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Effect of Magnetic Field on the Fe(II) \rightleftharpoons Fe(III) Transitions Induced by the Cooperative Molecular Distortions in Molecular Crystals of Iron Compounds

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Abstract

Effect of magnetic field on the cooperative Fe(II) \rightleftharpoons Fe(III) transitions in iron compounds are studied on the basis of the ligand field theory by using the model in which the coupling of the iron ion with the intramolecular distortions and the intermolecular coupling between the molecular distortions are taken into account. The model predicts that the Fe(II) \rightleftharpoons Fe(III) transition can be induced by a magnetic field.

1. Introduction

The Fe(II) \rightleftharpoons Fe(III) transitions in haemoproteins play a fundamentally important role in the photosynthetic and the respiratory chain systems. The transitions are essential to the function of various cytochromes as electron carriers in photosynthetic electron flow¹⁾; it is highly probable that O₂ evolution in the photosystem II is generated by the cooperative Mn(II) \rightleftharpoons Mn(III) transitions in the water dehydrogenase^{2,3)}. It has been found that the electrical conductivity of an anhydrous cytochrome c₃ changes drastically with temperature and the origin of the drastic change is due to the Fe(II) \rightleftharpoons Fe(III) transitions⁴⁻⁶⁾.

The redox transitions of transition-metal ions in organic compounds have been investigated in various manners. It has been found by Drickamer⁷⁾ that Fe(III) reduces to Fe(II) with increasing pressure in a very wide variety of compounds which include such prototype molecules for haemoglobin as protoporphyrin iron (III) chloride (haemin) and hydroxide (haematin). They concluded from the observation that the reduction of iron ions is a thermal process involving the transfer of an electron from the ligands to the iron and the thermal deformation of the potential well for the iron must be the dominating effect for the reduction in haemin and haematin.

Recently we have investigated the thermally and pressure induced transitions of valency and spin states of Fe ions in a molecular crystals on the basis of the microscopic model⁸⁻¹⁰⁾, where the cooperative couplings of d electrons with intramelecular distortions, in a state of intermolecular couplings and with a lattice strain are taken into account. It has been shown in the previous papers that the various types of thermally and pressure induced Fe(II) \rightleftharpoons Fe(III) transitions are possible depending on the relative energy positions of the ground states of Fe(II) and Fe(III) ions in the undistorted phase and on the coupling strength of the Fe ion with the molecular distortion and the lattice strain. The model predicts that the Fe(II) \rightleftharpoons Fe(III) transition can be induced by a magnetic field, though it has not been observed yet.

In the present paper we investigate the effect of a magnetic field on the Fe(II) \rightleftharpoons Fe(III) transition on the basis of our model and present the effect of the field on the temperature dependences of such physical quantities associated with the transition as the cooperative intramolecular distortions, the Fe(II) ion fraction, and magnetic susceptibilities.

2. Model and basic equations

2.1 Description of the model

We consider a system which is built up of N large molecules and has a cubic symmetry. Each molecule contains an Fe ion surrounded octahedrally by bulky ligand complexes. In the Fe(II) \rightleftharpoons Fe(III) transition we consider explicitly only d electrons of an Fe ion and π electrons in a molecular orbital which is extended on the ligands; the effect of the other electrons on the transition are taken into account as the

potential acting on the d and π electrons. We assume for simplicity that the symmetry of the molecular orbital treated explicitly is A_{1g} . The octahedral ligand field gives rise to two possible ground states in each Fe ion, the high-spin state ${}^5T_{2g}(t_2^4e^2)$ and the low-spin state ${}^1A_{1g}(t_2^6)$ for the Fe(II) ion, and the high-spin state ${}^6A_{1g}(t_2^3e^2)$ and the low-spin state ${}^2T_{2g}(t_2^5)$ for the Fe(III) ion¹¹⁾. When the Fe ion is in the orbital-degenerate state T_{2g} , the molecule is unstable under a uniaxial distortion of its nuclear framework¹²⁾. Therefore, we take account of the coupling within a molecule (intramolecular coupling) between d electrons in the Fe ion and the displacements of the ligands with E_g symmetry of the O_h point group. Since the interaction between the intramolecular displacements in different molecules is essential to the cooperative Fe(II) \rightleftharpoons Fe(III) transition⁸⁾, we take account of the intramolecular interaction by considering the dispersion of the molecular vibration modes corresponding to the E_g displacements.

