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Phase Transition without Spontaneous Symmetry Breaking between Hard and Soft Solid States

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The possibility of a new first-order phase transition between solid states with different stiffnesses but the same crystal symmetry is shown. The transition is not accompanied by spontaneous symmetry breaking, analogously to the liquid–gas transition. However, it is different from the liquid–gas transition in the aspect that it occurs between ordered phases. An ionic crystal that has two possible states with different ionic charges and close cohesive energies is a candidate in which such a transition is realized. We propose a simple model to describe such a transition, and examine the thermodynamic property in one, two and three dimensions. Expressions of the transition temperatures, the specific heats, and the latent heats are derived for a limiting case. We briefly discuss the possible relevance of the present mechanism of the phase transition to that observed in a biferrocene–fluorotetracyanoquinodimethane (F_1TCNQ) complex.

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The equilibrium state of a many-body system in a heat bath of temperature T has the minimum free energy $F = E - TS$, where E and S denote the total energy and the entropy of the system.[1] Therefore, the energy E tends to be low, and the entropy S tends to be large. Because of the factor T in the second term of the definition of F, the former tendency is dominant over the latter at low temperatures, whereas the latter is dominant over the former at high temperatures. Hence, in many systems, the phase transition occurs between the low-temperature ordered phase with a low energy E and the high-temperature disordered phase with a large entropy S. Since the disordered state has a higher symmetry than the ordered state, the phase transitions in those systems are accompanied by spontaneous symmetry breaking. For example, the ferromagnetic transition is accompanied by symmetry breaking in the spin space, while the superconducting transition is accompanied by that in the gauge space.

In contrast, the liquid–gas transition is not accompanied by symmetry breaking, since both of phases have translational symmetry. In this letter, we demonstrate that the first-order phase transition without any symmetry breaking can also occur between two solid states with different stiffnesses. We refer to those states as the hard and soft states in this letter. The present transition is a new transition without symmetry breaking, in the aspect that it occurs between ordered phases. One of the necessary conditions for the occurrence of such a phase transition is that the cohesive energies of those solid states be similar. It is also essential for the occurrence of the transition that the cohesive energy be lower and the excitation energies of phonons be higher in the hard state than in the soft state. This condition is physically reasonable. For example, it is known that the sound velocity of longitudinal acoustic phonons is proportional to the inverse of the square root of compressibility. The symmetries of the hard and soft states can be the same in the present mechanism of the phase transition. An ionic crystal with two possible states of ionic charges would be an example of the system in which such a transition occurs, if the above conditions are satisfied.

This study was motivated by the recent discovery of a first-order phase transition in a biferrocene–fluorotetracyanoquinodimethane (F_1TCNQ) complex near 100–150 K.[2] This complex has the crystal structure of the CsCl type, and each biferrocene cation has one Fe^{III} and one Fe^{II} ion in the high-temperature phase, while it has two Fe^{III} ions in the low-temperature phase.[2,3] Hence, it has been argued that the high- and low-temperature states are ionic crystals with ionic charges of ± 1 and ± 2, respectively. The magnitudes of the Curie constants in the high- and low-temperature phases are explained very well by this physical picture.[2] It seems impossible, because of the redox potential energy, to assume a physical picture for the high-temperature phase in which the cations with two Fe^{III} ions and those with two Fe^{II} ions are randomly distributed with the probability of $1/2$.[3] Furthermore, the ionic charges tend to be uniform in the ionic crystal so that the static Coulomb energy and the lattice deformation energy are lowered. Therefore, the entropy difference at the transition point is not the entropy due to the random distribution of the ionic charges at high temperatures. It has also been discussed that the entropies of the electrons in the high- and low-temperature phases are the same.[3,4]

