A Powder Neutron Diffraction Investigation of the Nuclear and Magnetic Structure of $Sr_2Fe_2O_5$

By C. Greaves,* A. J. Jacobson, B. C. Tofield† and B. E. F. Fender

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, England

The nuclear and magnetic structure of $Sr_2Fe_2O_5$ has been determined by profile analysis of powder diffraction data. The results indicate disorder in the displacements of the iron atoms in the approximately tetrahedral sites in space group *Icmm*. The relationship of this structure to those of $Ca_2Fe_2O_6$ (*Pcmn*) and $Ca_2(FeAl)_2O_6$ (*Ibm*2) is discussed. The values of the octahedral and tetrahedral site magnetic moments are compared with results for other Fe^{III} compounds.

Introduction

The structures and magnetic properties of the perovskite-related compounds $M_2Fe_2O_5$ where M = Ca, Sr and Ba, and $Ca_2(AlFe)_2O_5$ have been the subject of several investigations. The latter compound is an important constituent of Portland cement and the structures of the pure iron compounds are of particular interest in the relationships to the anion deficient phases $MFeO_{3-x}$.

$Ca_2Fe_2O_5$ has been examined in detail by single-crystal X-ray diffraction (Bertaut, Blum & Sagnières, 1959). The structure was found to be orthorhombic (*Pcmn*) and may be regarded as a distorted oxygen-deficient perovskite whose axes have the following relation to the simple ABO_3 perovskite cell parameter a_c: $a = \sqrt{2}a_c$, $b = 4a_c$ and $c = \sqrt{2}a_c$. Layers of corner-sharing FeO_6 octahedra alternate along **b** with FeO_4 distorted tetrahedra, and the large interstices between the layers, the perovskite *A* positions, are occupied by Ca^{2+} ions.

The similarity between the powder X-ray patterns and lattice parameters of $Ca_2Fe_2O_5$ and those of $Sr_2Fe_2O_5$ and $Ba_2Fe_2O_5$ led Gallagher, MacChesney & Buchanan (1964, 1965) to assume that all three compounds were isostructural. Smith (1962) reported brownmillerite, $Ca_2(Fe, Al)_2O_5$, to have the space group *Icmm* but more recently it has been shown to have a slightly modified structure with the space group *Ibm*2 (Colville & Geller, 1971).

The magnetic properties of $Ca_2Fe_2O_5$ have been investigated in detail by magnetic susceptibility measurements (Takeda, Yamaguchi, Tomiyoshi, Fukase, Sugimoto & Watanabe, 1968), neutron diffraction (Corliss, Hastings, Kunnmann & Banks, 1966; Friedman, Shakad & Shtrikman, 1967) and by linearly polarized recoilfree γ-rays (Geller, Grant & Gonser, 1971). It has been established that the compound is an antiferromagnet

($T_N \simeq 400\,°C$) with a *G*-type magnetic structure in which near-neighbour Fe^{3+} ions have spins oppositely directed along **c**. $Ca_2Fe_2O_5$ also shows weak ferromagnetism below T_N, which is consistent with this magnetic structure and the primitive space group. $Sr_2Fe_2O_5$ also has a *G*-type structure with the spin direction along **c** (Takeda *et al.*, 1968) with a high Néel temperature (700 K) but no parasitic ferromagnetism was detected. It was suggested that this last observation cast doubt on the assumption that the space group is *Pcmn* and that $Sr_2Fe_2O_5$ is isostructural with $Ca_2Fe_2O_5$.

In this work the nuclear and magnetic structures have been re-examined by profile refinement of neutron powder diffraction data collected at 4·2 K, and crystalline fragments of $Ca_2Fe_2O_5$ and $Sr_2Fe_2O_5$ have been examined with a JEM 100 U electron microscope. A study of the oxidized $SrFeO_{2.5+x}$ ($0 \le x \le 0.5$) system in which a new ordered phase ($\sim SrFeO_{2.75}$) has been observed is described elsewhere (Tofield, Greaves & Fender, 1975).

