Charge Transfer in Mixed-valence Solids. Part 9.[1] Preparation, Characterization, and Optical Spectroscopy of the Mixed-valence Mineral Voltaite [Aluminium Pentairon(II) Tri-iron(III) Dipotassium Dodecasulphate 18-Hydrate] and its Solid Solutions with Cadmium(II)

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Crystals of voltaite, $K_2Fe^{II}{}_5Fe^{III}{}_3Al[SO_4]_{12}\cdot 18H_2O$, and solid solutions $K_2Fe^{II}{}_xCd^{II}{}_{5-x}Fe^{III}{}_3Al[SO_4]_{12}\cdot 18H_2O$, have been prepared and characterized by chemical analysis and *X*-ray diffraction. The solid solutions are isostructural [O_h^8 (*Fd*3*c*)], *a* varying only from 27.25 ($x = 5$) to 27.49 Å ($x = 0$). Diffuse-reflectance spectra have been recorded at room temperature (5 000—50 000 cm^{-1}) and single-crystal transmission spectra at temperatures down to 4.2 K (5 000—25 000 cm^{-1}). From the spectrum of cadmium voltaite, iron(III) ligand-field transitions are found at 14 000 ($^6A_{1g}\rightarrow{}^4T_{1g}$), 19 000 ($^6A_{1g}\rightarrow{}^4T_{2g}$), and 23 500 cm^{-1} ($^6A_{1g}\rightarrow{}^4A_{1g},{}^4E_g$). In the mixed-valence crystals a broad absorption band centred at 16 500 cm^{-1} is the intervalence charge-transfer transition. Its half-width and integrated band area vary only slightly from room temperature to 4.2 K. The linear absorption constant of the intervalence transition in pure voltaite, extrapolated from the concentration dependence of the absorption constant in the crystals diluted with Cd^{II}, is 150 ± 3 cm^{-1}. The iron(II) ligand-field transition appears as a shoulder at 10 000 cm^{-1}. From the oscillator strength of the intervalence transition, the valence delocalization constant is estimated as 0.005 7. This value is compared with those of mixed-valence silicates and metal complexes.

MIXED valency, *i.e.* the simultaneous presence of two oxidation states of an element in the same crystal lattice, is quite common in minerals. In their review of mixed-valency chemistry, Robin and Day [2] collected many examples from the mineralogical literature, and the optical spectra of a number of these, in particular silicates containing Fe^{II} and Fe^{III}, have been examined in detail.[3-5] In this paper we report the optical spectra of voltaite, an iron(II), iron(III) sulphate, and a series of diluted voltaite crystals in which the Fe^{II} is partly replaced by Cd^{II}.

Voltaite is a convenient choice for a study of the temperature and concentration dependence of an iron(II)–iron(III) intervalence charge-transfer (c.t.) transition for several reasons; it is easily prepared and crystallized, its structure has been determined to good accuracy,[6] it is cubic, and is reported [7] to form homogeneous solid solutions with a wide variety of cations so that the concentration of Fe may be varied. The chemical formula of voltaite is $K_2Fe^{II}{}_5Fe^{III}{}_3Al[SO_4]_{12}\cdot 18H_2O$. It belongs to the space group O_h^8 (*Fd*3*c*) with a unit cell of 27.25 Å. There are two iron sites, one surrounded entirely by the oxygen atoms of sulphate groups, forming an almost regular octahedron [mean Fe(1)–O 2.004 Å], and the other surrounded by four sulphate oxygen atoms and two water molecules *trans* to one another. Around the second site, which contains the Fe^{II}, the average Fe–O distance is 2.090 Å. Since the two iron sites are crystallographically distinguishable we anticipate that the oxidation states are localized, but since the ligand fields around the sites differ only slightly the Franck–Condon energy required to transfer an electron from Fe^{II} to Fe^{III} will not be large. Thus, in crystalline form, voltaite is black, and belongs in class II of the Robin–Day [2] mixed-valence classification scheme. Magnetic-susceptibility measurements and Mössbauer spectra [8,9] confirm that the oxidation states are localized and that the ground states of both types of Fe are high spin ($^6A_{1g}$ and $^5T_{2g}$).