Thus, the Hamiltonian of the system is represented as

$$H = H_e + H_v + H_{ve} + H_z, \quad (1)$$

The first term H_e is the Hamiltonian for the electrons in the undistorted system and given by

$$H_e = \sum_i \sum_{n\nu} \varepsilon_n X_i^{n\nu}, \quad (2)$$

where ε_n is the energy of the electronic many body state $|in\nu\rangle$ of the i th molecule and

$$X_i^{n\nu} = |in\nu\rangle \langle in\nu|. \quad (3)$$

The second term H_v of eq. (1) is the Hamiltonian for the E_g intramolecular displacements Q_{2i} and Q_{3i} of the ligands in a state of intermolecular coupling and given by

$$H_v = \frac{1}{2} \sum_{\alpha} \sum_{\mathbf{k}} \left\{ \frac{1}{M} P_{\alpha}^*(\mathbf{k}) P_{\alpha}(\mathbf{k}) + M_{\alpha} \omega_{\alpha}(\mathbf{k})^2 Q_{\alpha}^*(\mathbf{k}) Q_{\alpha}(\mathbf{k}) \right\}, \quad (4)$$

$$Q_{\alpha}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_i \{ C_{\alpha 2}(\mathbf{k}) Q_{2i} + C_{\alpha 3}(\mathbf{k}) Q_{3i} \} e^{i\mathbf{k} \cdot \mathbf{R}_i}, \quad (5)$$

where $Q_{\alpha}(\mathbf{k})$ is the normal coordinate belonging to the α irreducible representation of the group of \mathbf{k} , Q_{2i} and Q_{3i} are the displacements of ligands in the molecule with E_g ($\propto x^2 - y^2$) and E_{gu} ($\propto 2z^2 - x^2 - y^2$) symmetries, respectively, and $C_{\alpha i}(\mathbf{k})$ is a symmetrization coefficient. The third term H_{ve} of eq. (1) is the interaction of the electrons with the intramolecular displacements Q_{ni} and written as

$$H_{ve} = \sum_i \sum_{n\nu} \{ Y_2(n\nu) Q_{2i} + Y_3(n\nu) Q_{3i} \} X_i^{n\nu}, \quad (6)$$

where

$$Y_l(n\nu) = \langle in\nu | (\partial V(i) / \partial Q_{li})_0 | in\nu \rangle, \quad (7)$$

$V(i)$ is the ligand field for the i th Fe ion and $(W)_0$ means the value of W for the undistorted system. The interaction H_{ve} is rewritten by using $Q_\alpha(\mathbf{k})$ for the latter convenience as

$$H_{ve} = \frac{1}{2} \sum_{\alpha\mathbf{k}} \sum_{n\nu} \{ Y_\alpha^{n\nu}(\mathbf{k})^* Q_\alpha(\mathbf{k}) + Y_\alpha^{n\nu}(\mathbf{k}) Q_\alpha^*(\mathbf{k}) \}, \quad (8)$$

where

$$Y_\alpha^{n\nu}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_i \sum_{l=2}^3 C_{\alpha l}(\mathbf{k}) Y_l(n\nu) e^{i\mathbf{k}\cdot\mathbf{R}_i} X_i^{n\nu}. \quad (9)$$

The final term H_z is the Zeeman term for d electrons in the external magnetic field B and written as

$$H_z = \sum_i (l_{iz} + 2s_{iz}) \mu_B B, \quad (10)$$

where μ_B is the Bohr magneton.

In order to obtain the eigenvalues of H , we eliminate the interaction H_{ve} by means of the unitary transformation⁸⁾,

$$A = \exp\left[-\frac{1}{2\hbar} \sum_{\alpha\mathbf{k}} \sum_{n\nu} \frac{Y_\alpha^{n\nu}(\mathbf{k})^* P_\alpha(\mathbf{k})^* + Y_\alpha^{n\nu}(\mathbf{k}) P_\alpha(\mathbf{k})}{M_\alpha \omega_\alpha(\mathbf{k})^2}\right]. \quad (11)$$

