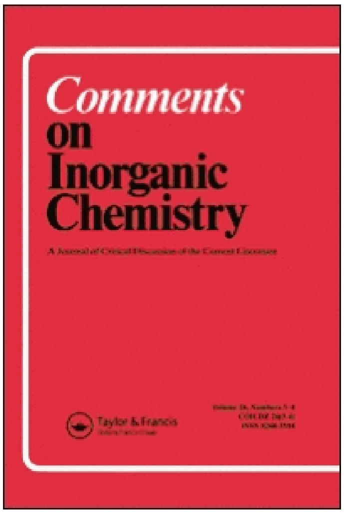

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Theory and Experiments on Valence Delocalization in Mixed-Valence Compounds

P. Day[a]
[a] Inorganic Chemistry Laboratory, Oxford University, Oxford, England

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Theory and Experiments on Valence Delocalization in Mixed-Valence Compounds

A simple perturbation model for calculating electron delocalization in valence-trapped (class II) mixed-valence compounds is described and its application illustrated. Optical absorption spectroscopy and polarized neutron diffraction are two experimental techniques for estimating valence delocalization. Both are described, with examples.

INTRODUCTION

Mixed-valence compounds are ones in which the same element is present in two different formal oxidation states. Since they are formed by nearly 40 elements in the Periodic Table their properties are clearly of great interest to inorganic chemists. Among the enormous variety of mixed-valence materials now known, examples can be found spanning the whole gamut of properties, from ones in which one has essentially a superposition of the behavior of the two oxidation states taken separately, to materials in which no vestige remains at all of behavior associated with the individual oxidation states.

As we first pointed out many years ago,[1] in principle two main factors determine how strongly metal ions of differing oxidation state interact with one another, either in a continuous lattice compound or in a discrete dimeric complex. The first is the similarity, or difference, between the ligand fields exerted by the two coordination sites. This comes about quite simply because the energy needed to transfer an electron from site to site determines how large the mixing is between two valence-bond configurations such as $Fe_A^{II}Fe_B^{III}$ and $Fe_A^{III}Fe_B^{II}$, where A and B label the two sites. The greater the energy difference, the smaller the admixture and the purer the single configuration. We have called the parameter describing the admixture the "valence delocalization coefficient," α.

Many physical properties depend on the magnitude of α, most notably the intensity of the intervalence optical transition. However close the energies of the two configurations are, they remain orthogonal unless there is

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some mechanism, describable as an off-diagonal matrix element, available to "mix" them together. That is the second factor which governs α, and is the one I shall concentrate on in this Comment. As an example I shall use the Fe(II, III) cyanides, in the form of the most famous mixed-valence compound of all, Prussian Blue, but also for simplicity the dimeric complex $Fe_2(CN)_{11}^{6-}$. Two questions will be addressed: can one make any *a priori* estimate of α starting from the properties of the constituent single-valence monomers, and if so, what methods are available to test the conclusions?

A PERTURBATION MODEL OF VALENCE DELOCALIZATION[2]

In most mixed-valence compounds the two metal ions of differing oxidation state are separated by bridging anions or neutral bifunctional organic ligands such as Cl^-, CN^-, pyrazine, 4,4′-bipyridine, etc. For example, the Fe(II)–Fe(III) distance in Prussian Blue [Figure 1(a)] is 5.1 Å and in $Fe_2(CN)_{11}^{6-}$ [Figure 1(b)] it is 4.9 Å. This is much too far apart for any direct interaction between them, and the orbitals of the bridging ligand have to be considered. The simplest representation of the situation is that in Figure 2, where χ_A and χ_B are nondegenerate orbitals centered on sites A and B, separated by a ligand L which has a doubly filled bonding orbital ϕ_L and an empty antibonding orbital ϕ_L^*. The ground-state wavefunction can be expressed as a Slater determinant

$$\psi_0 = |\chi_A \bar{\chi}_A \phi_L \bar{\phi}_L \chi_B|, \tag{1}$$

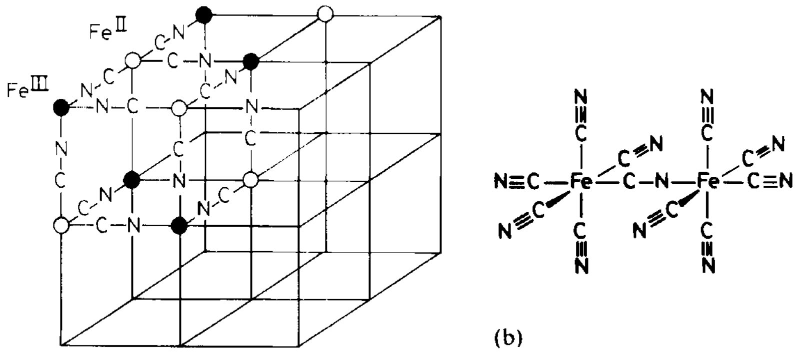

FIGURE 1 The structures of (a) Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$ and (b) the dimeric complex $Fe_2(CN)_{11}^{6-}$.