An unexpected feature of the low-temperature susceptibility, given the strength of the interaction between the two iron sites as indicated by the dark colour of the crystals, is the absence of a transition to an ordered state down to at least 3 K. Nevertheless, although many mixed-valence compounds appear deeply coloured to the eye, on measuring the absolute absorption constants by single-crystal transmission spectroscopy one often finds that the intervalence c.t. transitions are no more than an order of magnitude or so more intense than ligand-field transitions, compared with ligand-to-metal c.t. bands which are usually 2—3 orders of magnitude more intense. This is partly a consequence of the high concentration of absorbing ions in the solid, and partly due to the fact that the intensity of an intervalence c.t. transition is determined by the number of near-neighbour pairs of ions with differing oxidation state, and not simply by the number of individual ions.

EXPERIMENTAL

Sample Preparation.—Crystals of voltaite, and those in which some of the Fe^{II} is replaced by Cd^{II}, were prepared by a method similar to that used by Gossner and Arm.[10] To prepare voltaite, potassium sulphate (6—7 g), iron(II) sulphate heptahydrate (60.4 g), aluminium sulphate hexadecahydrate (37.0 g), and iron(III) sulphate enneahydrate (39.7 g) were dissolved in water (*ca.* 300 cm^3) in a large evaporating basin. The basin was transferred to a constant-temperature bath, and after adding concentrated sulphuric acid (45 cm^3), it was kept covered by a watch glass at 70 °C for *ca.* 10–14 d. After a week or so half the liquid had evaporated and large black crystals began to form. Subsequently, small quantities of water were added each day until the crystals, then 2—5 mm wide, did not grow any larger. The mother liquor was then decanted off and the mass of crystals washed with water followed by acetone. To prepare crystals diluted with Cd^{II}, the same method was used, simply replacing iron(II) sulphate by cadmium sulphate in the appropriate ratios.

The larger voltaite single crystals, which had an octahedral habit, were usually attached to a layer of white matrix material, mainly consisting of aluminium sulphate, underneath which was a dense mass of much smaller voltaite crystals. The large single crystals were therefore extracted individually by hand, and the white material was scraped off with a scalpel. They were stored in a desiccator over silica gel.

Analysis.—Total iron was determined both by titration of a solution of the sample with cerium(IV) sulphate, after reducing the iron(III) with tin(II) chloride, and by atomic-absorption spectroscopy. Excess of $SnCl_2$ was removed by adding mercury(II) chloride solution, which oxidised the Sn^{II} to Sn^{IV}, precipitating Hg_2Cl_2. Cadmium was also determined by atomic absorption spectroscopy. Iron(II) was determined by direct titration with Ce^{IV} and Fe^{III}, either by direct titration with Hg^{I} or by difference from the iron(II) and total iron results.

Diffraction.—*X*-Ray powder-diffraction measurements were made using a Guinier camera, with an internal standard of KCl, and a Philips counter diffractometer. Neutron powder-diffraction profiles were recorded on the D2 diffractometer at the Institut Laue Langevin, Grenoble, at temperatures between 3 and 250 K and a neutron wavelength of 1.222 Å.

Optical Spectroscopy.—The thin crystalline sections required for optical spectroscopy were prepared by fixing a natural face of a large single crystal to a microscope slide using Lakeside (glycol phthalate) cement, and then grinding a face parallel to it with successively finer grades of emery paper, followed by polishing with talc and a cloth pad. The section was then removed from the slide by gently warming the cement on a hotplate, and attached over a pinhole in a copper mounting plate with a small quantity of silicone grease. The mounted crystal was bolted to the base of an Oxford Instruments CF 100 continuous-flow helium cryostat, equipped with a Harwell temperature controller, and transmission spectra were recorded by a Cary 14R spectrophotometer. To obtain accurate values of optical density, and hence linear absorption constants, from the voltaite transmission spectra a number of precautions have to be taken. First the position of the sample on its pinhole mount, and a pinhole of the same size in the reference beam, are separately optimized by monitoring the output of the photomultiplier on an oscilloscope. If neutral density filters were used to balance the sample and reference beams when examining the spectra of samples with high optical densities, the following procedure was adopted: after recording the spectrum, the crystal was removed from the mounting plate and, after reversing the sample and reference channels in the spectrophotometer, a baseline including the optical density of the filter was recorded. Finally, the neutral density filter was removed, and a further baseline determined. Hence the contribution of the filter to the original spectrum could be found. Diffuse-reflectance spectra were also obtained on powdered samples at room temperature using a Unicam SP 700 spectrophotometer equipped with an SP 735 diffuse-reflectance attachment.

