Charge Transfer in Mixed Valence Solids. Part VII.[1] Perturbation Calculations of Valence Delocalization in Iron(II,III) Cyanides and Silicates

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A method is described for calculating coupling integrals between donor and acceptor ions in class II mixed valence compounds. Metal–ligand–metal interactions are simulated by a perturbation model, which is then used to calculate valence delocalization coefficients from empirical and theoretical information on metal ⟶ ligand and ligand ⟶ metal charge transfer in the component single-valence complexes. The model is tested by applying it to $Fe^{II,III}$ cyanides (Prussian Blue and its discrete molecular analogues) and silicates (*e.g.* biotite micas). Good agreement is found between observed and calculated intensities of the mixed valence charge transfer transitions.

MATERIALS containing ions of different valence which occupy similar but distinguishable sites (class II mixed-valence systems)[2] have certain properties attributable to co-operative interaction between the mixed-valence (m.v.) ions (*e.g.* light absorption in the near-i.r. or visible, enhanced conductivity in the solid state), whilst retaining many of the individual characteristics

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[1] Part VI, P. Day and I. D. Hall, *J. Chem. Soc.* (*A*), 1970, 2679.

[2] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 248.

of their constituent ions. Low-energy light absorption in these compounds is then ascribed to charge-transfer (c.t.) from low-valence (electron-donor) to high-valence (electron-acceptor) ions and the absorption intensity depends upon the small delocalization of the optical electron over donor and acceptor sites. Similarly, carrier transport may be treated by band or polaron theory, in which carriers move over like sites (*e.g.* excess holes move over low-valence ions, excess electrons over high-valence ions). In addition, the m.v. metal ions may contain spin-free electrons, which are expected to couple ferromagnetically due to valence delocalization between sites (Zener double exchange [3]).

To achieve any quantitative understanding of the co-operative properties of class II m.v. systems, it is necessary to estimate the coupling integrals between donor and acceptor ions, which are of fundamental importance in determining metal ⟶ metal c.t. band intensities, mobilities of carriers in transport processes, and the ferromagnetic coupling energy due to m.v. interaction. The purpose of this paper is to describe a method of calculating coupling integrals and to apply it to calculate valence delocalization coefficients in some model class II m.v. systems. The model, and the coefficients extracted from it, may be validated by comparing the calculated intensities of the mixed-valence c.t. transitions with those observed experimentally.

GENERAL THEORY

Consider a system in which metal ions A(↑ ↓), B(↓) are each co-ordinated to a ligand L(↑ ↓). If orbitals Φ_L, Φ_L^* (which may be A.O.s or M.O.s) are localized on L, and orbitals χ_A, χ_B are localized on A, B respectively, the zeroth-order ground state, ψ_0 may be written:

$$\psi_0 = |\chi_A\bar{\chi}_A\Phi_L\bar{\Phi}_L\bar{\chi}_B| \qquad (1)$$

The metal ⟶ metal electron transfer (e.t.) configuration is then:

$$\psi_{ET1}(\chi_A \longrightarrow \chi_B) = |\chi_B\bar{\chi}_A\Phi_L\bar{\Phi}_L\bar{\chi}_B| \qquad (2)$$

Ground and first excited states are written to admit the effect of valence delocalization between metal ion sites (*cf.* ref. 2):

$$\psi_G = (1 - \alpha_1^2)^{\frac{1}{2}}\psi_0 + \alpha_1\psi_{ET1}(\chi_A \longrightarrow \chi_B) \qquad (3)$$

$$\psi_{E1} = (1 - \alpha'^2_0)^{\frac{1}{2}}\psi_{ET1}(\chi_A \longrightarrow \chi_B) + \alpha'_0\psi_0 \qquad (4)$$

As is usual in evaluating coupling (or resonance) integrals zero differential overlap (z.d.o.) is assumed so that the integral $<\psi_0|\mathscr{H}|\psi_{ET1}(\chi_A \longrightarrow \chi_B)>$, which to first order determines α_1, α'_0, simply reduces to $\langle\chi_A|H|\chi_B\rangle$, where H is an appropriate one-electron Hamiltonian. Since A, B are generally well separated in m.v. compounds, this integral is negligible. Consequently, the metal ions must interact *via* higher-order perturbations involving the metal ⟶ ligand, ligand ⟶ metal e.t. configurations $\psi_{ET2}(\chi_A \longrightarrow \Phi_L^*)$, ψ_{ET3}-$(\phi_L \longrightarrow \chi_B)$:

$$\psi_{ET2}(\chi_A \longrightarrow \Phi_L^*) = |\Phi_L^*\bar{\chi}_A\Phi_L\bar{\Phi}_L\bar{\chi}_B| \qquad (5)$$

$$\psi_{ET3}(\Phi_L \longrightarrow \chi_B) = |\chi_A\bar{\chi}_A\chi_B\bar{\Phi}_L\bar{\chi}_B| \qquad (6)$$

The valence delocalization coefficients α_1, α'_0 are given by second-order perturbation theory as:

$$\alpha_1 = \sum_{i=2,3} \frac{<\psi_0|\mathscr{H}|\psi_i> \cdot <\psi_1|\mathscr{H}|\psi_i>}{(E_1 - E_0)\cdot(E_i - E_0)} \qquad (7)$$

$$\alpha'_0 = \sum_{i=2,3} - \frac{<\psi_0|\mathscr{H}|\psi_i> \cdot <\psi_1|\mathscr{H}|\psi_i>}{(E_1 - E_0)\cdot(E_i - E_1)} \qquad (8)$$

where $\psi_{ET1}(\chi_A \longrightarrow \chi_B)$, $\psi_{ET2}(\chi_A \longrightarrow \Phi_L^*)$, $\psi_{ET3}(\Phi_L \longrightarrow \chi_B)$ are abbreviated as ψ_1, ψ_2, ψ_3 respectively; and where $E_n = <\psi_n|\mathscr{H}|\psi_n>$. Expressions (7) and (8) may be generalized to take into account interaction *via* a number of ligand orbitals by extending the summation i over all configurations $\psi_{ET}(\chi_A \longrightarrow \Phi_{Lj}^*)$, ψ_{ET}-$(\Phi_{Lk} \longrightarrow \chi_B)$.