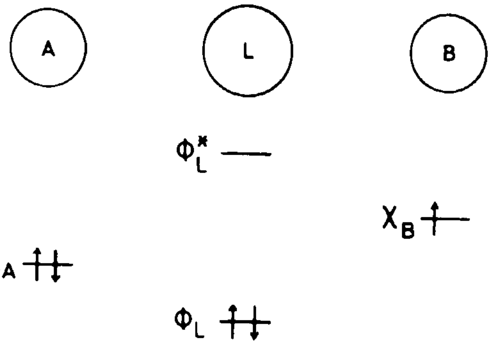

FIGURE 2 Orbitals involved in mixed-valence interaction.

where the bars represent spin functions for $m_s = -\frac{1}{2}$ and is written for $M_S = +\frac{1}{2}$. Correspondingly there is an intervalence charge-transfer configuration, described as

$$\psi_1 = |\chi_A\phi_L\bar{\phi}_L\chi_B\bar{\chi}_B|. \tag{2}$$

If the interaction between the centers is weak enough for the valence-bond model to be a good approximation then, in the spirit of the classical Mulliken model for molecular donor–acceptor complexes, a closer approximation to the time-independent wavefunction of the ground state is an admixture of ψ_0 and ψ_1:

$$\psi_G = (1 - \alpha_1^2)^{1/2}\psi_0 + \alpha_1\psi_1 \tag{3}$$

and for the intervalence state

$$\psi_{E_1} = (1 - \alpha_0)^{1/2}\psi_1 + \alpha_0\psi_0. \tag{4}$$

Assuming zero differential overlap the "mixing" matrix element $V_{01} = \langle\psi_0|\mathcal{H}|\psi_1\rangle$ is approximately $\langle\chi_A|\mathcal{H}|\chi_B\rangle$ which, if A and B are 5 Å apart, must be effectively zero. Consequently any interaction taking place between χ_A and χ_B must occur through the overlap of each of them with the orbitals of L. If the overlap remains small and the mixing described by α is also small, the most appropriate model for the interaction is a perturbation one, bringing in configurations containing ϕ_L and ϕ_L^*.

Configurations arising from excitations entirely localized on L, e.g., $|\chi_A\bar{\chi}_A\phi_L\bar{\phi}_L^*\chi_B|$, have no effect on mixing between ψ_0 and ψ_1 so we have to invoke what might be called "local" charge-transfer states. The latter are of two types, $\chi_A \rightarrow \phi_L^*$ and $\phi_L \rightarrow \chi_B$, corresponding to charge transfer from the lower valent metal ion to empty orbitals of L, or from filled orbitals on L to the hole in the metal orbital on the higher valent ion:

$$\psi_2 = |\chi_A\phi_L\bar{\phi}_L\phi_L^*\chi_B|;\ \psi_3 = |\chi_A\bar{\chi}_A\phi_L\chi_B\bar{\chi}_B|. \tag{5}$$

Since these determinants only differ by one electron each from ψ_0 and ψ_1, second-order perturbation provides a pathway to "mix" ψ_0 and ψ_1 via ψ_2 and ψ_3. Specifically

$$\begin{aligned} \alpha_1 &= \sum_{i=2,3} (V_{0i}V_{1i})/(E_1 - E_0)(E_i - E_0), \\ \alpha_0 &= \sum_{i=2,3} - (V_{0i}V_{1i})/(E_1 - E_0)(E_i - E_1), \end{aligned} \tag{6}$$

where $V_{ij} = \langle \psi_i | \mathcal{H} | \psi_j \rangle$ and $E_i = \langle \psi_i | \mathcal{H} | \psi_i \rangle$. In practice, of course, one may have a number of ligand orbitals, both filled and empty, which generate local charge-transfer configurations $\chi_A \rightarrow \phi^*_{Lj}$ and $\phi_{Lk} \rightarrow \chi_B$, but the summations are easily extended to take account of them. It would be pointless even to attempt to evaluate Eqs. (6) for any real inorganic complexes by *a priori* calculations, but we can gain a lot of insight by a mixture of theory and empiricism, as we shall now describe.