Sample preparation and characterization

The starting materials, $SrCO_3$ and Fe_2O_3 (Johnson Matthey 'Specpure' Chemicals), were dried by heating at 800 °C in CO_2 and 950 °C in air, respectively. The reagents were intimately ground together in the molar ratio 2:1 and the mixture fired in a platinum-lined alumina boat at 1300 °C. The final material was ground under hexane to preclude atmospheric oxidation. From the weight change on reaction the stoichiometry of the product was estimated to be $SrFeO_{2.505(10)}$. To determine the Fe^{IV} content of the sample, a weighed amount was dissolved under nitrogen in a standard Fe^{II} solution. Back titration of Fe^{II} with $K_2Cr_2O_7$ indicated no detectable amount of Fe^{IV}. The iron:strontium ratio was determined by atomic absorption spectroscopy and gave the overall stoichiometry as $Sr_{0.99(3)}FeO_{2.49(3)}$.

X-ray diffraction data for $SrFeO_{2.5}$ were collected with a Guinier–Hägg focusing camera of diameter 8·7 cm which covered Bragg angles $0° < \theta < 45°$. KCl was used as an internal calibrant. All 55 observed lines

could be indexed with the orthorhombic (*Pcmn*) unit cell of Gallagher, MacChesney & Buchanan (1964) and moreover satisfactory indexing could be accomplished assuming the body-centred condition $h+k+l=2n$. The lattice parameters obtained from a least-squares analysis were $a=5.6727$ (7), $b=15.582$ (2) and $c=5.5303$ (7) Å, in good agreement with the results of Gallagher *et al.* The results are given in Table 1.

Table 1. *Guinier X-ray diffraction data for* $SrFeO_{2.50}$
(Cu $K\alpha_1$ *radiation*)

$\lambda = 1.54051$ Å

hkl	d_{obs}	d_{calc}
020	7.8099	7.7908
110	5.3294	5.3305
101	3.9744	3.9599
130	3.8372	3.8379
121	3.5310	3.5301
200	2.8385	2.8364
141	2.7784	2.7770
002	2.7658	2.7651
150	2.7378	2.7313
022	2.6019	2.6059
211	2.4906	2.4913
240	2.2945	2.2929
042	2.2570	2.2548
132	2.2429	2.2421
161	2.1731	2.1716
202	1.9803	1.9800
080	1.9485	1.9477
222	1.9186	1.9190
062	1.8937	1.8930
301	1.7892	1.7892
330	1.7762	1.7768
242	1.7653	1.7650
271	1.6701	1.6694
341	1.6258	1.6259
350	1.6158	1.6166
280	1.6060	1.6056
143	1.5989	1.5987
082	1.5920	1.5923
0,10,0	1.5580	1.5582
213	1.5382	1.5381
332	1.4951	1.4948
361	1.4729	1.4734
163	1.4534	1.4531
1,10,1	1.4493	1.4499
400	1.4179	1.4182
352	1.3956	1.3956
282	1.3891	1.3885
004	1.3825	1.3826
411	1.3691	1.3684
303	1.3201	1.3200
183	1.3043	1.3030
402	1.2620	1.2619
343	1.2504	1.2502
204	1.2431	1.2428
154	1.2333	1.2335
2,10,2	1.2245	1.2245
442	1.2004	1.2005
244	1.1841	1.1840
363	1.1762	1.1767
471	1.1695	1.1690
1,10,3	1.1649	1.1647
480	1.1470	1.1465
084	1.1273	1.1274
413	1.1209	1.1211
314	1.1130	1.1132

$a=5.6727$ (7), $b=15.582$ (2), $c=5.5303$ (7) Å.

Neutron diffraction

Neutron diffraction measurements on polycrystalline $Sr_2Fe_2O_5$ were made at 4.2 K with neutrons of wavelength 1.545 Å obtained by reflexion from the (511) planes of a germanium monochromator with a take-off angle of 90°. Although the high Néel temperature (700 K) would enable the magnetic structure to be studied at room temperature, the collection of data at 4.2 K simplifies the structure refinement since the adoption of an overall temperature factor for all atoms in the unit cell introduces no significant errors.