To estimate the intensity of the transition $\psi_G \longrightarrow \psi_{E1}$ from calculated values of α_1, α'_0 we use the dipole length operator. The reliability of this operator in the present case is supported by a theoretical study [4] of the $\sigma(1s) \longrightarrow \sigma(2p)$ excitation in H_2^+, which indicates that dipole length transition moments are the most accurate for long-range interactions, and by the observation that both dipole length and velocity calculations of c.t. intensities in metal complexes of conjugated ligands are in good agreement with experiment, when the Linderberg [5] expression $\beta_{rs} = (h^2/m)$-(∇_{rs}/R) is used to calculate metal–ligand resonance integrals. The coupling integrals $<\psi_i|\mathscr{H}|\psi_j>$ reduce in form to metal–ligand resonance integrals, which are calculated by the Linderberg method whenever possible, otherwise they are chosen to reproduce (with the dipole length operator) the observed intensities of appropriate metal ⟶ ligand, ligand ⟶ metal c.t. bands. The denominator terms $(E_i - E_0)$ are set equal to the energies of corresponding c.t. transitions observed in the spectrum of the m.v. compound. When these transitions cannot be recognized in the reported spectrum, energies of similar excitations in related compounds are employed. Using these procedures we now apply equations (7) and (8) to two representative sets of class II m.v. compounds, in which Fe^{II} and Fe^{III} ions are bridged respectively, by cyanide and oxide ions. The delocalization parameters α_1 and α'_0 are calculated and then employed to estimate the intensity of the m.v. charge transfer transition.

Prussian Blue.—The Mössbauer spectrum [6] and magnetic susceptibility [7] of Prussian Blue indicate that low-spin Fe^{II} ions occupy strong-field sites, surrounded

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[3] C. Zener, *Phys. Rev.*, 1951, **21**, 440.

[4] D. R. Bates, *J. Chem. Phys.*, 1951, **19**, 1122.

[5] J. Linderberg, *Chem. Phys. Letters*, 1967, **1**, 39.

[6] E. Fluck, W. Kerler, and W. Nenwirth, *Angew. Chem. Internat. Edn.*, 1963, **2**, 277.

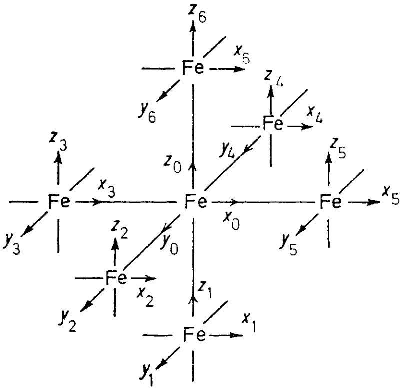
[7] D. Davidson and L. A. Welo, *J. Phys. Chem.*, 1928, **32**, 1191.

by six carbon atoms, whilst high-spin Fe^{III} ions occupy weak field octahedral sites. A recent *X*-ray study of a single crystal of Prussian Blue[8] reveals three different co-ordination units: $3Fe^{II}C_6$, $1Fe^{III}N_6$, and $3Fe^{III}N_4O_2$ in which the oxygen co-ordination is provided by water molecules. The final interatomic distances were Fe^{II}–C 1·93, Fe^{III}–N 2·00, Fe^{III}–O, 2·16, and C–N 1·15 Å.

The spectrum of an aqueous colloidal dispersal of Prussian Blue was measured by Robin,[9] who suggested the following band assignments:

14·1 kK	ε = 10 000	$Fe^{II}(t_{2g})$	$\longrightarrow Fe^{III}(t_{2g})$
24·5 kK	1 000	$Fe^{II}(t_{2g})$	$\longrightarrow Fe^{III}(e_g)$
34—38 kK	8 000	CN (π)	$\longrightarrow Fe^{III}(t_{2g})$
48 kK	25 000	$Fe^{II}(t_{2g})$	$\longrightarrow$ CN (π *)

The bands at 34—38 kK were assigned by Jørgenson[10] to crystal field excitations of the $Fe^{II}(CN)_6^{4-}$ ion; the observed extinction coefficients are, however, more consistent with Robin's interpretation. The band at 24·5 kK is probably the theoretically forbidden CN(σ) $\longrightarrow$ $Fe^{III}(t_{2g})$ excitation, which is observed with approximately the same energy and intensity in $Fe^{III}(CN)_6^{3-}$, rather than $Fe^{II}(t_{2g}) \longrightarrow Fe^{III}(e_g)$ which is also forbidden.



The co-ordinate axes used in defining the orbitals in the $Fe^{II}(CN)_6Fe_6^{III}$ subunit of Prussian blue