Motivated by the discovery of the above-described compound, we examine a system in which the ionic charges are uniformly distributed over all N lattice sites in both the high- and low-temperature phases. Hence, we introduce a macroscopic variable s, which represents the soft and hard phases by $s = 0$ and 1, respectively. In this model, the entropy difference at the transition temperature is attributed to the phonons, i.e., the lattice vibrations, which is appropriate for the biferrocene–F_1TCNQ complex, as discussed above. We define the cohesive energy per site $\epsilon^{(s)}$ and the frequency $\omega_{q\alpha}^{(s)}$ of the phonon of mode α and crystal momentum $\boldsymbol{q}$ in state s. Therefore, the Hamiltonian is expressed as

$$H = N\epsilon^{(s)} + \sum_{\boldsymbol{q}\alpha} \hbar\omega_{\boldsymbol{q}\alpha}^{(s)} \left(\hat{n}_{\boldsymbol{q}\alpha}^{(s)} + \frac{1}{2} \right), \tag{1}$$

where $\hat{n}_{\boldsymbol{q}\alpha}^{(s)}$ denotes the phonon number operator. We express the difference in the cohesive energies per site with corrections due to the zero-point fluctuations as

$$\Delta = \epsilon^{(0)} - \epsilon^{(1)} + N^{-1} \sum_{\boldsymbol{q}\alpha} \frac{1}{2} \left(\hbar\omega_{\boldsymbol{q}\alpha}^{(0)} - \hbar\omega_{\boldsymbol{q}\alpha}^{(1)} \right). \tag{2}$$

From the definition of s, we assume that $\Delta > 0$ and $\omega_{\boldsymbol{q}\alpha}^{(1)} > \omega_{\boldsymbol{q}\alpha}^{(0)}$, which is appropriate for the biferrocene–F_1TCNQ complex, because the crystal becomes harder for higher ionic charges. We disregard intramolecular vibrations, because they are irrelevant to the present phase transition.

The free energy is calculated as $F = -k_B T \ln Z$, where Z denotes the partition function $Z = \mathrm{Tr}(\mathrm{e}^{-\beta H})$ with $\beta = 1/k_B T$. Using eq. (1), we obtain

$$F(s) = -sN\Delta + k_B T \sum_{\boldsymbol{q}\alpha} \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega_{\boldsymbol{q}\alpha}^{(s)}}\right), \tag{3}$$

where we have omitted constant terms. Equation (3) can be rewritten as $F(s) = E(s) - TS(s)$ in terms of

$$\begin{aligned} E(s) &= -sN\Delta + \sum_{\boldsymbol{q}\alpha} \hbar\omega_{\boldsymbol{q}\alpha}^{(s)} n_{\boldsymbol{q}\alpha}^{(s)} \\ S(s) &= -k_B \sum_{\boldsymbol{q}\alpha} \left[n_{\boldsymbol{q}\alpha}^{(s)} \ln n_{\boldsymbol{q}\alpha}^{(s)} - (1 + n_{\boldsymbol{q}\alpha}^{(s)}) \ln(1 + n_{\boldsymbol{q}\alpha}^{(s)}) \right], \end{aligned} \tag{4}$$

where $n_{\boldsymbol{q}\alpha}^{(s)} = 1/(\mathrm{e}^{\beta\hbar\omega_{\boldsymbol{q}\alpha}^{(s)}} - 1)$. We define the free energy per site as $f(s) \equiv F(s)/N$. We refer to the sets of modes α of the acoustic and optical phonons as M_{ac} and M_{op}, respectively. We adopt the Debye approximation for the acoustic phonons. Hence, we set $\omega_{\boldsymbol{q}\alpha}^{(s)} \equiv c_\alpha |\boldsymbol{q}|$ for $\alpha \in M_{\mathrm{ac}}$. Furthermore, we set $\omega_{\boldsymbol{q}\alpha}^{(s)} \equiv \omega_\alpha^{(s)}$ for the optical phonons of $\alpha \in M_{\mathrm{op}}$, where $\omega_\alpha^{(s)}$ does not depend on $\boldsymbol{q}$, as in the Einstein model. Therefore, eq. (3) is rewritten as

$$f(s) = -s\Delta + f_{\mathrm{ac}}(s) + f_{\mathrm{op}}(s) \tag{5}$$

with

$$\begin{aligned} f_{\mathrm{ac}}(s) &= k_B T \sum_{\alpha \in M_{\mathrm{ac}}} N^{-1} \sum_{\boldsymbol{q}} \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega_{\boldsymbol{q}\alpha}^{(s)}}\right), \\ f_{\mathrm{op}}(s) &= k_B T \sum_{\alpha \in M_{\mathrm{op}}} \ln\left(1 - \mathrm{e}^{-\beta\hbar\omega_\alpha^{(s)}}\right). \end{aligned} \tag{6}$$

