Covalency in FeF_2 from magnetisation density data and from ab initio theory

Covalency in FeF$_2$ from magnetisation density data and from *ab initio* theory

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Abstract. A further analysis of the polarised neutron diffraction data on FeF$_2$ has been carried out using a valence orbital population model of the spin density. The fit to the data, $\chi^2 = 1.8$ for all reflections, is considerably better than for ligand field models used previously. The improvement is traced to the fact that the new model emphasises covalent interaction between iron and fluorine, whereas the earlier treatments introduced it only after spin–orbit interactions within the free Fe^{2+} ion had been taken into account. The amount of covalence required to explain the results is considerable, at least 10% of the spin of the iron atom being delocalised. However, the amount of spin seen on each fluorine atom is not correspondingly large, because cancellation takes place on account of the antiferromagnetic nature of the compound. An *ab initio* approximate calculation carried out on FeF$_6^{4-}$, units using the DV-X$_\alpha$ method lends strong support to the picture introduced by the valence orbital population model, and confirms that there are strong elements of covalence in the Fe–F interaction.

1. Introduction

Polarised neutron diffraction (PND) experiments on magnetically ordered crystals provide magnetic structure factors that arise from the magnetisation density in the unit cell. In most cases classical magnetochemistry and spectroscopy provide a good first approximation to the magnetisation density in the form of a wavefunction assigned to a free metal ion subject to a ligand field of symmetry corresponding to the site in the crystal, often idealised. For example, the Ni^{2+} ion in approximately octahedral sites may be taken to lead to the electron configuration $t_{2g}^6 e_g^2$. Improvements to these models must take account of a number of generally smaller factors whose balance varies from case to case. These factors include covalence, electron–electron correlation effects, magnetic exchange between ion sites, large orbital contributions to the magnetic moment, and complex ground terms.

In the simplest cases, paramagnets with small magnetic exchange, little orbital moment, collinear magnetisation, and simple ground terms, the magnetic structure factors are simply the Fourier transforms of the magnetisation density. This latter can be related to the spin density of the magnetically isolated fragments. This spin density shows very significant covalent and electron–electron correlation effects for many metal complexes. Those effects can be explained, in principle at least, both by *ab initio* methods for calculating the wavefunction and, qualitatively, by the usual chemical models of bonding [1].

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In other cases orbital moments may be larger and magnetic exchange may modify the ground state of the system. These complications can often be accommodated within an ionic, crystal field model, and then formulation and exact prediction of the observed magnetic structure factors, which are no longer simply related to the spin density, can be performed. Although covalency and associated correlation effects have been neglected in these treatments, agreement with experiment has often been obtained. Examples are the fluorides of bivalent iron and nickel, FeF_2 and NiF_2. The magnetic structures of these compounds are not simple, nor are the ground states uncomplicated. A simple crystal field model provides a fit to the observed PND results [2, 3].

However, the fit to the data for those compounds is not excellent, and the neglect of covalence is a likely cause of the deficiency. Brown [4] and de Almeida and Brown [3] showed that covalence is significant for FeF_2 by fitting the difference between theory and experiment to a simple model with a covalent wavefunction, but it has many parameters, often highly correlated.

On the other hand, empirical multipole models have been used to fit magnetic structure factors, and generally they provide a goodness-of-fit close unity, in contrast to either the *ab initio* or the single-ion type of calculations. The resulting model magnetisation densities, mapped in real space, show covalence effects directly. A relevant example is the $[CoCl_4]^{2-}$ ion in Cs_3CoCl_5 [5] where empirical modelling is a substantial improvement on even quite sophisticated calculated *ab initio* molecular wavefunctions [6], although those do show qualitatively the observed behaviour.

To illuminate the role of covalence in FeF_2 and NiF_2 we decided to apply empirical modelling to the PND data. In addition, we performed a number of local density approximation discrete variational X_α (DV-X_α) *ab initio* calculations of spin densities, both as a guide to the modelling and as an explanation of the results. In other systems, for example the $[Cr(CN)_6]^{3-}$ ion, this method has been remarkably successful in its predictions [1, 7]. In this paper we deal with FeF_2, and in the subsequent one NiF_2.

2. Previous work on FeF_2

2.1. Crystal and magnetic structures

FeF_2 at room temperature has a tetragonal structure, space group $P4_2/mnm$ [8, 9]. The iron atoms occupy the sites $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and there are four fluorine atoms at $\pm(x, x, 0; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2})$, with $x \simeq 0.3$. Thus each iron atom is on a site of mmm symmetry with almost octahedral coordination by six fluorine atoms. Conversely, the mm sites of the fluorine atoms are almost trigonally coordinated by three iron atoms. This is illustrated in figure 1.

