Charge Transfer in Mixed-valence Solids. Part VIII.[1] Contribution of Valence Delocalisation to the Ferromagnetism of Prussian Blue

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The contribution of mixed-valence electron delocalisation to the ferromagnetic exchange between the iron(III) ions in Prussian Blue $\{Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 14H_2O\}$ has been estimated theoretically. Agreement between the calculated and observed values of the Curie temperature is quite good.

PRUSSIAN BLUE, $Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 14H_2O$, is an interesting compound not only because it is one of the classical examples of a Class II[2] mixed-valence compound whose physical properties have been very comprehensively investigated but also because at low temperatures the iron(III) spins order ferromagnetically. Ionic transition-metal compounds, especially co-ordination complexes, which order as three-dimensional ferromagnets, are extremely rare,[3] so any insight which can be gained into the mechanism of the exchange interaction in Prussian Blue would be valuable.

The first report on the low-temperature magnetic properties of Prussian Blue[4] gave the Curie temperature as 3.5 K, and the Mössbauer spectrum recorded at 1.3 K certainly shows[5] the magnetic hyperfine structure expected of a ferromagnet. However, in neither of these studies was the chemical composition of Prussian Blue particularly well characterised, especially with regard to the potassium content of the samples. More recently, Ludi and his co-workers[6] prepared and analysed single crystals of Prussian Blue. They verified that the

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[1] Part VII, B. Mayoh and P. Day, *J.C.S. Dalton*, 1974, 846.

[2] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

[3] For some examples, see A. K. Gregson, P. Day, D. H. Leech, M. J. Fair, and W. E. Gardner, *J.C.S. Dalton*, 1975, 1306.

[4] A. N. Holden, B. T. Matthias, P. W. Anderson, and H. W. Lewis, *Phys. Rev.*, 1956, **102**, 1463.

[5] A. Ito, M. Suenaga, and K. Ono, *J. Chem. Phys.*, 1968, **48**, 3597.

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

limiting formula was $Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 14H_2O$ and determined the crystal structure by single-crystal *X*-ray diffraction. For their samples, powder neutron diffraction[7] suggested that the Curie temperature was *ca.* 10 K and indeed, at 4.2 K, the Mössbauer spectrum[8] showed fully developed magnetic hyperfine structure and the magnetic circular dichroism[9] saturated in very small applied fields. The existence of these more recent data make it worth examining the magnetic-ordering mechanism in more detail.

Most mixed-valence compounds which order as ferromagnets, for example the well known[10] series of manganites(III,IV) such as $La_xSr_{1-x}MnO_3$, are also metallic conductors. In that case the ferromagnetism arises from the 'double-exchange' mechanism first proposed by Zener:[11] coupling occurs between the unpaired electron spins localised on the metal ions *via* the delocalised conduction electrons. A perturbation procedure similar to the one we used earlier to calculate valence-delocalisation coefficients would then serve to derive the relevant coupling integrals. However, the ferromagnetism of Prussian Blue cannot come from this mechanism because, being a class II mixed-valence compound, it is not a metal, but a high-resistance semiconductor. Furthermore, in the cubic lattice the high-spin iron(III) ions are separated along each axis of the unit cell by low-spin diamagnetic Fe^{II}, and are thus no less than 10.16 Å apart. Consequently the basic mechanism of the exchange interaction must lie in what we[1,12] have called 'valence delocalisation' in the ground state between the Fe^{II} and Fe^{III}.

In essence the mechanism we envisage relies on the partial delocalisation of electrons formally occupying t_{2g} orbitals on Fe^{II} on to neighbouring high-spin iron(III) sites. Since each iron(III) site may only accept electron density of one particular spin, because the t_{2g} and e_g orbitals are both exactly half occupied, a t_{2g} electron with α spin originating on Fe^{II} may spend a larger fraction of its time on iron(III) sites than one of β spin. Some of the coulomb- and exchange-repulsion terms are sensitive to differences in the extent of delocalisation of α and β spins. The effect of this is that it is energetically more favourable to delocalise only one type of spin (either α or β) from Fe^{II} to Fe^{III}. In the crystal, however, each Fe^{II} is surrounded by six equivalent Fe^{III}, over which the spin density originating on the central Fe^{II} must therefore be correlated. The ferromagnetic coupling energy is the difference between the energy per iron(II) centre when the spins of the neighbouring Fe^{III} are ordered parallel to one another, compared to the energy when they are arranged randomly. It is this energy difference which we shall calculate.