The first-order transition temperature T_c is determined from the condition $F(s=1) = F(s=0)$, which is rewritten as

$$\begin{aligned} \beta_c \Delta = &\sum_{\alpha \in M_{\mathrm{ac}}} N^{-1} \sum_{\boldsymbol{q}} \ln \frac{1 - \mathrm{e}^{-\beta_c\hbar\omega_{\boldsymbol{q}\alpha}^{(1)}}}{1 - \mathrm{e}^{-\beta_c\hbar\omega_{\boldsymbol{q}\alpha}^{(0)}}} \\ &+ \sum_{\alpha \in M_{\mathrm{op}}} \ln \frac{1 - \mathrm{e}^{-\beta_c\hbar\omega_\alpha^{(1)}}}{1 - \mathrm{e}^{-\beta_c\hbar\omega_\alpha^{(0)}}}, \end{aligned} \tag{7}$$

where $\beta_c \equiv 1/k_B T_c$.

For the acoustic phonons, the summation of an arbitrary function $G(\omega_{\boldsymbol{q}\alpha}^{(s)})$ of the form $N^{-1} \sum_{\boldsymbol{q}} G(\omega_{\boldsymbol{q}\alpha}^{(s)})$ is replaced with

$$\int \frac{\mathrm{d}^d q}{(2\pi)^d} \, G(\omega_{\boldsymbol{q}\alpha}^{(s)}) \approx \int_0^{\omega_{\mathrm{D}\alpha}^{(s)}} \mathrm{d}\omega \, \rho_{d\alpha}^{(s)}(\omega) \, G(\omega), \tag{8}$$

where d, $\rho_{d\alpha}^{(s)}$ and $\omega_{\mathrm{D}\alpha}^{(s)}$ denote the dimensions of the system, the density of states of the acoustic phonons, and the Debye frequency. Since $\rho_{d\alpha}^{(s)}(\omega) \propto \omega^{d-1}$ in the Debye model and $N^{-1} \sum_{\boldsymbol{q}} 1 = 1$, we obtain $\rho_{d\alpha}^{(s)}(\omega) = d\omega^{d-1}/(\omega_{\mathrm{D}\alpha}^{(s)})^d$. Here, it is convenient to define the function

$$A_d(t) \equiv -\int_0^1 \mathrm{d}p \, p^{d-1} \ln(1 - \mathrm{e}^{-p/t}). \tag{9}$$

We can rewrite f_{ac} as $f_{\mathrm{ac}}(s) = -k_B T d \sum_{\alpha \in M_{\mathrm{ac}}} A_d(t_\alpha^{(s)})$, where $t_\alpha^{(s)} \equiv k_B T/\hbar\omega_{\mathrm{D}\alpha}^{(s)}$. It is easy to derive

$$A_d(t) = t^d \Gamma(d) \zeta(d+1) - \Gamma(d) \sum_{k=1}^{d} \frac{t^k g_{k+1}(t)}{\Gamma(d-k+1)}, \tag{10}$$

where Γ and ζ denote the gamma function and Reimann's zeta function ($\zeta(2) = \pi^2/6$, $\zeta(3) = 1.202\cdots$, $\zeta(4) = \pi^4/90$), and the function $g_k(t)$ is defined as $g_k(t) \equiv \sum_{n=1}^{\infty} \mathrm{e}^{-n/t}/n^k = \mathrm{O}(\mathrm{e}^{-1/t})$. Therefore, we obtain the following expression for the acoustic phonon part of the free energy,