FeF_2 undergoes magnetic ordering at 78 K and the structure remains rigorously tetragonal, becoming antiferromagnetic with opposing moments at $0, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, each aligned along c [10]. Since the sites of opposite spin are related not by only translation but also by a 90° rotation, two distinct domains are both possible and observed. These two domains scatter polarised neutrons differently. Thus in a PND experiment one should select a crystal with the greatest imbalance of domain populations, and estimate a correction to the data for their ratio [3, 11].

The nuclear structure of FeF_2 has been investigated by unpolarised neutron diffraction, as a preliminary to the polarised experiment [2, 3]. The agreement factors were satisfactory ($R(F) = 0.045$) but extinction was severe enough to be a source of error in the interpretation of the PND results. The structural details produced no new features.
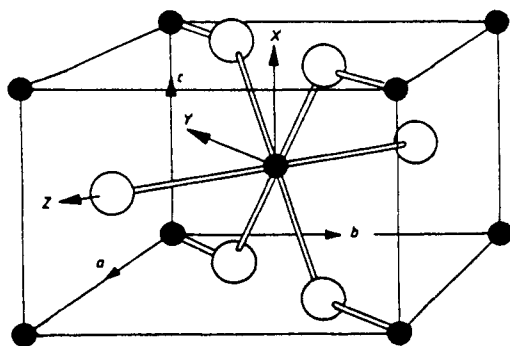
Figure 1. The tetragonal unit cell of FeF$_2$, which has the rutile structure. Each iron atom is octahedrally coordinated by fluorine atoms, and the quantisation axes X, Y and Z are shown for the atom at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$).

2.2. Other experiments and wavefunctions

The ground state wavefunctions for Fe^{2+} ions can be estimated in a crystal field approximation, and a detailed exposition is given elsewhere [2, 3]. From that we repeat only enough to illuminate the previous PND experimental interpretation.

FeF$_2$ has been studied by Mössbauer spectroscopy with temperature dependence [12–17] and pressure dependence [18–23], by optical spectroscopy [24–26], and by paramagnetic resonance of Fe^{2+} in ZnF$_2$ and of ^{19}F in FeF$_2$ [25, 28, 29]. As data accumulated it was found more and more necessary to interpret them in terms of an orthorhombic symmetry rather than a tetragonal crystal field model. If z is defined as the quantisation axis along the crystal $[1, -1, 0]$ axis and x along $[0, 0, 1]$, a ^{5}D Fe^{2+} free ion term is split by such a crystal field into terms differing in 3d orbital composition. These terms, in order of increasing energy (E_1 to E_5) as determined by experiment, correspond to approximately, $3d_{x^2-y^2}$, $3d_{xz}$, $3d_{yz}$, $3d_{xy}$, and $3d_{z^2}$, taken with the spin wave functions for $S = \frac{5}{2}$, with the label referring to the doubly occupied orbital or the spin hole, as required.

The introduction of spin–orbit coupling lifts the fivefold spin degeneracy of each term and mixes in small amounts of other states. Within the crystal field model the mixing coefficients are determined by the spin–orbit coupling constant and the energy differences between the various terms. Two acceptable wavefunctions, derived by means of slightly different approximations, have been given by Balcar *et al* [30] and by Okiji and Kanamori [31]. The use of the most general crystal field wavefunction, namely one derived from the complete 3d^4 (hole) manifold, has not been attempted.

The neglect of covalence in the above treatments contradicts the observation from resonance experiments that there is spin on the fluorine ligand, interpreted as 0.46(3)% on each, mainly in 2s orbitals, with both σ- and π-transfers involved [25, 27]. Reschke *et al* [32] attempted a molecular orbital model for the wavefunction to explain the data. They used a [FeF$_6$]$^{4-}$ cluster as the basis and took spin–orbit coupling and electron–electron correlation into account in a limited way to obtain fair agreement with experiment. The resulting 3d-like states correlate well with the crystal field model and show limited covalence and 4s/4p participation. The ground state is again dominated by the $3d_{x^2-y^2}$ contribution (coefficient 0.965).

We note that the energy order is thus rationalised in terms of the short Fe–F bonds along z exerting a stronger influence than the four longer bonds perpendicular, making $E_5 > E_4$ and E_2, $E_3 > E_1$. Further, the order $E_3 > E_2$ correlates well with the angular distortion in the xy plane, the fluorine atoms being closer to the yz than to the xz plane.