The complex nature of the powder pattern excluded the possibility of refinement based on integrated intensities and instead the structural parameters were refined by least-squares analysis of the diffraction profile (Rietveld, 1967). The program minimizes the function

$$\chi^2 = \sum_i w_i \left[y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc}) \right]^2$$

and all values refer to the quantity

$$R(\text{profile}) = \frac{100 \sum |y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc})|}{\sum |y_i(\text{obs})|}$$

where w is the weight, y the number of counts at a point in 2θ and c is the scale factor. The counter was stepped every 0.02° and counts accumulated every 0.1° interval. All the data collected in the range $8° < 2\theta < 95°$ were used in the refinement and the contribution to the profile from the background was estimated by hand. The free ion Fe^{3+} form factor (Watson & Freeman, 1961) and the following scattering lengths were used: $b_O = 0.58 \times 10^{-12}$ cm; $b_{Fe} = 0.951 \times 10^{-12}$ cm (Neutron Diffraction Commission, 1972) and $b_{Sr} = 0.692 \times 10^{-12}$ cm (Cooper & Rouse, 1972).

Initial refinement was carried out in *Pcmn*. The total number of variables refined was 24: a scale factor, 13 positional parameters, an overall temperature factor, 2 magnetic moments (one each for the octahedral and tetrahedral iron atoms), 3 cell constants, 3 half-width parameters and the 2θ zero correction. The refinement converged to a profile R of 11.0% which may be compared with an 'expected' R of 4.3%. The latter is calculated in terms of the number of variables, the number of observations and the statistical reliability of each observation. Correct structural models have normally been found to refine to give R profile $\leq 2R$ expected, and hence although there were no major discrepancies in the observed and calculated intensities this structural model does not appear to be completely satisfactory. Moreover, refinement of the individual temperature factors led to unacceptably high values (0.8 Å²) for the tetrahedral iron atom Fe(2) and for one of the oxygens, O(3), which is in the first coordination sphere of Fe(2). The other temperature factors were in the range 0.1–0.2 Å² as expected.
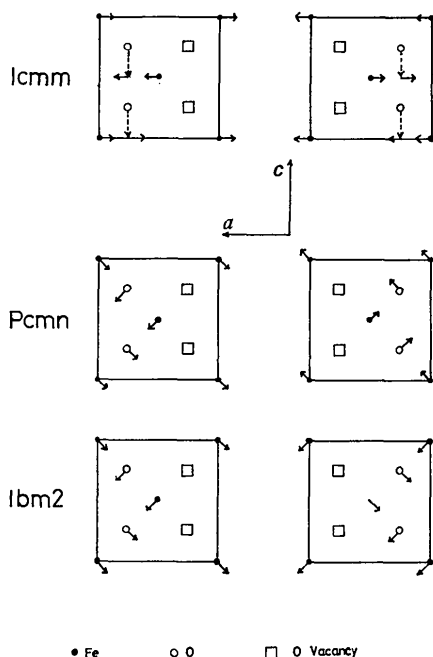
Fig. 1. Allowed displacements of atoms at $y=0.25$ and $y=0.75$ for space groups *Icmm*, *Pcmn* and *Ibm2*.

Table 2. *Atom positional parameters: space group Pcmn*

		x	y	z
Fe(1)	4(a)	0.0	0.0	0.0
Fe(2)	4(c)	0.569 (1)	0.25	0.482 (2)
Sr	8(d)	0.516 (1)	0.6088 (2)	0.000 (1)
O(1)	8(d)	0.255 (2)	0.9908 (3)	0.250 (3)
O(2)	8(d)	0.0531 (7)	0.1406 (3)	0.002 (2)
O(3)	4(c)	0.639 (2)	0.25	0.123 (2)

The atom positions are given in Table 2 from which it can be seen that the positions of Sr, O(1) and O(2) obey the restrictions of the higher symmetry *Icmm* although this space group also requires the 2 coordinates of Fe(2) and O(3) to be fixed at 0.5 and 0.0 respectively if these atoms are placed at 4(e) positions. A similar situation exists for a refinement in *Ibm2* [R(profile) = 11.2%]. Fe(1), Sr, O(1) and O(2) do not depart significantly from the positions demanded by *Icmm* but anomalously large temperature factors are observed for Fe(2) and O(3). The differences between *Ibm2*, *Icmm* and *Pcmn* with respect to the fractional coordinates of Fe(2) and O(3) are illustrated in Fig. 1. Both *Pcmn* and *Ibm2* allow satisfactory tetrahedral coordination to be achieved by every iron atom at $y=$