$$f_{\mathrm{ac}}(s) = \sum_{\alpha \in M_{\mathrm{ac}}} \hbar\omega_{\mathrm{D}\alpha}^{(s)} \bar{f}_{\mathrm{ac}}^{(d)}(t_\alpha^{(s)}), \tag{11}$$

with

$$\bar{f}_{\mathrm{ac}}^{(d)}(t) = d! \sum_{k=1}^{d} t^{k+1} \left[\frac{g_{k+1}(t)}{(d-k)!} - \zeta(d+1)\delta_{k,d} \right]. \tag{12}$$

We consider three possible cases: (1) a case in which the acoustic phonons are relevant and the optical phonons are negligible (i.e., $\omega_\alpha^{(s)} \gg T$ for $\alpha \in M_{\mathrm{op}}$), (2) a case in which the optical phonons are relevant and the acoustic phonons are negligible (i.e., $\omega_{\mathrm{D}\alpha}^{(s)} \gg T$ for $\alpha \in M_{\mathrm{ac}}$), and (3) a case in which both types of phonons are relevant at the same time. For simplicity, we consider a system in which there are one cation and one anion in a unit cell. In this case, the acoustic and optical phonons have three modes, because the ions oscillate in three dimensional space, even when the crystal structure is of low dimension. Furthermore, we set $\omega_\alpha^{(s)} = \omega_{\mathrm{op}}^{(s)}$ and $\omega_{\mathrm{D}\alpha}^{(s)} = \omega_{\mathrm{D}}^{(s)}$, which do not depend on α, as an example, because their values for the biferrocene–F_1TCNQ complex are unknown at present. Hence, the summations $\sum_{\alpha \in M_{\mathrm{ac}}}$ and $\sum_{\alpha \in M_{\mathrm{op}}}$ only result in factor 3. These simplifications do not cause any qualitative difference in the present mechanism of the phase transition.

First, we examine case (1), in which the acoustic phonons are relevant. The temperature dependences of the free energies for $s = 1$ and $s = 0$ are shown in Fig. 1. As an example, we set $\Delta = 0.1\hbar\omega_{\mathrm{D}}^{(0)}$ and $\omega_{\mathrm{D}}^{(1)} = 1.1\omega_{\mathrm{D}}^{(0)}$. The curves of the free energies for $s = 0$ and $s = 1$ cross at a finite temperature in any dimension. This result indicates the occurrence of the first-order phase transition, since the state with the lower free energy is realized at each temperature. At high temperatures, the soft state occurs since the entropy due to the lattice vibrations overcomes the increase in energy.

In this case, we can omit the second term of eq. (7). Then we obtain

$$\beta_c \Delta = 3d \left[A_d(t_c^{(0)}) - A_d(t_c^{(1)}) \right], \tag{13}$$

where $t_c^{(s)} = k_B T_c/\hbar\omega_{\mathrm{D}}^{(s)}$. Figure 2 shows the numerical solutions of eq. (13). It is found that the phase transition occurs at a finite temperature in any dimension, as long as $\Delta > 0$ and $\omega_{\mathrm{op}}^{(1)} > \omega_{\mathrm{op}}^{(0)}$. The transition temperature is higher in higher dimensions, although the dependence of T_c on the dimensionality is not very strong. When the value of Δ is fixed, the transition temperature T_c increases as the ratio $\omega_{\mathrm{op}}^{(1)}/\omega_{\mathrm{op}}^{(0)}$ decreases and approaches 1.