2.3. Polarised neutron diffraction experiments

PND data provides a stringent test of both the assumptions behind and the results of the crystal field calculation. The diffractometer used in the PND experiment measures the intensity of scattered neutrons initially polarised parallel or antiparallel to the applied magnetic field, which is perpendicular to the 'basal plane' of the diffractometer. If, for clarity, we omit some experimental corrections including degree of neutron polarisation, flipping efficiency and extinction, we can express the ratio of the two scattered intensities, the 'flipping ratio', $R(k)$, in terms of the crystal magnetisation density, $M(r)$.

$$R(k) = (F_N(k)^2 + 2F_N(k)F^{\perp}_{M,Z}(k) + |F^{\perp}_M(k)|^2)/(F_N(k)^2 - 2F_N(k)F^{\perp}_{M,Z}(k) + |F^{\perp}_M(k)|^2)$$

(1)

where

$$F^{\perp}_M(k) = k \times F_M(k) \times k$$

(2)

$$F_M(k) = (mc/eh) \int \exp(ik \cdot r)M(r) \, dr.$$

(3)

k is the experimental wavevector, r the position in the unit cell and $F_N(k)$ the nuclear structure factor.

This is a rather formidable set of vector equations, but it simplifies for many practical situations. For FeF_2 the $0kl$ and $h0l$ reflections in the magnetic model presented have flipping ratio of unity. For the reflections with $h + k + l$ odd the scattering arises from the difference of the magnetic densities on the two iron atom sites. For an ionic description of the compound this will be dominated the large spherical component of the Fe^{2+} 3d density, since each site has the opposite direction of magnetisation. In contrast, for reflections with $h + k + l$ even, there is no 3d spherical component, since the two-site contributions now cancel. The only magnetic scattering contribution comes from aspherical components on the Fe^{2+} ion and from covalent delocalisation of spin onto the F^- ions. The direction of the site magnetisation can be determined through equation (2) by refining the direction and thus altering the angle between $F_M(k)$ and the various reflection wavevectors k.

3. Previous analysis of PND data

de Almeida and Brown [3] fitted the parameters of crystal field models to only the twelve highest angle odd 'allowed' reflections. The orbital contribution was calculated exactly [33]. The wavefunction of Balcar *et al* [30] gave a reasonable fit with $\chi^2 = 5.8$. The slightly more flexible wavefunction of Okiji and Kanamori [31] gave $\chi^2 \simeq 4.7$, with values for the three coefficients of the various $|L, M_L\rangle$ components not significantly different from those previously obtained from the non-PND experiments. The results correspond to most of the spin in the $3d_{x^2-y^2}$ orbital with a small population in $3d_{xy}$. Subsequently, using the results of this fitting, the crystal field contribution to the remaining fourteen $h + k + l$ even reflections was calculated. The difference between these and the observed values was then fitted to a model wavefunction involving covalence, constructed from metal 3d and fluorine 2s and 2p atomic functions [3, 4]. This model has large numbers of highly correlated parameters. Neglecting some parameters, because they correspond to small densities, and noting those coefficients which were perfectly

correlated for $h + k + l$ even reflections, left seven parameters. The resultant model decreased χ^2 from the single-ion value of 65 to 3.0, a very significant improvement. However, there were still large correlations and physically rather unsatisfactory values for some parameters. Inclusion of an extra low angle $h + k + l$ reflection, to give fifteen in all, and application of further constraints to ensure more physically acceptable values, gave $\chi^2 \simeq 7$ for four variables.

Although part of the improvement on including covalence may reflect inadequacy in the Okiji and Kanamori single-ion model, it is clear that covalency is significant. The calculated amount of spin delocalised agrees qualitatively with that seem in maps obtained by Fourier transformation of the observed data. The dominant covalent interaction extracted from the fit is between the iron $3d_{yz}$ orbital and the short bonded fluorine atom (along the $[1, -1, 0]$ direction) $2p_y$ orbital and the longer bonded fluorine atom (approximately along the $[1, 1, 1]$ direction) $2p_z$ orbital. However, such a covalent interaction is basically π in symmetry, a surprising conclusion in view of the excellent opportunity for σ-spin delocalisation.

4. Valence orbital analysis of PND data

Empirical conventional multipole modelling of the magnetisation in FeF_2 could probably provide better fits than those above, but at the expense of a proliferation of parameters. The number of parameters can be reduced by using not only the site symmetry of the centres but also imposing additional constraints suggested on chemical grounds by the atomic orbitals available for hybridisation and molecular geometry. For example, the four multipoles allowed in mm symmetry may be reduced to three (sp^2) hybrid populations if one notes the trigonal symmetry imposed on F by the three nearest-neighbour Fe atoms.

We employ a model which uses on fluorine an (sp^2) hybrid orbital pointing along the short Fe–F bond, $(sp^2)_1$, and two similarly populated such hybrids pointing almost at the other two Fe atoms, $(sp^2)_{2,3}$, and a $2p_\pi$ orbital perpendicular to the trigonal plane. On the iron atom we have five 3d orbital populations, corresponding to the diagonal terms in the density matrix. In addition we use a 3d radial parameter to allow expansion or contraction of the 3d distribution. In other cases a mid-bond population (usually a Gaussian function with $\langle U^2 \rangle = 1600$ pm^2) was found useful in improving the fit and it is incorporated here. Another option which we employ is to allow 4p populations on the metal atom.

