Spin Density and Bonding in the CrF_6^{3-} Ion in $K_2Na[CrF_6]$

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The spin-density data previously obtained by a polarised neutron diffraction experiment on $K_2Na[CrF_6]$ have been reanalysed. A chemically-based model for the CrF_6^{3-} ion, involving conventional atomic orbitals, has been fitted to the 92 observed magnetic structure factors using a least-squares procedure. The best refinement, with seven variable parameters, converged with the agreement factors R 0.0861, R' 0.0579, and χ^2 1.569. The spin density in chromium 3*d* orbitals has t_{2g} symmetry $[t_{2g}^{2.66(5)}, e_g^{-0.06(5)}]$. There is also a region of spin density centred on the chromium atom which is radially much more diffuse than the theoretical 3*d* orbitals and contains 0.4(1) spins parallel to the spin density of t_{2g} symmetry closer to the chromium centre. The model indicates a small parallel spin population [0.020(5)] in each $2p_\pi$ orbital of fluorine, and an antiparallel spin population [−0.02(1)] in a fluorine $2p_\sigma$ orbital. The model also indicates further antiparallel spin density along the Cr–F vector, and no significant spin population of the fluorine 2*s* orbital. The spin-transfer coefficients f_{s^*}, f_{σ^*}, and f_π from the present modelling [0.001(3), −0.021(12), 0.020(5) respectively] are shown to be in good agreement with the values determined from other resonance and neutron diffraction techniques.

POLARISED neutron diffraction experiments are valuable as a means of studying chemical bonding by defining the valence electron densities in the highest partially filled molecular orbitals of paramagnetic transition-metal complexes.[1] Precise magnetic structure factors [$F(hkl)$] at each Bragg point can be obtained from a polarised neutron diffraction experiment using a paramagnetic single crystal in an external magnetic field.[2] Fourier inversion of a complete set of magnetic structure factors gives the magnetisation density throughout the crystallographic unit cell. In the absence of any magnetisation density produced from orbital angular momentum in the ground state of the complex, the magnetisation density is, apart from a change of units, the spin density.

The compound $K_2Na[CrF_6]$ is well suited for a polarised neutron diffraction determination of the spin-density distribution. Crystals [space group $Fm3m$, cell length $a = 8.232(5)$ Å, $Z = 4$] contain isolated CrF_6^{3-} ions.[3] The chromium(III) atoms have high (cubic) site symmetry, simplifying molecular-orbital calculations. Furthermore, the orbital angular momentum is quenched, with a g factor of 1.998,[4] so that the observed magnetic structure factors are directly related only to the spin density. The compound (Cr^{3+}, $S = \frac{3}{2}$) is paramagnetic down to at least 1.5 K. At 4.2 K and in an applied magnetic field of reasonable strength (*e.g.* 1.8 T), a reasonably large [1.08(2) B.M.† per Cr] magnetisation is induced. However, this compound has a number of disadvantages. Covalency in the CrF_6^{3-} complex ions is weak, due to the high electronegativity of the fluorine ligands. In practice, this means that the departure from the simple free-ion case, where all the spin density is localised on the chromium atom (Cr^{3+}, $t_{2g}^3e_g^0$), is expected to be small. The half-filled antibonding molecular orbital is, by symmetry considerations, not σ bonding, thus restricting the information about σ bonding obtainable from the spin-density distribution. Finally, all classes of Bragg reflections contain a large magnetic structure factor contribution from the spin density on the chromium atom which may swamp any covalency effects. This is in contrast to the Cs_3CoCl_5 system[5,6] where certain classes of reflections are only present if there is covalence.

A very elegant polarised neutron diffraction experiment on $K_2Na[CrF_6]$ has been performed by Wedgwood.[3] Magnetic structure factors, corrected for extinction effects, are tabulated for 91 Bragg reflections. These data, complete within $(\sin\theta)/\lambda \leqslant 0.726$ Å^{-1}, are used in the spin-density analysis reported below.