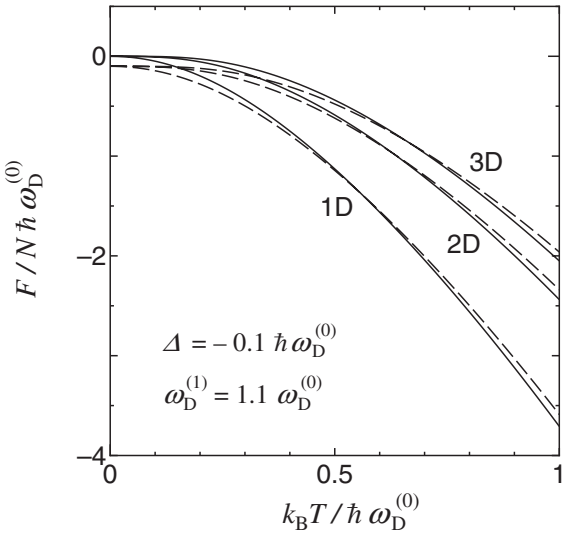

Fig. 1. Temperature dependences of the free energies when the acoustic phonons are relevant. The solid and dashed curves correspond to $s = 0$ and $s = 1$, respectively. The labels 1D, 2D and 3D indicate one, two and three dimensions, respectively.

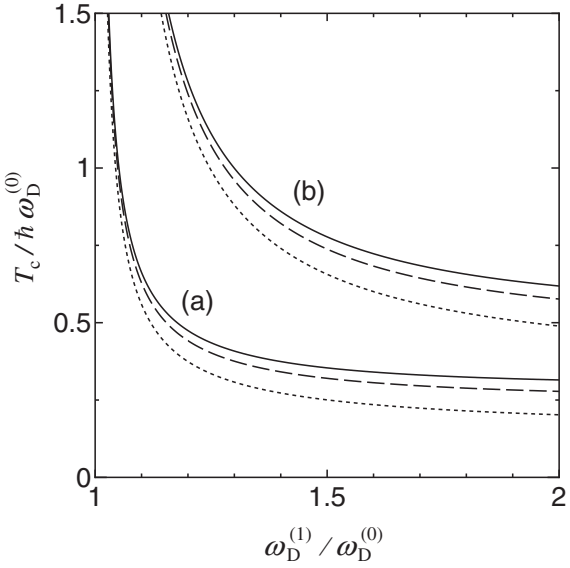

Fig. 2. Transition temperatures when the acoustic phonons are relevant. (a) $\Delta/\omega_{\rm D}^{(0)} = 0.1$ and (b) $\Delta/\omega_{\rm D}^{(0)} = 0.5$. The solid, dashed and dotted curves show the results in three, two and one dimensions, respectively.

When $k_{\rm B}T \ll \hbar\omega_{\rm D}^{(s)} \ll \hbar\omega_{\rm op}^{(s)}$, the free energy per site is expressed as

$$f(s) = -s\Delta - 3d!\,\zeta(d+1)\hbar\omega_{\rm D}^{(s)}\left(\frac{k_{\rm B}T}{\hbar\omega_{\rm D}^{(s)}}\right)^{d+1}, \qquad (14)$$

in d dimensions. Hence, we obtain the entropy and the specific heat as

$$S = 3(d+1)!\,\zeta(d+1)Nk_{\rm B}\left(\frac{k_{\rm B}T}{\hbar\omega_{\rm D}^{(s)}}\right)^{d},$$
$$C_{\rm V} = 3d(d+1)!\,\zeta(d+1)Nk_{\rm B}\left(\frac{k_{\rm B}T}{\hbar\omega_{\rm D}^{(s)}}\right)^{d}, \qquad (15)$$