A difficulty which must be considered is the relation of magnetisation density to the spin density. We employ the dipole approximation [34] to substract the orbital component of the magnetisation density to leave the spin component, which we model. Recently an examination has been made of the PND results for the $CoCl_4^{2-}$ ion in Cs_3CoCl_5 and the magnetically anistropic Co(phthalocyanine) molecule using both the dipole approximation and a crystal field calculation of the orbital scattering to calculate magnetisation density and the magnetic scattering [35]. The examination reveals that deficiencies in the dipole approximation may be less severe than has been suspected for systems where the ground state is well defined and orbital contributions are not large, as is the case for FeF_2.

A last point to emphasise is that we refine all the data simultaneously, rather than using stepwise methods and neglecting at times certain reflections expected to be poorly modelled.

Table 1. Population parameters for FeF_2 from the valence orbital refinements (spins), on experimental data.

Refinement atom		$R1$ valence orbital	$R2$ constrained valence orbital
Fe	$3d_{x^2-y^2}$	$-0.37(14)$	$0.04(7)$
	$3d_{z^2}$	$0.73(18)$	$0.90(4)$
	$3d_{xy}$	$1.14(21)$	$=3d_{z^2}$
	$3d_{xz}$	$0.90(25)$	$0.86(5)$
	$3d_{yz}$	$0.83(14)$	$=3d_{xz}$
	$4p_x$	$2.1(3)$	0
	$4p_y$	$-1.0(3)$	0
	$4p_z$	$=4p_y$	0
	3d radius	$0.84(3)$	$0.91(2)$
F	$(sp^2)_1$	$0.004(4)$	$0.012(4)$
	$(sp^2)_2$	$-0.016(4)$	$=-(sp^2)_1$
	$(sp^2)_3$	$=(sp^2)_2$	$=-(sp^2)_1$
	$2p_\pi$	$0.016(14)$	$0.012(4)$
G†	short	$-0.01(3)$	$-0.01(1)$
G	long	$-0.02(1)$	$=$short

† Gaussian function; see text.

The above model is minimal by the standards of our previous work in the analysis of the PND data for systems when there are many reflections available. However, it still has fourteen parameters for only thirty reflections, a barely acceptable ratio for least-squares refinement purposes. It gives $\chi^2 = 1.8$ and $R(F) = 0.021$, which values are a great improvement on the two previous partial refinements. The results are listed in table 1 as $R1$. The total magnetisation around each Fe site is predicted as $\pm 7.3\mu_B$. The total, bulk magnetisation is thus zero, as required for an antiferromagnet. Within the limitations of the dipole approximation and employing the experimental value of g of 2.25, this corresponds to 3.2 spins for each iron atom. The equivalent 'full' multipole model has two more parameters and gives an almost identical fit, with the parameters of table 1 essentially unchanged. We do not quote its detail because of the poorer data/variable ratio.

We also made a more constrained refinement in which spin donation from Fe to F was assumed equal for *all* bonds. This introduced the following population constraints; $3d_{z^2} = 3d_{xy}$, $3d_{xz} = 3d_{yz}$, $(sp^2)_1 = -(sp^2)_2$, and mid-bond Gaussian functions are equal. To attain comparability with the results of earlier refinements [3] we omitted four low angle reflections. The 4p orbital populations therefore could not be well determined, and consequently were omitted from the refinement. This left 7 parameters and 26 reflections, and gave $\chi^2 = 3.5$, $R(F) = 0.048$, $F(000) = 3.5$ spins per Fe atom. These results also are listed in table 1 as $R2$. Removing in a further refinement the four low angle $(\sin\theta/\lambda < 2.5$ nm$^{-1})$ reflections and the 4p population parameters gives $\chi^2 = 0.8$ for unconstrained valence refinement. The large anisotropy in the initial fit $R1$ thus derives from the low angle reflections. In another refinement we constrained $F(000)$ to be $9.0\mu_B$ $(= 4g)$, and χ^2 rose from 0.8 to 3.6.

Examination of correlation coefficients, and test refinements showed that a low value of $F(000)$, low 3d populations and a contracted 3d radius, while partly correlated, are well determined from the refinement. In a last refinement we replaced (sp^2) hybrids on

the fluorine with 2p orbitals. The χ^2 rose from 1.8 to 2.8, indicating that the dipolar contribution on the fluorine atom is significant.

