Mysterious Charge Ordering on $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$

Tsuyoshi Takeno$^1$, Kei Kobayashi$^1$, Yutaka Nishio$^1$, Koji Kajita$^1$, Hatsumi Mori$^2$, Toshikazu Nakamura$^3$

$^1$Department of Physics, Faculty of Science, Toho University, Miyama 2-2-1, Funabasi, Chiba, 274-8510, Japan
$^2$Institute for Solid State Physics University of Tokyo 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
$^3$Institute for Molecular Science, Myodaji, Okazaki, Aichi, 444-8585, Japan

E-mail: nishio@ph.sci.toho-u.ac.jp

Abstract. We have performed thermal studies of a charge disproportionation induced metal–insulator transition in $\theta$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ system. We have detected a sharp peak in a heating process and a broad hump in a cooling process with a remarkable hysteresis. This peculiar transition could be easily suppressed by a rapid-cooling. In the successive heating process, system shows a reentrant metal-insulator-metal transition. At the transition, a drastic lattice modulation brings about this mysterious first order phase transition accompanying a notable hysteresis and the rapid-cooling effect.

1. Introduction

Competitions of a band width and intermolecular Coulomb interaction drive the various phase transitions in the theta type BEDT–TTF systems [1]. One of the most attractive characters in these systems is the charge disproportionation of ET molecule with a metal–insulator transition essentially driven by intermolecular electron-electron correlation [2]. In this new phase observed in RbZn(SCN)$_4$ salt, the ET molecules are separated into two different valence states with 0.2+ and 0.8+ from 0.5+ [3–6]. This charge disproportionation accompanies a noticeable lattice modulation. The short range order of super lattice (3a×4c) causes a diffuse scattering in the high temperature metallic phase. It is replaced by 2c satellite spots across the phase transition [7]. The degrees of freedom for the lattice modulation in $\theta$–(BEDT–TTF)$_2$(RbZn)$_4$ salts should be discussed based on the value observed in $\alpha$–(BEDT–TTF)$_2$I$_3$ [8, 9], in which the charge density on ET molecular is only modified without the lattice distortion.

Thermal study of the charge disproportionation in this system has not been reported yet. In this article, we obtained the information about the specific heat and the latent heat at this phase transition. We report remarkable sweep rate dependence of this phase transition and discuss the degrees of freedom for this peculiar charge ordering in order to qualitatively discuss the mechanism of this transition [10, 11].

2. Experimental
We have constructed a new type of thermal measurement system, which can detect the specific heat and the latent heat of a small sample with a weight of less than 0.3 mg. This system covers a wide temperature region from 1.5 K up to room temperature. The DTA method was adopted because temperature region is too wide for the other methods such as thermal relaxation method or adiabatic method to give the data with high accuracy.

3. Result and Discussion

Fig. 1 shows a plot of the specific heat at a slow sweep rate of less than 0.54 K/min. We observed a broad hump at 175 K in the cooling process and a sharp peak at 210 K in the heating process. This large hysteresis indicates that this phase transition should be of the first order. Above 215 K and below 155 K, the specific heat in the heating process traces the data in the cooling process.

![Figure 1](image_url)

**Figure 1.** Specific heat in the cooling and the heating processes with the slow sweep rate of 0.54 K/min.

We quantitatively discuss the entropy difference $\Delta S$ observed at this phase transition. We detected $\Delta S = 6.1$ J/mol·K in the cooling process and 6.8 J/mol·K in the heating process. We also determined whether the Clausius–Clapeyron relation $\Delta S = \Delta V (dP_C/dT_C)$ is obeyed. Here, $\Delta S$ is the entropy change; $\Delta V$, the volume expansion; and $T_C$ and $P_C$ are the critical temperature and pressure, respectively. Substituting $\Delta V = 1.55 \pm 0.15$ Å$^3$ and $dP_C/dT_C = 8 \times 10^6$ Pa/K, as reported by H. Mori [12], we obtained $\Delta S = 7.4$ J/mol·K. This value is nearly equal to the observed excess entropy, i.e. $\Delta S = 6.4 \pm 0.4$ J/mol·K. This estimation indicates that the transfer is a first-order phase transition.