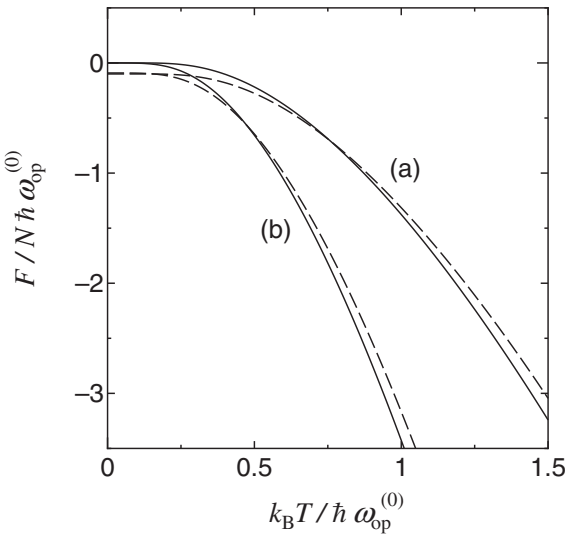

Fig. 3. Temperature dependences of the free energies (a) when only the optical phonons are relevant, and (b) when both the acoustic and optical phonons are relevant. The solid and dashed curves correspond to $s = 0$ and $s = 1$, respectively. We set $\Delta = 0.1\omega_{\rm op}^{(0)}$ and $\omega_{\rm op}^{(1)} = 1.1\omega_{\rm op}^{(0)}$. Furthermore, for curves (b), we set $\omega_{\rm D}^{(0)} = \omega_{\rm op}^{(0)}$ and assumed a three-dimensional system.

respectively. The transition temperature is derived as

$$T_{\rm c} = \frac{1}{k_{\rm B}[3d!\,\zeta(d+1)]^{\frac{1}{d+1}}}\left[\frac{\Delta}{(\hbar\omega_{\rm D}^{(0)})^{-d} - (\hbar\omega_{\rm D}^{(1)})^{-d}}\right]^{\frac{1}{d+1}}, \qquad (16)$$

when $\Delta \ll \hbar\omega_{\rm D}^{(0)} \lesssim \hbar\omega_{\rm D}^{(1)}$. We obtain the latent heat at the transition temperature as

$$Q = (d+1)N\Delta. \qquad (17)$$

Next, we examine case (2), in which the optical phonons are relevant and they all have the same frequency. The temperature dependences of the free energies for $s = 1$ and $s = 0$ are shown in Fig. 3. We set $\Delta = 0.1\hbar\omega_{\rm D}^{(0)}$ and $\omega_{\rm op}^{(1)} = 1.1\omega_{\rm op}^{(0)}$, as an example. The curves of the free energies of $s = 0$ and $s = 1$ cross at a finite temperature. Hence, it is found that the first-order transition occurs between the soft phase at high temperatures and the hard phase at low temperatures. The free energies when both the acoustic and optical phonons contribute [i.e., case (3)] are also plotted in Fig. 3. The transition temperature is lower than that when the acoustic phonons are irrelevant, because the entropy increases as the number of the relevant phonon modes increases.

In case (2), eq. (7) for the transition temperature $T_{\rm c}$ is simplified to

$$\beta_{\rm c}\Delta = 3\ln\left[\left(1 - {\rm e}^{-\beta_{\rm c}\hbar\omega_{\rm op}^{(1)}}\right)/\left(1 - {\rm e}^{-\beta_{\rm c}\hbar\omega_{\rm op}^{(0)}}\right)\right]. \qquad (18)$$

Figure 4 shows the numerical solution of eq. (18), and the latent heats calculated with eq. (4). When $\Delta > 0$ and $\omega_{\rm op}^{(1)} > \omega_{\rm op}^{(0)}$, we obtain a finite transition temperature. The transition temperature does not depend on the dimensionality. When the value of Δ is fixed, the transition temperature $T_{\rm c}$ increases as the ratio $\omega_{\rm op}^{(1)}/\omega_{\rm op}^{(0)}$ decreases, as in case (1). Since $F(1) = F(0)$ at $T = T_{\rm c}$, we have $Q = [TS(0) - TS(1)]_{T_{\rm c}} = [E(0) - E(1)]_{T_{\rm c}} \geq N\Delta$. It is analytically