The Hamiltonian takes the form

$$H = H_e + H_{ee} + \tilde{H}_v + H_z, \quad (12)$$

where

$$H_{ee} = -\frac{1}{2} \sum_{n\nu} \sum_{\mu m} \sum_{\alpha\mathbf{k}} \frac{Y_\alpha^{n\nu}(\mathbf{k})^* Y_\alpha^{\mu m}(\mathbf{k})}{M_\alpha \omega_\alpha(\mathbf{k})^2} \quad (13)$$

$$\tilde{H}_v = \frac{1}{2} \sum_{\alpha\mathbf{k}} \left\{ \frac{1}{M_\alpha} \tilde{P}_\alpha^*(\mathbf{k}) \tilde{P}_\alpha(\mathbf{k}) + M_\alpha \omega_\alpha(\mathbf{k})^2 \tilde{Q}_\alpha^*(\mathbf{k}) \tilde{Q}_\alpha(\mathbf{k}) \right\}, \quad (14)$$

$$\tilde{P}_\alpha(\mathbf{k}) = A^* P_\alpha(\mathbf{k}) A = P_\alpha(\mathbf{k}), \quad (15)$$

$$\tilde{Q}_\alpha(\mathbf{k}) = A^* Q_\alpha(\mathbf{k}) A = Q_\alpha(\mathbf{k}) + \sum_{n\nu} \frac{Y_\alpha^{n\nu}(\mathbf{k})}{M_\alpha \omega_\alpha(\mathbf{k})^2}, \quad (16)$$

In order to clarify the meaning of H_{ee} , we rewrite H_{ee} in terms of $X_i^{n\nu}$ as

$$H_{ee} = -\frac{1}{2} \sum_{i,i'=2i,j=1}^3 \sum_{n\nu} \sum_{\mu m} J_{ii',i'j} Y_l(n\nu) Y_{l'}(m\mu) X_i^{n\nu} X_j^{m\mu}, \quad (17)$$

where

$$J_{i,i'} = \sum_{\mathbf{k}} \frac{C_{a_i}(\mathbf{k}) C_{a_{i'}}(\mathbf{k})}{NM_a \omega_a(\mathbf{k})^2} i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_{i'}) \quad (18)$$

The terms with $i \neq j$ in eq. (17) represent intermolecular interactions between the electrons in the different molecules. We adopt the random phase approximation to investigate the effect of the intermolecular coupling H_{ee} on the Fe(II) ⇌ Fe(III) transition. The operators $X_i^{n\nu} X_j^{m\mu}$ with $i \neq j$ in H_{ee} are replaced by

$$\langle X_i^{n\nu} \rangle X_j^{m\mu} + \langle X_j^{m\mu} \rangle X_i^{n\nu} - \langle X_i^{n\nu} \rangle \langle X_j^{m\mu} \rangle, \quad (19)$$

where $\langle X_i^{n\nu} \rangle$ means the thermal average of the operator $X_i^{n\nu}$ and is written hereafter as $\langle X^{n\nu} \rangle$, because it does not depend on the suffix i . Substituting the expression (19) into (17) and making the symmetry consideration¹³⁾, we obtain

$$H_{ee} = - \sum_i \sum_l \sum_{n\nu} \left\{ \frac{1}{2} j_2 Y_l(n\nu) + K_2 \sum_{m\mu} Y_l(m\mu) \langle X^{m\mu} \rangle \right\} Y_l(n\nu) X_i^{n\nu} + \frac{1}{2} NK_2 \sum_l \left\{ \sum_{n\nu} Y_l(n\nu) \langle X^{n\nu} \rangle \right\}^2, \quad (20)$$

where

$$j_2 = J_{2i,2i} = \frac{1}{N} \sum_{\mathbf{k}} \frac{C_{a_2}(\mathbf{k}) C_{a_2}^*(\mathbf{k})}{M_a \omega_a(\mathbf{k})^2}, \quad (21)$$

$$K_2 = \frac{1}{M_2 \omega_2(0)^2} - j_2. \quad (22)$$

Thus, the Hamiltonian $H_e + H_{ee} + H_z$ for the electrons is written as the sum of the Hamiltonian h_i for single molecule, where

$$h_i = \sum_{n\nu} \varepsilon_{n\nu} [\langle X \rangle] X_i^{n\nu} + \frac{1}{2} K_2 \sum_l \left\{ \sum_{n\nu} Y_l(n\nu) \langle X^{n\nu} \rangle \right\}^2 + (l_{iz} + 2S_{iz}) \mu_B B, \quad (23)$$

$$\varepsilon_{n\nu} [\langle X \rangle] = \varepsilon_n - \sum_l \left\{ \frac{1}{2} j_2 Y_l(n\nu) + K_2 \sum_{m\mu} Y_l(m\mu) \langle X^{m\mu} \rangle \right\} Y_l(m\mu). \quad (24)$$

