8B/2009S2-008

Stepwise N-I phase transitions due to charge frustration in a covalently-bonded donor/acceptor compound

Hajime SAGAYAMA*[1] Taka-hisa ARIMA[1,2],
Natsuko MOTOKAWA[3], Tamiko CHIYO[3], Miho TAKEMURA[3],
Hitoshi MIYASAKA[4] and Masahiro YAMASHITA[3]
[1]IMRAM, Tohoku Univ., Katahira, Aoba-ku, Sendai 980-8577, Japan
[2]Sch. of Front. Sci., Univ. of Tokyo, Kashiwa, Chiba 277-8581, Japan
[3]Dept. of chem., Tohoku Univ., Aramaki-Aza, Aoba-ku, Sendai 980-8578, Japan
[4]Grad. Sch. of Nat. Sci. and Tech., Kanazawa Univ., Kakuma-machi, Kanazawa 920-1192, Japan

Introduction

Ru_2F_4Ph-DMDCNQI is the first example of a covalently-bonded donor (DMDCNQI) and acceptor (Ru_2F_4Ph) chain complex exhibiting neutral(N)-ionic(I) phase transitions. The [–{Ru_2}–(DMDCNQI)–] chains run along the *a* axis and make π-stack arrangements along the *b* and *c* axes. N-I transitions successively occur at two critical temperatures T_1~270K and T_2~210K. From crystal structure analysis at the laboratory level, averages of the charge transfer degree, δ, in high-temperature phase ($T>T_1$), intermediated phase ($T_1>T>T_2$), and low-temperature phase ($T<T_2$) are estimated at 0, 0.5, and 1, respectively. Since the covalent bonding prevents dimerization, ferrimagnetically-coupled magnetic moments are ordered in the low-temperature phase. The presence of large magnetic moments as well as the staging feature of the N-I transitions may provide a good arena for dynamical functionalities originating from the correlations among charge, spin, and lattice. In order to ascertain the valence state in the intermediate phase, an x-ray diffraction measurement on a single crystal was performed at BL8B, Photon Factory.

Experimental result and Analysis

Figure 1 shows oscillation photographs observed at the 200 K and 220 K. Superlattice reflections with the modulation vector (0 1/2 1/2) are clearly observed at 220 K. Result of the crystal structure analysis at 240K suggests that two neutral chains (II and IV) with δ~0 and two ionic chains (I and III) with δ~1 are aligned to form an alternating stacking of N and I layers in the intermediate phase as shown in figure 2. This is the first observation of the self-organization of the N and I moieties. It might be caused by frustration of interchain Coulomb interaction. Details of this study are published in the reference [1]

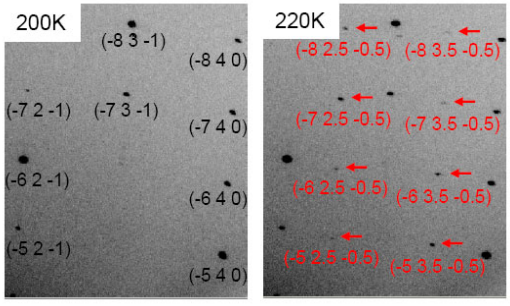

Figure 1 X-ray oscillation photographs observed at 200K and 220K.

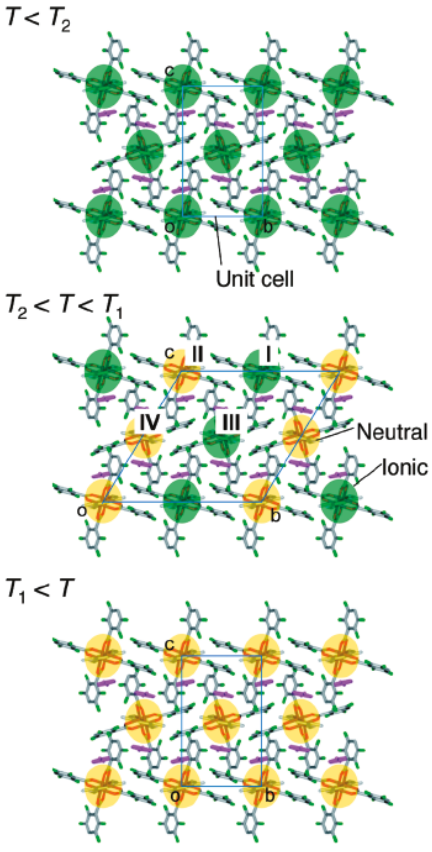

Figure 2 Arrangements of N and I chains in the ionic, intermediated, and neutral phase.

Reference

[1] H. Miyasaka, N. Motokawa, T. Chiyo, M. Takemura, M. Yamashita, H. Sagayama, and T. Arima, *J. Am. Chem. Soc.* **133**, 5338–5345 (2011).

*sagayama@tagen.tohoku.ac.jp