To calculate the spectrum of Prussian Blue, we consider for simplicity an isolated unit, $Fe^{II}(CN)_6Fe_6^{III}$, of O_h symmetry (Figure). The ground state of this system is written as a linear combination of ground and metal $\longrightarrow$ metal, metal $\longrightarrow$ ligand, ligand $\longrightarrow$ metal c.t. configurations of A_{1g} symmetry:

$$\psi_G(A_{1g}) = \psi_0(A_{1g}) + \alpha_1\psi_1(A_{1g}) + \alpha_2\psi_2(A_{1g}) + \alpha_3\psi_3(A_{1g}, \mathrm{I, II, III, IV}) \quad (9)$$

where

$$\psi_0(A_{1g}) = \psi[C^6(a_{1g})N^{30}(a_{1g})CN^{24}(a_{1g})] \quad (10)$$

$$\psi_1(A_{1g}) = \psi[C^5(t_{2g})N^{31}(t_{2g})CN^{24}(a_{1g})] \quad (11)$$

$$\psi_2(A_{1g}) = \psi[C^5(t_{2g})N^{30}(a_{1g})CN^{24}(a_{1g})CN^*(t_{2g})], \quad (12)$$

$$\begin{aligned}\psi_3(A_{1g}, \mathrm{I}) &= \psi[C^6(a_{1g})N^{31}(t_{2g})CN^{23}(t_{2g})],\\ \psi_3(A_{1g}, \mathrm{II}) &= \psi[C^6(a_{1g})N^{31}(t_{2g})CN^{23}(t_{2g})],\\ \psi_3(A_{1g}, \mathrm{III}) &= \psi[C^6(a_{1g})N^{31}(t_{2u})CN^{23}(t_{2u})]\\ \psi_3(A_{1g}, \mathrm{IV}) &= \psi[C^6(a_{1g})N^{31}(t_{1u})CN^{23}(t_{1u})] \quad (13)\end{aligned}$$

in which C^i, N^j represent numbers of *d* electrons in carbon, nitrogen holes respectively; and CN^k, CN* represent electrons in cyanide π, π^* orbitals.

Spectrally active excited states are formed as linear combinations of T_{1u} symmetry. Writing metal $\longrightarrow$ metal c.t. state wavefunctions to first order in metal–metal electron delocalization (*i.e.* second order in metal–ligand electron delocalization), and metal $\longrightarrow$ ligand, ligand $\longrightarrow$ metal c.t. state wavefunctions to first order in metal–ligand electron delocalization:

$$\psi_{E1}(T_{1u}, N) = \psi_1(T_{1u},N) + \alpha_2\psi_2(T_{1u},N) + \alpha_3\psi_3(T_{1u},N);\ N = \mathrm{I, II} \quad (14)$$

$$\psi_{E2}(T_{1u},N) = \psi_2(T_{1u},N);\ N = \mathrm{I, II} \quad (15)$$

$$\psi_{E3}(T_{1u},N) = \psi_3(T_{1u},N);\ N = \mathrm{I, II, III, IV, V, VI, VII, VIII} \quad (16)$$

where

$$\begin{aligned}\psi_1(T_{1u},\mathrm{I}) &= \psi[C^5(t_{2g})N^{31}(t_{1u})CN^{24}(a_{1g})],\\ \psi_1(T_{1u},\mathrm{II}) &= \psi[C^5(t_{2g})N^{31}(t_{2u})CN^{24}(a_{1g})] \quad (17)\end{aligned}$$

$$\begin{aligned}\psi_2(T_{1u},\mathrm{I}) &= \psi[C^5(t_{2g})N^{30}(a_{1g})CN^{24}(a_{1g})CN^*(t_{1u})],\\ \psi_2(T_{1u},\mathrm{II}) &= \psi[C^5(t_{2g})N^{30}(a_{1g})CN^{24}(a_{1g})CN^*(t_{2u})] \quad (18)\end{aligned}$$

$$\begin{aligned}\psi_3(T_{1u},\mathrm{I}) &= \psi[C^6(a_{1g})N^{31}(t_{1u})CN^{23}(t_{2g})],\\ \psi_3(T_{1u},\mathrm{III}) &= \psi[C^6(a_{1g})N^{31}(t_{2g})CN^{23}(t_{1u})],\\ \psi_3(T_{1u},\mathrm{IV}) &= \psi[C^6(a_{1g})N^{31}(t_{2g})CN^{23}(t_{2u})],\\ \psi_3(T_{1u},\mathrm{V}) &= \psi[C^6(a_{1g})N^{31}(t_{1g})CN^{23}(t_{1u})],\\ \psi_3(T_{1u},\mathrm{VI}) &= \psi[C^6(a_{1g})N^{31}(t_{1u})CN^{23}(t_{1g})],\\ \psi_3(T_{1u},\mathrm{VII}) &= \psi[C^6(a_{1g})N^{31}(t_{1g})CN^{23}(t_{2u})],\\ \psi_3(T_{1u},\mathrm{VIII}) &= \psi[C^6(a_{1g})N^{31}(t_{2u})CN^{23}(t_{1g})] \quad (19)\end{aligned}$$

Transition moments of the bands *ca.* 14, 34—38, 48 kK are given by applying the dipole length operator (with the point dipole approximation) to the excitations $\psi_G(A_{1g}) \longrightarrow \psi_{E1}(T_{1u}),\ \psi_{E2}(T_{1u}),\ \psi_{E3}(T_{1u})$:

$$\begin{aligned}&<\psi_G(A_{1g})|\sum_i er_i|\psi_{E1}(T_{1u})> = \alpha_1<\psi_1(A_{1g})|\sum_i er_i|\psi_i(T_{1u},\mathrm{I})>\\ &+ \alpha_2\alpha'_2<\psi_2(A_{1g})|\sum_i er_i|\psi_2(T_{1u},\mathrm{I})>\\ &+ \alpha_3\alpha'_3[<\psi_3(A_{1g},\mathrm{I})|\sum_i er_i|\psi_3(T_{1u},\mathrm{I})>\\ &+ <\psi_3(A_{1g},\mathrm{IV})|\sum_i er_i|\psi_3(T_{1u},\mathrm{I})>]\\ &= \alpha_1\mu_1 + \alpha_2\alpha'_2\mu_2 + \alpha_3\alpha'_3\mu_3 \quad (20)\end{aligned}$$

$$\begin{aligned}&<\psi_G(A_{1g})|\sum_i er_i|\psi_{E2}(T_{1u},\mathrm{I})> = \alpha_2<\psi_2(A_{1g})|\sum_i er_i|\psi_2(T_{1u},\mathrm{I})>\\ &= \alpha_2\mu_2 \quad (21)\end{aligned}$$

$$\begin{aligned}&<\psi_G(A_{1g})|\sum_i er_i|\psi_{E3}(T_{1u},\mathrm{I})> = \alpha_3[<\psi_3(A_{1g},\mathrm{I})|\sum_i er_i|\text{-}\\ &\psi_3(T_{1u},\mathrm{I})>\\ &+ <\psi_3(A_{1g},\mathrm{IV})|\sum_i er_i|\psi_3(T_{1u},\mathrm{I})>]\\ &= \alpha_3\mu_3 \quad (22)\end{aligned}$$