The eigenvalues and eigenfunctions of h_i are calculated within the ${}^2T_{2g}(t_2^5 a^2)$, ${}^6A_{1g}(t_2^3 e^2 a^2)$, ${}^2A_{1g}(t_2^6 a^1)$, ${}^6T_{2g}(t_2^4 e^2 a^1)$, and ${}^4T_{2g}(t_2^4 e^2 a^1)$ manifold whose wave functions are represented as

$$|^2T_{2g} r M_s\rangle, |{}^6A_{1g} M_s\rangle, |{}^2A_{1g} M_s\rangle, |{}^6T_{2g} r M_s\rangle, \text{ and } |{}^4T_{2g} r M_s\rangle,$$

respectively, where $\gamma = \xi, \eta, \zeta$ and M_s denotes a z -component of spin. The eigenvalues are written as

$$F_{1,r} = E_{3L} - K_2 Y(III) \left[\frac{\sqrt{3}}{2} \langle Y_2 \rangle - \frac{1}{2} \langle Y_3 \rangle \right] + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2] + (3 - 2r + \kappa) \mu_B B \quad (r = 1, 2), \quad (25)$$

$$E_{2,r} = E_{3L} - K_2 Y(III) \left[\frac{\sqrt{3}}{2} \langle Y_2 \rangle + \frac{1}{2} \langle Y_3 \rangle \right] + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2] \\ + (3-2r-x) \mu_B B \quad (r = 1, 2), \quad (26)$$

$$E_{3,r} = E_{3L} - K_2 Y(III) \langle Y_3 \rangle + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2] \\ + (3-2r) \mu_B B \quad (r = 1, 2), \quad (27)$$

$$E_{4,r} = E_{3H} + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2] + (7-2r) \mu_B B \quad (r = 1 \sim 6), \quad (28)$$

$$E_{5,1} = E_{2L} + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2], \quad (29)$$

$$E_{6,r} = E_{2H} - K_2 Y(II) \left[\frac{\sqrt{3}}{2} \langle Y_2 \rangle - \frac{1}{2} \langle Y_3 \rangle \right] + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2] \\ + (6-2r+x) \mu_B B \quad (r = 1 \sim 5) \quad (30)$$

$$E_{7,r} = E_{2H} + K_2 Y(II) \left[\frac{\sqrt{3}}{2} \langle Y_2 \rangle + \frac{1}{2} \langle Y_3 \rangle \right] + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2] \\ + (6-2r-x) \mu_B B \quad (r = 1 \sim 5) \quad (31)$$

$$E_{8,r} = E_{2H} - K_2 Y(II) \langle Y_3 \rangle + \frac{1}{2} K_2 [\langle Y_2 \rangle^2 + \langle Y_3 \rangle^2] \\ + (6-2r) \mu_B B \quad (r = 1 \sim 5), \quad (32)$$

where E_{3L} is the energy of the $Fe^{3+}a^2$ low-spin state $|^2T_{2g}\gamma M_s\rangle$ in the undistorted phase ($\langle Y_2 \rangle = \langle Y_3 \rangle = 0$) and so forth, $Y(II)$ and $Y(III)$ are the coupling constants $Y_l(n\nu)$ of electrons with the intramolecular displacement Q_3 in the high-spin state $|^6T_{2g}\xi M_s\rangle$ or $|^4T_{2g}\xi M_s\rangle$ of the $Fe^{2+}a^1$ configuration and in the low-spin state $|^2T_{2g}\xi M\rangle$ of the $Fe^{3+}a^2$ configuration, respectively, and

$$\langle Y_l \rangle = \sum_{n\nu} Y_l(n\nu) \langle X^{n\nu} \rangle. \quad (33)$$

κ is the orbital reduction factor⁸⁾ for which we take 0.8 in the following calculation.