A WORKED EXAMPLE: $Fe_2(CN)_{11}^{6-}$

For a model calculation of valence delocalization using the approach we have just described, consider the $Fe_2(CN)_{11}^{6-}$ ion of Figure 1(b). There is good evidence[3] that the valences are trapped, with the Fe surrounded by six carbon atoms being low-spin Fe(II) while the other, surrounded by five carbons and one nitrogen, is low-spin Fe(III). However, the mixed-valence ion has an intervalence absorption band at 7700 cm^{-1} with a molar extinction coefficient of about 3000 l mol^{-1} cm^{-1}. It is a typical class II complex. The "operative" part for our purpose is shown in Figure 3, where we have drawn the relevant orbitals in the yz plane. Of course, an equivalent set could be drawn in the xz plane.

In an obvious notation

$$\psi_0 = |yz_A\overline{yz}_A\,\pi y\,\overline{\pi y}\;yz_B|\psi_0', \tag{7}$$

where ψ_0' is the remainder of the valence shell electrons:

$$\psi_0' = |xy_A\overline{xy}_A\,xz_A\overline{xz}_A\,\pi x\,\overline{\pi x}\,xy_B\overline{xy}_B\,xz_B\overline{xz}_B|. \tag{8}$$

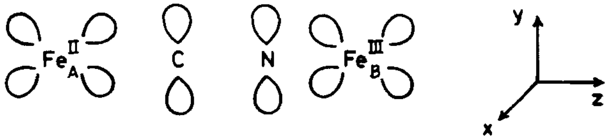

FIGURE 3 Metal and ligand orbitals in $Fe_2(CN)_{11}^{6-}$.

Then the three types of excited state defined in Eqs. (1), (2) and (5) are

$$\begin{aligned}\psi_1 &= |\mathrm{yz_A}\overline{\mathrm{yz_B}}\pi\mathrm{y}\,\overline{\pi\mathrm{y}}\,\mathrm{yz_B}|\psi_0', \\ \psi_2 &= |\mathrm{yz_A}\overline{\pi\mathrm{y}}{}^*\pi\mathrm{y}\,\overline{\pi\mathrm{y}}\,\mathrm{yz_B}|\psi_0', \\ \psi_3 &= |\mathrm{yz_A}\overline{\mathrm{yz_A}}\pi\mathrm{y}\,\overline{\mathrm{yz_B}}\mathrm{yz_B}|\psi_0'.\end{aligned} \tag{9}$$

Following the perturbation the ground and excited intervalence charge-transfer states from Eqs. (3) and (4) are

$$\begin{aligned}\psi_G &= \psi_0 + \gamma_1\psi_1, \\ \psi_E &= \psi_1 + \gamma_0\psi_0.\end{aligned} \tag{10}$$

Then the valence delocalization coefficients can be written explicitly as

$$\gamma_{1,0} = \pm\frac{\langle \mathrm{yz_A}|H|\pi\mathrm{y}^*\rangle\langle \mathrm{yz_B}|H|\pi\mathrm{y}^*\rangle}{(E_2 - E_0)(E_1 - E_0)} - \frac{\langle \mathrm{yz_A}|H|\pi\mathrm{y}\rangle\langle \mathrm{yz_B}|H|\pi\mathrm{y}\rangle}{(E_3 - E_0)(E_1 - E_0)}, \tag{11}$$

where the + refers to γ_1 and the − to γ_0. Next we have to make some assumptions about the form of the molecular orbitals πy and πy* on the cyanide bridging group. Let

$$\pi\mathrm{y} = a\mathrm{y_C} + b\mathrm{y_N}; \qquad \pi\mathrm{y}^* = b\mathrm{y_C} - a\mathrm{y_N} \tag{12}$$

with y_C and $\mathrm{y_N}$ being py orbitals on the atoms C and N. The off-diagonal matrix elements in Eq. (11) then reduce to two-center metal–ligand resonance integrals in an effective one-electron approximation like that of extended Hückel theory or other CNDO or INDO schemes:

$$\begin{aligned}&\langle \mathrm{yz_A}|H|\pi\mathrm{y}^*\rangle = b\beta(\mathrm{Fe^{II}\text{-}C}); \quad \langle \mathrm{yz_B}|H|\pi\mathrm{y}^*\rangle = -a\beta(\mathrm{Fe^{III}\text{-}N}), \\ &\langle \mathrm{yz_A}|H|\pi\mathrm{y}\rangle = a\beta(\mathrm{Fe^{II}\text{-}C}); \quad \langle \mathrm{yz_B}|H|\pi\mathrm{y}\rangle = -b\beta(\mathrm{Fe^{III}\text{-}N}).\end{aligned} \tag{13}$$

For the sake of simplicity in the present case we put $a = b = 1/\sqrt{2}$ but better values could be obtained from molecular orbital calculations on $\mathrm{CN^-}$ at an appropriate level of sophistication. It is worth noticing that when bifunctional aromatic heterocycles are used as bridging groups in mixed-valence compounds simple Hückel or Pariser–Parr–Pople calculations would probably be sufficient to get an idea of the magnitudes of the molecular orbital coefficients at the ligating atoms.

