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Thermal Study of Monovalent-Divalent Phase Transition in npBifc-F$_1$TCNQ System

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Abstract. In a new molecular solid composed of di-neopentyl-biferrocene (npBifc) and fluorotetracyanoquinodimethane (F$_1$TCNQ)$_3$, Mochida reported the discovery of a reversible valence transfer that can be regarded as an "ionic(I)-ionic(II)" phase transfer between the monovalent state (D$^+$A$^-$) and the divalent state (D$^{2+}$A$^{2-}$). We have studied thermo-dynamical properties of this transformation for this complex using the differential thermal analyses (DTA). We observed a broad excess specific heat with multi-peaks attributed to micro-domain structure over the corresponding temperature range (100-150K) accompanied by temperature hysteresis of 7K. The transition entropy ($\Delta S$) was determined to be 22 ± 2 J/mol-K and almost satisfied a Clausius-Clapeyron relation. These experimental results provide an experimental confirmation of the first order phase transition for the monovalent-divalent transfer. At the transition, we observe that the electronic degrees of freedom remained constant values, while large entropy absorbed crossing from low temperature phase to high temperature one is contributed by the lattice one. We finally estimated the internal energy and concluded that delicate energy valance between Madelung, ionization and affinity energies enable this system to exhibit a temperature induce monovalent-divalent phase transition.

1. Introduction

The valences of molecules in ionic crystals are usually stable against the change in temperature because of large internal energy differences between states with different valences. However, in the charge-transfer solid of TTF–Chloranil, phase change between the neutral state and monovalent state occurs [1]. It is because the balance of the energy gain due to Madelung energies and the cost due to ionization energy is almost perfect. Therefore, we can control the phase change by manipulating temperature or external pressure. Recently, Mochida synthesized new ionic molecular crystal composed of (npBifc) and a tetracyanoquinodimethane (TCNQ) derivative [2]. In this material, he discovered a reversible valence transition that can be regarded as an "ionic(I)-ionic(II)" phase transition between the monovalent state (D$^+$A$^-$) and the divalent state (D$^{2+}$A$^{2-}$). This work is motivated by the anomalous magnetic property of this material. This system changes from monovalent state at high temperature to the divalent state at low temperatures. Entering into low temperature state, the magnetic susceptibility is found to be enhanced. It means that entropy for the spin system increases with lowering the temperature. This, however, conflicts with the thermodynamic rule. Some freedoms other than spins, therefore, should accompany this phase change.
2. Experimental

We constructed a new type of thermal measurement system, which can detect the specific heat and the latent heat of the sample with a weight of less than 0.3 mg. It covers a wide temperature region from 5K up to room temperature. The DTA method was adopted because temperature region is too wide for other methods such as thermal relaxation method or adiabatic method to give the data with high accuracy. In the DTA method, we use a reference sample in addition to the sample. They are placed in a vacuum space with weak heat links to the heat bath. When the temperature of heat bath is changed, heat flow occurs between bath and the sample and reference. It then causes a temperature change as is given by next two equations,

\[ C_s \Delta T_s = K_s (T_b - T_s) \]

\[ C_r \Delta T_r = K_r (T_b - T_r) \]

where \( C_s \) is heat capacity of sample, \( T_s \) temperature of sample, \( K_s \) heat link between sample and heat bath, \( T_b \) temperature of bath. For the reference, we get a similar equation:

\[ C_r \Delta T_r = K_r (T_b - T_r) \]

where the suffix r indicates reference. From these equations, we obtain the following relation:

\[ C_s = C_r \frac{K_s}{K_r} \frac{\Delta T_s}{\Delta T_r} \]

We measure the temperatures of the sample, reference and the heat bath. Putting them into the equation, we can calculate the heat capacity of the sample. In the present system, the sample and the reference are placed in the same condition. It can reduce the noise due to irregularity of the temperature change, thermal radiation and etc. In present work, chromel-constantan thermo-couple and polystyrene are used as thermometer and reference sample, respectively.