RESULTS

Analysis.—In Table 1 are given the analyses of all the samples used in this work, together with elemental compositions calculated by assuming that the formulae were $K_2Fe^{II}_xCd_{5-x}Fe^{III}_3Al[SO_4]_{12}\cdot 18H_2O$. Also tabulated are the values of x for each sample which best fit the analytical data. In assigning a value of x to each sample we have given greater weight to the total iron and the cadmium analyses which were performed by atomic-absorption spectroscopy, than to the iron(II) and total iron analyses obtained by volumetric methods.

TABLE 1

Observed and calculated analyses for voltaite and cadmium-diluted voltaites

Analysis (%)							
Total Fe			Cd		Fe^{II}		
a	*b*	Calc.	*a*	Calc.	*b*	Calc.	x
22.0	21.7	22.0			13.0	13.75	5.00
15.95	16.6	15.95	9.70	10.0	7.6	8.10	3.10
12.9	13.4	13.0	14.55	14.85	5.3	5.35	2.10
10.0	9.9	10.05	19.3	19.7	2.2	2.60	1.05
8.65	8.4	8.65	21.75	22.0	0.8	1.30	0.55
7.85	8.0	7.85	23.75	23.3	0.5	0.60	0.25
7.75	7.6	7.75	23.25	23.5	0.2	0.45	0.20
7.85	7.7	7.25	23.6	24.3	0	0	0

[a] Determined by atomic-absorption spectroscopy. [b] Determined by titration.

Diffraction.—For each sample, some 80 peaks in the powder pattern could be indexed in the O_h^8 ($Fd3c$) space group, and the unit-cell parameter found by least-squares fitting. Thus the mixed crystals, and also the pure cadmium voltaite, are isostructural with normal voltaite with only very small changes in lattice dimensions. The unit-cell parameters as a function of x (see Table 1) are listed in Table 2. They vary linearly with x, the best least-squares line being represented by the equation $a_0 = 0.05x + 27.50$.

TABLE 2

Lattice parameters of voltaite samples: variation with composition. The final figure in parentheses is the standard deviation

x	a_0/Å	x	a_0/Å
5.00	27.249(2)	0.53	27.484(2)
3.10	27.347(3)	0.24	27.481(3)
2.10	27.383(2)	0.19	27.497(2)
1.05	27.444(2)	0	27.491(2)

TABLE 3

Variation with temperature of the unit-cell parameter of voltaite

T/K	a_0/Å	T/K	a_0/Å
248	27.278	48	27.190
173	27.246	4.2	27.191
89	27.241	3	27.222

The object of the neutron-diffraction experiments was to see if voltaite underwent any phase transitions on cooling from room to liquid-helium temperature, to observe the unit-cell parameter as a function of temperature, and to look for evidence of magnetic ordering at low temperature. As shown in Table 3 the unit-cell contracts slightly with decreasing temperature but there is no evidence for any phase transformation nor, even at the lowest temperature, any intensity variations or new peaks which could be ascribed to the onset of magnetic order. The latter conclusion agrees with the magnetic-susceptibility experiments.[8]

Optical Spectroscopy.—The single-crystal transmission spectra of four diluted voltaite samples in the visible and near-i.r. regions are shown in Figure 1, the intensity of absorption being indicated as the linear absorption constant. These spectra were recorded at room temperature,

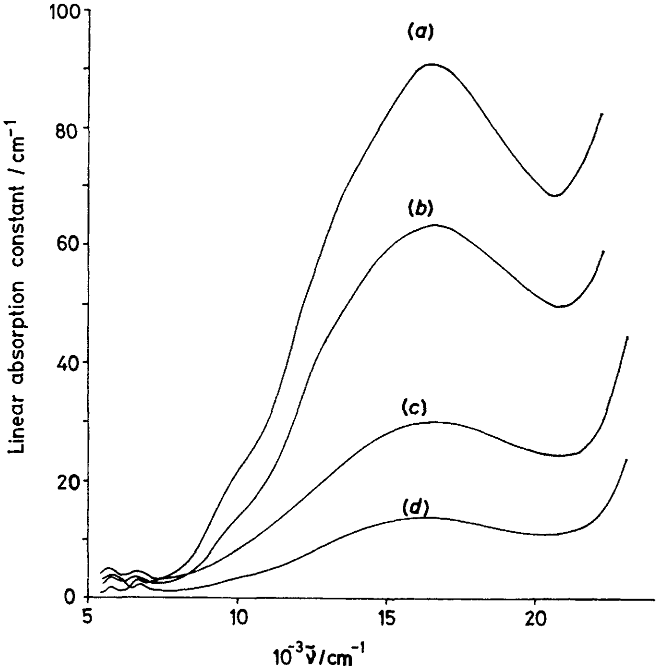


FIGURE 1 Absorption spectra of single crystals of cadmium-diluted voltaites. $x = 3.10$ (*a*), 2.10 (*b*), 1.05 (*c*), 0.53 (*d*)