Two different methods have been used to estimate the metal–ligand resonance integrals. It has been observed[4] that the intensities of both metal-to-ligand and ligand-to-metal charge-transfer transitions, calculated either with the dipole-length or the dipole velocity operator, agree quite well with experiment when the so-called Linderberg criterion[5] is used to calculate the resonance integral. To apply Linderberg's expression

$$\beta_{rs} = (h^2/m)(\nabla_{rs}/R) \tag{14}$$

one needs to know the Fe^{II}-C and Fe^{III}-N distances, which we take from crystallographic data on related ions. For the atomic wavefunctions we have used Richardson's[6] for Fe and Clementi's[7] for C and N. In this way, in the present case one finds $\beta(Fe^{II}\text{-}C)$ is $-6350\ cm^{-1}$ and $\beta(Fe^{III}\text{-}N)$ $-7300\ cm^{-1}$. These numbers are quite similar in magnitude to those which reproduce the observed intensities of the charge-transfer bands[8] in such complexes as $Fe(bpy)_3^{3+}$and $Fe(CN)_6^{4-}$. In fact an alternative, and simpler, way to estimate the β's is just to choose them to reproduce the observed intensities of such bands.

The final set of quantities in Eq. (11) which have to be estimated are the various excitation energies $(E_n - E_0)$. Rather than make any attempt to calculate them (a more or less hopeless task for such large molecules) we take them directly from experiment: either from the complex itself or from closely related ones where the transitions in question can be definitely assigned. We have already said that $(E_1 - E_0)$ for $Fe_2(CN)_{11}^{6-}$ is 7700 cm^{-1}. Bands corresponding to the other states happen to be rather ill-defined for this particular ion, so we use bands which have been assigned in Prussian Blue[9] and $Fe(CN)_6^{3-}$ to estimate $(E_2 - E_0)$ as 35 000 and $(E_3 - E_0)$ as 48 000 cm^{-1}.

Putting all these numbers together γ_1 is 0.15 and γ_0 -0.19. Although the "hole" in the t_{2g} shell on the Fe^{III} is most probably located in xz or yz because of the mixed valence interaction, its distribution actually depends on a balance of spin-orbit coupling and the tetragonal distortion of the ligand field arising from the FeC_5N coordination. Since we have no evidence about the magnitude of these effects it seems best to assume that the hole is equally distributed among the three t_{2g} orbitals. Then the valence delocalization coefficients are

$$\alpha_1 = \sqrt{(\tfrac{2}{3})}\gamma_1 = 0.12; \quad \alpha_0 = \sqrt{(\tfrac{2}{3})}\gamma_0 = -0.15. \tag{15}$$

Physically, the significance of these numbers is that in the ground state the hole in the t_{2g} shell, formally localized on the Fe^{III} at the N end of the cyano group, has a probability $\alpha_1^2 \sim 1\%$ of being found on the other Fe. Considering the various approximations made in obtaining them, one would not wish to give credence to these numbers much beyond the first significant figure, but they should provide a guide to the orders of magnitude, at least. The question is, can we check them against experiment, and it is to answering that that the last part of this Comment will be devoted.

INTENSITIES OF INTERVALENCE OPTICAL TRANSITIONS

Like all optical absorption bands, the metal-to-metal charge-transfer transitions of mixed-valence compounds provide us with three experimental observables: the energy of the band maximum, the integrated area under the band envelope, and the shape of the envelope. Sometimes these are called the first three moments. The energy is related to the change in internal energy at the two sites when an electron is transferred between them, and must depend on the ionization potential of the ion at site A and the electron affinity of the one at B. However, it is extremely difficult, if not impossible, to calculate the energy *a priori* in any specific case. Similarly the shape of the band depends on details of vibrational–electronic coupling too subtle to expound here, though the question has been covered elsewhere.[10] The integrated band area, on the other hand, gives us a direct measure of the valence delocalization.