Table 3. *Refined structural parameters of* $SrFeO_{2.50}$: *average unit cell (Icmm)*

		x	y	z	Occupation parameter
Fe(1)	4(a)	0.0	0.0	0.0	1.0
Fe(2)	8(i)	0.5686 (5)	0.25	0.4584 (7)	0.5
Sr	8(h)	0.5165 (6)	0.6092 (2)	0.0	1.0
O(1)	8(g)	0.25	0.9909 (2)	0.25	1.0
O(2)	8(h)	0.0513 (5)	0.1401 (2)	0.0	1.0
O(3)	8(i)	0.641 (1)	0.25	0.123 (1)	0.5

Effective spin	Overall temperature factor 0.13 (3) $Å^2$
Fe(1) 1.99 (6)	
Fe(2) 2.05 (7)	

Table 4. *Interatomic distances* (Å) *and bond angles* (°)

The numbers of equivalent distances per polyhedron are shown in square parentheses.

Fe(1) polyhedron

Fe(1)–O(1)	1.985 (1) [4]	O(1)–O(1)	2.7651 (3) [2]
Fe(1)–O(2)	2.203 (3) [2]	O(1)–O(1)	2.8505 (10) [2]
Mean Fe(1)–O	2.057	O(2)–O(1)	3.000 (6) [4]

O(1)--Fe(1)–O(1)	88.27 (6)	O(2)–O(1)	2.930 (6) [4]
O(1)--Fe(1)–O(1)	91.73 (6)	O(1)–Fe(1)–O(2)	88.64 (12)
		O(1)–Fe(1)–O(2)	91.36 (12)

Fe(2) polyhedron

Fe(2)–O(2)	1.857 (6) [2]	O(2)–O(2)	3.425 (7) [1]
Fe(2)–O(3)	1.90 (1) [1]	O(2)–O(3)	2.91 (1) [2]
Fe(2)–O(3)	1.88 (1) [1]	O(2)–O(3)	2.97 (1) [2]
Mean Fe(2)–O	1.874	O(3)–O(3)	3.03 (1) [1]

O(2)--Fe(2)–O(2)	134 (1)	O(2)–Fe(2)–O(3)	105 (1)
O(2)--Fe(2)–O(3)	102 (1)	O(3)–Fe(2)–O(3)	107 (2)

Sr polyhedron

Sr——O(1)	2.658 (5) [2]	Sr——O(2)	2.499 (7) [1]
Sr——O(1)	2.575 (5) [2]	Sr——O(3)	2.456 (7) [1]
Sr——O(2)	2.814 (2) [2]	Mean Sr——O	2.632

0·25 and 0·75. They differ only in the direction of the cooperative displacements of Fe(2) and O(3) at $y=0·75$ relative to those at $y=0·25$. *Icmm* differs from *Pcmn* only in the fixed z coordinates for Fe(2) and O(3).

Though both *Pcmn* and *Ibm*2 inadequately describe the positions of Fe(2) and O(3) a satisfactory description of the structure can be obtained by allowing disordered displacements of these atoms in *Icmm* with half occupation of position 8(i). A significantly improved refinement [R(profile) = 8·6%] is obtained and all the individual temperature factors in this final refinement fall in the range 0·1–0·2 Å². The observed and calculated profiles are shown in Fig. 3 with the refined parameters in Table 3. The interatomic distances and angles are presented in Table 4. The average unit cell observed by neutron diffraction is illustrated in Fig. 2(a).

The magnetic contribution to the profile was simultaneously refined with the nuclear data and gave for the effective spins of the two iron atoms S(Fe oct) = 1·99 (6) and S(Fe tet) = 2·05 (7). The spins are directed along **c**.