Wedgwood used Fourier methods to analyse the data.[3] A Fourier map clearly shows the aspherical t_{2g} symmetry of the spin density on the chromium atom and a small amount of parallel spin density transferred to each fluorine atom. The wave-vector dependences of the first two multiple components of the spin density around the chromium atom (zero- and fourth-order terms) were extracted by the double-Fourier transform method.[7] These were interpreted by a simple molecular-orbital model involving one parameter, A_π, the covalency parameter associated with the highest half-filled molecular orbitals. The zero- and fourth-order multipole components gave A_π equal to 0.15 and 0.24 respectively (implying 0.02 to 0.06 spins in each fluorine $2p_\pi$ orbital). A more advanced model, involving spin in the e_g or more diffuse chromium orbitals, or in the fluorine $2p_\sigma$ orbital, or in the σ-overlap region, was not attempted. The main reason why only a simple model could be fitted to the data was that series termination errors, inherent in any Fourier method, gave rise to effects on the derived form factors at least as large as those associated with covalency.[3]

The use of a least-squares modelling method is not limited by such series termination errors. Furthermore, again unlike Fourier methods, one is able to take account of the differing reliability of different reflections, in this case a 100-fold spread in the weights assigned to the individual reflections. An argument against the least-squares method is that it is model-dependent. The errors in the values of derived parameters, or even their reality, are dependent on the model used. It is

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† Throughout this paper: 1 B.M. $= 9.274 \times 10^{-24}$ A m^2.

therefore important to use a model sufficiently flexible that the goodness-of-fit index (χ^2) can approach unity, *and* that the model is consistent with previous experimental results.

A preliminary report of the results from our least-squares method of analysis of the $K_2Na[CrF_6]$ data has been made.[1] The spin populations on the chromium atom were determined as $t_{2g}^{2.61(6)}e_g^{0.01(6)}$, and there was found to be 0.04(1) parallel spins (of the same sign as on Cr) in a spherically symmetric *s*-type function centred on each fluorine atom (this fluorine spin population was in error by a factor of three in the original report). The fact that the sum of the spin density on each CrF_6^{3-} complex (2.86) was not three electrons, together with the departure of the goodness-of-fit index ($\chi^2 = 3.20$) from unity, indicate that this model was not sufficiently flexible and can be significantly improved. This has been accomplished by including the following features in the model reported below; (*a*) the 3*d* functions on the chromium atom have been allowed to expand or contract by means of a refineable radial parameter; (*b*) provision has been made for spin population of a diffuse 4*s*-type orbital; (*c*) the spin density on each fluorine atom can now be distributed amongst $2p_\sigma$ or $2p_\pi$ orbitals, also of variable radial extent; and (*d*) provision has been made for spin density in the overlap region along the Cr–F vector.

A second method for analysing spin-density data by the least-squares technique, developed in parallel with the approach used below, is the use of local multipole expansions.[8] This method also avoids many of the errors and limitations of Wedgwood's Fourier methods. The spin density is parametrised in terms of sufficient multipole functions of the lowest order that χ^2 is minimised, or nearly so. Unlike the angular functions whose choice is rationally determined, the radial functions used are empirical, and may or may not be optimised in the least-squares process. The fit of the refined model to the data is expected to be better than for other methods of analysis since there is no restriction on the order of multipole or type of radial function used. However, the problem remains that although the derived multipoles *describe* the data, they do not do so *uniquely*, being derived by the method of least squares. Moreover, unless constraints on the order of multipole used and the type of radial dependence allowed are made, then an interpretation in physically significant terms (of relevance to other systems) is not possible. If such constraints are applied, a way of doing this in terms of atomic orbital populations has been suggested,[8] and applied to the Wedgwood data for $K_2Na[CrF_6]$. This multipole analysis yields the spin populations in chromium atomic orbitals $t_{2g}^{2.70(3)}e_g^{0.10(4)}$, with $p_\sigma^{-0.04(1)}$ and $p_\pi^{0.10(2)}$ on each fluorine atom. In this model no provision was made for a diffuse 4*s*-type orbital on the chromium atom, and overlap spin density was not included except by allowing an expansion of the fluorine radial function. The goodness-of-fit index, χ^2, was 1.48. The method of analysis used below is based on a simple chemical model of the molecular orbitals and, although less flexible than the empirical multipole method, yields directly a chemically meaningful description of the spin density of the CrF_6^{3-} complex ion in terms of conventional orbital populations. This method has already been successfully applied in the case of the $CoCl_4^{2-}$ ion in Cs_3CoCl_5.[6] In this paper we discuss in some detail a suitable spin-density model and the results of fitting it to the data. Finally, we summarise these results and place them in their chemical context.