Using the mixed-valence wavefunctions of Eq. (10) the transition electric-dipole moment of the intervalence band is

$$\begin{aligned}\mu_{GE} &= \langle \psi_G | \mathbf{m} | \psi_E \rangle \sim \gamma_1 \langle \psi_1 | \mathbf{m} | \psi_1 \rangle + \gamma_0 \langle \psi_0 | \mathbf{m} | \psi_0 \rangle, \\ &= \gamma_1 \mu_1 + \gamma_0 \mu_0\end{aligned} \tag{16}$$

where we have neglected the cross-terms and hence the overlap charge distribution. There has been a lot of discussion about the relative merits of the electric dipole moment, dipole velocity and dipole acceleration operators to calculate the intensities of optical transitions, and for exact wavefunctions all three should give identical results.[11] However, the evidence is that for approximate wavefunctions the dipole moment operator $e\mathbf{r}$ becomes a better approximation relative to the other two as the distance between the atoms in a molecule increases.[12] Taking $Fe_2(CN)_{11}^{6-}$ as our example, we choose the origin of coordinates at the center of the Fe–Fe axis, and so have

$$\mu_0 = -(\tfrac{1}{2})eR; \quad \mu_1 = +(\tfrac{1}{2})eR \tag{17}$$

so that

$$\mu_{GE} = (\tfrac{1}{2})eR(\gamma_1 - \gamma_0), \tag{18}$$

where R is the distance between the two Fe atoms. With the parameters from Eq. (15) and R of 4.9 Å we find μ_{GE} is 0.67 eÅ, in quite reasonable agreement with the observed value of 0.80 eÅ. We have calculated valence delocalization coefficients for several prototype mixed-valence compounds with the perturbation model, and in general found that agreement between observed and calculated intensities was quite acceptable.[2] Recently, however, Richardson and Taube[13] have measured the spectra of a dozen or so

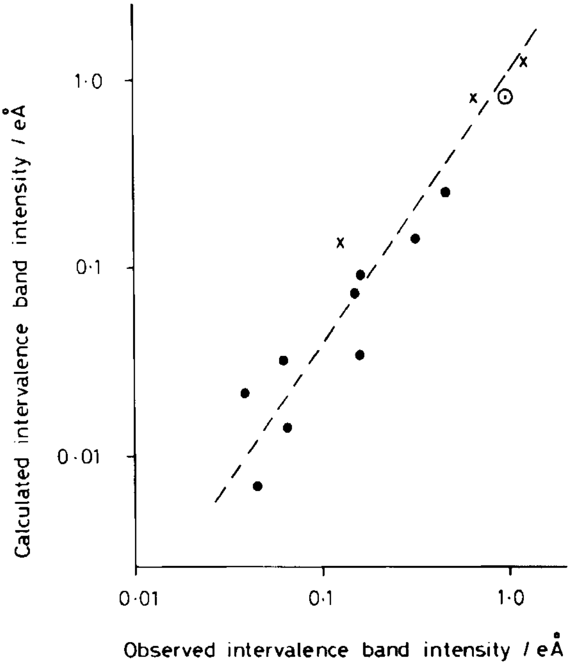

FIGURE 4 Observed and calculated intensities of intervalence transitions in Fe(II, III) and Ru(II, III) complexes. Crosses are from Ref. 2 and dots from Ref. 13.

complexes $(NH_3)_5Ru(L)Ru(NH_3)_5^{5+}$, where L is a substituted pyridine, pyrimidine, bisubstituted naphthalene, etc., and also calculated the intensities of their intervalence bands with the model. Over such a large set of closely related complexes, Figure 4 (which also includes our own data) shows a very nice correlation of theory and experiment suggesting that the perturbation model gives a good description of weakly coupled mixed-valence compounds.

GROUND-STATE VALENCE DELOCALIZATION: POLARIZED NEUTRON DIFFRACTION

Using excited-state properties such as the intensities of intervalence transitions to estimate delocalization in the ground state is necessarily an indirect procedure (albeit, as we have seen, quite a successful one). It would be more logical, as well as more direct, to employ physical methods based only on properties of the electronic ground state. Mössbauer and EPR spectroscopy come to mind, but most direct of all would be to determine the distribution of unpaired electron density between the two metal-ion

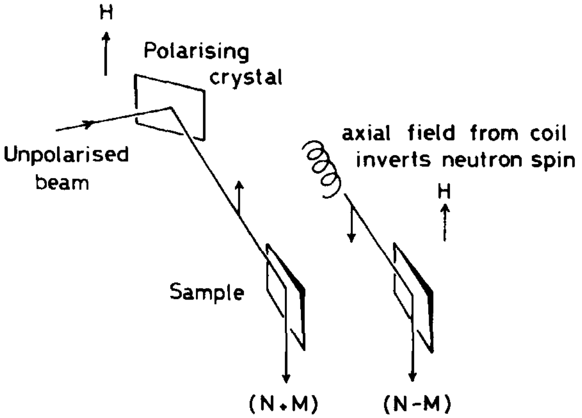

FIGURE 5 Schematic view of a diffractometer for polarized neutrons.

sites. The ultimate technique for making this kind of measurement is polarized neutron diffraction, and it happens that the classical mixed-valence complex, Prussian Blue, is in some ways a particularly suitable case to study.