5. *Ab initio* DV-X_α calculations

The calculations we performed were of the DV-X_α-type (see [36] and [37] and references therein). DV-X_α calculations of the wavefunction, as currently implemented, make only two necessary assumptions. Firstly that the wavefunction is single determinantal in nature, and secondly, the usual X_α approximation, that the non-local exchange–correlation term can be replaced by the local Hartree–Fock–Slater term [38]. Other approximations used in earlier work, for example the *self-consistent charge* or the *muffin tin* potentials, are unnecessary and are no longer used here. Because numerical rather than analytical bases are employed, with a sufficient number of integration points, and sufficient multipoles used in fitting the potential, the only serious remaining deficiency relative to Hartree–Fock (HF) limit calculations is in the quality of basis sets [39]. In calculations of properties including spin it is important to take an account of electron–electron correlation in some way. This is conveniently done, but with only semiquantitative accuracy, by use of the *unconstrained* HF formalism in which up and down spin molecular orbitals can differ.

We have used as a basis, a single numerical function per valence orbital along with diffuse polarisation functions, obtained by HF numerical solution of the atom or ion problem. It is useful to confine the atom/ion in a potential well to localise the diffuse polarisation functions, but taking care that occupied orbitals are not significantly changed. This basis set contains atomic occupied basis functions of about double-zeta quality. However, the atomic functions while accurate for atoms, are not sufficiently flexible for molecular calculations of the highest accuracy. The iron (Fe^{2+}) basis functions are 1s–3d plus 4s and 4d. For fluorine (F^-) the functions are 1s–2p plus 3d. No orbitals were frozen. The experimental geometry in the FeF_2 crystal, D_{2h} for the $[FeF_6]^{4-}$ unit, was used, and the cluster was placed in an electric field modelling the point charge ion distribution of the crystal. With this basis set and the UHF procedure we might expect a reasonable account of covalent transfers and inter-atom polarisation effects, but poor account of intra-atom spin polarisation. As an illustration of basis set dependence, a calculation with a neutral atom basis wavefunction was also carried out.

The calculated energies of the five components of the ^5D term can be compared to results of optical and Mössbauer spectroscopy. We use in table 2 the eigenvalue differences which, in the X_α approximation, providing there is no orbital relaxation, give the optical transition energies. As a check on the absence of relaxation phenomena,

Table 2. Term energy separations from $^5A_{1g}$ ground state (cm^{-1}) for the $[FeF_6]^{-4}$ cluster.

State	Spin hole	Empirical MO [32] theory	X_α theory atom basis	X_α theory ion basis	Experiment	Reference
$^5B_{2g}$	$3d_{xz}$	607	2160	1046	770	[18, 42]
$^5B_{1g}$	$3d_{yz}$	873	2391	896	1100	[41]
$^5B_{3g}$	$3d_{xy}$	11 285	13 067	19 312	7400	[23]
$^5A_{1g}$	$3d_{z^2}$	17 020	13 774	11 000	10 900	[23]

Table 3. Theoretical charge and spin population changes in the overlap matrix from free ions in the $[FeF_6]^{4-}$ cluster.

		Spin			Charge	
	Fe	F(short)	F(long)	Fe	F(short)	F(long)
Fe	−0.063	−0.130	−0.236	0.323	0.018	0.052
F(short)		0.219	−0.033		−0.041	−0.305
F(long)			0.242			−0.048

which are expected to be small for these $3d \rightarrow 3d$ transitions, we performed transition state calculations with a basis set 1s–3d on iron and 1s–2p on fluorine [38]. The transition state results all differed by less than 5% from the eigenvalue differences of the ground state calculation. We can also make comparison with the empirical molecular orbital calculations of Reschke *et al* [32], also listed in table 2. The Fermi energy of the ionic basis calculation was 0.01 eV and of the neutral atom basis 3.4 eV compared to an experimental value of $\simeq -2$ eV.

Removal of the external crystal field gave a Fermi energy of 18.8 eV for the ionic basis, but with little change in relative level ordering. The electrostatic crystal field thus corrects 90% of the Fermi energy error, almost stabilising the cluster in the crystal. The ionic basis, as expected in this quite ionic system, gives better agreement with the optical experiments, as well as a better Fermi energy. Although both ionic and atomic bases give qualitatively similar results for both energies and charge and spin densities, they are sufficiently different that use of more flexible sets may give yet further improvement. In this case, perhaps because it is more ionic, a fully ionic basis may be more adequate than in more covalent systems.

Table 4. Theoretical Mulliken populations for spin and charge in the $[FeF_6]^{4-}$ cluster.