A SPIN-DENSITY MODEL FOR THE DATA

The observed magnetic structure factors are used with the least-squares refinement program ASRED [9] to optimise the parameters of some chemically-based model. In ASRED a set of quantisation axes is chosen, using chemical intuition and/or local symmetry for each atom. The spin populations of *s*, *p*, or *d* orbitals on each atom can be refined by a least-squares procedure, using the formalism of Weiss and Freeman.[10]

The choice of atomic orbitals is constrained in our program to those which produce no cross terms in proceeding from the coefficients in the molecular orbitals to the electron (or spin) density distribution. For example, on chromium in CrF_6^{3-}, given 3*d* orbitals, we cannot introduce other orbitals such as 3*p*, since there would arise *dp* overlap spin density which is not yet included within the Weiss and Freeman formalism.[10] The use of a set of diffuse functions is allowable providing the overlap of the radial part with the '3*d*' radial function is negligible. This problem is essentially that also faced in transforming from a description of the data in terms of multipoles to chemically significant, atomic orbital, information.

Single-electron scattering factor curves $<j_0>_{s,p,d}$, $<j_2>_{p,d}$, and $<j_4>_d$ for each atom type and each orbital type from the literature,[11,12] or calculated from an atomic wavefunction,[13] are used in conjunction with the equations for the scattering by *p* [14] and *d* electrons.[10] Because such single-electron scattering curves apply to the theoretical free atom or ion, for real atoms in a chemical environment it is desirable to allow some refinement of the scattering-curve shape. This is accomplished in ASRED by a least-squares refinement of a radial parameter r, defined by $f(s) = f_0(rs)$ where $f(s)$ is the single-electron scattering factor at $(\sin\theta)/\lambda = s$ and $f_0(rs)$ is the free atom or ion scattering factor at $(\sin\theta)/\lambda = rs$. The refinement of r is associated with variation of the radial exponents of the atomic wavefunction.

Because the phases of the magnetic structure factors are experimentally determined, the function minimised in the least-squares procedure is $\Sigma w(F_o - F_c)^2$ where w is the weight assigned to the F_o values, and F_o and F_c are the observed and calculated magnetic structure factors.

If an independent measurement of the magnetisation of the sample, at the same temperature and field strength and aligned in the same direction as for the polarised neutron diffraction experiment, is available then the moment per metal atom can be included in the data as the observation $F(000)$. This is providing no experimental complications, such as depolarisation, arise. Furthermore, if this value is known it can be used in ASRED to scale the structure-factor calculation from the model so that spin populations on absolute and not just relative scale are obtained. We are thus using the magnetisation as an observable, with S

Table 1

Scattering factors for the unfilled $4s$ orbital for Cr^{3+} *

$[(\sin\theta)/\lambda]$/Å^{-1}	f	$[(\sin\theta)/\lambda]$/Å^{-1}	f
0.00	1.0000	0.25	−0.0609
0.02	0.9709	0.30	−0.0434
0.04	0.8880	0.35	−0.0206
0.06	0.7634	0.40	−0.0064
0.08	0.6141	0.50	0.0018
0.10	0.4584	0.60	0.0014
0.12	0.3122	0.70	0.0006
0.14	0.1868	0.80	0.0002
0.16	0.0884	0.90	0.0001
0.18	0.0181	1.00	0.0000
0.20	−0.0269		

* Scattering-factor values calculated from a wavefunction with $\zeta = 1.5$,[13] using a published method.[15]

(the spin quantum number of the ion) assumed to be well determined by other spectroscopic and resonance experiments.