Next, we investigated the rapid cooling effect of this phase transition [13] by varying the sweep rate between 0.54 K/min~2.72 K/min. We plotted the specific heat under the most rapid cooling condition of 2.72 K/min and the slowest cooling condition of 0.54 K/min in Fig. 2. We could not detect a clear peak over the entire temperature range in the most rapid cooling process. In this condition, the system does not exhibit the metal-insulator transition and maintains a metallic phase at the lowest temperatures. In the subsequent heating process, the specific heat traces the cooling process data line up to 160 K. We observed a small dip at 180 K and a sharp peak at 210 K. We attributed this small dip and the sharp peak to the released latent heat in the case of the metal-insulator transition and the released absorption heat in the insulator-metal transition, respectively. We compared the specific heat for the slow and rapid cooling rates in Fig. 2. In the rapid cooling process, the specific heat does not exhibit any hump or dip across the transition temperature $T_C$. Another point we should mention about data in Fig.2 is the background specific heat. As shown in the figure, the background can be approximated by two straight lines with slightly different slopes. The system changes from high temperature metallic phase to insulating phase at low temperatures Therefore, two lines represent the specific heat of the metallic phase and insulating phase. We observed a large specific heat difference $\Delta C = C_{\text{Metal}} - C_{\text{Insulator}}$ of 30~40 J/mol·K, which is ten times larger than free electron degrees of
freedom of $\gamma T_c = 4 \text{ J/mol-K}$ assuming that the $\gamma$ value is 0.02 J/mol-K$^2$ as observed in the case of the organic metal $\kappa$-(BEDT-TTF)$_2$I$_3$[14]. Most of this specific heat difference is believed to be contributed by the lattice degrees of freedom.

We thermodynamically discuss these drastic hysteresis behaviours of this mysterious phase transition. In Fig. 2, we observed a dip in the rapid heating process. This dip is caused by the released entropy at the phase transition in the heating process. This entropy-reduction cannot be realized in the steady states. We plotted a schematic view of the Gibbs free energy $G$ vs. order parameter $\delta$ in Figure 3(a) and Gibbs energy vs. temperature in Figure 3(b) in high-temperature metal phase A and low-temperature charge ordering insulator phase B. At a temperature higher than the critical temperature $T_C$, $G_A(T) < G_B(T)$. Then, phase A is stabilized. The temperature then crosses $T_C$, where $G_A(T_C) = G_B(T_C)$. At a temperature lower than $T_C$, some parts of the sample transfer from phase A to phase B accompanied by significantly large lattice modulations. In this transition process, the space group changes from I222 (phase A) to P2$_1$2$_1$2$_1$ (phase B) [15]. In this process, the molecular configuration has to transfer through the energy barrier between the stable and metastable states by thermal excitation.

**Figure 2.** (a) Specific heat under the slow and rapid cooling rate conditions. We detected a linear dependence of the specific heat in the metallic (upper line) and the insulating states (lower line). (b)(c) Sweep rate dependence of excess specific heat in the heating process (b) and cooling process (c).

**Figure 3.** (a) Schematic view of the free energy vs. the order parameter in each temperature across the phase transition, in each temperatures ($T_a > T > T_c$). (b) Temperature dependence of free energies for phase A and phase B.
In the rapid cooling process, a majority of the system cannot transfer and therefore the specific heat does not exhibit visible anomalies at the transition temperature. Below 160 K, the specific heats in the cooling and heating processes coincide. In this lowest-temperature region, transfer from phase A to phase B cannot occur since the energy barrier exceeds the thermal energy, i.e. $\Delta E > k_B T$. In the heating process, a number of sites in the metastable phase A transfer to phase B in the temperature range $T_d \sim \Delta E/k_B < T_c$. At $T_d$, entropy $S_A(T_d) = -(dG_A/dT)$ is larger than $S_B(T_d)$. A transfer from phase A to phase B leads to the released entropy $\Delta S = S_A - S_B > 0$ and an exothermic reaction $T_d(S_A - S_B)$ in the heating process, contrary to the endothermic reaction in the steady state. The strong dependence of this phase transition on the sweep rate is caused by the drastic lattice symmetrical transformation.

4. Summary
At the charge disproportionation transition, we observed a remarkable temperature-induced hysteresis. In the heating process, we observed a large peak, while in the cooling process, we observed a broad hump. At the transition temperature, a significant lattice modulation due to change in the space group from $P2_12_12_1$ to $I222$ results in a large entropy difference $\Delta S = 6.1$–$6.7$ J/mol·K. A rapid cooling process suppresses the phase transition. In the subsequent heating process, we could observe the metal–insulator–metal transition. We thermodynamically discussed the mechanism of this mysterious phase transition.

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