2.2 Basic equations in the thermodynamic equilibrium

The thermodynamic equilibrium state of the system is found by minimizing the free energy F with respect to $\langle Y_2 \rangle$ and $\langle Y_3 \rangle$ subject to the condition that the values of $\langle Y_l \rangle$ should satisfy eq. (33) selfconsistently. The free energy of the system is given by

$$F = -kT \ln \left[\sum_{n=1}^8 \sum_{r=1}^{n_r} \exp\left(-\frac{E_{n,r}}{kT}\right) \right] + F_{vib}, \quad (34)$$

where F_{vib} is the free energy for the harmonic vibrations described by the Hamiltonian \hat{H}_v (eq. (14)). The equilibrium values of $\langle Y_2 \rangle$ and $\langle Y_3 \rangle$ are

$$\langle Y_2 \rangle = \frac{\sqrt{3}}{2} Y(III) (\rho_1 - \rho_2) + \frac{\sqrt{3}}{2} Y(II) (\rho_6 - \rho_7), \quad (35)$$

$$\langle Y_3 \rangle = \frac{1}{2} Y(III) (2\rho_3 - \rho_1 - \rho_2) + \frac{1}{2} Y(II) (2\rho_8 - \rho_6 - \rho_7), \quad (36)$$

where ρ_n is the population of the n th level per ion and is defined by

$$\rho_n = \sum_{r=1}^{n_r} \rho_{n,r} = \frac{\sum_{r=1}^{n_r} \exp\left(-\frac{E_{n,r}}{kT}\right)}{\sum_{n=1}^8 \sum_{r=1}^{n_r} \exp\left(-\frac{E_{n,r}}{kT}\right)}. \quad (37)$$

The low-spin fractions, ρ_{III}^L and ρ_{II}^L , and the high-spin fractions ρ_{III}^H and ρ_{II}^H , for the Fe(III) and Fe(II) ions are given by

$$\rho_{III}^L = \rho_1 + \rho_2 + \rho_3 \quad (38)$$

$$\rho_{II}^L = \rho_5 \quad (39)$$

$$\rho_{III}^H = \rho_4 \quad (40)$$

$$\rho_{II}^H = \rho_6 + \rho_7 + \rho_8. \quad (41)$$

Since the equilibrium value of $\tilde{Q}_a(\mathbf{k})$ is zero, that of the real displacement $Q_a(\mathbf{k})$ of the ligands is obtained from eq. (16) as

$$\langle Q_a(\mathbf{k}) \rangle = - \sum_{n\nu} \frac{\langle Y_a^{n\nu}(\mathbf{k}) \rangle}{M_a \omega_a(\mathbf{k})^2} \quad (42)$$

Using eqs. (5), (9), and (33), we obtain

$$\langle Q_{li} \rangle = \frac{-\langle Y_l \rangle}{M_a \omega_a(0)^2} \quad (43)$$

This means that $\langle Y_l \rangle$ may be interpreted as a quantity describing the cooperative intramolecular distortion.

The magnetic susceptibility is the observable quantity which may show us efficiently the existence of the Fe(II) \rightleftharpoons Fe(III) transition. Therefore we calculate the magnetic susceptibility χ_{ij} of the system in the magnetic field parallel to the z axis. This is evaluated by¹⁴⁾

$$\chi_{ij} = -N \sum_{n=1}^8 \sum_{r=1}^{n_r} \frac{\partial E_{n,r}}{\partial B} \rho_{n,r}. \quad (44)$$

2.3 The values for E_{3L} , E_{3H} , E_{2L} , E_{2H} , $\sqrt{K_2} Y(III)$ and $\sqrt{K_2} Y(II)$

In order to obtain the temperature dependence of the cooperative intramolecular distortion, we require an information about the physically reasonable ranges of values for E_{3L} , E_{3H} , E_{2L} , E_{2H} , $\sqrt{K_2} Y(III)$ and $\sqrt{K_2} Y(II)$. Those for $(E_{3L} - E_{3H})$, $(E_{2H} - E_{2L})$, $(E_{2L} - E_{3H})$, $\sqrt{K_2} Y(III)$, and $\sqrt{K_2} Y(II)$ were estimated already from the previous studies^{10,11)} of the high-spin \rightleftharpoons low-spin transitions in the Fe(III) and Fe(II) compounds: The value for the energy separation $(E_{3L} - E_{3H})$ between the ${}^2T_{2g}$ and ${}^6A_{1g}$ states in the relevant Fe(III) compounds ranges from -2000 to 1500 cm^{-1} , the value for $(E_{2H} - E_{2L})$ between the ${}^5T_{2g}$ and ${}^1A_{1g}$ states in the relevant Fe(II) compounds ranges from 0 cm^{-1} to 2000 cm^{-1} and the value for $(E_{2L} - E_{3H})$ between the Fe(II) and Fe(III) ions in the undistorted system from -2000 cm^{-1} to 2000 cm^{-1} ; both the coupling parameters, $\sqrt{K_2} Y(III)$ and $\sqrt{K_2} Y(II)$, of the iron with the intramolecular distortion take a value in the region of $0 \sim 50 \text{ cm}^{-1/2}$.