If metal *d* orbitals, xy_i, xz_i, yz_i, are defined according

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[8] H. J. Buser, A. Ludi, W. Petter, and D. Schwarzenbach, *J.C.S. Chem. Comm.*, 1972, 1299.

[9] M. B. Robin, *Inorg. Chem.*, 1962, **1**, 337.

[10] C. K. Jørgensen, quoted in J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, 1961.

to the co-ordinate scheme of the Figure, and if Φ_d represents a symmetry-adapted linear combination of Fe^{III} d orbitals, μ_1 reduces to:

$$\mu_1 = <\psi_1(A_{1g})|\sum_i er_i|\psi_1(T_{1u})> = 3<\Phi_d(t_{2g})|\sum_i er_i|\Phi_d(t_{1u})>$$

where the factor $3(=\sqrt{3} \times \sqrt{3})$ accounts for the degeneracy of the Φ. Substituting the linear combinations of d orbitals for $\Phi_d(t_{2g})$ and $\Phi_d(t_{1u})$, expanding and taking only one-centre terms, we find that:

$$\mu_1 = -\sqrt{3}R(\mathrm{Fe^{II} - Fe^{III}}) \qquad (23)$$

μ_2, μ_3 are derived by a similar procedure using appropriate combinations of π, π^* orbitals:

$$\mu_2 = -\sqrt{3}R(\mathrm{Fe^{II}\text{-}CN}) \qquad (24)$$

$$\mu_3 = -\sqrt{3}R(\mathrm{Fe^{III}\text{-}NC}) \qquad (25)$$

Taking into account the degeneracies of the transitions $\psi_G \longrightarrow \psi_{E1}$, ψ_{E2}, ψ_{E3}, the corresponding bands have total theoretical dipole length transition moments as follows:

14·1 kK, $\psi_G(A_{1g}) \longrightarrow \psi_{E1}(T_{1u},N)$, $-\sqrt{2}(\alpha_1\mu_1 + \alpha_2\alpha'_2\mu_2 + \alpha_3\alpha'_3\mu_3)$
34—38 kK, $\psi_G(A_{1g}) \longrightarrow \psi_{E3}(T_{1u},N)$, $-2\sqrt{2}\alpha_3\mu_3$
48·0 kK, $\psi_G(A_{1g}) \longrightarrow \psi_{E2}(T_{1u},N)$, $-\sqrt{2}\alpha_2\mu_2$ (26)

The coefficients α_2, α'_2, α_3, α'_3 may be derived from first-order perturbation theory, and the coefficient α_1 from second-order perturbation theory [equation (7)], as:

$$\alpha_1 = \frac{2(xz_0|H|\pi x_1)(xz_1|H|\pi x_1)}{(E_3 - E_0)\,(E_1 - E_0)} - \frac{2(xz_0|H|\pi\overset{*}{x}_1)(xz_1|H|\pi\overset{*}{x}_1)}{(E_2 - E_0)\,(E_1 - E_0)} \qquad (27)$$

$$\alpha_2 = \frac{2\sqrt{2}(xz_0|H|\pi x_1)}{(E_2 - E_0)};\quad \alpha'_2 = \frac{(xz_1|H|\pi\overset{*}{x}_1)}{\sqrt{2}(E_2 - E_1)} \qquad (28)$$

$$\alpha_3 = \frac{(xz_1|H|\pi x_1)}{(E_3 - E_0)};\quad \alpha'_3 = \frac{2(xz_0|H|\pi x_1)}{(E_3 - E_1)} \qquad (29)$$

where E_0, E_1, E_2, E_3 are the energies of the configurations ψ_0, ψ_1, ψ_2, ψ_3 respectively.

If the cyanide ion M.O.s π, π^* are written in terms of C, N p A.O.s, x_C, x_N:

$$\pi x = ax_C + bx_N,$$
$$\pi\overset{*}{x} = bx_C - ax_N \qquad (30)$$

then

$$(xz_0|H|\pi x_1) = a\beta(\mathrm{Fe^{II}—C}),$$
$$(xz_1|H|\pi x_1) = b\beta(\mathrm{Fe^{III}—N}),$$
$$(xz_0|H|\pi\overset{*}{x}_1) = b\beta(\mathrm{Fe^{II}—C}),$$
$$(xz_1|H|\pi\overset{*}{x}_1) = -a\beta(\mathrm{Fe^{III}—N}) \qquad (31)$$

where the β's are Fe^{II}, Fe^{III} d_{xz}—C, N p_X resonance integrals for the appropriate bond distances in Prussian Blue, and are calculated using the Linderberg[5] expression from Richardson Fe(0),[11] Clementi C, N A.O. functions:[12]

$$\beta(\mathrm{Fe^{II}—C}),\ 6·35\ \mathrm{kK};\ \ \beta(\mathrm{Fe^{III}—N}),\ 4·80\ \mathrm{kK} \qquad (32)$$

The a, b coefficients in (31) are assigned the approximate value $1/\sqrt{2}$; and the E_i terms in (27)—(29) are taken from the energies of the $\psi_G \longrightarrow \psi_{Ei}$ transitions in Prussian Blue as:

$(E_1—E_0)$ 14·1 kK; $(E_2—E_0)$ 48·0 kK; $(E_3—E_0)$ 36·0 kK (33)

Using (27)—(33) the calculated α_i, α'_i values are:

α_1 0·106, α_2 —0·265, α'_2 —0·070, α_3 —0·095, α'_3 —0·423

If $R(\mathrm{Fe^{II}—Fe^{III}})$, $R(\mathrm{Fe^{II}—CN})$, $R(\mathrm{Fe^{III}—NC})$ are set as 5·1, 2·5, and 2·6 Å respectively, expressions (23)—(26) give the calculated transition moments:

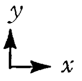
Band energy/kK	Calculated transition moment/eÅ	Observed transition moment/eÅ
14·1	1·69	1·23
34—38	1·23	0·96
48	1·63	1·50

The calculated transition moment for $Fe^{II} \longrightarrow Fe^{III}$ charge transfer is rather high. This appears to be due to the weakness in equations (17) and (27) that small errors in the evaluation of metal–ligand coupling integrals may be compounded in the calculation of metal–metal valence delocalization coefficients. Use of semi-empirical metal–ligand resonance integrals derived from the observed intensities of the 34—38, 48 kK bands of Prussian Blue leads to a calculated moment for the 14·1 kK transition of 1·25 eÅ.

$[Fe_2(CN)_{11}]^{6-}$.—Following earlier work by Emschwiller,[13] Ludi and his colleagues[14] have recently prepared a series of complex ions of general formula $[(R_1)_5M_1R_3M_2(R_2)_5]^{n-}$, in which $R_1 = NH_3$, CN; R_2 = CN; R_3 = CN, pyrazine; M_1, M_2 = Fe, Ru. The spectrum of the m.v. ion $[Fe_2(CN)_{11}]^{6-}$, measured by Ludi and Roder,[14] contains a band at 25 kK, which is generally observed in cyanide complexes of Fe^{III}, and is presumably due to $CN(\sigma) \longrightarrow Fe^{III}$ c.t. excitation. This indicates trapping of metal ion valences in the complex ion. A band at 7·7 kK may then be safely assigned to an $Fe^{II} \longrightarrow Fe^{III}$ c.t. transition. $CN(\pi) \longrightarrow Fe^{III}$, $Fe^{II} \longrightarrow CN(\pi^+)$ c.t. excitations are responsible for absorption from 30 to 40, 45 to 50 kK respectively, as in Prussian Blue and the ferricyanide, ferrocyanide ions.

In the theoretical treatment of $[Fe_2(CN)_{11}]^{6-}$ only the simple linear system

Fe_1-C-N-Fe_2



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[11] J. W. Richardson, W. C. Nienwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

[12] E. Clementi, *I.B.M. Journal Res. Devel.*, 1965, **9**, 2.

[13] G. Emschwiller, *Compt. rend.*, 1967, **265C**, 281.

[14] A. Ludi, personal communication.

need be considered. It is assumed that the *C*-co-ordinated Fe_1 ion is formally divalent, the *N*-co-ordinated Fe_2 ion being formally trivalent. Both metal ions are expected to be low spin.

The component of the zeroth-order ground state in which the unpaired electron in Fe^{III} occupies d_{yz} may be written:

$$\psi_0 = |\overline{yz}_1\, yz_1\, \pi\bar{y}\, \pi y\, yz_2| \times \psi'_0 \qquad (34)$$

where $\psi'_0 = |xy_1\ x\bar{y}_1\ xz_1\ x\bar{z}_1\ \pi z\ \bar{\pi}z\ xy_2\ \bar{x}y_2\ xz_2\ x\bar{z}_2|$; *xy, xz, yz* are Fe_1, Fe_2 *d* orbitals; and πy, πz are CN^- ion π M.O.s, of form (30). Corresponding metal ⟶ metal, metal ⟶ ligand, and ligand ⟶ metal e.t. configurations are then:

$$\psi_1 = |yz_1\, \overline{yz}_2\, \pi y\, \pi y\, yz_2| \times \psi'_0 \qquad (35)$$

$$\psi_2 = |yz_1\, \bar{\pi}y^*\, \pi y\, \bar{\pi}y\, yz_2| \times \psi'_0 \qquad (36)$$

$$\psi_3 = |yz_1\, \overline{yz}_1\, \pi y\, \overline{yz}_2\, yz_2| \times \psi'_0 \qquad (37)$$

Ground and metal ⟶ metal c.t. states are formed as linear combinations of ψ_0, ψ_1:

$$\begin{aligned}\psi_G &= \psi_0 + \gamma_1\psi_1,\\ \psi_{E1} &= \psi_1 + \gamma'_0\psi_0\end{aligned} \qquad (38)$$

The transition dipole of the excitation $\psi_G \longrightarrow \psi_{E1}$ is given by:

$$\begin{aligned}\mu(\psi_G \longrightarrow \psi_{E1}) &= \gamma_1 < \psi_1|\sum_i er_i|\psi_1>\\ &\quad + \gamma'_0 < \psi_0|\sum_i er_i|\psi_0>\\ &= \gamma_1\mu_1 + \gamma'_0\mu_0\end{aligned} \qquad (39)$$

where, if the origin of the *z*-axis is chosen using expression (34),

$$\begin{aligned}\mu_0 &= -R(Fe^{II}—Fe^{III})/2,\\ \mu_1 &= R(Fe^{II}—Fe^{III})/2\end{aligned} \qquad (40)$$