Atom	Orbital	Wavefunction	
		Spin	Charge
Fe	$3d_{z^2}$	0.860	1.125
	$3d_{xy}$	0.915	1.083
	$3d_{xz}$	0.954	1.031
	$3d_{yz}$	0.954	1.043
	$3d_{x^2-y^2}$	0.081	1.869
	Total 3d	3.763	6.150
	4s	0.006	0.128
	4d	−0.025	0.092
	Total spin/charge	3.749	+1.630
F(short)	2s	0.001	1.998
	2p	0.068	5.911
	3d	0.003	−0.004
	Total spin/charge	0.072	−0.905
F(long)	2s	0.001	1.997
	2p	0.029	5.900
	3d	−0.003	0.060
	Total spin/charge	0.027	−0.957

The spin and charge populations are listed in tables 3 and 4. The Mulliken populations which change significantly are, as expected, 3d, 4s and 4p on Fe^{2+} and 2s and 2p on F^-. The u-type orbitals contribute less than 10% to the spin, but larger amounts, $\simeq 50\%$, than the g-type orbitals in the charge transfer.

6. Discussion

6.1. DV-X_α calculations and expected results for $[FeF_6]^{4-}$

The wavefunctions of the calculations can be interpreted qualitatively rather simply. We note that the cores do not contribute to the bonding. Examination of molecular orbital eigenvectors shows noticeable covalent interaction, up to 20% on the ligand in supposedly metal-centred orbitals. Table 3 shows the large spin transfers to ligand and metal–ligand overlaps in both spin and charge resulting from these distinctly 'molecular' orbitals.

The spin density distribution can be interpreted as delocalisation of the spin onto the ligands (positive F–F terms) via antibonding orbitals (negative M–F terms). The charge transfer is a little more complex. There is a noticeable antibonding F–F overlap term, but other overlaps are small. The iron atom gains some charge from fluorines.

Examination of the eigenvectors shows that the antibonding spin-unpaired negative contribution to overlap is only just overbalanced by the positive contribution from the 'spin-paired' bonding orbitals. There are more of the latter but each has a smaller overlap than the antiboding orbitals. The corresponding overlaps are almost balanced. The fluorine atoms lose charge and iron gains it.

We can summarise the result by saying that the complex is in fact quite covalent. If remember the greater experimental sensitivity of PND compared with x-ray diffraction experiments we note that the spin density is delocalised to a degree highly significant experimentally, while the charge density is not. The orbitals contributing to the interaction are dominantly iron 3d and fluorine 2p. The metal 4s and 4d and fluorine 3d orbitals contribute a small amount to the charge, but much less to the spin density. σ-donation from $3d_{z^2}$ and $3d_{xy}$ is approximately double the π-donation from $3d_{xz}$ and $3d_{yz}$.

The short Fe–F bond shows over twice the spin and charge transfers of the long Fe–F bond. In general the covalent Fe–F(short) interaction eigenvector coefficients are much larger than for the long bonds. The long Fe–F interaction is dominantly σ in symmetry with a negligible π-component, while the short bond is divided approximately 3 to 1 between σ- and π-donation. Given the greater sensitivity of π-overlaps to bond lengths and bond length changes than σ, these results are expected.

A last point to emphasise is that the calculated spin transfers to the ligands and to the overlaps are quite large; 10% of the spin population for FeF_6 unit lies on the fluorine atoms, and -9% in the metal–fluorine overlap region.

6.2. The wavefunctions of the $[FeF_6]^{4-}$ cluster and FeF_2 crystals

To connect with the PND experiment we must use the cluster calculation to tell us about the crystal. If we retain a localised bond description as a first approximation we can estimate that the spin and charge densities are a superposition of those for the cluster. That is to say, the iron atom configuration is unaltered, while the fluorine atom adds the contribution from the three neighbouring irons. The more covalent the system the less likely is this to be true. However, we might expect it to be at least a qualitative guide to the fluorine atom spin distribution.

We do not discuss the calculated charge distribution results in detail as they are so close to the free ions, and simply add. The resulting net predicted charges are $+1.63e$ and $-0.82e$ for the iron and fluorine sites respectively.

The spin distribution is more complex, because of the vector nature of the magnetisation density. Two of the iron neighbours of fluorine atoms have down spin, and that along the short Fe–F bond, up spin. Thus, as is well known for antiferromagnets [40], the net fluorine spin transfers tend to cancel, depending on the precise distribution on the fluorine atom. A simple σ/π model, and assuming *all* spin cancels in the σ-plane, leaves -0.012 spins in the σ-plane and $+0.018$ in the π-plane, while the crystal has now a net spin count of 3.6 spins per Fe–F(short) unit, a substantial reduction from the ideal ionic value of 4. The cancellation in the full molecular wavefunction may be less dramatic since we note that use of fluorine 2p orbitals results in less cancellation and a quadrupolar distribution in the fluorine σ-plane. In addition, 2s or 3d hybridisation is important because firstly, the total spin is reduced to a lesser extent and secondly, we expect a dipolar spin distribution to be present on the fluorine atoms, with a positive lobe directed towards the short Fe–F bond and a negative lobe along each long such bond.