THEORY

Spin Orientations and Wavefunctions.—If the spins of the six Fe^{III} around an iron(II) centre are randomly oriented the statistical weights of all the possible spin-coupling schemes are respectively 1/64 for 6α or 6β, 6/64 for 5α + 1β or 5β + 1α, 15/64 for 4α + 2β or 4β + 2α, and 20/64 for 3α + 3β. A general Slater-determinant wavefunction for the optical electrons, which we assume to be Fe^{II} t_{2g}, in the ground state is as in equation (1) where i labels the coupling case and $t_n^{\alpha,\beta}$ take the forms (2a) and (2b) where t_C are t_{2g}

$$\Psi_G = |t_{1i}{}^{\alpha}t_{1i}{}^{\beta}t_{2i}{}^{\alpha}t_{2i}{}^{\beta}t_{3i}{}^{\alpha}t_{3i}{}^{\beta}| \qquad (1)$$

$$t_n{}^{\alpha} = [(1 - kc^2)t_C{}^2 + kc^2\phi(t_N)^2)]^{\frac{1}{2}} \qquad (2a)$$

$$t_n{}^{\beta} = [(1 - jc^2)t_C{}^2 + jc^2\phi(t_N)^2]^{\frac{1}{2}} \qquad (2b)$$

orbitals on Fe^{II} at the carbon ends of the cyanide groups, $\phi(t_N)$ is an appropriate combination of t_{2g} orbitals on Fe^{III} at the nitrogen ends of the cyanides, and $k/(k + j)$ is the fraction of the delocalised electron density c^2 which has α spin [$j/(k + j)$ is the similar fraction for β spin], and $k + j = 1$. In writing equations (2a) and (2b) we have made use of the small degree of overlap between t_C and $\phi(t_N)$, *i.e.* (3). In the various spin-coupling combinations acces-

$$t_n{}^{\alpha} = (1 - kc^2)^{\frac{1}{2}}t_C + (kc^2)^{\frac{1}{2}}\phi(t_N) \qquad (3)$$

sible to the six Fe^{III} around our reference Fe^{II} the appropriate values of k and j are as in equations (4)—(10). In

$$6\alpha: k = 0, \quad j = 1 \qquad (4)$$

$$6\beta: k = 1, \quad j = 0 \qquad (5)$$

$$5\alpha + 1\beta: k = 1/6, j = 5/6 \qquad (6)$$

$$5\beta + 1\alpha: k = 5/6, j = 1/6 \qquad (7)$$

$$4\alpha + 2\beta: k = 1/3, j = 2/3 \qquad (8)$$

$$4\beta + 2\alpha: k = 2/3, j = 1/3 \qquad (9)$$

$$3\alpha + 3\beta: k = 1/2, j = 1/2 \qquad (10)$$

order to write the wavefunctions of the different coupling combinations in the form of Slater determinants, it is now convenient to rewrite $t_n^{\alpha,\beta}$ as in (11) and (12) where $\phi(t_C,t_N) = [t_C{}^2 - \phi(t_N)^2]^{\frac{1}{2}}$, again assuming small overlap between t_C and $\phi(t_N)$.

$$t_n{}^{\alpha} = [t_C{}^2 - kc^2\phi(t_C,t_N)^2]^{\frac{1}{2}} \qquad (11)$$

$$t_n{}^{\beta} = [t_C{}^2 - jc^2\phi(t_C,t_N)^2]^{\frac{1}{2}} \qquad (12)$$

Since for our purposes the energies of $(x - 6)\alpha + x\beta$ and $x\alpha + (6 - x)\beta$ are the same, we shall write only one component of each, for example $k = 1$, $j = 0$. Then substituting into equation (1), we have:

Case (*a*) (6α, 6β):

$$\Psi_{Ga} = |[t_C{}^2 - c^2\phi(t_C,t_N)^2]_1{}^{\frac{1}{2}\alpha}\, t_{C1}{}^{\beta}[t_C{}^2 - c^2\phi(t_C,t_N)^2]^{\frac{1}{2}\alpha}{}_{-}\, t_{C2}{}^{\beta}[t_C{}^2 - c^2\phi(t_C,t_N)^2]_3{}^{\frac{1}{2}\alpha}t_{C3}{}^{\beta}| \qquad (13)$$

Case (*b*) (5α + 1β, 5β + 1α):

$$\Psi_{Gb} = |[t_C{}^2 - \tfrac{5}{6}c^2\phi(t_C,t_N)^2]_1{}^{\frac{1}{2}\alpha}[t_C{}^2 - \tfrac{1}{6}c^2\phi(t_C,t_N)^2]_1{}^{\frac{1}{2}\beta}\ etc.| \qquad (14)$$