3. Experimental result and discussion

![Figure 1](image)

Figure 1 Specific heat for npBifc-F1TCNQ (black line) and npBifc-TCNQ (red line). The inset shows specific heat for npBifc-F1TCNQ in the cooling (blue line) and heating processes (red line).

1.1. Confirmation of Phase transition

Fig.1 shows the plots of the specific heat of npBifc-F1TCNQ and npBifc-TCNQ salt that does not exhibit ionic(I)-ionic(II) transfer. The plot for the F1TCNQ salt shows a excess specific heat in the temperature range 100-150 K. This region coincides with the region in which the magnetization anomaly is observed. These results indicate that the excess specific heat can be attributed to the ionic (I)-ionic (II) transfer. The excess enthalpy (\( \Delta H \)) of this transition has been estimated to be 2.5 ± 0.3 kJ/mol-K, and the transition entropy (\( \Delta S \)) was determined to be 22 ± 2 J/mol-K.

We have observed hysteresis of 7K during the heating and cooling excess specific heat (see inset of Fig.1). The hysteresis is the key feature suggesting that this ionic (I) – ionic (II) transition is a 1st order phase transition. To confirm that the phase transition is a 1st order phase transition, we checked whether the Clausius-Clapeyron relation 

\[ \Delta S = \Delta V (dP_c/dT_c) \]

is obeyed. Here, \( \Delta S \) is the entropy change, \( \Delta V \), volume expansion and \( T_c \) and \( P_c \) are the critical temperature and pressure, respectively.
Substituting $\Delta V = 30 \\text{Å}^3$ and $dP_c/dT_c = 1.5 \times 10^6 \text{Pa/K}$, reported by Uruichi et al.[3], we obtain $\Delta S = 27 \text{ J/mol-K}$. This value is nearly equal to the observed excess entropy, i.e. $\Delta S = 22 \pm 2 \text{ J/mol-K}$. In this section, we have shown that the transfer from monovalent to divalent state is 1st order phase transition and not a crossover phenomenon.

1.2. Degrees of freedom

To ascertain the origin of driving factor behind this phase transition, we estimate the degrees of freedom for spin, electron, and lattice systems. In this phase transition, it is noted that electronic entropy is completely invariant under the phase transition. In the high-temperature (HT) phase, the donor is in the mono-cationic state, containing one Fe$^{2+}$ ion and one Fe$^{3+}$ ion, as shown in figure 2. These ions undergo rapid exchange. The acceptor unit has an excess electron. At the transition temperature, the intermolecular electron transfer takes place from the donor to the acceptor unit. In the low-temperature (LT) phase, the donor is in the dicationic state, containing two Fe$^{3+}$ ions, and the acceptor unit has two excess electrons. In the HT phase, the contribution from $S_{\text{mo}} = R \ln 2$ (valence tautomerization) + $R \ln 4$ ($\text{Fe}^{3+}$ spin with $J = 3/2$) + $R \ln 2$ ($\pi$ spin with $s = 1/2$) amounts to $4R \ln 2$. In the LT phase, the total electronic entropy is $S_{\text{di}} = 2 \times R \ln 4$ (two Fe$^{3+}$ spins with $J = 3/2$) = $4R \ln 2$, which is equal to that of the HT phase. It is confirmed that the total degrees of freedom for electrons and the localized spins remains constant when the system crosses the transition region. Therefore, the degrees of freedom do not contribute to the excess specific heat.

1.3. Change of stiffness

The large excess entropy observed at the boundary should be caused by the lattice expansion. It is plausible, because we have detected a change in stiffness of the system in two phases by comparing specific heat $C_{\text{F1TCNQ}}$ of npBifc-F1TCNQ with $C_{\text{TCNQ}}$ of npBifc-TCNQ salt; npBifc-TCNQ salt does not exhibit phase transition and remains in the monovalent state even at the lowest temperature. In Fig.1, we can verify that $C_{\text{F1TCNQ}} > C_{\text{TCNQ}}$ at temperatures higher than the transition temperature ($T > T_c$), while $C_{\text{F1TCNQ}} < C_{\text{TCNQ}}$ at temperatures lower than the transition temperature ($T < T_c$). The anion of F1TCNQ salt has a higher weight and a larger size as compared to that of TCNQ. In F1TCNQ salt the anion is located far away from the cation and the attractive force between them is weaker. These facts lead to the reduction in the frequency of harmonic-oscillation and the Debye characteristic temperature [4]. After the transition, the induration of ionic bonds shifts the frequency of harmonic oscillation to higher frequency. Therefore, system changes from a soft solid ($T > T_c$) to hard one ($T < T_c$).