6.3. The PND results and the ab initio predictions

On examining the valence population results of table 1 for the Fe^{2+} ion we see the spin hole in the $3d_{x^2-y^2}$ orbitals, just as expected from previous PND and other evidence. The new feature is the large anistropy in 4p populations. This, being defined by low angle reflections, possibly reflects anistropy in the orbital contribution rather than in the spin. Barnes *et al* [35] show that the dipole approximation produces its most significant errors at low scattering angles.

Evidence for covalence is clear. Firstly, the low total moment (spins/Fe) of $R1$ corresponds to a large delocalisation of magnetisation onto the fluorine atoms; approximately 20% of the spin of each Fe centre is transferred. Secondly on the fluorine atoms we see positive spin pointing towards the iron atom at the origin of the cell and negative towards that at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. This dipolar arrangement is just that expected given the antiferromagnetic arrangement of iron atom lattice and a σ-bonding mechanism. The observed separation is evidence that the fluorine 2p orbitals are hybridised, either with 2s or 3d orbitals, or more generally that there is some polarisation on fluorine. The overlap populations are negative as expected for antibonding molecular orbitals.

The constrained valence refinement strengthens these conclusions; halving the number of parameters increases χ^2 from 1.8 to 3.5 but improves the precision of those derived greatly. These latter approach highly reasonable values—the population of $3d_{x^2-y^2}$ becomes close to zero and those of the other 3d orbitals become slightly less than unity, having lost spin by covalent delocalisation, with both σ- and π-transfers significant with a total spin loss on Fe of 11%. The mid-bond overlap is scarcely significant, but seems to be negative as expected from delocalisation via antibonding molecular orbitals, and the fluorine atoms are reasonable.

In particular, the positive π- and negative σ-populations indicate that, while σ-donation via the long Fe–F bond is comparable with that of the short bond, the corresponding π-donation is much smaller. The greater sensitivity of π-overlap to bond length changes predicted by theory, relative to σ-bond overlaps, makes us expect this to happen. Lastly, the 3d spin radial extent is less than for the free Fe^{2+} ion, a feature commonly observed when covalence is present.

When we turn to the theoretical *ab-initio* X_α results we see that with one exception,

and apart from the 3d radial change which this UHF *ab initio* calculation cannot duplicate, each of these observations is just what has been predicted, and we do not repeat the previous discussion. The calculated energy levels agree well with the optical spectra (table 2). The exception concerns the experimentally significant dipole on fluorine contrasted with the pure 2p spin in the calculation. It may be that our 3d polarisation function and/or the 2s orbital are not adequate bases to give this effect by 2s–2p or 2p–3d mixing.

The agreement with the ionic basis is better than that of the empirical MO model, and therefore, since it is also an *ab initio* method, the X_α interpretation is to be preferred. These results, $\chi^2 \simeq 3.5$ with seven parameters and thirty reflections used, are a marked improvement on those of the earlier analyses [3] where χ^2 was 4.7 and 3.0 for seven parameters using respectively twelve and fourteen reflections. It is not clear why in that treatment of covalence the dominant contribution was found to be Fe $3d_{yz}$ donation into a F $2p_y$ orbital, an unexpected result theoretically. Perhaps it resulted from the large correlations, and resulting necessary constraints applied.

Both theory and experiment support a model in which the dominant contribution to the spin density is the covalent delocalisation from an Fe^{2+} ion with a $3d_{x^2-y^2}$ spin hole, via antibonding orbitals, with σ- and smaller π-contributions from the short Fe–F bond and σ only from the long Fe–F bond, into fluorine orbitals which are mainly 2p but with some 2s and 3d hybridisation, and with all the partially filled Fe 3d orbitals contributing. This, of course, is the normal chemical bonding model. The limitations in our treatment of the orbital magnetisation density contribution do not appear to be important. The assumption of bond additivity so as to be able to progress from a $[FeF_6]^{4-}$ cluster to the FeF_2 crystal appears to be adequate. That is, the Fe–F bond properties seem to be at least semi-quantitatively transferable.

7. Conclusions

It is clear that for crystals such as FeF_2 in which orbital magnetisation is not large, a better description of the experimental PND results is provided by neglecting spin–orbit coupling effects, other than as involved in the scaling and in the application of the dipole correction, and considering covalence in detail, rather than vice versa. The incorporation of both adequately and self-consistently is not yet possible.