but in Figure 2 are shown the spectra at room temperature and 4.2 K of the crystal with $x = 3.10$. One can see that decreasing the temperature has only a very small effect, narrowing the broad band at 16 500 cm^{-1} to a marginal extent and causing the near-u.v. absorption edge to shift somewhat to the blue, exposing a small narrow band at 23 200 cm^{-1}. Apart from the band at 16 500 cm^{-1}, the only other spectral features in Figures 1 and 2 are a shoulder near 10 000 cm^{-1}, which becomes a little weaker and also better resolved at 4.2 K, and two very weak bands in the near-i.r. at 5 800 and 6 900 cm^{-1}. The latter are assigned to O–H vibrational overtones.

Voltaite samples containing the highest proportion of Cd did not form crystals large enough, or of sufficiently good optical quality, for transmission measurements. Diffuse-reflectance spectra were therefore recorded as shown in Figure 3. From this Figure one can see that with increasing dilution the broad absorption band at 16 500 cm^{-1} becomes progressively weaker, exposing two other bands, which occur at 14 000 and 19 000 cm^{-1} for the pure cadmium(II) compound. The sharp O–H vibrational overtones remain almost unaffected by changing composition, as do the much more intense bands in the u.v. at 29 000, 36 000, and 49 000 cm^{-1}.

To define the energies of the iron(II) and iron(III) ligand-field transitions for sites co-ordinated by groups similar to those occurring in voltaite, crystal transmission and powder diffuse-reflectance spectra of a number of model compounds were also measured. No single-valence iron(II) compound could be found with a co-ordination geometry precisely mimicking the *trans*-$(H_2O)_2(SO_4)_4$ co-ordination of the iron(II) site in voltaite: $Fe[SO_4]\cdot 7H_2O$, containing $[Fe(OH_2)_6]^{2+}$, is probably the closest analogy. In the latter, the $^5T_{2g}$ state, split by the Jahn–Teller effect, is represented by two broad bands with maxima at 8 900 and 11 250 cm^{-1}. The linear absorption constant of a crystal of $Fe[SO_4]\cdot 7H_2O$ at 11 250 cm^{-1} (the more intense of the two components of $^5T_{2g}$) was estimated as 5.3 cm^{-1}. The closest available analogy to the iron(III) site in voltaite is in $Fe_2[SO_4]_3$, where the Fe^{III} is also co-ordinated by six oxygen atoms from SO_4 groups,[11–13] although in voltaite the iron(III) site is closer to a regular octahedron. No crystals of $Fe_2[SO_4]_3$ could be made large enough for transmission measurements, but a diffuse-reflectance spectrum showed peaks (cm^{-1}) which can be assigned as follows:

14 400	$^6A_{1g}\rightarrow{}^4T_{1g}$
18 600	$\rightarrow{}^4T_{2g}$
23 400 23 600	$\rightarrow{}^4A_{1g},{}^4E_g$