Electron diffraction

Icmm and *Ibm*2 demand identical Bragg absences with atoms in general positions but in *Pcmn* additional reflexions are allowed for which $h+k+l \neq 2n$. Crystalline fragments of both Sr₂Fe₂O₅ and Ca₂Fe₂O₅ were examined with a JEM 100 U electron microscope and although the assignment of *Pcmn* symmetry was confirmed for Ca₂Fe₂O₅ the patterns of Sr₂Fe₂O₅ indicated one of the body-centred space groups. The neutron measurements which appear to point to the *Icmm* structure cannot however distinguish between a fully

disordered structure, correctly described in *Icmm*, and a situation where order persists over several unit cells and the symmetry of a typical cell in such a domain is best described as *Ibm*2. The latter situation is illustrated in Fig. 2 where (b) and (c) show the displacements of Fe(2) and O(3) projected perpendicular to **a**. Disorder is indicated in (c).

Because the wavelength employed in electron diffraction is shorter than the neutron wavelength the former technique may reveal ordered regions (down to about 20 Å) which remain undetected by X-rays or neutrons. In the present study a good many of the crystals gave patterns indicative of a larger cell than
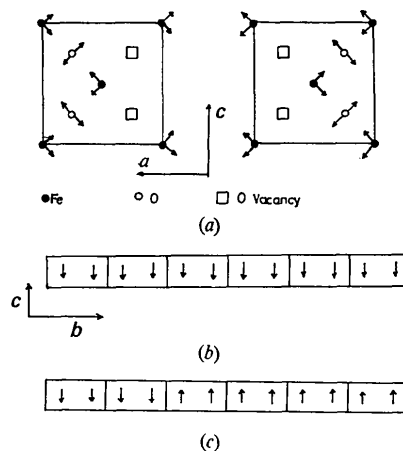

Fig. 2. Displacements of atoms in an average unit cell are shown in (a). Representations of the structure based on (b) *Ibm*2 complete order, (c) *Ibm*2 partial order.
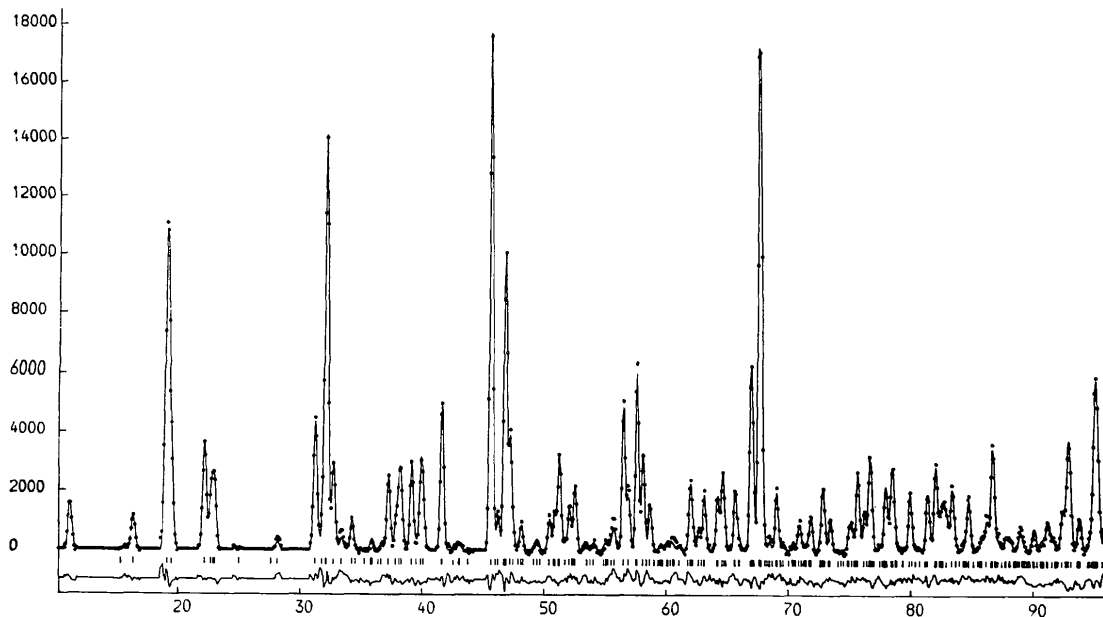

