

# Cooperative electron delocalization of mixed-valence biferrocenium complexes

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# Cooperative Electron Delocalization of Mixed-Valence Biferrocenium Complexes

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Intramolecular electron transfer in the mixed-valence biferrocenium complexes in crystals shows qualitatively different behavior from that in the complexes in solutions. The "extra" electron in a mixed-valence complex in the crystal may be localized at low temperature and delocalized at higher temperature. The electron localization-delocalization transition induced thermally corresponds to a kind of order-disorder phase transition. In order to clarify the mechanism of the transition, a statistical mechanical model is proposed. The temperature dependences of the physical quantities relevant to the cooperative electron localization-delocalization transition are calculated based on the model. Those calculated values are compared with the observed ones for various kinds of mixed-valence biferrocenium trihalide crystals and reasonable agreements are obtained.

## Introduction

The electron transfer process between metal ions in binuclear mixed-valence complexes has been studied mainly in dilute solutions<sup>1</sup>. However, recently it has been

found from the study of the process in the solid state<sup>2-5</sup> that a new type of intramolecular electron transfer occurs due to the cooperative interaction between the mixed-valence complexes. At very low temperature the "extra" electron in each complex locates on one specified metal ion. When the temperature increases, the electron transfers to the other metal ion in some complexes. At a definite temperature the electron in all of the complexes begins transferring between the two metal ions. This electron localization-delocalization transition corresponds to a kind of order-disorder Phase transition<sup>5,6</sup>.

We have propose a statistical mechanical model<sup>5</sup> for binuclear mixed-valence trihalides, which may clarify the mechanism of various types of electron localization-delocalization phase transitions. The basic idea of the model is as follows : A binuclear mixed-valence biferrocenium cation has the two vibronic states  $[\text{Fe}_A^{\text{II}}\text{Fe}_B^{\text{III}}]$  and  $[\text{Fe}_A^{\text{III}}\text{Fe}_B^{\text{II}}]$ , corresponding to the electronic states in which the "extra" electron locates on  $\text{Fe}_A$  and  $\text{Fe}_B$  ions, respectively. The electrons in the states are coupled to an out-of phase combination of symmetric ligand-metal stretching modes. Each trihalide counteranion  $X_A^- - YX_B^-$  also has the two vibronic states,  $[\text{X}_A^- \cdots - Y - \text{X}_B^-]$  and  $[\text{X}_A^- - Y \cdots \text{X}_B^-]$ . The intramolecular vibronic interaction induces the electron transfer between the two states in these ions. The cation-cation and cation-anion intermolecular interactions may induce cooperatively the electronic localization in the mixed-valence cation, that is, only one state (say  $[\text{Fe}_A^{\text{II}}\text{Fe}_B^{\text{III}}]$ ) is occupied. The localized state ( $[\text{Fe}_A^{\text{II}}\text{Fe}_B^{\text{III}}]$ ) becomes more unstable with increasing temperature. that is, the "extra" electron transfers more and more rapidly between the two iron ions,  $\text{Fe}_A$  and  $\text{Fe}_B$ , and the mixed-valence cation becomes delocalized at temperatures above a critical temperature  $T_C$ . The model has consistently explained the various observed data from Mossbauer spectra, heat capacity measurements, X-ray crystallography, and infrared spectroscopy<sup>5</sup>.

In the model<sup>5</sup> the intermolecular interactions were treated by the molecular field approximation. Specifically, the molecular field was assumed the keep on crystallographic direction of the compound. What this assumption suggests a degeneration of the two vibronic states in the cation for  $T > T_C$ .

However, recently Sorai et al<sup>6</sup> indicated based on the results of heat capacity measurements that the ground state of the cation is not degenerate even at tempera-

tures above  $T_c$ . Therefore, in the preceding paper<sup>7</sup> we have reconsidered the problem by taking into account a variation of the direction of the molecular field. In the present paper we consider only the case in which there is no anion effects. We calculate the temperature dependences of the localization rate, the heat capacity, and the energy separation between the two vibronic states in the cation for various kinds of biferrocenium trihalide crystals. These calculated results are in a reasonable agreement with the observed ones<sup>2-4,6</sup>.