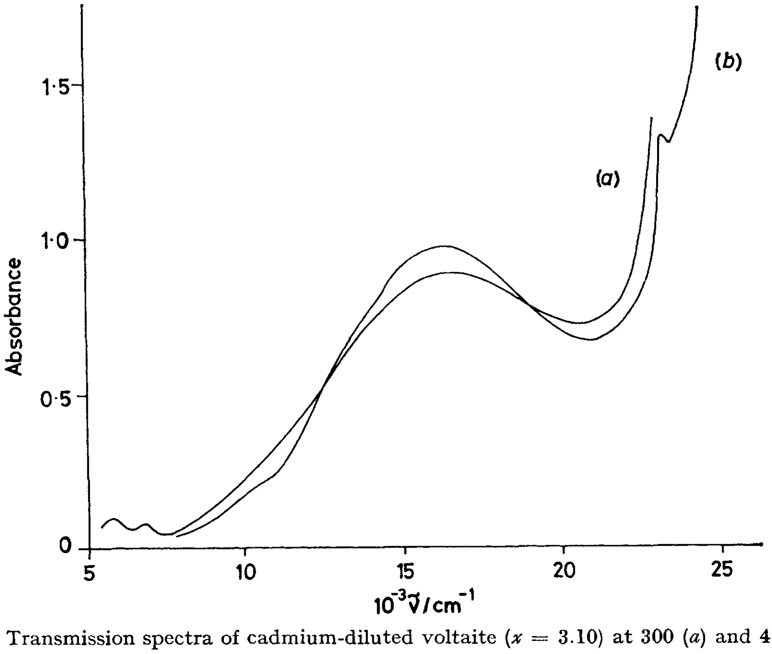


FIGURE 2 Transmission spectra of cadmium-diluted voltaite ($x = 3.10$) at 300 (*a*) and 4.2 K (*b*)

In addition, a number of much more intense and broad peaks, assigned as $[SO_4]^{2-} \rightarrow Fe^{III}$ c.t. transitions, were found at 27 600, 34 000, 38 200, and 45 500 cm^{-1}. Making a comparison with the ligand-field spectrum of $[Fe(OH_2)_6]^{3-}$,[14,15] one sees that the sulphate ion exerts a ligand field quite similar to, but a little smaller than, that of water, and that it also lies slightly below water in the nephelauxetic series. Values of the octahedral ligand-field parameters and the nephelauxetic ratio are respectively 14 300 cm^{-1} and 0.75 for the aqua-ion and 13 000 cm^{-1} and 0.72 for the sulphate. Since the ligand-field splitting parameters of sulphate and water differ by less than 10% in their iron(III) complexes, one anticipates a comparably small difference between the values for the corresponding iron(II) complexes. Given that the baricentre of the two Jahn–Teller components of $^5T_{2g}$ in $Fe[SO_4]\cdot 7H_2O$ is at 10 100 cm^{-1}, and assuming that the 'rule of average environment'[16] applies to the spectra of iron(II) ions co-ordinated by a mixture of sulphate ions and water molecules, the baricentre of the $^5T_{2g}$ Jahn–Teller components for the *trans*-$(H_2O)_2(SO_4)_4$ co-ordinated site in voltaite is expected to fall just below 10 000 cm^{-1}. With these considerations in mind we can now examine the voltaite spectra in more detail.

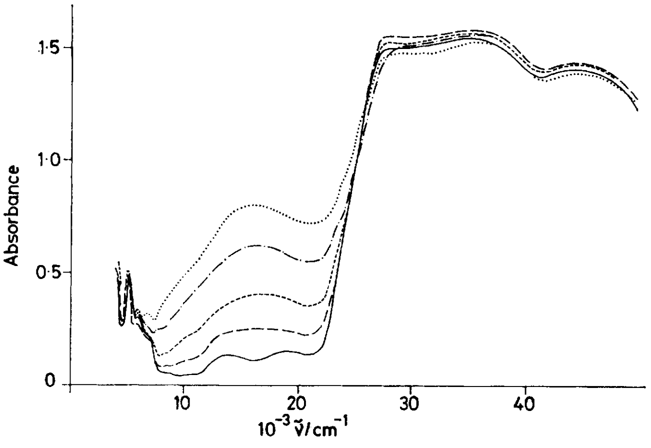


FIGURE 3 Diffuse-reflectance spectra of cadmium-diluted voltaites. The full line is for pure cadmium voltaite. The remainder with increasing intensity of the band at 16 000 cm^{-1}, correspond to $x = 0.19$, 0.24, 0.53, and 1.05