The method just described has been successfully applied [6] in fitting a model to the spin-density data for the $CoCl_4^{2-}$ ion in Cs_3CoCl_5.[5] In the case of $K_2Na[CrF_6]$, the moment per Cr site has been determined at 4.2 K and 1.76 T (the conditions of the polarised neutron diffraction experiment) as $F(000) = 1.08 \pm 0.02\mu_B$.[3] There are therefore 92 observations of magnetic structure factors [including $F(000)$] for use in the model fitting. Each F_o value will be given a weight $1/\sigma^2(F_o)$ in the least-squares refinement, where $\sigma(F_o)$ is the estimated error [3] in an F_o value. The local quantisation axes sets for Cr and for the unique F atom are directed along the corresponding unit-cell axes as dictated by local symmetry and chemical intuition. The single-electron scattering factor curves from ref. 11 will be used for the $3d$ electrons of Cr^{3+} and for the $2p$ electrons of neutral F. The spherically symmetrical 'overlap' scattering will be included with the fluorine $2p$ $\langle j_0 \rangle$ curve. The '$4s$' scattering curve for Cr^{3+} has been calculated from a wavefunction with $\zeta = 1.5$,[13] using a published method,[15] and is presented in Table 1.

SPIN-DENSITY MODEL RESULTS FOR THE CrF_6^{3-} ION

The simplest ionic model for the CrF_6^{3-} ion is one in which all the spin density is localised on the Cr^{3+} ion, which has cubic site symmetry. The Cr^{3+} configuration is then $t_{2g}^3e_g^0$ or $d_{xy}^{1.0}d_{xz}^{1.0}d_{yz}^{1.0}d_{z^2}^{0.0}d_{x^2-y^2}^{0.0}$. From Table 2, it is seen that this ionic model does not fit the observed data at all well ($\chi^2 = 12.6$). However, a considerable improvement is achieved by allowing the spin populations of the t_{2g} and e_g sets and of a diffuse $4s$-type orbital centred on chromium to vary (refinement 1, Table 2) ($\chi^2 = 2.0$). The possibility of a small parallel spin population of the empty e_g or $4s$ orbitals in this case has previously been suggested,[16] and is supported by Wedgwood's analysis of the data.[3] For the cobalt atom in $CoCl_4^{2-}$, the spin-density analysis indicates large spin population in diffuse regions around the cobalt atom.[6]

The effects of covalency in the Cr^{3+}–F^- bonding are included in the model by allowing spin occupancy of the $2p_\sigma$ and $2p_\pi$ orbitals on the fluorine atom. Further, the 'overlap' region can be approximated by placing a spherically symmetric scattering source on the Cr–F vector. The 'overlap' may not necessarily be modelling overlap spin density, but could also be accommodating spin density from diffuse chromium orbitals. The 'overlap' spin density was centred at the position, of fractional co-ordinates (0, 0, 0.17), suggested from the Fourier map of Wedgwood.[3] The refinement including these parameters (refinement 2, Table 2) produces a further improvement in the fit with the observed data ($\chi^2 = 1.68$). Previous experiments [6,9] and the theoretical relative independence of $3d$ radial functions from total charge lead one to assume that in CrF_6^{3-} the Cr^{3+} $3d$ orbitals would be very similar to the theoretical free-ion functions. However, in the case of electronegative fluorine, the $2p$ orbitals of F^- in the complex are likely to be considerably expanded in space from the free-atom functions used in the above refinements. Therefore, the model may be further improved by allowing radial changes in the chromium $3d$ orbitals and, particularly, in the fluorine $2p$ orbitals. This has been done (refinement 3, Table 2), and yields a spin-density model which is not significantly different from that of refinement 2 but produces a small improvement in the goodness-of-fit index ($\chi^2 = 1.63$) The refined value of the radial parameter, $r(3d)$, indicates that the chromium $3d$ orbitals may be slightly expanded from the theoretical functions calculated

