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Structural studies on charge ordering in organic conductors based on a π-reduced donor DODHT

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Introduction

Modification of the π-electron system of organic donor molecules in organic conductors leads to unique physical properties relating to the strong electron correlation, such as charge ordering and superconductivity. We synthesized a new donor molecule DODHT [(1,4-dioxane-2,3-diyldithio)dihydrotetrathiafulvalene], in which the π-electron system is reduced compared with that of TTF derivatives, and succeeded in preparing new pressure-induced superconductors, β''-$(DODHT)_2X$ (X = PF_6, AsF_6, $BF_4{\cdot}H_2O$) [1]. At ambient pressure, β''-$(DODHT)_2PF_6$ exhibits phase transition to an insulator state accompanied by charge ordering (CO) with a stripe-type charge pattern along molecular side-by-side direction (*a*-axis) [2]. The DODHT salts with counter anions with same octahedral symmetry exhibts different electrical and magnetic behaviors; only the PF_6 and AsF_6 salts show superconductivity under pressure of above *ca*. 1.3 GPa, whereas the SbF_6 salt is semiconducting without any distinct anomaly accompanying insulator transition.

In order to investigate the difference in the physical properties of β''-DODHT salt with octahedral anions in different sizes, we carried out X-ray structural studies by synchrotron radiation and found difference in the superstructure resulting from the CO.

Results and Discussion

We have already found that the insulating phase of β''-$(DODHT)_2PF_6$ is the CO state with a stripe-type charge pattern along *a*-axis by the observation of satellite reflections below transition temperature using monochromatized Mo Ka X-rays of 30 kV, 40 mA. In the CO phase, the unit cell becomes double along *a*-axis due to CO and satellite spots associated with the 2*a* superlattice structure should be observed. The same satellite reflections were observed in the oscillation photograph taken at 40 K using synchrotron radiation at BL1B as shown in Figure 1, confirming the CO in this salt.

On the other hand, in β''-$(DODHT)_2AsF_6$, very weak satellite reflections corresponding to 2*a* superstructure similarly to the PF_6 salt was observed at 210 K. Intensity of the satellite peak increased with decreasing temperature, and the wave vectors varied to merge to strong diffuse reflections at (0.5a*, 0.5b*, 0) below 80 K. The result is completely different from that for the PF_6 salt, indicating strong disorder and different charge pattern of the CO state emerged in the AsF_6 salt.

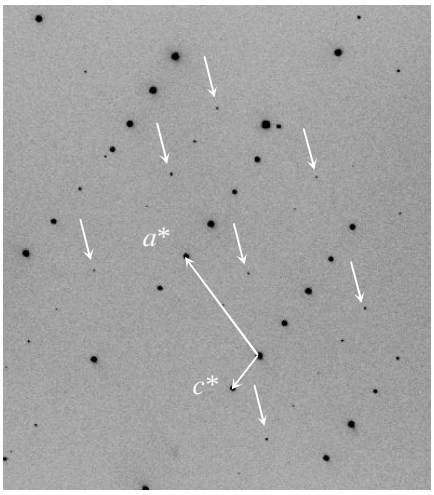

Figure 1. X-ray oscillation photograph taken at 40 K of β''-$(DODHT)_2PF_6$. Reflections indicated by white arrows are satellite spots of $q = a^*/2$.

In summary, comparison of the temperature dependence of satellite reflections resulting from the CO between β''-$(DODHT)_2PF_6$ and β''-$(DODHT)_2AsF_6$ indicates that the different CO state was realized in the AsF_6 salt, which causes the difference in the electrical and magnetic behavior between two salts.

References

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