]. At $T_{FM} > T = 20$ K $> T_{MI}$, no satellite reflection nor diffuse scattering was found. The reliable factor $R = 5\%$. Compared with the structures at 90 K and 300 K, all atomic positions at 20 K are almost the same. Only small anomalies are found in an electron density map

as shown Fig. 1(b). We can see unique deformations around Se and S atoms in BETS. We shall return to this point later.

Secondly, to detect a small structural change, we investigated the detailed peak profile of the Bragg reflection. A Huber 4-circled diffractometer equipped with a cryostat (Iwatani HE05) down to 4 K was used for this experiment. We focused on the (0 0 7) Bragg reflection, because the large cryostat on the diffractometer limited the χ angle to $30^\circ - 110^\circ$. The (0 0 7) is the observable highest angle Bragg reflection in the c^* direction. Figure 2(c) shows the temperature dependence of the $1/c^*$. The $1/c^*$ corresponds to the so-called d -spacing of the c -plane, but is not the same as the c since the unit cell is triclinic. We can see a discontinuous expansion about 0.0008 \AA at T_{MI} [3]. This discontinuity indicates the nature of a first-order structural phase transition at T_{MI} . On the other hand, no clear anomaly was found around T_{FM} . What we can only see is the deviation from the fitting curve based on the Debye model shown with the solid line in Fig. 2(c). Thus, to reveal more details, we measured again the peak profiles with much higher resolution [4]. By a 3D map scan for the peak of the (0 0 7) reflection, we found a small peak splitting. The amount of splitting reached $0.017 a^* - 0.010 b^* + 0.002 c^*$. Such small splitting can only be observed with the high resolution. Figure 3 shows the temperature variation of the peak profile along this direction. At 100 K, the peak has a shoulder at the lower angle side. With decreasing temperature, this shoulder developed into a peak, and became sharper as opposed to the higher angle peak that became broader. Below T_{MI} , only a single broad peak was observed. Each of the two peaks has a different d^* value. Therefore, the coexistence of two kinds of crystals was indicated. We conjecture the coexistence of ferroelectric (or antiferroelectric) and paraelectric region sat $T_{FM} > T > T_{MI}$ to interpret the complicated peak profiles mentioned above. This heterogeneous phase is responsible for the anomalous dielectric enhancement similar to a relaxor in the anomalous metallic phase.

We can now consider the anomalous electron density distribution at 20 K. These anomalies may be a circumstantial evidence of the heterogeneous phase, because these anomalies can be considered as an artificial result of averaging the heterogeneous structure. Schematic inset figures in Fig. 2(a) illustrate the temperature variation of the ferroelectric (or antiferroelectric) regions and the paraelectric regions. In the inset figures, both black and white areas denote

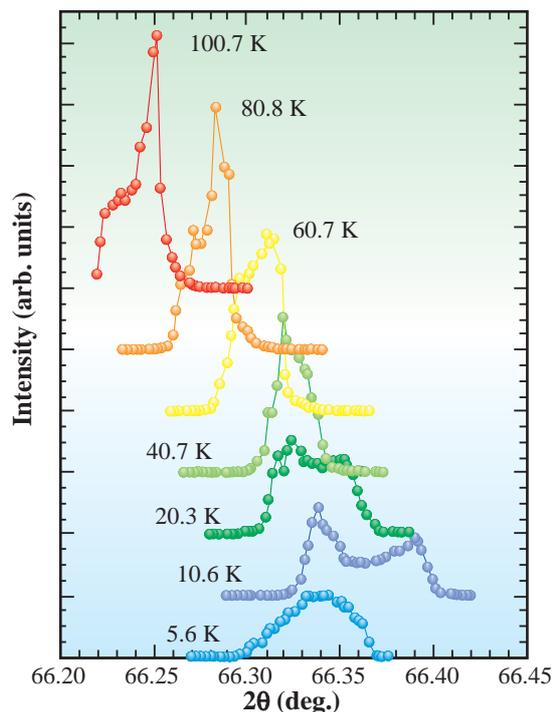


Fig. 3. Peak profiles of the (0 0 7) Bragg reflection measured with high resolution. Scan direction is parallel to $0.017 a^* - 0.010 b^* + 0.002 c^*$ [4].

ferroelectric domains (or antiphase domains in the antiferroelectric region), and the gray area is a paraelectric region. Above T_{FM} , the crystal is as homogeneous as that in the paraelectric state. In the temperature region of $T_{FM} > T > T_{MI}$, it takes a heterogeneous structure. Below T_{MI} , the crystal is dominated by the ferroelectric (or antiferroelectric) state. However, the detailed crystal structure below T_{MI} is still unclear, and should be revealed to clarify the origin of spontaneous polarization and relation to the π - d interaction.

Masashi Watanabe, Satoshi Komiyama and Yukio Noda

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University

E-mail: m-wat@tagen.tohoku.ac.jp

References

- [1] H. Kobayashi *et al.*: Synth. Met. **70** (1995) 867.
- [2] H. Matsui *et al.*: J. Phys. Soc. Jpn. **70** (2001) 2501.
- [3] M. Watanabe, S. Komiyama, Y. Noda, E. Negishi and N. Toyota: J. Phys. Soc. Jpn. **72** (2003) 452.
- [4] S. Komiyama *et al.*: submitted to J. Phys. Soc. Jpn.