1.4. Condition of this transition

Phase transition takes place where the Gibbs free energy of two phases crosses under the constant pressure and temperature conditions. At just transition temperature, an equation $U_{\text{mo}} + PV_{\text{mo}} - T_cS_{\text{mo}} = U_{\text{di}} + PV_{\text{di}} - T_cS_{\text{di}}$, is satisfied. From this equation, a simple relation is obtained. $\Delta U + PV \Delta V = T_c \Delta S$ where $\Delta U = U_{\text{mo}} - U_{\text{di}}$ is internal energy difference, $\Delta V = V_{\text{mo}} - V_{\text{di}}$ is unit cell volume difference and $\Delta S = S_{\text{mo}} - S_{\text{di}}$ is entropy difference between monovalent and divalent phases.

At ambient pressure, Uruichi reported the volume shrinkage $\Delta V = 1.8 \times 10^5 \text{ m}^3/\text{mol}$ across the transition and estimate $P \Delta V$ to be 1.8 J/mol at ambient pressure. On the other hand, $\Delta S_{T_c} = 120 \text{ K} \times 22 \text{ J/mol-K} = 2.6 \text{ kJ/mol}$, which is about 1000 times larger than that of $P \Delta V$. Neglecting the term $P \Delta V$, we
get the difference in the internal energy between two phases $\Delta U$ to be 2.6 kJ/mole. We compare this value with the Madelung energy and the ionization energy. We can roughly estimate the Madelung energy $E$ assuming the CsCl type crystal structure of this material, $E = -\alpha q^2 / 4\pi \varepsilon_0 R$, where $q$, $\alpha$, $\varepsilon_0$ and $R$ is electron charge, Madelung constant, dielectric constant and distance between anion and cation, respectively. We obtain the value of $E_{\text{mo}} = -250.2$ kJ/mol, $E_{\text{di}} = -4 \times 254.7$ kJ/mol using $q_{\text{mo}} = 1$, $q_{\text{di}} = 2$, $\varepsilon_0 = 1$, $R_{\text{mo}} = 9.646$ Å and $R_{\text{di}} = 9.571$ Å and have the large value of $\Delta E = E_{\text{mo}} - E_{\text{di}} = 768.6$ kJ/mol. This Madelung energy difference is related to the internal energy difference $\Delta U$ and the difference between ionization and affinity energies $\Delta I$ by a relation, $\Delta U = \Delta E - \Delta I$ (4).

![Figure 3](image-url) Schematic view of energy balance between the Madelung energies $E$ in the monovalent and divalent states, the difference between ionization and affinity energies $\Delta I$.

From this relation, we obtain $\Delta I = 766.0$ kJ/mol. Both $\Delta E$ and $\Delta I$ are larger than $\Delta U$ by a factor 300, as shown in figure 3. We conclude that a delicate energy valance between Madelung energy and ionization energy is realized in this system which enables this system to undergo monovalent–divalent transition at low temperatures.

4. Summary
We carried out the specific heat and latent heat measurements on Bifferocene-F1TCNQ using the DTA method and detected huge specific heat with the excess entropy exceeding $\Delta S \sim 3R \ln 2$. This specific heat shows a thermal hysteresis and obeys the Clausius-Clapeyron relation. From these results, we concluded that the monovalent-divalent transfer is the first order phase transition. We have discussed the degrees of freedom of spin, electron and the lattice and clarified that the lattice contribution critically drives the phase transition, while the sum degrees for electrons and spins remains constant. Finally we estimate the difference of internal energy and Madelung energy in both phase and conclude that the delicate balance of the Madelung, ionization and affinity energies can undergo such a temperature induced monovalent-divalent phase transition.

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