Structural study on charge ordered states of β''-DODHT salts

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We are currently investigating the development of new donor molecules based on the new organic donor with reducing π-electron system, DODHT ((1,4-dioxane-2,3-diyldithio)dihydrotetrathiafulvalene) [1]. We have already found three pressure-induced organic superconductors, β''-$(DODHT)_2X$ (X = PF_6, AsF_6 and $BF_4{\cdot}H_2O$), which exhibit insulator transition at T_I = ca. 250 K at ambient pressure [2]. X-ray diffraction measurement revealed that the satellite reflections corresponding to twofold superstructure along a-axis were observed below the transition temperature T_I for β''-$(DODHT)_2PF_6$. The magnetic susceptibility data above 60 K was well reproduced by one-dimensional S = 1/2 alternating Heisenberg chain model. These results indicate that the insulating state of this salt comprises a charge ordered state and the application of hydrostatic pressure above 13.2 kbar brings the superconducting phase by suppression of the charge ordered insulating phase [3]. In this context, the nature of the insulating state under pressure of this salt is important issue for investigation of the relationship between charge ordering and superconductivity. Among β''-DODHT salts with octahedral anions, only the PF_6 and AsF_6 salts showed transition to superconducting states under pressures of above *ca*. 1.3 GPa. Their magnetic behaviors, however, are rather different; temperature dependence of magnetic susceptibility of PF_6 salt followed 1-dimensional alternating Heisenberg model, while that of AsF_6 salt did not and an abrupt drop of susceptibility was observed at around 90 K. On the other hand, β''-DODHT salts with larger octahedral anions such as SbF_6 and TaF_6 did not show the superconducting transition under the pressure. Nevertheless the magnetic susceptibility was well reproduced by alternating Heisenberg model for both the salts. In order to clarify the difference of physical behaviors among β''-DODHT salts, we carried out X-ray structural experiments using synchrotron beam line at Photon Factory in KEK (BL-8A).

For the AsF_6 salt, satellite reflections corresponding to (a*/2, b*/2, c*) appears with broadness of the spots below 95 K, where the magnetic susceptibility decreased to non-magnetic state abruptly. This result was in contrast with the PF_6 salt, indicating a different CO structure. The precise structural analysis including superlattice reflections was difficult due to the streak-like spots, we collected the data at 150 K and 250 K; just below and above the temperature where the length of the *b*-axis were significantly changed (Figure 1). We will compare the structure at these two temperatures and discuss the insulating state of this salt.

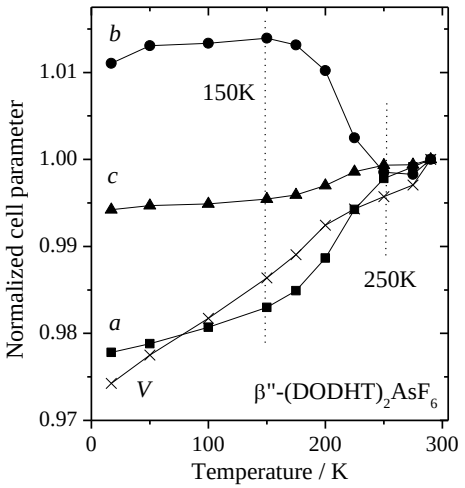

Fig 1. Temperature dependence of cell parameter of β″- $(DODHT)_2AsF_6$.

[1] H. Nishikawa *et al.*, *Chem. Commun.*, 494-495 (2003). [2] H. Nishikawa *et al.*, *J. Am. Chem. Sco.*, 730-731 **124** (2002). [3] H. Nishikawa *et. al.*, *Phys. Rev. B*, **72**, 052510 (2005).