Diffraction of polarized neutrons has a long history in solid state physics as a means of determining magnetization densities,[14] but has not been applied very frequently to inorganic complexes.[15] Put briefly, the cross section for elastic scattering, and hence diffraction, of neutrons by unpaired electrons in a crystal lattice depends on the relative orientation of the electron and nuclear spins. The nuclear scattering cross section is independent of the orientation of the neutron spin. Thus in principle one can separate the nuclear and magnetic contributions to the total scattering by aligning the electron spins and then carrying out diffraction measurements with the spins of the incoming neutrons polarized first parallel and then antiparallel to the electron spins. A schematic picture of such a device is shown in Figure 5.

Polarized neutrons are obtained from the unpolarized beam coming out of the reactor by reflecting them from a suitable plane of a magnetized crystal such as a Heusler alloy. They are then used in a classical diffraction experiment, just as unpolarized neutrons or x rays, but with the difference that the spins of the neutrons arriving at the sample are "flipped" periodically from up to down by an axial coil so that two diffraction measurements are made in succession at the same Bragg angle. If the nuclear and magnetic structure factors are denoted by F_N and F_M in the former case we measure $F_\mathrm{N} + F_\mathrm{M}$ and in the latter $F_\mathrm{N} - F_\mathrm{M}$. The intensities of the two diffraction peaks are[16]

$$\begin{aligned} I^{\uparrow} &= F_\mathrm{N}^2 + m^2F_\mathrm{M}^2 + 2mF_\mathrm{N}F_\mathrm{M}P, \\ I^{\downarrow} &= F_\mathrm{N}^2 + m^2F_\mathrm{M}^2 - 2mF_\mathrm{N}F_\mathrm{M}P, \end{aligned} \tag{19}$$

where m is the magnetization of the sample and P the efficiency of the polarizer. In practice P can be close to unity, but the magnetization depends on the strength of the applied field and the temperature. Clearly, one can achieve magnetic saturation ($m \sim 1$) in almost any substance, given a large enough field and a low enough temperature, but compounds which order spontaneously as ferromagnets have a substantial advantage. Prussian Blue, $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$, is just such a compound.[17]

The structure of Prussian Blue is shown in outline in Figure 1(a). All the physical evidence agrees that it is a deeply trapped class II mixed-valence compound, with low-spin Fe(II) at the carbon-coordinated sites and high-spin Fe(III) at the nitrogen. Interaction between the two sites is evidenced by the appearance of an intervalence band at 14 100 cm^{-1}, whose intensity suggests a value of α_1 of about 0.1,[9] in agreement with the estimate[2] of 0.11 from the perturbation model we described earlier. Prussian Blue is one of a very small number of ionic insulators which order as three-dimensional ferromagnets.[18] Its Curie temperature is only[19] 5.5 K but even that is surprising when one realizes that the nearest "through bond" approach of the Fe(III) which carry the spin is no less than 10.16 Å, and that the exchange pathway lies through five atoms: N–C–Fe^{II}–C–N. It seems reasonable to hypothesize that the existence of a low-lying intervalence excited state which can be mixed into the ground state provides the dominant mechanism of the exchange interaction. Indeed, we have demonstrated that with $\alpha_1 \sim 0.1$ this mechanism predicts a ferromagnetic exchange constant with T_c of the correct magnitude. I shall not describe the model here, but refer the reader to the earlier paper[20] for details. Suffice to say here that the compound is ferromagnetic, and that susceptibility measurements show that in a field of 4.8 T the magnetization varies from 0.96 at 4.2 K to 0.99 at 1.7 K.

That is the good news. The bad news is that Prussian Blue, being a coordination polymer, cannot be grown in single crystals large enough for neutron diffraction. Consequently the experiment must be done with a powder. Recently we carried out such an experiment on the D5 polarized beam diffractometer at the Institut Laue–Langevin, Grenoble.[21] The sample was held at 3 K in a field of 4.8 T and the neutron wavelength was 1.074 Å. Since Prussian Blue is cubic[22] (Pm3m) there are not very many reflections, and the magnetic form factor falls off steeply with increasing Bragg angle 2θ. The experimental strategy, therefore, was to measure only the (111), (200) and (400) reflections, but to vary 2θ in 0.1° steps and use long counting times to obtain good statistics. Part of the data is shown in Figure 6.