DISCUSSION

From the *X*-ray and neutron-diffraction experiments it is clear that the voltaite unit cell is practically unaffected, either by replacing Fe^{II} by Cd^{II} or by changing the temperature from 300 to 4 K. All the spectra can therefore be discussed within the same structural framework. Referring to Figures 1 and 2 one can see that in voltaite itself, and in the diluted crystals containing only a small proportion of Cd, the two lowest iron(III) ligand-field transitions are completely obscured by the broad band at 16 500 cm^{-1}, although in the 4.2 K spectrum (Figure 2) the $^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$ band stands out clearly at 23 200 cm^{-1}. This is almost at the same frequency as found in pure cadmium voltaite, and demonstrates that the localized excitations are essentially unchanged in going from the single- to mixed-valence samples. The iron(II) ligand-field transitions in the mixed-valence compounds, on the other hand, are represented by the weak shoulder seen in all the spectra of Figure 1 at 10 000 cm^{-1}. Consequently, the dominant contribution to the absorption profile in the visible region comes from the band at 16 500 cm^{-1}. As indicated by Figure 4, the linear absorption constant of that band is quite accurately proportional to the iron(II) content of the crystals, and if the linear plot in Figure 4 is extrapolated to the composition of pure voltaite, whose transmission spectrum could not be measured, a value for the maximum linear absorption constant at the peak of 150 cm^{-1} is found. Recalling that the linear absorption constant of $Fe[SO_4]\cdot 7H_2O$ in the region of the spin-forbidden ligand-field band at 10 000 cm^{-1} was only 5 cm^{-1}, and that the spin-forbidden ligand-field bands of the high-spin d^5 iron(III) site are certain to be even weaker, one concludes that in making a rough assessment of the oscillator strength of the band at 16 500 cm^{-1} the contribution of both iron(II) and iron(III) ligand-field bands can be neglected. Any calculation of valence delocalization based on this hypothesis would then be an upper estimate. It should also be noted that the area of the envelope of the band at 16 500 cm^{-1} scarcely changes with temperature, although its half-width slightly decreases. Hence, again, the overwhelming proportion of the oscillator strength in this region comes from a transition which is electric-dipole allowed.

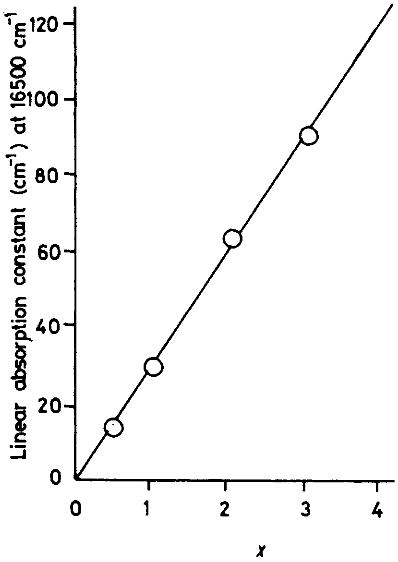


FIGURE 4 Variation of the linear absorption constant at the peak of the intervalence band in cadmium-diluted voltaites as a function of composition

Since the iron(II) and iron(III) valences are localized, so that the compound belongs in class II of the Robin–Day[2] classification scheme for mixed-valence compounds, the band at 16 500 cm^{-1} is then assigned as the $Fe^{II} \rightarrow Fe^{III}$ c.t. transition. Its oscillator strength is a direct measure of what we have called[17] the 'valence delocalization coefficient'. Consider two metal ion sites, A and B such as the iron(II) and iron(III) sites in voltaite, distinguishable crystallographically and carrying different numbers of localized *d* electrons. In the present instance they have ground-state electron configurations $t_{2g}^4e_g^2$ and $t_{2g}^3e_g^2$. Considering only one *d* orbital on each of two atoms, a zero-order ground-state wavefunction (1) could be written. With a certain

$$\psi_0 = |\chi^+{}_A\chi^-{}_A\chi^+{}_B| \qquad (1)$$

expenditure of energy one might create an excited state by transferring an electron from A to B, giving (2). The

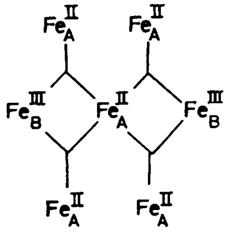
$$\psi(A\rightarrow B) = |\chi_A{}^+\chi^+{}_B\chi^-{}_B| \qquad (2)$$

time ground state is an admixture of ψ_0 and $\psi(A\rightarrow B)$, depending on the energy difference between the two zero-order states and the size of the resonance or transfer integral linking them together. In the new wavefunctions (3) for the ground and excited states α and β

$$\begin{aligned}\psi_g &= (1-\alpha^2)^{\frac{1}{2}}\psi_0 + \alpha\psi(A\rightarrow B) \qquad (3)\\ \psi_e &= (1-\beta^2)^{\frac{1}{2}}\psi(A\rightarrow B) + \beta\psi_0\end{aligned}$$

are called the valence delocalization coefficients for the ground and excited states respectively. In the present case there is more than one iron(III) neighbour around each Fe^{II} so that strictly speaking one ought to write $\psi(A\rightarrow B)$ as a linear combination of functions in each of which the electron originally on the Fe^{II} has been transferred to one of the iron(III) neighbours.