### Model

Since a detailed explanation of the model has been given in reference<sup>5</sup>, we describe here only an essential part of the model for later convenience. The two vibronic states in the cation are denoted by the Pauli spin operators,  $\sigma_{cz}$ :  $[\text{Fe}_A^{\text{II}}\text{Fe}_B^{\text{III}}]$  and  $[\text{Fe}_A^{\text{III}}\text{Fe}_B^{\text{II}}]$  are assigned to  $\sigma_{cz} = 1$  and  $-1$ , respectively. The two states in each ion couple with each other through the intramolecular interaction which is denoted by  $\alpha$ ;  $\alpha$  is positive. We consider the two types of arrangements of mixed-valence cations and trihalide anions in the solid state, where one arrangement shown in Figure 5 of reference 5 corresponds to biferrocenium trihalide and dialkylbiferrocenium trihalide crystals, and the other shown in Figure 6 of reference 5 corresponds to dihalobiferrocenium trihalide crystals.

The various states of the mixed-valence cations in a crystal are determined by the Hamiltonian  $H$ ,

$$H = \alpha \sum_{i=1}^N \sigma_{cx,i} - J_c \sum_{i>j} \sigma_{cz,i} \sigma_{cz,j} \quad (1)$$

where the first term is the Hamiltonians for the  $N$  free cations, the second term is the cation-cation interactions, and the double summation is made only over nearest neighbor pairs. Here,  $2J_c$  is the energy difference between the parallel localized state ( $\sigma_{cz,i} = \sigma_{cz,j}$ ) and the antiparallel ( $\sigma_{cz,i} = -\sigma_{cz,j}$ ) and is positive.

In order to calculate analytically the thermal average of relevant quantities of the system, we transform  $\sigma_{cz,i}$  and  $\sigma_{cx,i}$  into the new spin operators,  $S_{cz,i}$  and  $S_{cx,i}$  such as

$$\sigma_{cz,i} = S_{cz,i} \cos \theta_c - S_{cx,i} \sin \theta_c, \quad (2)$$

$$\sigma_{cx,i} = S_{cz,i} \sin \theta_c + S_{cx,i} \cos \theta_c. \quad (3)$$



We introduce a model Hamiltonian  $H_0$  which approximates reasonably the real Hamiltonian  $H$ :

$$H_0 = -y_c \sum_{i=1}^N S_{cz,i}. \quad (4)$$

The strength  $y_c$  and the direction  $\theta_c$  of the molecular fields for the cation is determined so as to minimize the free energy  $F$  of the system.  $F$  is given as

$$F = -k_B T \ln Z_0 + \langle H - H_0 \rangle, \quad (5)$$

where the partition function  $Z_0$  of the model system is

$$Z_0 = \text{Tr} \left[ \exp \left( -\frac{H_0}{k_B T} \right) \right], \quad (6)$$

and the thermal average of a quantity  $Q$  is given by

$$\langle Q \rangle = \frac{1}{Z_0} \text{Tr} \left[ Q \exp \left( -\frac{H_0}{k_B T} \right) \right]. \quad (7)$$

The equations for  $y_c$  and  $\theta_c$  are obtained as

$$\sin \theta_c = -\alpha / y_c, \quad (8)$$

$$y_c \cos \theta_c - j_c Y_c \cos \theta_c = 0, \quad (9)$$

where  $j_c = 2J_c$  and

$$Y_c = \tanh(y_c / k_B T).$$

### Relevant Quantities

Although there exist various physical quantities relevant to the cooperative electron localization-delocalization transition, the quantities which have been measured experimentally are the electron localization rate of the mixed-valence cations, heat capacity, and the effective energy difference between the two vibronic states in the cation. These quantities also can be calculated based on the present model.

The localization rate  $\eta_c$  for the cation in the crystals is given by

$$\eta_c = \rho_{cA} - \rho_{cB} = \tanh \left( \frac{y_c}{k_B T} \right) \cos \theta_c, \quad (10)$$

where  $\rho_{cA}$  and  $\rho_{cB}$  are the thermally averaged population probabilities of the localized states,  $[\text{Fe}_A^{\text{II}}\text{Fe}_B^{\text{III}}]$  and  $[\text{Fe}_A^{\text{III}}\text{Fe}_B^{\text{II}}]$ , respectively. When the "extra" electron locates only on the  $\text{Fe}_A$  ion,  $\eta_c$  becomes unity. When the electron transfers frequently between  $\text{Fe}_A$  and  $\text{Fe}_B$ , the populations of the two states becomes equivalent and  $\eta_c$  becomes zero.