Fig. 3. Powder neutron diffraction pattern for Sr₂Fe₂O₅. Small circles are the experimental points and the continuous line passes through the calculated points. The small vertical lines are the calculated *hkl* positions and the bottom trace is a difference plot.

expected and this was taken as a sign that oxygen vacancy ordering had occurred along different (but crystallographically equivalent) cubic sub-cell directions. A completely random intergrowth of domains is ruled out however because the X-ray/neutron structure would appear cubic. Unfortunately, probably owing to the weak nature of the superstructure reflexions the presence of such domains could not be demonstrated either by dark-field microscopy or by lattice imaging. In any case there is not necessarily a direct correspondence between these domains and any described by *Ibm2*.

Discussion

The combination of neutron and electron-diffraction techniques demonstrates that $Sr_2Fe_2O_5$ has body-centred symmetry but still leaves open the question as to whether randomly disordered displacements of Fe(2) and O(3) on the *Icmm* model represent a sufficient description of the structure. It seems plausible that short-range order reminiscent of the *Ibm2* structure should persist over a few unit cells but this suggestion is conjectural at present.

Both the body-centred space groups are compatible with the magnetic structure determined in the present study and the earlier magnetic measurements. The magnetic moments of the octahedral [1·99 (6)] and tetrahedral [2·05 (7)] Fe^{3+} ions are, as expected, reduced from the Fe^{3+} free ion value. For the octahedral ion, the moment reduction may be related to covalency parameters defined in terms of simple molecular orbitals (Hubbard & Marshall, 1965) thus

$$S/S_0 = 1 - 1\cdot2(A_\sigma^2 + 2A_\pi^2 + 2A_s^2)$$

where S is the measured spin, S_0 the value expected for the free ion and A_σ, A_π and A_s the σ, π and s covalency parameters. For an antiferromagnet, S_0 must be corrected for the zero-point spin deviation and here the value of 0·975 S calculated by Davis (1960) has been used. The covalency parameter sum is calculated as $A_\sigma^2 + 2A_\pi^2 + A_s^2 = 15\cdot3 \pm 2\cdot1\%$. This value is somewhat higher than the results of Tofield & Fender (1970) for $YFeO_3$ and $LaFeO_3$ which gave 11·0 (1·0) and 10·0 (0·5)% respectively, although the bond lengths are similar. In $Sr_2Fe_2O_5$ four Fe–O distances are 1·99 Å and two 2·20 Å compared with bond lengths between 2·00 and 2·01 Å in $YFeO_3$ and in $LaFeO_3$.

For the tetrahedral site the relationship between the moment reduction and covalency parameters can also be deduced. However, the tetrahedral site is considerably distorted and as resonance data (which would give $A_\sigma^2 - A_\pi^2$) is in any case not available a separation into σ, s and π contributions is not significant. We therefore write

$$S/S_0 = 1 - 0\cdot8 \sum_{\pi,\sigma,s} A^2$$

where $\sum A^2$ is the covalency parameter sum. A further problem is encountered in that the zero-point spin deviation may be less reliably estimated because of the

large site distortion. Use of the Anderson (1952) relation however gives an estimate for the covalency parameter sum of 17·5 ± 3·3%. This appears to be larger than the octahedral site value, indicating an increased covalent interaction per bond which is consistent with the shorter Fe–O distance (1·874 Å, *i.e.* 0·18 Å less than for the octahedral site).

The results given above for the magnetic moments of the octahedral and tetrahedral Fe^{3+} ions may be compared with the results obtained in a room-temperature polarized-beam study of the magnetic-moment density distribution in yttrium iron garnet (Bonnet, Delapalme, Tcheou & Fuess, 1974). Yttrium iron garnet also has both octahedral and tetrahedral iron atoms and the moment density shows clearly the covalent spin transfer to the oxygens. The magnetic moments associated with the two metal sites were obtained by integration over a sphere of radius 1·73 Å and a cube of side $a/2 = 1\cdot55$ Å, taking the yttrium position as the background level. For the cube integration the results agree well with the bulk magnetization and give for the moments of the octahedral and tetrahedral sites 1·85 and 1·875 respectively. These results cannot be directly compared with our values because they refer to room temperature and also as Bonnet *et al.* point out there is a discrepancy between their neutron values and those obtained by Strenzwilk & Anderson (1968) from an Oguchi effective-field treatment of the bulk magnetization data. However, the neutron measurements on yttrium iron garnet and $Sr_2Fe_2O_5$ both indicate closely similar moments for octahedral and tetrahedral Fe^{3+}. The mean Fe–O distances in the garnet are tetrahedral 1·84 Å and octahedral 2·02 Å, similar to those in $Sr_2Fe_2O_5$ (1·874 and 2·057 Å respectively).

