An Explanation of the Temperature Dependence of the Mössbauer Spectra of Mixed Valence Biferrocenium Derivatives with a (Valence-State) Order-Disorder Transition

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Synopsis. The temperature dependence of the quadrupole splitting values in the Mössbauer spectra for monooxidized biferrocenium derivatives is well explained in term of an order-disorder transition with regard to the valence state of two iron atoms in the cations.

It has been reported that several kinds of triiodide salts of monooxidized 1′,1‴-dialkylbiferrocenium derivatives [Fe(II)·Fe(III)] ($R_2bfc \cdot I_3$) show a characteristic temperature dependence in their Mössbauer spectra,[1,3-5] where two well resolved doublets are observed at low temperatures. With an increase in the temperature, the quadrupole splitting (*Q.S.*) values of the outer and inner doublets decrease and increase respectively, until finally these two doublets are superimposed on each other, giving only one doublet, as is shown in Figs. 1 and 2. No line-broadening is observed in the process of the temperature dependence of *Q.S.*, although it might be expected for a relaxation process. There has thus far been no explanation for the characteristic temperature dependence of the quadrupole split lines commonly observed in the triiodide salts of ethyl, propyl, butyl, and benzyl derivatives.[5] In the present paper, this characteristic temperature dependence of the Mössbauer spectra is explained in terms of an order-disorder transition of the valence state of two iron atoms in the biferrocenium cations caused by a cooperative intermolecular interaction in a crystal.

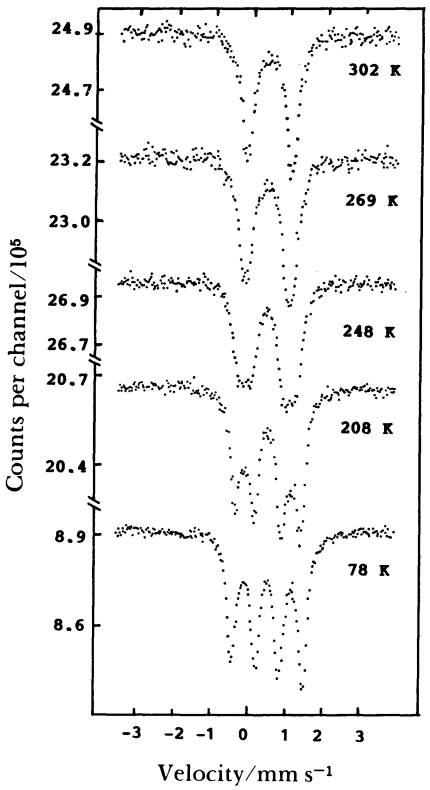

Fig. 1. Variable temperature ^{57}Fe Mössbauer spectra for 1′,1‴-dibutylbiferrocenium triiodide. The data are taken from Ref. 4.

I. Explanation of the Temperature Dependence of the Mössbauer Spectra. In order to explain the temperature dependence characteristic of the dialkylbiferrocenium triiodides, the following two hypotheses are assumed:

(i) The two iron atoms, Fe_A and Fe_B, in a cation are inequivalent in the crystal state, i.e., the potential energies between State I, [Fe_A(II)·Fe_B(III)], and State II, [Fe_A(III)·Fe_B(II)], differ from each other.

(ii) The electrontransfer rate between the two iron atoms becomes much faster than the Mössbauer time scale, $\approx 10^{-7}$ s, at higher temperatures, where the two ΔE_Q values start to change.

The (i) assumption is supported by the crystal structure of dipropylbiferrocenium triiodide.[2,3] The two iron atoms in the cation are found not to be

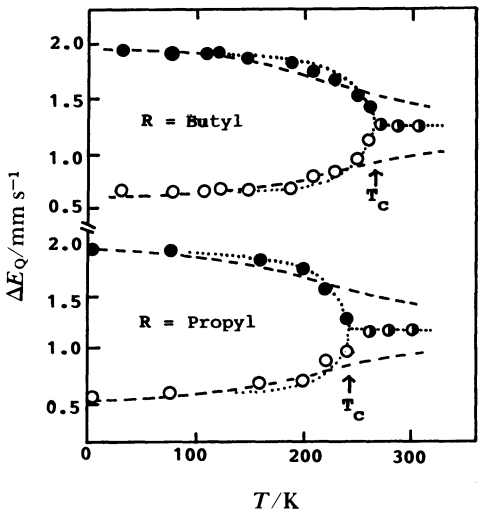

Fig. 2. Temperature dependence of quadrupole splitting for 1′.1‴-dialkylbiferrocenium triiodide ($R_2bfc \cdot I_3$). The open and closed circle corresponds to ferrocene and ferrocenium potion, respectively. The data were taken from Refs. 1 and 4 and the meanings of the dotted and broken lines in the figure are given in the text.

equivalent in the crystal packing. The (ii) assumption is important in explaining why no line-broadening is observed upon a change in the ΔE_Q values (see below). An intramolecular electron exchange rate faster than the Mössbauer time scale, as assumed above, has actually been found in, for example, 1′,1‴-dibromo and diiodobiferrocenium triiodides, even at 4.2 K, in the crystal state.[6,7]