The coefficients γ_1, γ'_0 can be derived from (7), (8) as:

$$\gamma_1 = \frac{(yz_1|H|\pi y^*)(yz_2|H|\pi y^*)}{(E_2 - E_0)(E_1 - E_0)} - \frac{(yz_1|H|\pi y)(yz_2|H|\pi y)}{(E_3 - E_0)\,(E_1 - E_0)} \qquad (41)$$

$$\gamma'_0 = -\frac{(yz_1|H|\pi y^*)(yz_2|H|\pi y^*)}{(E_2 - E_1)\,(E_1 - E_0)} - \frac{(yz_1|H|\pi y)(yz_2|H|\pi y)}{(E_3 - E_0)\,(E_1 - E_0)} \qquad (42)$$

The cyanide M.O. coefficients *a*, *b* of (31) are once again given the approximate value $1/\sqrt{2}$, while the interatomic distances in the complex are assessed from crystallographic data on related ions[15] as:

$R(Fe^{II}—C)$ 1·92 Å; $R(C—N)$ 1·15 Å
$R(Fe^{III}—N)$ 1·85 Å; $R(Fe^{II} - Fe^{III})$ 4·92 Å

Resonance integrals $\beta(Fe^{II}—C)$, $\beta(Fe^{III}—N)$ for the appropriate metal–ligand distances are again calculated from the Linderberg[5] expression from Richardson Fe(0),[11] Clementi C,N A.O. functions[12] giving $\beta(Fe^{II}—C)$: 6·35 kK; $\beta(Fe^{III}—N)$: 7·30 kK. Metal ⟶ ligand (π^*), ligand (π) ⟶ metal c.t. bands are not clearly defined in the reported spectrum of $[Fe_2(CN)_{11}]^{6-}$. Consequently, $(E_1 - E_0)$, $(E_2—E_0)$, $(E_3—E_0)$ have to be taken from the spectra of $[Fe_2(CN)_{11}]^{6-}$, Prussian Blue, and $Fe(CN)_6^{3-}$ respectively as $(E_1—E_0)$ 7·7 kK; $(E_2—E_0)$ 35 kK; $(E_3—E_0)$ 48 kK. With these various assumptions, equations (31), (41), and (42) lead to values of γ_1 and γ'_0 of 0·149 and −0·186 respectively.

The next step is to take account of the distribution of the hole in the d_{xy}, d_{xz}, d_{yz} orbitals of the Fe^{III} ion, which depends upon the balance of spin–orbit coupling and the tetragonal distortion of the ligand field from octahedral symmetry. Location of the hole in the d_{xz}, d_{yz} orbitals of Fe^{III} is favoured by $Fe^{II} \longrightarrow Fe^{III}$ c.t. interaction. However, the effect of the distortion in cyanide co-ordination about Fe^{III} cannot be ascertained, so it seems safest to assume that $C(yz, xz) = \sqrt{\tfrac{2}{3}}$, $C(xy) = \sqrt{\tfrac{1}{3}}$. Then the 'true' coefficients of valence delocalization, α_1, α'_0, are given by:

$$\begin{aligned}\alpha_1 &= \sqrt{\tfrac{2}{3}}\,\gamma_1 = 0{\cdot}117,\\ \alpha'_0 &= \sqrt{\tfrac{2}{3}}\,\gamma'_0 = -\,0{\cdot}153\end{aligned}$$

The transition moment $\mu(\psi_G \longrightarrow \psi_{E1})$ is now dependent upon α_1, α'_0 rather than γ_1, γ'_0 in (39), and is calculated as 0·67 eÅ, in reasonable agreement with the observed 0·80 eÅ.

Biotite Micas.—Many naturally occurring minerals contain Fe^{II}, Fe^{III}, both as major constituents and as impurities. As long ago as 1926, MacCarthy[16] was able to correlate the wide variation in their colour with the oxidation state of the iron and to demonstrate that the darkest colours were found when Fe^{II} and Fe^{III} were similtaneously present. Robbins and Strens[17] have recently reported polarized spectra for fifteen biotite micas of various Fe^{II}, Fe^{III} composition, in which there is clear evidence that absorption at 15 kK is due to $Fe^{II} \longrightarrow Fe^{III}$ charge transfer, and which are therefore suitable model systems to test our perturbation model of class II m.v. interactions.

Biotite micas are built up of composite sheets in which a layer of octahedrally co-ordinated cations (Mg^{II}, Fe^{II}, Al^{III}, Fe^{III}, and Ti^{IV}) is sandwiched between two layers of corner-sharing SiO_4, AlO_4 tetrahedra.[18] Discrete sheets are weakly held together by layers of K^+ ions, which form cleavage planes of the crystal. Neighbouring Fe^{II}, Fe^{III} ions share two common ligands ($2OH^-$ or OH^-, O^{2-}).

Robbins and Strens give the following spectral data and assignments for biotites containing appreciable quantities of Fe^{II}, Fe^{III}:

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[15] V. A. Pospdov and G. S. Zhdanov, *J. Phys. Chem. U.S.S.R.*, 1947, **21**, 279; A. K. van Bever, *Rec. Trav. chim.*, 1938, **57**, 1259.

[16] G. R. MacCarthy, *Amer. J. Sci.*, 1926, **12**, 16.

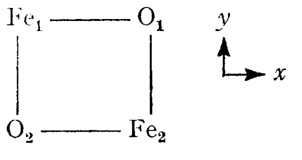
[17] D. W. Robbins and R. G. Strens, *Mineral Mag.*, 1972, **38**, 551.

[18] A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon Press, Oxford, 1962.

Band energy/kK	Variation of intensity with mineral composition	Assignment
8·7 10·9	Proportional to Fe^{II} content	$Fe^{II}(t_{2g}) \longrightarrow Fe^{III}(e_g)$ *
13·9	Proportional to the product of Fe^{II}, Fe^{III} concentrations	$Fe^{II}(t_{2g}) \longrightarrow Fe^{III}(t_{2g})$
20—25	? ?	$O^{2-}(\pi) \longrightarrow Ti^{IV}(t_{2g})$
>50	Proportional to Fe^{II} content	$O^{2-}(\pi) \longrightarrow Fe^{II}(t_{2g})$

The 13·9 kK band is polarized exclusively in the cleavage plane of the crystal, which lends further support to its assignment to $Fe^{II} \longrightarrow Fe^{III}$ charge transfer.