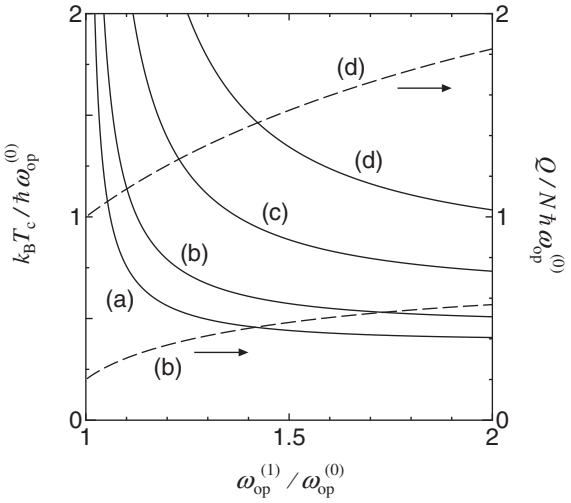

Fig. 4. Transition temperatures (solid curves and the left scale) and latent heats (dashed curves and the right scale) when the optical phonons are relevant. (a) $\Delta/\omega_{op}^{(0)} = 0.1$, (b) $\Delta/\omega_{op}^{(0)} = 0.2$, (c) $\Delta/\omega_{op}^{(0)} = 0.5$, and (d) $\Delta/\omega_{op}^{(0)} = 1$.

verified that Q increases as the ratio $\omega_{op}^{(1)}/\omega_{op}^{(0)}$ increases. It is found, from the numerical results, that Q/N is of the order of $k_B T_c$ in a large area of parameter space.

We obtained sharp transitions, as described above. However, the transition in the present compound has a finite width of $\sim$50 K.[2] This can be explained by the effect of inhomogeneity of the ionic charge distribution in the temperature region of the transition. A study of this effect will be presented in a separate paper.[5]

The valence transition observed in the compound $YbInCu_4$[6,7] is a similar phenomenon. In this compound, it was observed that the first-order transition from the high-temperature phase with Yb^{3+} to the low-temperature phase with $Yb^{2.9+}$ occurred at $T_V \approx 42$ K. Hence, the difference in the valence number is much smaller than that in the transition of the biferrocene–F_1TCNQ complex. Furthermore, the electron state changes qualitatively around the transition temperature in $YbInCu_4$. For example, the magnetic susceptibility changes from that described by the Curie law to the Pauli paramagnetic susceptibility. Hence, the transition in $YbInCu_4$ seems different from that in the present compound.[8]

The neutral-ionic transition observed in the TTF–chloranil compound[9,10] was also accompanied by changes of the ionic charges from ± 0 to ± 1. However, since the transition was accompanied by the spin-Peierls transition, the lattice symmetry changed at the transition point. Furthermore, the electron state also changed qualitatively there. Therefore, the neutral-ionic transition also seems quite different from the transition in the present compound.

In conclusion, it has been shown that the first-order phase transition without any symmetry breaking can occur between hard and soft solid states. An ionic crystal which has two possible states with different ionic charges would be a typical example of this phenomenon, if its cohesive energies are similar. The transition occurs between the high-temperature state with a high energy and a large entropy and the low-temperature state with a low energy and a small entropy, as in other phase transitions. The difference in the entropies at the transition temperature is attributed to the phonons. Both the optical and acoustic phonons can be relevant to the phase transition. The present theory is the only one proposed to explain the mechanism of the transition in the biferrocene–F_1TCNQ complex at present, to the author's knowledge. However, its quantitative confirmation based on future experimental data, such as phonon frequencies, remains as a topic of a future study.

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4) The entropies S_e of electrons are estimated as follows.[2] In the high-temperature phase, the F_1TCNQ anion has one electron with spin 1/2, and the biferrocene cation has a pair of one Fe^{III} and one Fe^{II}. Therefore, the state number is estimated to be $2 \times 2 \times (2J + 1) = 16$, where $J = 3/2$ denotes the quantum number of the electron on the Fe^{III} site, and one of the factor of 2 is the number of ways of choosing one Fe^{III} from two Fe ions. Thus, $S_e = k_B N \ln 16$. In the low-temperature phase, the two electrons on the F_1TCNQ anion form a singlet state, and the biferrocene cation has two Fe^{III}'s. Therefore, $S_e = k_B N \ln[(2J + 1)^2] = k_B N \ln 16$.
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