From the crystal structure of voltaite[6] we see that each iron(II) site has two iron(III) sites as nearest neighbours, co-ordinated in a linear arrangement as shown below. The triangles in this diagram represent projections of the $[SO_4]^{2-}$ tetrahedra along their three-fold axes. Thus, only two B sites have to be considered, and there are two $\psi(A\rightarrow B)$, formed from the symmetric and antisymmetric combinations of $\psi_{B_1}{}^{II}\psi_{B_2}{}^{III}$ and $\psi_{B_1}{}^{III}$-$\psi_{B_2}{}^{III}$ with $\psi_A{}^{III}$. For α and β to be non-zero, ψ_0 and $\psi(A\rightarrow B)$ must transform under the same irreducible representation of the point group for the linear AB_2 cluster. Thus the symmetric combination of $\psi_{B_1}{}^{II}\psi_{B_2}{}^{III}$ and $\psi_{B_1}{}^{III}\psi_{B_2}{}^{II}$ combines with ψ_0 in forming the ground state ψ_g [equation (3)], but the electric-dipole selection rule requires that the optical transition be to an antisymmetric combination. Hence in the optically accessible excited state (ψ_e), β = 0.[18] Further simplification comes from our observation that the energy and lineshape of the mixed-valence absorption band is unchanged when Fe^{II} on the A sites is progressively replaced by Cd^{II}, and that its intensity is quite accurately proportional to the iron(II) concentration. This amounts to saying that the effect of each iron(II) donor is simply additive, and that the optical properties may be thought of as resulting from the sum of pairwise near-neighbour AB interactions. Additional evidence against the importance of longer-range interactions is the vanishingly low temperature of magnetic ordering. Similar conclusions were reached in a number of other mixed-valence model systems in which the concentration dependence of the mixed-valence absorption band could be followed,[19,20] but the present case is interesting in that the iron(II) and iron(III) sites are bridged by sulphate ions in contrast to the other compounds we have examined, which were molecular ionic lattices.



If we only consider pairwise interactions, the electric-dipole transition moment μ for the transition from ψ_g to ψ_e with degeneracy *g* is (4) which, if all except single-

$$\mu = g^{\frac{1}{2}}\langle\psi_g|e\boldsymbol{r}|\psi_e\rangle \qquad (4)$$

centre terms are neglected (because overlap between ψ_A and ψ_B is small), becomes (5) where R_{AB} is the distance between the A and B sites.

$$\mu = \tfrac{1}{2}e(\alpha+\beta)R_{AB} \qquad (5)$$

To estimate (α + β) from the spectra in Figure 1 we need to determine the oscillator strength associated with each iron(II)–iron(III) near-neighbour pair. There is a complication when calculating the number of such pairwise interactions, because the stoicheiometry of the voltaite formula determined by chemical analysis can only be reconciled with the degeneracies of the two iron sites assigned on the crystallographic structure determination by assuming that one sixth of the Fe^{III} occupies iron(II) sites. Thus, Mereiter[6] assigns degeneracies of 32, 32, 96, and 16 to the K, Fe_A, Fe_B, and Al sites respectively, whilst the observed stoicheiometry is $K_2Fe^{II}{}_5Fe^{III}{}_3Al[SO_4]_{12}\cdot 18H_2O$. Mereiter refined structure factors from 726 reflections down to a residual *R* of only 0.032 so there can be no doubt of the essential correctness of his structure. By ordering the octahedral $[Al(OH_2)_6]^{3+}$ groups he further reduced *R* to 0.029,[21] but makes no comment about the possibility of ordering $Fe^{III} + 5Fe^{II}$ on the Fe_B sites. In computing the number of iron(II)–iron(III) contacts we therefore assume that they are randomly distributed. As shown above, every A site is surrounded by two B sites, containing Fe^{III}, and four A sites, each of which has a one-sixth probability of containing Fe^{III}. In undiluted voltaite the number of iron(II)–iron(III) contacts is $2\frac{2}{3}$ times the concentration of Fe^{II}. The latter is Zx/NV, where *Z* is the number of Fe^{II} per formula unit, *N* the number of formula units per mol, and *V* the volume of the unit cell. For voltaite $x = 5$, $V = 20\,235$ Å³, and the concentration of iron(II)–iron(III) pairs is 17.506 mol dm^{-3}.