In general, if "flipping ratios" $I^{\uparrow}/I^{\downarrow}$ could be measured for a large number of reflections, we could obtain a map of the magnetization density in the unit cell by means of a Fourier transformation, much as one would do for the total electron density by x-ray diffraction. The very small

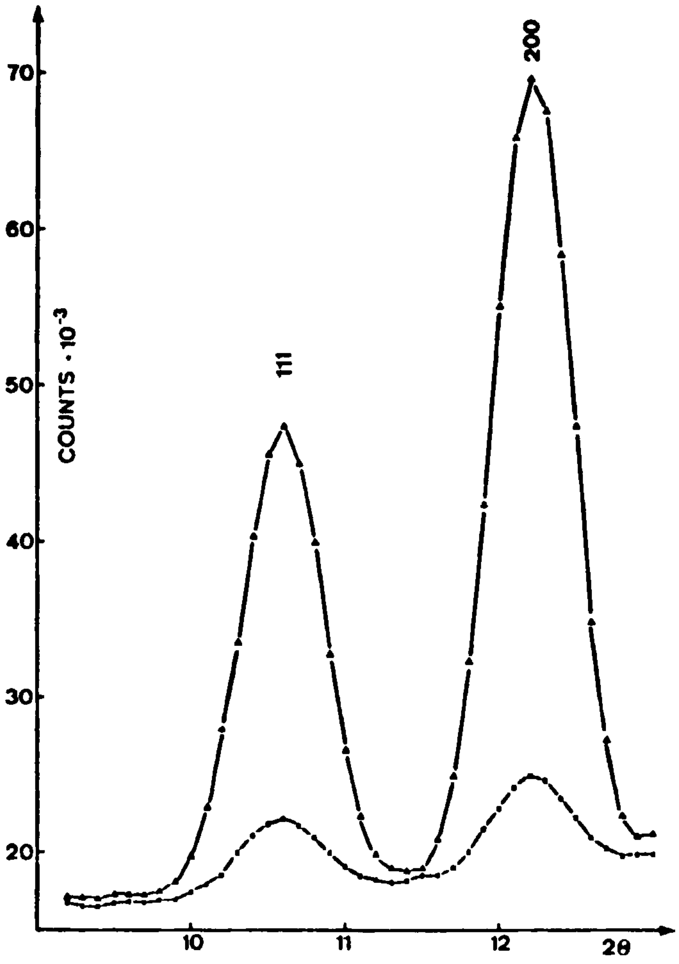

FIGURE 6 Part of the neutron diffraction profile of Prussian Blue powder at 3 K and 4.8 T for neutron spin up (triangles), and down (squares) (Ref. 21).

number of peaks precludes this approach, however, and we aim simply to obtain the magnitude of the unpaired spin transferred from the low-spin Fe(II) to the high-spin Fe(III). The magnetic form factor of a reflection (hkl) is[23]

$$F_{\mathrm{M}}^{hkl} = (e^2\gamma/mc^2)\sum_i \langle S_i\rangle f_i^{hkl} \exp\{2\pi i[(hx+ky+lz)/a]\}, \qquad (20)$$

where $\langle S_i\rangle$ is the expectation value of the spin S_z at site i, f_i^{hkl} are magnetic scattering factors, x, y, z are atomic coordinates and a is the unit cell parameter. The total spin in each unit cell is

$$4\langle S_{\mathrm{Fe(III)}}\rangle + 3\langle S_{\mathrm{Fe(II)}}\rangle = 10 \qquad (21)$$

and the observed magnetic structure factors are refined to extract a value of $\langle S_{\mathrm{Fe(II)}}\rangle$.

In terms of Eq. (3) there is a simple relationship between $\langle S_{\mathrm{Fe(II)}}\rangle$ and α_1. The zero-order ground state has

$$\langle \psi_0 | S_{z\mathrm{Fe(III)}} | \psi_0 \rangle = \tfrac{5}{2}; \quad \langle \psi_0 | S_{z\mathrm{Fe(II)}} | \psi_0 \rangle = 0 \tag{22}$$

while in the intervalence charge-transfer excited state

$$\langle \psi_1 | S_{z\mathrm{Fe(III)}} | \psi_1 \rangle_{\mathrm{av}} = (\tfrac{5}{2}) - (\tfrac{1}{6})(\tfrac{1}{2}); \quad \langle \psi_1 | S_{z\mathrm{Fe(II)}} | \psi_1 \rangle = \tfrac{1}{2} \tag{23}$$

where the "av" means an average over all six Fe(III) sites neighboring on Fe(II). On the other hand for the true ground state ψ_G

$$\begin{aligned} \langle \psi_G | S_{\mathrm{Fe(III)}} | \psi_G \rangle &= (\tfrac{5}{2}) - (\tfrac{1}{12})\alpha_1^2; \\ \langle \psi_G | S_{\mathrm{Fe(II)}} | \psi_G \rangle &= (\tfrac{1}{2})\alpha_1^2 \end{aligned} \tag{24}$$

Thus we find $\alpha_1^2 = 2\langle S_{\mathrm{Fe(II)}}\rangle$.