Case (*c*) (4α + 2β, 4β + 2α):

$$\Psi_{Gc} = |[t_C{}^2 - \tfrac{2}{3}c^2\phi(t_C,t_N)^2]_1{}^{\frac{1}{2}\alpha}[t_C{}^2 - \tfrac{2}{3}c^2\phi(t_C,t_N)^2]_1{}^{\frac{1}{2}\beta}\ etc.| \qquad (15)$$

Case (*d*) (3α + 3β):

$$\Psi_{Gd} = |[t_C{}^2 - \tfrac{1}{2}c^2\phi(t_C,t_N)]_1{}^{\frac{1}{2}\alpha}[t_C{}^2 - \tfrac{1}{2}c^2\phi(t_C,t_N)^2]_1{}^{\frac{1}{2}\beta}\ etc.| \qquad (16)$$

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[7] H. J. Buser, A. Ludi, P. Fischer, T. Studach, and B. W. Dale, *Z. phys. Chem.* (*Frankfurt*), 1974, **92**, 354.

[8] A. Ludi and B. W. Dale, personal communication.

[9] H. U. Güdel and E. R. Krausz, personal communication.

[10] G. H. Jonker and J. H. van Santen, *Physica*, 1950, **16**, 337, 599.

[11] C. Zener, *Phys. Rev.*, 1951, **81**, 440.

[12] B. Mayoh and P. Day, *Inorg. Chem.*, 1974, **13**, 2273.

Ferromagnetic Coupling Energy.—In order to find the ferromagnetic coupling energy the energies of the four cases (*a*)—(*d*) must be compared, that is, the values of (17) for $i = a, b, c, d$, and d. Energy differences between the

$$E_{Gi} = \langle \Psi_{Gi} | \mathscr{H} | \Psi_{Gi} \rangle \tag{17}$$

various states i arise from differences in the coulomb- and exchange-repulsion integrals $\langle t_n{}^{\alpha} t_n{}^{\alpha} | e^2/r_{12} | t_n{}^{\beta} t_n{}^{\beta} \rangle$, $\langle t_n{}^{\alpha} t_p{}^{\alpha} | e^2/r_{12} | t_n{}^{\alpha} t_p{}^{\alpha} \rangle$, and $\langle t_n{}^{\beta} t_p{}^{\beta} | e^2/r_{12} | t_n{}^{\beta} t_p{}^{\beta} \rangle$. In fact, if we define equations (18) and (19), we find the energy differences (20)—(22)

$$J_{11} = \langle \phi^2(t_C,t_N)_1 | e^2/r_{12} | \phi^2(t_{C,N})_1 \rangle \tag{18}$$

$$K_{12} = \langle \phi(t_C,t_N)_1 \phi(t_C,t_N)_2 | e^2/r_{12} | \phi(t_C,t_N)_1 \phi(t_C,t_N)_2 \rangle \tag{19}$$

between the different coupling cases (*a*)—(*d*). The ferro-

$$E_{Ga} - E_{Gb} = (15c^4/36)J_{11} + (30c^4/36)K_{12} \tag{20}$$

$$E_{Ga} - E_{Gc} = (6c^4/9)J_{11} + (12c^4/9)K_{12} \tag{21}$$

$$E_{Ga} - E_{Gd} = (3c^4/4)J_{11} + (6c^4/4)K_{12} \tag{22}$$

magnetic coupling energy depends not only on these energy differences but also on the weighting to be given to each case. Relative to case (*a*) the weighting factor w_b of (*b*) is 12/64, of (*c*) is 30/64, and of (*d*) is 20/64. Then the total ferromagnetic coupling energy resulting from the mixed-valence interaction is (23).

$$E_{fm} = \sum_{i=b,c,d} (E_{Ga} - E_{Gi})w_i = (1/8)(5J_{11} + 10K_{12})c^4 \tag{23}$$