At a sufficiently low temperature, if State I, [Fe_A(II)·Fe_B(III)], is assumed to be predominant, the two *Q. S.* values for iron A and B, atoms $\Delta E_{Q,A}$ and $\Delta E_{Q,B}$, will the approximately equal to those for the ferrocene and ferrocenium species corresponding to an outer doublet and an inner doublet in the Mössbauer spectrum respectively. At increased temperatures, the population of State II, [Fe_A(III)·Fe_B(II)], can be expected to increase. If the intramolecular valence exchange occurs sufficiently faster than the Mössbauer time scale, as assumed in the (ii) hypothesis, the observed $\Delta E_{Q,A}$ and $\Delta E_{Q,B}$ values can be represented by using the populations of State I, P_I, and State II, P_{II};

$$\Delta E_{Q,A} = P_I \cdot \Delta E_Q(\text{Fe(II)}) + P_{II} \cdot \Delta E_Q(\text{Fe(III)})$$
$$= P_I \cdot \Delta E_Q(\text{Fe(II)}) + (1-P_I) \cdot \Delta E_Q(\text{Fe(III)}) \quad (1)$$

because:

$$P_I + P_{II} = 1$$

and:

$$\Delta E_{Q,B} = P_I \cdot \Delta E_Q(\text{Fe(III)}) + (1-P_I) \cdot \Delta E_Q(\text{Fe(II)}) \quad (1)'$$

where ΔE_Q(Fe(II)) and ΔE_Q(Fe(III)) stand for the *Q. S.* values for the ferrocene-like and ferrocenium-like moieties in the R_2bfc·I_3 respectively; those values are determined by extrapolating the temperature dependences of the $\Delta E_{Q,A}$ and $\Delta E_{Q,B}$ values to 0 K. With an increase in the temperature, P_I decreases from unity, accompanied by both a decrease in the $\Delta E_{Q,A}$ value and an increase in the $\Delta E_{Q,B}$ value because $\Delta E_Q(\text{Fe(II)}) > \Delta E_Q(\text{Fe(III)})$. At sufficiently high temperatures, both the P_I and P_{II} populations both approach 0.5, and the values of $\Delta E_{Q,A}$ and $\Delta E_{Q,B}$ both also approach a mean value of ΔE_Q(Fe(II)) and ΔE_Q(Fe(III)), showing only one doublet just superimposed by the two doublets of the Fe_A and Fe_B absorbances in the Mössbauer spectrum. In this process, if the valence-exchange rate between the two iron atoms is sufficiently faster than the Mössbauer time scale, no line-broadening is observed in the Mössbauer absorptions. The observed Mössbauer spectra shown in Fig. 1 are qualitatively explained by the above consideration.

At 110 K and room temperature, the X-ray structure of the *n*-propyl derivative also supports this consideration. In the X-ray structure of Pr_2bfc·I_3 at 110 K, the cations have two kinds of inequivalent ferrocene and ferrocenium units, of which one corresponds to the Fe(II) unit, and the other, to the Fe(III) unit. These two units in the cations are aligned in the crystal in an orderly manner, as is schematically illustrated in Fig. 3(a). On the contrary, these two ferrocene and ferrocenium units become equivalent at room temperature; i.e., the configuration of the ferrocene or ferrocenium units in the cation is aligned in a disorderly manner at room temperature, as is demonstrated in Fig. 3(b).[3,7] If this disordering is dynamic, the time averaged population in the divalent and trivalent state for all the iron atoms will become nearly 0.5 in the crystal at room temperature.

II. Simple Model for the Order-Disorder Transition of the Valence State by Means of Cooperative Intermolecular Interaction. In the previous section, an energy difference between the states of [Fe_A(II)·Fe_B(III)] and [Fe_A(III)·Fe_B(II)] was assumed to explain the temperature dependence of the *Q.S.* values. If this energy difference remains constant over the temperature range where the Mössbauer spectra are observed, the population of State I or II, P_I or P_{II}, is related to the free-energy difference between State I and II, ΔG, as is expressed in the following equation:

$$P_I = (\exp(-\Delta G/RT) + 1)^{-1} \quad (2)$$

Table 1. Transition Temperatures and Interaction Energies

R	T_c/K	ε/kJ mol^{-1}		ΔG/kJ mol^{-1} c)
		2-Dimensional[a]	3-Dimensional[b]	
Butyl	262	1.08	0.72	2.6
Propyl	242	1.01	0.67	2.4
Ethyl	272	1.13	0.75	2.8
Benzyl	262	1.08	0.72	2.7

a) The values assuming a square lattice. b) The values assuming a cubic lattice. c) See Eq. 2 in the text.