The concentrations of Fe^{II}, Fe^{III} in biotite minerals are such that nearest-neighbour Fe^{II}, Fe^{III} ions must predominantly occur in isolated pairs. If, initially, no account is taken of distortion of the octahedral sites, the model system



may be chosen to illustrate Fe^{II}—Fe^{III} interaction.

An octahedral array of O^{2-}, OH^- ions constitutes a rather weak ligand field, so that both Fe^{II}, Fe^{III} are high spin. The lowest energy $Fe^{II} \longrightarrow Fe^{III}$ e.t. excitation responsible for the 13·9 kK absorption band in biotites is then of form

$$Fe_1{}^{II}(t_{2g}{}^4)(\uparrow\uparrow\uparrow\downarrow)\,Fe_2{}^{III}(t_{2g}{}^3)(\uparrow\uparrow\uparrow) \longrightarrow Fe_1{}^{III}(t_{2g}{}^3)\,(\uparrow\uparrow\uparrow)\,Fe_2{}^{II}(t_{2g}{}^4)\,(\uparrow\uparrow\uparrow\downarrow)$$

assuming that the free spins on interacting Fe^{II}, Fe^{III} ions are ferromagnetically aligned.

If the t_{2g} d orbitals of Fe_i and the p orbitals of O_j are written as xy_i, xz_i, yz_i and x_j, y_j, z_j respectively, the ferromagnetic zeroth-order ground state of the system may be written:

$$\psi_0 = |xy_1xz_1yz_1\bar{d}_1x_1\bar{x}_1y_1\bar{y}_1z_1\bar{z}_1x_2\bar{x}_2y_2\bar{y}_2z_2\bar{z}_2xy_2xz_2yz_2| \quad (43)$$

where d_i expresses the distribution of the 'excess' t_{2g} electron in xy_i, xy_i, yz_i. The $Fe_1{}^{II} \longrightarrow Fe_2{}^{III}$ e.t. configuration is then:

$$\psi_1 = |xy_1xz_1yz_1\,\bar{d}_2x_1\bar{x}_1y_1\bar{y}_1z_1\bar{z}_1\,x_2\bar{x}_2y_2\bar{y}_2z_2\bar{z}_2\,xy_2\,xz_2\,yz_2| \quad (44)$$

ψ_0, ψ_1 interact at second order *via* O_1, $O_2 \longrightarrow Fe_2{}^{III}$ $(p_1, p_2 \longrightarrow d)$ e.t. configurations,* so that ground and excited state valence delocalization coefficients, γ_1, γ'_0, are given by (7), (8) as:

$$\gamma_1 = \sum_{\substack{p=x,y,z;\\ j=1,2}}\sum - \frac{(d_1|H|p_j)(d_2|H|p_j)}{[E(p_j \longrightarrow d_2) - E_0](E_1 - E_0)} \quad (45)$$

$$\gamma'_0 = \sum_{\substack{p=x,y,z;\\ j=1,2}}\sum \frac{(d_1|H|p_j)(d_2|H|p_j)}{[E(p_j \longrightarrow d_2) - E_1](E_1 - E_0)} \quad (46)$$

The integrals $(d_i|H|p_j)$ are expressed in terms of Fe^{II}—O, Fe^{III}—O ($d\pi$—$p\pi$) resonance integrals at the appropriate bond distances by:

$$\begin{aligned}&(xy_1|H|y_1) = \beta(Fe^{II}\text{—}O),\ (xy_1|H|x_2) = -\beta Fe^{II}\text{—}O),\\ &(xy_2|H|x_1) = \beta(Fe^{III}\text{—}O),\ (xy_2|H|y_2) = -\beta(Fe^{II}\text{—}O),\\ &(xz_1|H|z_1) = \beta(Fe^{II}\text{—}O),\ (xz_2|H|z_2) = -\beta(Fe^{III}\text{—}O),\\ &(yz_1|H|z_2) = \beta(Fe^{II}\text{—}O),\ (yz_2|H|z_1) = \beta(Fe^{III}\text{—}O)\end{aligned} \quad (47)$$

with other $(d_i|H|p_j) = 0$.

Equations (45), (46) then give for the particular cases $d_1 = xy_1$, xz_1, yz_1:

$$\gamma_1(d_1 = xy_1) = \gamma'_0\,(d_1 = xy_1) = 0,\dagger$$

$$\gamma_1(d_1 = xz_1) = -\frac{\beta(Fe^{II}\text{—}O)\cdot\beta(Fe^{III} - O)}{[E(z_1 \longrightarrow yz_2) - E_0](E_1 - E_0)},$$

$$\gamma'_0(d_1 = xz_1) = \frac{\beta(Fe^{II}\text{—}O)\cdot\beta(Fe^{III}\text{—}O)}{[E(z_1 \longrightarrow yz_2) - E_1](E_1 - E_0)},$$

$$\gamma_1(d_1 = yz_1) = -\frac{\beta(Fe^{II}\text{—}O)\cdot\beta(Fe^{III}\text{—}O)}{[E(z_2 \longrightarrow xz_2) - E_0](E_1 - E_0)},$$

$$\gamma'_0(d_1 = yz_1) = \frac{\beta(Fe^{II}\text{—}O)\cdot\beta(Fe^{III}\text{—}O)}{[E(z_2 \longrightarrow xz_2) - E_1](E_1 - E_0)} \quad (48)$$