Therefore, the state of  $\eta_c=1$  corresponds to the completely localized state, while that of  $\eta_c=0$  corresponds to the completely delocalized state. In the case where the intermolecular interactions,  $J_c$ , are much larger than the intramolecular couplings,  $\alpha$ ,  $\eta_c$  becomes unity. However, in the case where  $\alpha$  is much larger than  $j_c$ ,  $\eta_c$  becomes zero.

The effective energy separation  $\Delta E_c$  in the cation is given by

$$\Delta E_c = 2 |j_c|. \quad (11)$$

The value of  $\Delta E_c$  becomes  $2 j_c$  in the case of  $j_c > \alpha$ , while  $\Delta E_c$  becomes  $2 \alpha$  in the case of  $\alpha > j_c$ .

The heat capacity  $C_p$  is generally obtained from the thermodynamic equation,

$$C_p = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_p. \quad (12)$$

The expression of  $C_p$  in the present system is obtained by using the free energy  $F$  given in Eq. (5). If the transition between the electronically localized ( $\eta_c > 0$ ) and delocalized ( $\eta_c = 0$ ) states in cations is induced cooperatively by the intermolecular interactions, that is, the transition is a kind of phase transition,  $C_p$  should show an irregular temperature dependence around the transition temperature  $T_c$ .

#### Effect of Crystal Environments to Electron Localization-Delocalization Transition

The electron localization-delocalization transition in the mixed-valence complexes is affected in various ways by crystal environments. The effects of environments are represented in the present model through the cation-cation interaction  $j_c$  and the coupling strength  $\alpha$  in the cation. In order to see how these factors affect the localization-delocalization transition, we have calculated the temperature dependences of  $\eta_c$ ,  $\Delta E_c$ , and  $C_p$  for various values of  $\alpha$  and  $j_c$ .

We show the calculated temperature dependences of the electron delocalization rate  $\eta_c$  in Figure 1 for the three cases, (a), (b), and (c), where the values of  $\alpha$  and  $j_c$  are chosen so that  $\eta_c$  may reproduce the observed values for (a) biferrocenium  $I_3^-$ , (b) biferrocenium  $IBr_2^-$ , and (c) di-n-butylbiferrocenium  $I_3^-$ . The adjusted values (in  $\text{cm}^{-1}$  unit) of  $\alpha$  and  $j_c$  are 40, 280 for (a), 40, 155 for (b), and 35, 215 for (c), respectively. The agreement of the calculated temperature dependence of  $\eta_c$  with the observed one

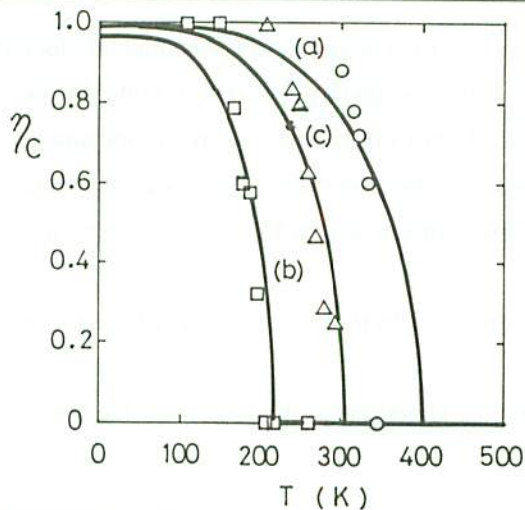


Fig. 1 Temperature dependences of the localization rate  $\eta_c$  for the cases of (a), (b), and (c) whose meanings are explained in the text. The observed relevant values<sup>2,3</sup> are also plotted.