3. The effect of magnetic field on the Fe(II) \rightleftharpoons (III) transitions

In this section we show how the temperature and magnetic field dependence of the physical quantities relevant to the Fe(II) \rightleftharpoons Fe(III) transition changes with the energy separation between the Fe(II) and Fe(III) states and with the coupling strength between the iron and the molecular distortion.

3.1 The case of the energy separation $(E_{2L} - E_{3H}) \leq 0$

Various types of transition may occur thermally by changing values of parameters⁸⁾. We show in Fig. 1 the thermal variation of the population of the ferrous state, ρ_{II} , as a function of magnetic field, in the case where $E_{2L} - E_{3H} = -600 \text{ cm}^{-1}$, $E_{3L} - E_{3H} = -500 \text{ cm}^{-1}$, $E_{2H} - E_{2L} = 500 \text{ cm}^{-1}$, $\sqrt{K_2} Y(III) = 15 \text{ cm}^{-1/2}$, and $Y(II)/Y(III) = 2$. It is seen in Fig. 1 that the thermal variation of the redox transition is much effected by magnetic field. The thermal variation of the cooperative molecular distortion $\langle Y_3 \rangle$ is shown in Fig. 2 as a function of magnetic field, where the parameter values are the same as those in Fig. 1. The equilibrium value of $\langle Y_2 \rangle$ is always zero. At the mediate strength of magnetic field, the discontinuous transition occurs twice. The first transition temperature T_{c1} decreases with strengthening magnetic field. The second transi-

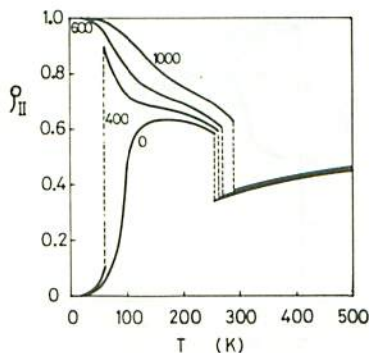


Fig. 1 Thermal and magnetic field variation of the population of ferrous state ρ_{II} in the case where $E_{2L} - E_{3II} = -600 \text{ cm}^{-1}$, $E_{3L} - E_{3II} = -500 \text{ cm}^{-1}$, $E_{2II} - E_{2L} = 500 \text{ cm}^{-1}$, $\sqrt{K_2} Y(III) = 15 \text{ cm}^{-1/2}$ and $Y(II)/Y(III) = 2$. The figures attached to the curves give values of B in kG.

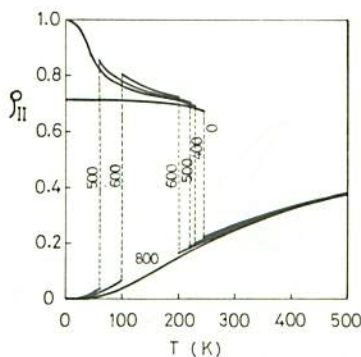


Fig. 2 Temperature and magnetic field variation of the cooperative distortion $\langle Y_3 \rangle$. The values of parameters are the same as those in Fig. 1. The figures attached to the curves give values of B in kG.

tion temperature T_{c2} at which the distortion disappears increases with magnetic field but the rate of the change is much smaller than that of T_{c1} . The temperature dependence of magnetic susceptibility x_{II} is also shown as a function of magnetic field in Fig. 3 where the parameter values are the same as those in Figs. 1 and 2. It is seen from a comparison of Fig. 2 with Figs. 1 and 3 that the effect of a magnetic field on the temperature dependence of cooperative intramolecular distortion is reflected on those of the physical quantities such as ρ_{II} and x_{II} .