Table 2

Orbital spin populations and agreement factors for spin-density distribution models of the CrF_6^{3-} ion [a]

Centre [b]	Variable [c]	Ionic model	Refinement 1	Refinement 2	Refinement 3
Cr	$3d_{z^2}, d_{x^2-y^2}$	0.0	0.00(2)	0.009(22)	0.031(24)
	$3d_{xy}, d_{xz}, d_{yz}$	1.0	0.84(2)	0.844(15)	0.854(16)
	'$4s$'	0.0	0.47(6)	0.51(9)	0.34(13)
	$r(3d)$	1.0	1.0	1.0	1.016(8)
F	$2p_\sigma$	0.0	0.0	−0.021(12)	−0.025(17)
	$2p_{\pi x}, p_{\pi y}$	0.0	0.0	0.019(5)	0.027(10)
	$r(2p)$			1.0	1.3(3)
'Overlap'	'$2s$'	0.0	0.0	−0.020(13)	−0.017(13)
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$		0.2145	0.0965	0.0937	0.0888
$R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$		0.1687	0.0673	0.0603	0.0586
$\chi^2 = \Sigma w(\Delta F)^2/(n - v)$		12.590	2.024	1.682	1.625
Number of variables, v		0	3	6	8
$F(000)$ calculated		1.080	1.079	1.093	1.093

[a] A parameter which has been varied in the least-squares refinement is given an estimated standard deviation in parentheses. A negative spin population indicates antiparallel spin density to that in the chromium t_{2g} orbitals. $\Delta F = F_o = F_c$ where F_o and F_c are the observed [3] and calculated phased magnetic structure factors; n (=92) is the number of observations; $w = 1/\sigma^2(F_o)$ where $\sigma(F_o)$ is the estimated error in F_o.[3] $\sigma(F_o)$ has been assigned the value 0.02 for each of the five reflections for which Wedgwood reports no estimate of the error. [b] The Cr and F centres are at the positions and have the thermal parameters determined from the 4.2 K neutron diffraction structural analysis. The overlap is centred at (0,0,0.17) and is given the same thermal parameters as F. [c] The symbols s,p,d are used here to represent populations of the corresponding orbitals. Where several symbols appear on the one line, the population in the Table refers to each orbital individually. The radial expansion parameter r is defined by $f(s) = f_0(rs)$, where $f(s)$ is the single-electron scattering factor at $(\sin\theta)/\lambda = s$ and is related to $f_0(rs)$, the free atom or ion scattering factor at $(\sin\theta)/\lambda = rs$.

for Cr^{3+} (significant at the 2σ level). The value of $r(2p)$, 1.3(3), is not determined from the data to be significantly different from unity and hence the amount of any expansion of the fluorine $2p$ orbitals is not determined.

As indicated in Table 2, the atom centres in the tabulated refinements were given the thermal parameters determined in Wedgwood's 4.2 K neutron diffraction structural analysis.[3] The value obtained for the U value of the isotropic thermal parameter of chromium was $-0.000\,3(6)$ Å^2 and this was set to zero in the refinements of Table 2. This is an unrealistic value for U(Cr) because, at 4.2 K, zero-point motion is responsible for a U value generally significantly greater than zero.[17,18] A more realistic value for U(Cr), similar to the values obtained for the other atoms in the refinement,[3] is 0.003 Å^2 and this value has been used in the refinements given in Table 3.

TABLE 3

Orbital spin populations for ' best ' spin-density distribution models of the CrF_6^{3-} ion *

Centre	Variable	Refinement 4	Refinement 5
Cr	$3d_{z^2},d_{x^2-y^2}$	$-0.025(26)$	$-0.031(25)$
	$3d_{xy},d_{xz},d_{yz}$	0.890(17)	0.888(17)
	' $4s$ '	0.34(13)	0.39(11)
	$r(3d)$	1.002(8)	1.001(7)
F	$2p_\sigma$	$-0.025(17)$	$-0.021(12)$
	$2p_{\pi x},p_{\pi y}$	0.026(10)	0.020(5)
	$r(2p)$	1.3(3)	1.0
' Overlap '	' $2s$ '	$-0.015(13)$	$-0.016(13)$
R		0.0862	0.0861
R'		0.0576	0.0579
χ^2		1.574	1.569
Number of variables		8	7
F(000) calculated		1.092	1.086

* Footnotes to Table 2 apply here also, with the exception that Cr has been given an isotropic thermal parameter $U = 0.003$ Å^2.