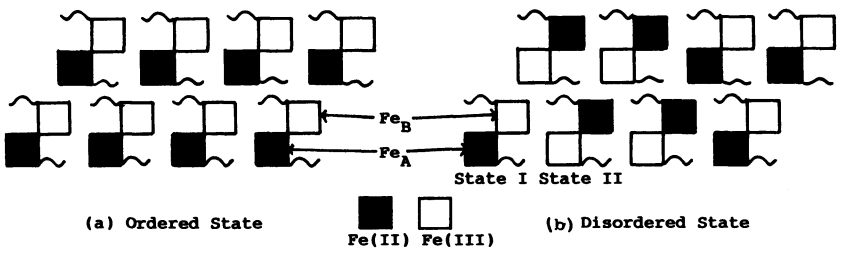

Fig. 3. Schematic representation of ordered (a) and disordered (b) state with regard to valence state of 1′,1‴-dialkylbiferrocenium triiodide.

The calculated temperature dependence of the ΔE_Q values for Fe_A and Fe_B, based on Eq. 1 and Eq. 2 with the ΔG values listed in Table 1, are shown in Fig. 2 by the broken lines. For all the cases, the calculated values do not fit well to the temperature dependence of the observed ΔE_Q values, especially the sudden change of ΔE_Q at 200—270 K.

This sudden change in the observed ΔE_Q values suggests an abrupt change in the population of the State I or II (see the previous section); i.e., an ordered state in which most cations remain in either one of the two states (I or II) changes to a disordered state, in which the populations of the two state of the cations are approximately equal, within a narrow temperature range, as is schematically illustrated in Fig. 3. This feature of the temperature dependence of the population in the valence states resembles the well-known order-disorder phase transitions, such as a ferro-to-para magnetic or electric transition. The small endothermic peak observed in the DSC measurements near the temperature showing a sudden change in the ΔE_Q value (e.g., several hundred J mol^{-1} for dipropylbiferrocenium triiodide) also indicates that change can be regarded as an order-disorder transition with regard to the valence state of the cations. In the crystal, the valence state of a cation may be affected by that of the neighboring cations, i.e., the energy difference between the two valence states, e.g., States I and II, of a cation are affected by those of the neighboring cations. This cooperative intermolecular interaction between cations is considered to cause an order-disorder transition. It seemed worthwhile to examine whether or not the Ising model could be applied to this system in order to explain such a cooperative intermolecular interaction. The states of I and II are represented by $\sigma_i=1$ and $=-1$ respectively, and an interaction Hamiltonian, H_{ij}, for the Ising model is geven with an intermolecular interaction energy, ε, that is:

$$H_{ij}=-(\varepsilon/2)\sum_{ij}\sigma_i\sigma_j \qquad (\sigma_i, \sigma_j=\pm 1) \tag{3}$$

where the intermolecular interaction, ε, is defined by considerig the interaction with the first neighboring cations, neglecting any anisotropic interaction. The values of P_I and P_{II} at various temperatures are obtained by using a molecular field approximation.[8] The ΔE_Q values for Fe_A and Fe_B can also be obtained by using the P_I and P_{II} values estimated based on Eq. (1). The results for butyl and propyl derivatives with ε values satisfactorily reproduce the observed ΔE_Q values at various temperature as is shown in Fig. 2 by dotted lines. The estimated interaction energies, ε, assuming a two- and three- dimensional interaction and the (second order) transition temperature, T_C, are listed in Table 1. Similarly good coincidences between the theoretical curves and the experimental data are also obtained for the ethyl and benzyl derivatives.

In this treatment, an isotropic interaction between neighboring cations placed on the square (for a two dimensional alignment) or the cubic (for a three dimensional alignment) lattice points is assumed, although the environment of a cation is not actually isotropic. For example, in the X-ray structure of $Pr_2bfc{\cdot}I_3$, the alignment of the cations shows a step-by-step slipping π-π stack between cycropentadienyl rings in one direction, while those same cations are aligned across one triiodide anion in two directions.[2] In spite of the different interaction in different direction in an actual crystal, the results show a fairly good coincidence between the experimental and theoretical results in which an isotropic interaction is assumed. This means that the valence state of the cations is determined by the alignment of the neighboring cations and by their interaction and that two- or three-dimensional[9] intermolecular interactions have a similar interaction energy value, ε, as is tabulated in Eq. 3.

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8) The calculation of P_I and P_{II} based on the molecular field approximation at various temperatures is equivalent to that of spontaneous magnetization for a 1/2 spin system. Regarding States I ($\sigma_i=1$) and II ($\sigma_i=-1$) as the +1/2 and −1/2 spin states respectively, the values (P_I-P_{II}) at various temperatures correspond to the values proportional to the spontaneous magnetization of the spin system. Such calculation of the magnetization based on the molecular-field approximation is carried out according to the procedure in such textbooks as "Introduction to Solid State Physics," ed by C. Kittel, Jhon Willey & Sons Inc., New York (1975), Chap. 15, and "The Structures and Properties of Solids. **6**, The Magnetic Properties of Solids," ed by J. Crangle, Edward Arnold, London (1976), Chap. 2.

9) It has been theoretically proved that one dimensional interaction in the Ising model shows no phase transition: in the exact solution for the one-dimensional Ising model, the population of the two states does not show any such steep temperature dependence as is shown in Fig. 2.