3.2 The case of energy separation $(E_{2L} - E_{3II}) \geq 0$

Various types of transition may occur thermally by changing values of the parameters⁸⁾. We show in Fig. 4 the thermal variation of the population of ferrous

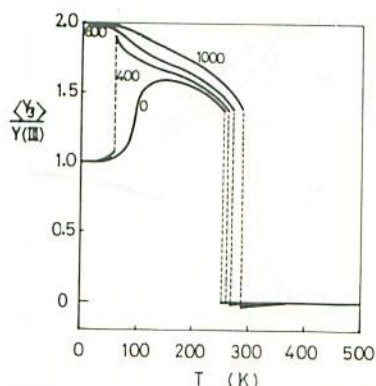


Fig. 3 Thermal and magnetic field variation of the magnetic susceptibility χ_{II} for the same values of parameters as in Fig. 2. The figures attached to the curves give values of B in kG.

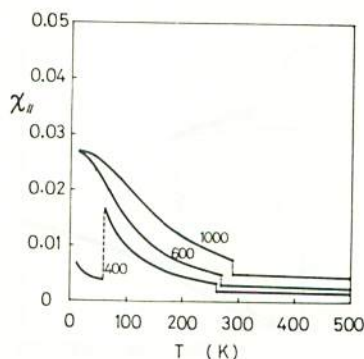


Fig. 4 Thermal and magnetic field variation of the population of ferrous state ρ_{II} in the case where $E_{2L} - E_{3H} = 0 \text{ cm}^{-1}$, $E_{3L} - E_{3H} = E_{2H} - E_{2L} = 500 \text{ cm}^{-1}$, $\sqrt{K_2} Y(III) = 32 \text{ cm}^{-1/2}$, and $Y(II)/Y(III) = 1$. The figures attached to the curves give values of B in pG.

state, ρ_{II} , as a function of magnetic field, in the case where $E_{2L} - E_{3H} = 0$, $E_{3L} - E_{3H} = E_{2H} - E_{2L} = 500 \text{ cm}^{-1}$, $\sqrt{K_2} Y(III) = 32 \text{ cm}^{-1/2}$, and $Y(II)/Y(III) = 1$. The temperature dependence of the cooperative molecular distortion $\langle Y_3 \rangle$ is shown as a function of magnetic field in Fig. 5. As increasing magnetic field the discontinuous transition occurs twice, i.e., firstly from the Fe(III) HS state to the Fe(II) HS due to the occurrence of the cooperative distortion and secondly from the Fe(II) HS to the Fe(III) HS due to its disappearance. When magnetic field is very strong, the cooperative distortion is unstable to occur and the continuous redox transition takes place. Figure 6 shows the effect of the field on the temperature dependence of magnetic susceptibility χ_{II} . It is seen from a comparison of Fig. 5 with Figs. 4 and 6 that the temperature dependence

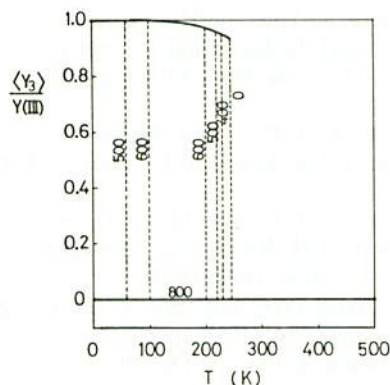


Fig. 5 Temperature and magnetic field distortion of the cooperative distribution $\langle Y_3 \rangle$. The values of parameters are the same as those in Fig. 4. The figures attached to the curves give values of B in kG.

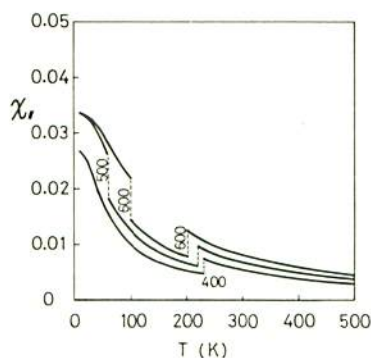


Fig. 6 Thermal and magnetic field variation of the magnetic susceptibility χ_i for the same values of parameters as in Fig. 5. The figures attached to the curves give values of B in kG.

of the cooperative intramolecular distortions is reflected on those of the physical quantities such as ρ_{II} and x_{ij} .

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