Refinement 4 (Table 3) is the same as refinement 3 except for the value of U(Cr). The use of the assumed value of 0.003 Å^2 rather than zero for U(Cr) in the refinement produces a better goodness-of-fit index ($\chi^2 = 1.574$), and is therefore believed to yield a more correct spin-density model. Finally in refinement 5 (Table 3), the radial parameter $r(2p)$ for fluorine, which was not determined as significantly different from unity in previous refinements, has been held invariant with a value of unity. The orbital spin populations from refinement 5 ($\chi^2 = 1.569$) are believed to be the best estimates of these parameters as indicated by the present data.

In order to check various aspects of this best model, a number of other refinements were performed. These are not discussed in detail, but the qualitative answers they provide to the following questions are given. *Is the diffuse orbital population on chromium real?* Because the form factor for this diffuse ' $4s$-type ' orbital (Table 1) falls off rapidly at relatively low $(\sin\theta)/\lambda$ values, it is possible that errors in the two lowest angle observations, 000 and 111 [$(\sin\theta)/\lambda = 0.105$ Å^{-1}], could be the major source of the apparent diffuse spin population. A refinement omitting both these data yielded a ' $4s$ ' spin population 0.36(18) indicating that the diffuse component of spin density about the chromium atom is real.

How well does the ' 4s-type ' function of Table 1 represent the diffuse component of spin density about chromium? A refinement was performed in which the radial extent of the orbital represented by the form factor of Table 1 was allowed to vary. The radial parameter $r(4s)$ (Table 2), refined together with all other variables, had a value 1.08(14), indicating that the form factor of Table 1 is a good representation of the radial extent of the diffuse spin density on the chromium centre. The changes in magnetic structure factors caused by changes in the angular nature of the diffuse orbital, *e.g.* $4s$ to $4d$ (t_{2g} symmetry), would have a small effect, since the population is also small. Hence we can say nothing about the angular nature of this diffuse density except to note that the ' overlap ' included in the model may also be associated with diffuse chromium orbitals rather than true overlap.

Is the spin density on fluorine non-centrosymmetric? Hybridisation of s and p orbitals could shift the centroid of spin density from the position of the fluorine nucleus. A refinement varying the positional parameter of the fluorine spin-density centroid did not shift it significantly from the nuclear position. The data therefore do not warrant an attempt to include sp hybrid-type orbitals on fluorine in the refinement.

How well is the ' overlap ' region represented by an s-type scatterer at position (0,0,0.17)*?* A refinement varying the positional parameter of the ' overlap ' yielded a value [0,0,0.18(7)] which is not significantly different from (0,0,0.17). In another refinement the ' overlap ' was treated as a p-type scatterer, and p_π populations were refined. The goodness-of-fit index increased slightly and the p_π spin populations were not well determined. Therefore, for the present data set, an s-type scatterer at position (0,0,0.17) on the Cr–F vector is the best model of this ' overlap ' region.

How accurate is the assumed value of 0.003 Å^2 *for* U(Cr)*?* A refinement varying all other parameters and U(Cr) converged with a value 0.006(5) Å^2 for U(Cr). In this refinement the thermal parameter for chromium is highly correlated with the orbital spin populations. However, it serves as an indication that the value chosen, 0.003 Å^2, is reasonable considering the thermal parameters determined [3] for the other atoms.