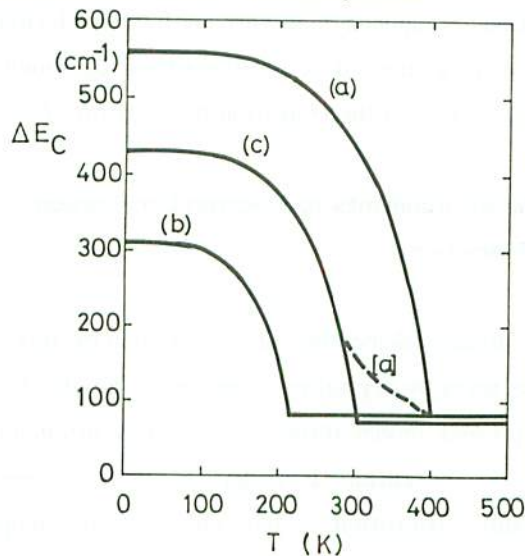


Fig. 2 Thermal variations of the energy separation  $\Delta E_c$  for the cases of (a), (b), and (c). The observed values<sup>6</sup> for (a) are also plotted by a broken line.

is quite reasonable. It is suggested from these calculations that the change of counter-anion from  $\text{I}_3$  to  $\text{IBr}_2$  induces a drastic change in the cation-cation interaction strength  $j_c$ , whereas the transition temperature  $T_c$  is rather insensitive to a change of  $\alpha$ . The substitution of butyl into the cation induces a noticeable change in the cation-cation interaction  $j_c$ .

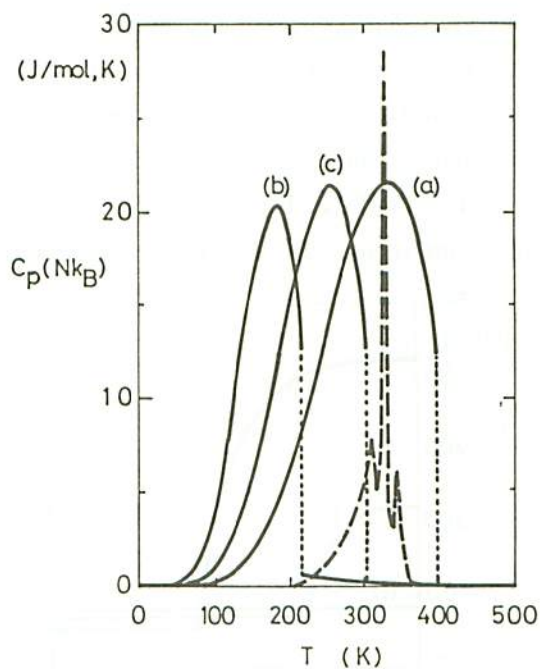


Fig. 3 Thermal variations of the heat capacity  $C_p$  for the cases of (a), (b), and (c). The observed values<sup>6</sup> for (a) are also plotted by a broken line.

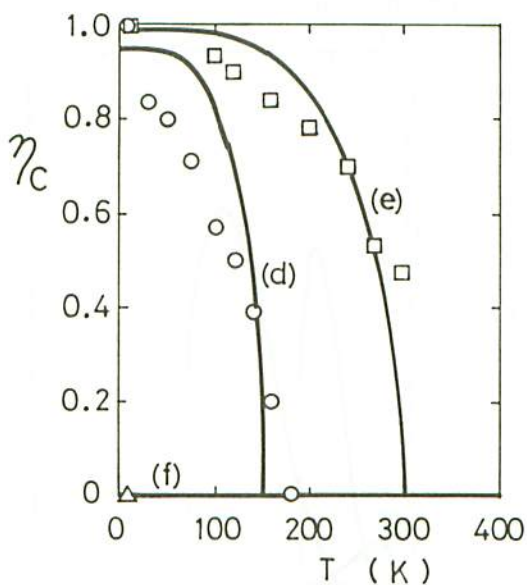


Fig. 4 Temperature dependences of  $\eta_c$  for the cases of (d), (e), and (f) corresponding to dihalobiferrocenium trihalides. The observed values are also plotted<sup>6</sup>.