Unfortunately it must be stated at this point that the experiments performed so far do not yield values of α_1^2 which are larger than the standard deviations placed on them by statistical and other errors. The latter is currently ±0.056, somewhat greater than the values of about 0.01 predicted by the optical absorption intensity and our perturbation model. Nevertheless, polarized neutron diffraction is the *only* technique which can give a direct experimental determination of α_1^2 to compare with theories of mixed-valence delocalization, and, in principle, with sufficiently long counting times, or in samples which can be obtained as large enough single crystals, there is no reason why it should not.

CONCLUSION

In this article I have tried to point out the interest in calculating the valence delocalization coefficient α_1 for mixed-valence compounds by means of a simple perturbation model, and also indicated some ways of estimating it experimentally. Of the experimental methods, measuring the intensity of the intervalence optical transition is the easiest, but polarized neutron diffraction is potentially the most direct and unambiguous. To my knowledge it has only been tried out so far on one compound, Prussian Blue, which has the disadvantage of being available only as a powder. Apart from its simplicity, an advantage of the perturbation model as a framework for calculation is that it can draw on empirical data such as the energies of local charge-transfer states in complexes of the individual oxidation states. With its emphasis on the excited states involving the bridging ligands, it should also bring about a clearer understanding of the electronic factors underlying the strength or weakness of the interaction in the many mixed-valence compounds known, or yet to be prepared.

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P. DAY
Inorganic Chemistry Laboratory,
Oxford University,
South Parks Road, Oxford OX1 3QR, England

References

1. M. B. Robin and P. Day, Adv. Inorg. Chem. Radiochem. **10,** 248 (1967).
2. B. Mayoh and P. Day, J. Chem. Soc. Dalton Trans. **1974**, 846 (1974).
3. R. Glauser, U. Hauser, F. Herren, A. Ludi, P. Roder, E. Schmidt, H. Siegenthaler and F. Wenk, J. Am. Chem. Soc. **95,** 8457 (1973).
4. N. Sanders and P. Day, J. Chem. Soc. A **1970**, 1190 (1970).
5. J. Linderberg, Chem. Phys. Lett. **1,** 39 (1967).
6. J. W. Richardson, W. C. Nieuwpoort, R. R. Powell and W. F. Edgell, J. Chem. Phys. **36,** 1057 (1962).
7. E. Clementi, I.B.M. Journal Res. Dev. **9,** 2 (1965).
8. N. Sanders, J. Chem. Soc. A **1971**, 1564 (1971); J. Chem. Soc. Dalton Trans. **1972**, 345 (1972); B. Mayoh and P. Day, Theoret. Chim. Acta **49**, 259 (1978).
9. M. B. Robin, Inorg. Chem. **1,** 337 (1962).
10. See chapters by P. Day, N. S. Hush and P. N. Schatz, in *Mixed Valence Compounds*, ed. D. B. Brown (Reidel, Dordrecht, 1980).
11. H. Eyring, J. Walter and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944).
12. D. R. Bates, J. Chem. Phys. **19,** 1122 (1951).
13. D. E. Richardson, Ph.D. Thesis, Stanford Univ. (1981); H. Taube, Am. Chem. Soc. Meeting, Atlanta, 1981.
14. A recent review is J. B. Forsyth, Phys. Scr. **15,** 69 (1977).
15. Recent examples are CrF_6^{3-}, F. A. Wedgwood, Proc. Roy. Soc. **A349,** 447 (1976) and $CoCl_4^{2-}$, P. J. Brown, J. B. Forsyth and R. Mason, Phil. Trans. Roy. Soc. B **290,** 481 (1980).
16. G. E. Bacon, *Neutron Diffraction* (Oxford Univ. Press, Oxford, 1964).
17. A. N. Holden, B. T. Matthias, P. W. Anderson and H. W. Lewis, Phys. Rev. **102,** 1463 (1956).
18. For a list see P. Day, Accounts Chem. Res. **12,** 236 (1979).
19. A. Ito, M. Suenaga and K. Ono, J. Chem. Phys. **48,** 3597 (1968).
20. B. Mayoh and P. Day, J. Chem. Soc. Dalton Trans. **1976**, 1483 (1976).
21. P. Day, F. Herren, A. Ludi, H. U. Güdel, F. Hulliger and D. Givord, Helv. Chim. Acta **63,** 148 (1980).
22. H. J. Buser, D. Schwarzenbach, W. Petter and A. Ludi, Inorg. Chem. **16,** 2704 (1977).
23. W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon Press, Oxford, 1971).