To evaluate the resonance integrals in (48) we again make use of the Linderberg [5] expression using Richardson Fe^0 3*d*, Clementi O 2*p* functions to give:

$$\beta(Fe^{II}\text{—}O),\ 4{\cdot}0\ \text{kK};\quad \beta(Fe^{III}\text{—}O),\ 5{\cdot}1\ \text{kK}$$

The energy of O^{2-} $(p\pi) \longrightarrow Fe^{III}(t_{2g})$ electron transfer depends upon the nature of the other ions to which O^{2-} is co-ordinated. However, for simplicity, baricentre of the energies of *all* O^{2-} $(p\pi) \longrightarrow Fe^{III}(t_{2g})$ e.t. configurations is taken as 30 kK, from the O^{2-} $(p\pi) \longrightarrow Fe^{III}(t_{2g})$ c.t. band in alkali amphiboles.[19] If we now set $(E_1$—$E_0)$ equal to the observed energy of $Fe^{II}(t_{2g}) \longrightarrow Fe^{III}(t_{2g})$ charge transfer in biotites, 13·9 kK, (48) then gives the valence delocalization coefficients:

$$\gamma_1(d_1 = xz_1, yz_1),\ 0{\cdot}049;\quad \gamma'_0(d_1 = xz_1, yz_1),\ 0{\cdot}091$$

To calculate the true valence delocalization coefficients α_1, α'_0, we also need to consider two further points. First, the distribution of the optical electron in xy_1, xz_1, yz_1. The observation of two polarized *d–d* transitions of weak-field Fe^{II} at *ca.* 10 kK indicates that these orbitals are non-degenerate. Unfortunately there is not enough experimental information concerning the nature of Fe^{II} ion sites to calculate the splitting of xy_1, xz_1, yz_1 levels, so it is necessary to assume that the optical electron spends about one third of its time in each, *i.e.* $2\gamma_1{}^2/3$ of its time in xy_2 or yz_2. Secondly, there is the question of the spin alignment in Fe^{II}—

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* $Fe_1{}^{II} \longrightarrow O_1$, O_2 $(d_1 \longrightarrow 3p_1, 3p_2)$ e.t. configurations are too high in energy and too diffuse to warrant consideration.

† It should, however, be noted that the excess electron in xy_2 may become delocalized into $(x^2 - y^2)_2$, since $[x_2|H|\,(x^2 - y^2)_2]$, $[y_1|H|\,(x^2 - y^2)_2]$ are non-zero. $Fe^{II}(dxy) \longrightarrow Fe^{III}\ (dx^2 - y^2)$ charge-transfer is then optically allowed, and may be observed at *ca.* 13·9 kK + 10 *Dq*, where 10 *Dq* is the energy separation of the e_g, t_{2g} orbitals of an Fe^{II} site, *i.e. ca.* 10^2kK. Clearly, some part of the biotite absorption from 20—25 kK has such an origin.

[19] J. G. F. Littler and R. J. P. Williams, *J. Chem. Soc.*, 1965, 6368.

Fe^{III} ion-pairs. Ferromagnetic coupling of the interacting Fe^{II}, Fe^{III} ions is favoured by delocalization superexchange, the coupling energy being $\gamma_1^2(E_1—E_0)$ *ca.* 40 cm^{-1}. At the temperature to which the data of Robbins and Strens relate (*ca.* 300 K) we thus expect almost random interionic alignment of Fe^{II}, Fe^{III} spins, which reduces valence delocalization by a factor of about one half. Under these circumstances α_1, α'_0 are then related to γ_1, γ'_0 by:

$$\alpha_1 = \sqrt{\tfrac{2}{3}}\,\sqrt{\tfrac{1}{2}}\,\gamma_1 = -0{\cdot}028,$$

$$\alpha'_0 = \sqrt{\tfrac{1}{3}}\,\gamma'_0 = 0{\cdot}053$$

The calculated moment of the $Fe^{II}(t_{2g}) \longrightarrow Fe^{III}(t_{2g})$ c.t. excitation is given by $\frac{1}{2}(\alpha_1 - \alpha'_0)R(Fe^{II}—Fe^{III})$ as 0·125 eÅ. In comparing the calculated moment with that observed by Robbins and Strens [17] one must take account of the observation that the 13·9 kK band is anisotropically polarized within the cleavage plane of the crystal. This indicates that $Fe^{II} \longrightarrow Fe^{III}$ c.t. transitions *via* bridging ($2OH^-$), (OH^-, O_2^-) ligands occur with different probabilities, a fact not taken into account by our simple model, which assigns all $E(p_i \longrightarrow d_2)$ the same energy and distributes the optical electron equally in xy_1, xz_1, yz_1. However, we note that the calculated average transition moment is nicely bracketed by the experimental values for charge transfer *via* ($2OH^-$), (OH^-, O^{2-}) bridging ions respectively, 0·134, 0·080 eÅ.

CONCLUSIONS

In general, even bearing in mind that the calculations contain a degree of in-built self-compensation by the fact that a number of the quantities required to evaluate equations (7) and (8) are obtained empirically, the level of agreement between observed and calculated transition moments for the metal ⟶ metal charge transfer excitations is most encouraging. It certainly suggests that for weakly coupled class II m.v. systems, whether bridged by monoatomic anions or molecular ligands, a simple perturbation model, reminiscent of the conventional Mulliken theory of donor–acceptor complexes, is an adequate starting point. Although, aside from the intensities of m.v. charge transfer transitions, there are few direct experimental tests of the magnitudes of the calculated valence delocalization parameters, their orders of magnitude are certainly reasonable, for example, the probability of finding the optical electron at a nitrogen site in Prussian Blue (α_1^2) is 1%. Perhaps, now that well characterized crystalline samples of Prussian Blue are available,[8] it may prove possible to determine α_1 from, *e.g.*, the transferred hyperfine interaction measured by the Mössbauer spectrum.

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