The calculated temperature dependences of  $\Delta E_c$  and  $C_p$  are shown in Figures 2 and 3, respectively, where the observed values for biferrrocenium trihalide, (a), are also plotted. The energy separation  $\Delta E_c$  in the very low temperature region is induced by the intermolecular interaction,  $j_c$ , where the ground and excited states correspond to the two localized states,  $[\text{Fe}_A^{\text{II}}\text{Fe}_B^{\text{III}}]$  and  $[\text{Fe}_A^{\text{III}}\text{Fe}_B^{\text{II}}]$ , respectively. On the other hand, in the higher temperature region ( $T > T_c$ )  $\Delta E_c$  is induced by the intramolecular

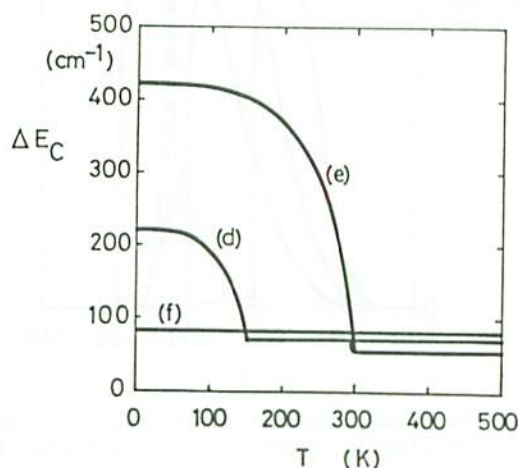


Fig. 5 Thermal variations of  $\Delta E_c$  for the cases of (d), (e), and (f).

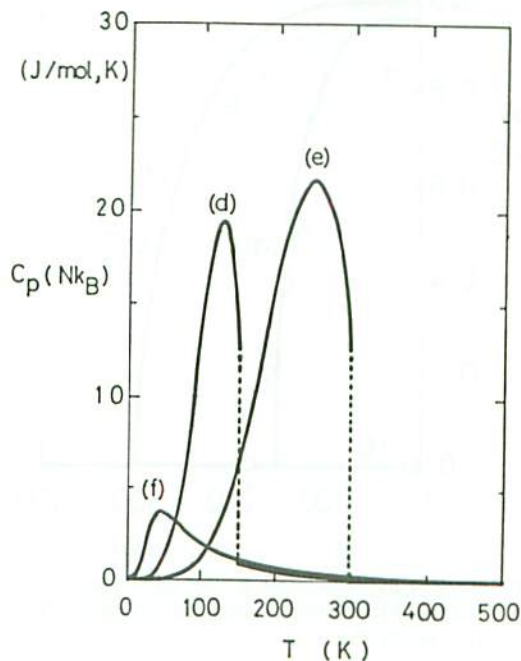


Fig. 6 Thermal variations of  $C_p$  for the cases of (d), (e), and (f).

coupling  $\alpha$  and is independent of  $T$ . Where both the ground and excited states correspond to the delocalized electron tunneling states, that is,  $\Delta E_c$  is the tunneling splitting. It is seen from Figures 1, 2, and 3 that the present model may reproduce the essential features of the observed temperature dependences. Therefore it is highly possible that the energy splitting for  $T > T_c$  is due to the tunneling of "extra" electron.

We show the calculated temperature dependence of  $\eta_c$  with the observed values in Figure 4 for the three cases, (d), (e), and (f) with the dihalobiferrocenium ( $X_2 - \text{BiFc}$ ) trihalide crystal structure, where (d), (e), and (f) correspond to  $\text{Cl}_2 - \text{BiFc} \cdot \text{IBr}_2$ ,  $\text{Br}_2 - \text{BiFc} \cdot \text{IBr}_2$ , and  $\text{I}_2 - \text{BiFc} \cdot \text{I}_3$ , respectively. The values of  $\alpha$  and  $j_c$  in  $\text{cm}^{-1}$  unit are 35, 110, respectively for (d), 30, 210, respectively for (e), and 40,  $\cong 40$ , respectively for (f). The calculated curves reproduce well the observed temperature dependences.

The calculated temperature dependences of  $\Delta E_c$  and  $C_p$  are shown for the cases of (d), (e), and (f) in Figures 5 and 6. Unfortunately, at the present time we have no experimental datum of  $\Delta E_c$  and  $C_p$  for dihalobiferrocenium trihalide crystals.

It is clear from these considerations that the present model may reproduce well the essential features of the observed electron localization-delocalization transitions in the crystals. Therefore, it is reasonably concluded that the electron delocalization process observed in the various kinds of mixed-valence biferrocenium complexes is due to the cooperative intermolecular interactions which do not exist in solutions.

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