Finally from the yttrium iron garnet data and the moments obtained by integration over the cube, the form factors were deduced. The octahedral Fe^{3+} results closely follow the free ion curve but the tetrahedral values show a marked contraction. In our powder experiment no information could be obtained concerning the shape of the form factor and the free ion data of Watson & Freeman (1961) have been used. A contraction of the Fe^{3+} form factor would result in our value of the tetrahedral moment being too low by 2–3%.

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Scaling of Intensities

BY T. R. LOMER AND A. J. C. WILSON

Department of Physics, University of Birmingham, Birmingham B15 2TT, England

The supposed object of a scaling factor is to make the calculated intensity of reflexion, on the average, equal to the observed intensity. Refinement of an adjustable scaling factor by least-squares procedures does not achieve this aim; there is a systematic error whose magnitude depends on the residual refined.

Ideally the calculated and observed values for the intensity of an X-ray reflexion should agree exactly. In practice, there are always differences between the observed intensities I and the calculated intensities H; the various residuals used in least-squares refinement are different average measures of the differences. Only if certain conditions are satisfied will refinement of different residuals lead to the same values of the parameters refined, and still other conditions must be satisfied if the values of the parameters are to be unbiased (see, for example, Wilson, 1973). Observed intensities are normally on a relative scale, and the calculated intensities must therefore be multiplied by a scaling factor E before making the comparison. [The reasons for including the scaling factor in H rather than in I have been given by, for example, Cruickshank (1970).] Appropriate values of the scaling factor can be obtained at each stage of the refinement by making the average values of H and I agree, an extension of the approximate procedure proposed by Wilson (1942). Least-squares adjustment of the scaling parameter will normally give significantly different values of E. Wilson (1974a) has shown that if

$$R_1 = \langle (F-G)^2 \rangle / \langle F^2 \rangle \qquad (1)$$

is the residual based on the magnitude of the observed structure factor F and of the calculated structure factor G, scaled so that

$$\langle F^2 \rangle \equiv \langle I \rangle = \langle H \rangle \equiv \langle G^2 \rangle , \qquad (2)$$

then refinement of the scaling factor E_1 in the modified residual

$$S_1 = \langle (F-E_1G)^2 \rangle / \langle F^2 \rangle \qquad (3)$$

leads to

$$E_1 = 1 - \tfrac{1}{2} R_1 , \qquad (4)$$

$$(S_1)_{min} = R_1(1 - \tfrac{1}{4} R_1) . \qquad (5)$$

In typical cases E_1 will differ from the value 1 [expected from (2)] by some per cent. The present note discusses scaling in the case of the residual R_2. Ordinarily this gives simpler calculations than R_1 does (Wilson, 1969; Lenstra, 1974), but here the results are more complex and less straightforward in interpretation.

The residual R_2 is defined by

$$R_2 = \langle (I-H)^2 \rangle / \langle I^2 \rangle , \qquad (6)$$

where H has been scaled in accordance with (2). The residual modified by including an adjustable scaling factor is

$$S_2 = \langle (I-E_2H)^2 \rangle / \langle I^2 \rangle . \qquad (7)$$

Multiplying out and minimizing with respect to E_2 gives

$$R_2 = 1 - 2\langle HI \rangle / \langle I^2 \rangle + \langle H^2 \rangle / \langle I^2 \rangle , \qquad (8)$$

$$E_2 = \langle HI \rangle / \langle H^2 \rangle , \qquad (9)$$

$$(S_2)_{min} = 1 - \langle HI \rangle^2 / \langle H^2 \rangle \langle I^2 \rangle . \qquad (10)$$