CHEMICAL IMPLICATIONS OF THE SPIN DENSITY DISTRIBUTION IN CrF_6^{3-}

Major features of the spin density that our model reveals (Tables 2 and 3) are (i) the largely t_{2g} nature of the spin density centred on the chromium atom [$t_{2g}^{2.66(5)}$-$e_g^{-0.06(5)}$]; (ii) a region of parallel spin density centred on the chromium atom which is radially much more diffuse than the $3d$ orbitals and contains 0.4(1) spins. This diffuse density, the angular variation of which is not well defined by the data, is adequately modelled by a $4s$-type function; (iii) the presence of a small parallel spin population [0.020(5)] in each $2p_\pi$ orbital of fluorine; (iv) antiparallel spin density along the Cr–F vector close to the fluorine centre. In the present treatment, this antiparallel spin density has been modelled as $2p_\sigma$ density centred on fluorine [$-0.02(1)$ spins] plus a poorly defined spherical ' blob ' of ' overlap ' density closer to fluorine than to chromium [$-0.02(1)$ spins]; and (v) no significant $2s$ contribution to the spin density on fluorine.

The best comparison between our results and the results of other studies of the bonding in the CrF_6^{3-} ion is by use of the spin-transfer coefficients, f_{s*}, $f_{\sigma*}$, and f_π[19] (Table 4). Apart from the present experimental method, other resonance and neutron diffraction techniques do not give estimates of both f_π and f_σ individually. Therefore, the results of several techniques must be combined by use of a model of bonding such as we have used, to yield the individual parameters. Our f values are in very good agreement with those obtained by this combination of resonance and neutron diffraction data. It is difficult to understand why the multipole modelling[8] of Wedgwood's CrF_6^{3-} data does not yield f values compatible with the other techniques.

Wedgwood's derived covalency parameters ($A^2_\pi \simeq f_\pi = 0.02$ or 0.06) probably reflect the inadequacy of a single parameter model and the limitations, discussed above, of the double-Fourier transform method.

We can explain our observed spin-density distribution in the CrF_6^{3-} ion as being composed of two parts: (*a*) three spins in the π-antibonding molecular orbitals of t_{2g} symmetry, and (*b*) a net zero spin in spin-polarised σ-bonding e_g or a_{1g} orbitals. On entering into bonding, the $3d$ electrons become angularly polarised into a $t_{2g}{}^n e_g{}^0$ configuration. While the radial dependence of the electron density closer to the chromium nucleus changes little from that expected on theoretical grounds, a substantial diffuse ' tail ' develops at up to 1 Å distance from the chromium centre. The overlap between the fluorine $2p_\pi$ and chromium $3d$ t_{2g} orbitals is much increased by the development of such diffuse density. The resulting covalence implies that parallel spin density is delocalised into the fluorine $2p_\pi$ atomic orbitals in the antibonding t_{2g} molecular orbital. Since the orbital is antibonding, one would also expect the ' overlap ' region to contain less parallel spin density than a simple superposition of the atomic orbitals would give.

TABLE 4

Spin-transfer coefficients for Cr^{3+} in CrF_6^{3-}

	Present modelling	Multipole modelling	Wedgwood [a]	Combined resonance and neutron diffraction [b]	Spin polarised Hartree–Fock calculations	
					Brown and [c] Burton (semi-empirical)	Larsson and Connolly [d] ($X - \alpha$)
f_{s*}	0.001(3) [e]			−0.002(1)		
$f_{\sigma*}$	−0.021(12)	−0.04(1)		−0.027(4)	−0.022	−0.048
f_π	0.020(5)	0.05(1)	0.04(2)	0.022(4)	0.026	0.01

[a] Ref. 3. [b] Refs. 19 and 20. [c] Ref. 21. [d] Ref. 22. [e] f_{s*} from the present modelling has been estimated from the difference in the nuclear position of the fluorine atom and its refined centroid of spin density.