The next step in calculating the valence delocalization coefficient is to obtain the oscillator strength, and hence the electric-dipole transition moment of the mixed-valence band at 16 500 cm^{-1}. Following the arguments already given, we attribute all the absorption under the broad band envelope in Figure 1 to the Fe^{II}–Fe^{III} c.t.

band, and ignore any contribution from the iron(II) and iron(III) ligand-field transitions. Furthermore, as a rough approximation, we assume that the band is gaussian in shape. The oscillator strength is given by $f = 4.6 \times 10^{-9}\ \varepsilon w$ where ε is the maximum absorption coefficient of the band in units of $dm^3\ mol^{-1}\ cm^{-1}$ and w is the full width at half-height in cm^{-1}. Using the value of 150 cm^{-1} for the linear absorption constant of voltaite at 16 500 cm^{-1}, extrapolated from the diluted crystals as shown in Figure 4, and a value for w averaged from the spectra in Figure 1, we find $f = 3.62 \times 10^{-4}\ dm^3\ mol^{-1}\ cm^{-2}$. This is a remarkably small intensity for an electric-dipole-allowed c.t. band, although it follows from the fact that the absorption coefficient per iron(II)–iron(III) contact is only 8.6 $dm^3\ mol^{-1}\ cm^{-1}$. That voltaite itself is so black in appearance is the result of the very high concentration (17.5 mol dm^{-3}) of iron(II)–iron(III) pairs. The oscillator strength is related to the electric-dipole transition moment μ by $f = 1.096 \times 10^{11} \Delta E \mu^2$ where ΔE is the energy of the transition in cm^{-1}. For the band of voltaite, at 16 500 cm^{-1}, therefore, μ is 0.045 Å. Since the nearest-neighbour iron(II)–iron(III) pairs are separated by 7.9 Å we obtain a value of only 5.7×10^{-3} for the average of the ground- and excited-state valence delocalization coefficients in equation (5). Such a small value provides an explanation for the unusually low magnetic-ordering temperature of voltaite [8] because, if valence delocalization were the most important mechanism for electron exchange between the Fe^{II} and Fe^{III}, one could use the theory which we originally devised to account for the ferromagnetism of Prussian Blue [1] to estimate the Curie temperature: the Curie temperature obtained in this way is 10^{-4} K!

It is of interest to compare the valence delocalization coefficient of voltaite with those of other mixed-valence compounds, including minerals.[17] In Prussian Blue, $[Fe^{III}\{Fe^{II}(CN)_6\}]^-$, in which the iron(II) and iron(III) ions are bridged by cyanide groups, α is *ca.* 0.1, the metal–metal distance being 5.1 Å. In the biotite micas, on the other hand, α is only *ca.* 0.03 although the nearest metal–metal distance is somewhat shorter than in Prussian Blue. The reason for this would appear to be the absence of low-energy iron(II)-to-ligand c.t. states in the silicates, mixing of which into the metal-to-metal c.t. state provided one of the mechanisms of valence delocalization. The case of voltaite is analogous to the biotite micas since the bridging sulphate group, like the oxide ion in the micas, has no low-lying orbitals capable of acting as acceptors in an iron(II)-to-ligand charge transfer. Additionally, the Fe^{II}–Fe^{III} distance in voltaite is nearly 8 Å, so a valence delocalization coefficient even smaller than in the biotite micas is not surprising. What is perhaps surprising is that voltaite should appear so strongly coloured to the eye: as pointed out above, this is the result of the high effective concentration of near-neighbour iron(II)–iron(III) pairs in the crystal rather than the intrinsic oscillator strength associate with each pairwise interaction. A further point of interest concerns the relationship between voltaite and the two other well authenticated mixed-valence iron sulphate minerals, romerite and bilinite.[22,23] Their chemical formulae are respectively $Fe^{II}Fe^{III}_2[SO_4]_4 \cdot 14H_2O$ and $Fe^{II}Fe^{III}_2[SO_4]_4 \cdot 22H_2O$, differing therefore only in water content. Romerite is reported as yellow-brown and bilinite as colourless to yellow. Their structures are unknown but it is certainly significant that both have a much higher ratio of water molecules to Fe atoms than voltaite. Probably, the metal atoms are mainly co-ordinated by water and the number of sulphate bridges between ions of differing oxidation state is greatly reduced, so reducing the intensity of any intervalence absorption.

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