Evaluation of J_{11} *and* K_{12}.—The next step in calculating E_{fm} is to evaluate J_{11} and K_{12} explicitly. Substituting into equations (18) and (19) we obtain (24) and (25). In order

$$J_{11} = \langle t_{C1}{}^2 - \phi_1(t_N)^2 | e^2/r_{12} | t_{C1}{}^2 - \phi_1(t_N)^2 \rangle \tag{24}$$

$$K_{12} = \langle [t_{C1}{}^2 - \phi_1(t_N)^2]^{\frac{1}{2}} [t_{C2}{}^2 - \phi_2(t_N)^2]^{\frac{1}{2}} | e^2/r_{12} | [t_{C1}{}^2 - \phi_1(t_N)^2]^{\frac{1}{2}} [t_{C2}{}^2 - \phi_2(t_N)^2]^{\frac{1}{2}} \rangle \tag{25}$$

to expand these expressions in terms of single-centre $\mathrm{Fe^{II}}$ and $\mathrm{Fe^{III}}$ t_{2g} functions we need to define the axis of the $\mathrm{Fe^{II}(CN)_6Fe^{III}{}_6}$ cluster. Fortunately an axis definition is already available from our previous paper [1] on the optical spectrum of Prussian Blue. Using the labels we used in that paper, and arbitrarily fixing t_{C_1} as d_{xy} and t_{C_2} as d_{xz}, we obtain equations (26) and (27). In order to simplify

$$\phi_1(t_N) = (1/2)[d_{xy_2} + d_{xy_3} + d_{xy_4} + d_{xy_5}] \tag{26}$$

$$\phi_2(t_N) = (1/2)[d_{xz_1} + d_{xz_3} + d_{xz_5} + d_{xz_6}] \tag{27}$$

the expressions for J_{11} and K_{12}, all the interactions between d_{xy} on $\mathrm{Fe^{II}}$ and the d_{xyi} on the surrounding $\mathrm{Fe^{III}}$ are generalised in terms of d_{xy_1}. All the $\mathrm{Fe^{III}}$–$\mathrm{Fe^{III}}$ interactions are expressed in terms of either one-centre (d_i–d_i), adjacent two-centre (d_i–d_i; $i = 1$, $j = 2$), or distant two-centre (d_i–d_j; $i = 1$, $j = 6$) interactions. The resulting expressions are (28) and (29). In deriving these expressions we have also used the Mulliken approximation to set all other terms of the type $\langle d_i d_j | d_i d_j \rangle$, where d_i and d_j are on different centres, equal to zero.

$$\begin{aligned} J_{11} = {} & \langle d_{xy} d_{xy} | e^2/r_{12} | d_{xy} d_{xy} \rangle - 2\langle d_{xy} d_{xy} | e^2/r_{12} | d_{xy_2} d_{xy_2} \rangle \\ & + (1/4)[\langle d_{xy_2} d_{xy_2} | e^2/r_{12} | d_{xy_2} d_{xy_2} \rangle + 2\langle d_{xy_2} d_{xy_2} | e^2/r_{12} | d_{xy_3} d_{xy_3} \rangle + \langle d_{xy_2} d_{xy_2} | e^2/r_{12} | d_{xy_4} d_{xy_4} \rangle] \end{aligned} \tag{28}$$

$$\begin{aligned} K_{12} = {} & \langle d_{xy} d_{xz} | e^2/r_{12} | d_{xy} d_{xz} \rangle + (1/8)[\langle d_{xy_1} d_{xz_1} | e^2/r_{12} | d_{xy_1} d_{xz_1} \rangle + \langle d_{xy_1} d_{xz_1} | e^2/r_{12} | d_{xy_6} d_{xz_6} \rangle] \end{aligned} \tag{29}$$

Numerical Estimates of J_{11} *and* K_{12}.—The final stage in our calculation of E_{fm} is to estimate some numerical magnitudes for the various coulomb- and exchange-repulsion integrals which appear in (28) and (29). As our aim is only to obtain a rough idea of the magnitudes of the various terms which enter into the magnetic coupling, we used the point-charge approximation $J_{ij} = 14.4/R_{ij}$, where R_{ij} is the distance between the two centres, to estimate the two-centre repulsion integrals between orbitals localised on different iron(III) centres. The one-centre $\mathrm{Fe^{II}}$ and one-centre $\mathrm{Fe^{III}}$ coulomb integrals correspond to the γ_{11} terms of Pariser–Parr–Pople ZDO–MO theory,[13] while the one-centre exchange integrals are assumed to be proportional to the γ_{11} as in the INDO approximation.[14] The two-centre $\mathrm{Fe^{III}}$–$\mathrm{Fe^{III}}$ exchange integral is set equal to zero. With these approximations, we obtain (30) and (31), k being the proportionality constant just mentioned.*

$$J_{21} = \gamma_{11}(\mathrm{Fe^{II}}) + (1/4)\gamma_{11}(\mathrm{Fe^{III}}) - 4.30\ \mathrm{eV} \tag{30}$$

$$K_{12} = k\gamma_{11}(\mathrm{Fe^{II}}) + (1/8)k\gamma_{11}(\mathrm{Fe^{III}}) \tag{31}$$