To explain the negative (antiparallel) $2p_\sigma$ spin population on the fluorine atom, spin polarisation has been invoked.[16] Various exchange effects will cause the parallel spin e_g spin orbitals to become different spatially from the antiparallel spin spin orbitals (this is ' spin polarisation '). Qualitatively we expect parallel spin orbitals to become more concentrated near the metal centre, while in the antiparallel spin orbitals, antiparallel spin density will be delocalised away from the metal. This explains the negative $2p_\sigma$ spin density on the fluorine atom. A corresponding amount of parallel spin density must occupy an e_g or a_{1g} metal orbital. Since we observe no significant parallel e_g population, this must reside in the diffuse region (conventionally, as either a $4s$-type, or in the *tail* only of a $3d/4d$-type, distribution). The existence of such spin-polarisation effects in the σ-bonding orbitals implies that they may also be important in other molecular orbitals, such as the π-bonding t_{2g} orbitals. Therefore, the $2p_\pi$ and ' overlap ' spin populations may not bear a close resemblance to those expected from the coefficients of a simple π-antibonding t_{2g} molecular orbital.

Many theoretical calculations on the CrF_6^{3-} ion have been made. Semi-empirical,[21] X-α,[22] and *ab initio* calculations[23] all show the same qualitative features that we observe. The *ab initio* calculations (double-zeta, unrestricted Hartree–Fock),[23] being non-empirical are more reliable. They show a spin-density distribution in good qualitative agreement with that deduced from our model. More detailed features of the spin density may be revealed by theoretical calculations. However, since the present data are of limited resolution [(sin $\theta)/\lambda \leqslant 0.726$ Å^{-1}], they can show little or no evidence of such details.

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REFERENCES

[1] B. N. Figgis, R. Mason, A. R. P. Smith, and G. A. Williams, *J. Amer. Chem. Soc.*, 1979, **101**, 3673.

[2] B. C. Tofield, *Structure and Bonding*, 1975, **21**, 1.

[3] F. A. Wedgwood, *Proc. Roy. Soc.*, 1976, **A349**, 447.

[4] J. Hukin, M.Sc. Thesis, Clarendon Laboratory, Oxford University, 1965.

[5] B. N. Figgis, P. A. Reynolds, G. A. Williams, R. Mason, A. R. P. Smith, and J. N. Varghese, *J.C.S. Dalton*, 1980, 2333.

[6] B. N. Figgis, P. A. Reynolds, and G. A. Williams, preceding paper.

[7] J. Moss and P. J. Brown, *J. Phys. (F)*, 1972, **2**, 358.

[8] J. N. Varghese and R. Mason, personal communication.

[9] B. N. Figgis, E. S. Kucharski, and G. A. Williams, *J.C.S. Dalton*, 1980, 1515.

[10] R. J. Weiss and A. J. Freeman, *J. Phys. and Chem. Solids*, 1959, **10**, 147.

[11] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 103—146.

[12] R. E. Watson and A. J. Freeman, *Acta Cryst.*, 1961, **14**, 27.

[13] E. Clementi and C. Roetti, *Atomic Data and Nuclear Data Tables*, 1974, **14**, 177.

[14] R. McWeeney, *Acta Cryst.*, 1951, **4**, 513; B. Dawson, *ibid.*, 1964, **17**, 990, 997.

[15] J. Avery and K. J. Watson, *Acta Cryst.*, 1977, **A33**, 679.

[16] B. C. Tofield and B. E. F. Fender, *J. Phys. and Chem. Solids*, 1970, **31**, 2741.

[17] B. N. Figgis, R. Mason, A. R. P. Smith, and G. A. Williams, *Acta Cryst.*, 1980, **B36**, 509.

[18] G. A. Williams, B. N. Figgis, R. Mason, S. A. Mason, and P. E. Fielding, *J.C.S. Dalton*, 1980, 1688; B. N. Figgis, R. Mason, and G. A. Williams, *Acta Cryst.*, in the press.

[19] B. C. Tofield, *Progr. Inorg. Chem.*, 1976, **20**, 153.

[20] R. Shulman and K. Knox, *Phys. Rev. Letters*, 1960, **4**, 603.

[21] R. D. Brown and P. G. Burton, *Theor. Chim. Acta*, 1970, **18**, 309.

[22] S. Larsson and J. W. D. Connolly, *J. Chem. Phys.*, 1974, **60**, 1514.

[23] G. S. Chandler and R. A. Phillips, personal communication.