A simple localised chemical bond model in which 3d/4s/4p orbitals on the iron atom interact with 2s/2p/3d orbitals on the fluorine atoms via σ- and π-bonding appears adequate to describe both the experiments and the theoretical X_α calculations.

A surprising feature of both the experiment and the theory is the very large amount of covalence in this crystal which is traditionally thought 'ionic' in character.

A more stringent test of our model would be on modern PND data for MnF_2. In that compound orbital moment complications do not occur. Further investigation of the approximation of bond additivity in these systems, perhaps by use of larger clusters might also prove useful.

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References

[1] Figgis B N and Reynolds P A 1986 *Int. Rev. Phys. Chem.* **5** 265
[2] Brown P J and Forsyth J B 1981 *J. Phys. C: Solid State Phys.* **14** 517
[3] de Almeida M J M and Brown P J 1988 *J. Phys. C: Solid State Phys.* **21** 1111
[4] Brown P J 1986 *Chem. Scr.* **26** 433
[5] Figgis B N, Kucharski E S and Reynolds P A 1989 *Acta Crystallogr.* B **45** 232
[6] Figgis B N and Reynolds P A 1990 *J. Phys. Chem.* **94** 2211
[7] Figgis B N and Christos G A unpublished
[8] Ferrari A 1926 *Rend. Accad. Lincei* III **6** 224
[9] Stout J W and Reed S A 1954 *J. Am. Chem. Soc.* **76** 5279
[10] Erickson R A 1953 *Phys. Rev.* **90** 779
[11] Radhakrishna P, Brown P J, Herrmann-Ronzaud D and Alben R 1978 *J. Phys. C: Solid State Phys.* **11** 2851
[12] Wertheim C K 1961 *Phys. Rev.* **121** 63
[13] Ingalls R 1964 *Phys. Rev.* A **133** 787
[14] Werthaim C K and Buchanan D N E 1967 *Phys. Rev.* **161** 478
[15] Axtmann R C, Hazony Y and Hurley J W Jr 1968 *Chem. Phys. Lett.* **2** 673
[16] Ganiel U and Shtrikamn S 1969 *Phys. Rev.* **177** 503
[17] Johnson D P and Ingalls R 1970 *Phys. Rev.* B **1** 1013
[18] Champion A R, Vaughan R W and Drickamer H G 1967 *J. Chem. Phys.* **47** 2583
[19] Simanek E and Wong A Y C 1968 *Phys. Rev.* **166** 348
[20] Drickamer H G, Fung S C and Lewis G K Jr 1969 *Advances in High Pressure Research* vol 13 (New York: Academic)
[21] Christoe C W and Drickamer H G 1970 *Phys. Rev.* B **1** 1813
[22] Silva D M and Ingalls R 1972 *Phys. Rev.* B **5** 3725
[23] Silva D M 1973 *Phys. Rev.* B **7** 3306
[24] Jones G D 1967 *Phys. Rev.* **155** 259
[25] Stout J W and Shulman R G 1960 *Phys. Rev.* **118** 1136
[26] Brokopf H, Reinen D and Schmitz-Du Mont O 1969 *Z. Phys. Chem.* **68** 228
[27] Tinkham M 1956 *Proc. R. Soc.* A **236** 535, 549
[28] Jaccarino V, Shulman R G and Stout J W 1957 *Phys. Rev.* **106** 602
[29] Baker J M and Hayes W 1967 *Phys. Rev.* **106** 603
[30] Balcar E, Lovesey S W and Wedgewood F A 1973 *J. Phys. C: Solid State Phys.* **6** 3746
[31] Okiji A and Kanamori J 1964 *J. Phys. Soc. Japan* **19** 908
[32] Reschke R, Trautwein A and Harris F E 1977 *Phys. Rev.* B **15** 2708
[33] Brown P J, Welford P J and Forsyth J B 1977 *J. Phys. C: Solid State Phys.* **6** 1405
[34] Marshall W and Lovesey S W 1974 *Thermal Neutron Scattering* (Oxford: Oxford University Press)
[35] Barnes L A, Chandler G S and Figgis B N 1989 *Mol. Phys.* **68** 711
[36] Deeth R J, Figgis B N and Ogden M I 1987 *Chem. Phys.* **121** 115
[37] Deeth R J 1990 *J. Chem. Soc. Dalton Trans.* 355
[38] Slater J C 1972 *Adv. Quant. Chem.* **6** 1
[39] Delley B and Ellis D E 1982 *J. Chem. Phys.* **76** 1949
[40] Tofield B C 1976 *Struct. Bonding* **21** 1
[41] Stout J W, Steinfeld M I and Yazuri M 1968 *J. Appl. Phys.* **39** 1141
[42] Perkins H K and Hazony Y 1972 *Phys. Rev.* B **5** 7