Values of γ_{11} may of course be obtained from atomic Hartree–Fock calculations. However, it is well known that when they are used in molecular-orbital (m.o.) calculations they usually predict singlet–triplet separations much greater than those observed. Consequently, following other semiempirical m.o. calculations [13] we use the energy of the ' Pariser disproportionation reaction ' to find γ_{11}. As a function of the charge q on a metal ion, γ is given by the difference between two valence-orbital ionisation potentials

$$\gamma(q) = \mathrm{VOIP}(q-1) - \mathrm{VOIP}(q) \tag{32}$$

as in (32). Published tabulations [15] of VOIP(q) then lead to estimates for both $\gamma_{11}(\mathrm{Fe^{II}})$ and $\gamma_{11}(\mathrm{Fe^{III}})$ of 12.4 eV. Finally Watson's self-consistent-field calculations of γ_{dd}, $\gamma_{dd'}$, and $K_{dd'}$ for neutral atoms of the first transition series indicate that the ratio of γ_{dd} to $K_{dd'}$ (*i.e.* the proportionality factor k) is 0.0388. When the values of all these parameters are substituted into (30) and (31) the resulting estimates of J_{11} and K_{12} are 11.2 and 0.54 eV respectively. The ferromagnetic coupling energy E_{fm} from (23) is therefore equal to $7.675c^4$ eV.

RESULTS AND DISCUSSION

Calculation of the Curie Temperature.—In order to relate the magnitude of E_{fm} which we have calculated to the observed Curie temperature we assume that $E_{fm} \sim k_B T_c$, from which T_c is predicted to be $(8.9 \times 10^4)c^4$ K. The coefficient c, which we have called [1,12] the ' valence delocalisation coefficient,' can be approached in one of two ways. Either one can estimate it from the intensity of the mixed-valence absorption band or, for cases such as Prussian Blue, where the two metal ions of differing valency are bridged by an intervening ligand, it can be calculated from a perturbation model, mixing $\mathrm{Fe^{II}} \rightarrow \mathrm{CN}$ and $\mathrm{CN} \rightarrow \mathrm{Fe^{III}}$ local charge-transfer states into the ground state. In our earlier paper [1] on the perturbation

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* 1 eV ≈ 1.60×10^{-19} J.

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model for valence delocalisation we used Prussian Blue as a test case, and obtained estimates of the ground-state delocalisation coefficient in both ways, for comparison: that estimated from the intensity of the mixed-valence band was 0.106, while the estimate based on the perturbation calculation was 0.083. The former value leads to a calculated Curie temperature of 11.2 K and and the latter to 6.6 K.

A number of comments can be made on this result. First, the fact that the iron(III) ions in Prussian Blue are so far apart, and yet magnetic ordering is found at a modestly accessible temperature, strongly implicates the intervening diamagnetic iron(II) ions in the interaction process. Secondly, that the interaction should be ferromagnetic is highly unusual, and the fact that it occurs in a mixed-valence compound suggests that it is the mixed-valence interaction which provides the dominant exchange path. The calculations described above give strong support to both these hypotheses. We have demonstrated not only that the mixed-valence delocalisation mechanism indeed predicts ferromagnetic coupling but, further, that the extent of ground-state valence delocalisation as estimated from the optical spectrum or a perturbation calculation leads to a calculated Curie temperature very close to that observed. Of course, the level of agreement between the calculated and observed Curie temperatures is very remarkable, especially when one remembers that in our model T_c is proportional to c^4. Obviously it would be very interesting to examine the low-temperature magnetic properties of related compounds, such as the ruthenium and osmium analogues of Prussian Blue, and other heavy-metal ferro- and ferri-cyanides in which interionic charge-transfer states, though not strictly of the mixed-valence type, might make an important contribution to the exchange mechanism.

Finally it is worth mentioning that no direct correlation between the calculated magnetic interaction energy and any electrical-conductivity properties is to be expected in Prussian Blue and related class II mixed-valence compounds. In this kind of compound conduction is limited by electron trapping as a result of lattice polarisation. The diffusion coefficient in the hopping model depends on $\nu_0\exp(-\Delta G/\boldsymbol{k}T)$, where ν_0 is the frequency of the lattice mode and ΔG the work which must be done to bring the energies of the carbon-hole and nitrogen-hole sites to equivalence, so that electron transfer can take place.

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