JOURNAL OF SOLID STATE CHEMISTRY **97**, 179–185 (1992)

Structure and Oxygen Stoichiometry in $Sr_3Fe_2O_{7-y}$, $0 \leq y \leq 1.0$

S. E. DANN, M. T. WELLER,[1] AND D. B. CURRIE

Department of Chemistry, The University of Southampton, Southampton SO9 5NH, United Kingdom

Received August 2, 1991

Powder neutron diffraction has been used to determine the structure of four compounds from the series $Sr_3Fe_2O_{7-y}$, $y = 0, 0.25, 0.42$, and 1.0. All these compounds crystallize with structures based on that of $Sr_3Ti_2O_7$ with oxygen systematically removed from a site linking the FeO_6 octahedra together. Complete removal of oxygen from this site produces an unusual, square-pyramidal coordination around each iron(III) ion and a stoichiometry of $Sr_3Fe_2O_6$; this compound is isostructural with $La_2SrCu_2O_6$. A bond valence parameter, R_0, for Fe^{4+} has been derived as 1.788(2) Å.

Introduction

The chemistry of iron(IV) in complex oxides is poorly characterized due to the difficulty in synthesizing materials containing this oxidation state without access to highly oxidizing conditions. The known compounds are limited to the strontium and barium ternary phases such as $SrFeO_3$ (*1*), $BaFeO_3$ (*2*), and Sr_2FeO_4 (*3*). All these phases are synthesized by direct reaction of oxides containing Fe^{3+} under oxygen pressures of several hundred atmospheres; synthesis of large quantities and single crystals is therefore difficult. Partial oxidation of iron above the trivalent state can often be achieved by reaction in oxygen at ambient pressures, for example, the compounds $SrFeO_{2.78}$ (*4*) and $Sr_3Fe_2O_{6.16}$ (*5*).

The structural chemistry of Fe(IV) shows a number of similarities with that of Cu(II). The ionic radii of these ions are similar and if the iron exists in the high spin state both are Jahn–Teller ions. These similarities can be seen in the pairs of compounds Sr_2FeO_4/La_2CuO_4 and $La_2SrCu_2O_{6+y}$/$Sr_3Fe_2O_{7-y}$. The structural chemistry of $La_2SrCu_2O_6$ (212) and the related calcium doped compounds has been of considerable interest recently due to the discovery of superconducting behavior in $La_{2-x}Sr_xCaCu_2O_{6\pm y}$. The superconducting behaviour in the 212 system depends markedly upon the oxygen stoichiometry and distribution. Location of oxygen between the CuO_5 square planes destroys the superconducting potential of these materials. In the $La_2SrCu_2O_{6+y}$ system the level of this additional oxygen is relatively small with $6 \pm y$ at most 6.04. However, with barium doping the oxygen stoichiometry may rise much higher, for example $La_{1.9}Ba_{0.1}SrCu_2O_{6.30}$ (*6*).

The magnetic behavior of the $Sr_3Fe_2O_{7-y}$ system has been investigated previously (*7*). $Sr_3Fe_2O_{6.0}$ is antiferromagnetic at room temperature; increasing the oxygen content and

---

[1] To whom correspondence should be addressed.

0022-4596/92 $3.00

hence the Fe^{4+} level results in a rapid decrease in the Neél temperature approaching 0 K for $Sr_3Fe_2O_{6.5}$. Further increases in the oxygen stoichiometry cause the Neél temperature to rise again with a value of 130 K found for $Sr_3Fe_2O_{6.90}$. This unusual magnetic behavior was explained in terms of a weak ferromagnetic Fe^{4+}–O^{2-}–Fe^{4+} exchange interaction but a strong Fe^{3+}–O^{2-}–Fe^{3+} interaction. However, no account was taken of the changing oxygen stoichiometry in terms of its effect on coupling between the iron centers or alterations in their relative positions.

The structures of $SrFeO_3$ and Sr_2FeO_4 have both been determined (*1, 3*); the iron(IV) coordination geometries in these compounds are surprisingly regular, being octahedral in the former and a slightly axially elongated octahedron in the latter. No accurate structural data is available on the $Sr_3Fe_2O_{7-y}$ system. A powder X-ray structure determination on $Sr_3Fe_2O_{6.16}$ indicated that the unit cell was double that of $Sr_3Ti_2O_7$, though no refinements of the oxygen positions or distribution were undertaken (*5*).

In the present paper we have determined the structure of $Sr_3Fe_2O_{7-y}$ using powder neutron diffraction for four different values of y covering the full stoichiometry range. The results are interpreted in terms of the related effects of changing iron oxidation state and oxygen level.

Experimental

A sample of $Sr_3Fe_2O_{7-y}$ was synthesized by direct reaction of $SrCO_3$ (99.5) and Fe_2O_3 (99.99) mixed thoroughly together in the correct molar proportions and heated to 1100°C in air for 16 h and after regrinding, a further 16 h at 1300°C. Samples of this compound were then treated further to control the oxygen stoichiometry as shown in Table I. All products were shown to be single phase by powder X-ray diffraction using a Siemens D5000 diffractometer with primary monochromator operating with Cu$K\alpha_1$ radiation; refined lattice parameters from this X-ray data are given in Table I. Oxygen stoichiometries were determined by thermogravimetric analysis under hydrogen; samples were heated to 750°C in platinum crucibles to effect complete reduction to Fe(III), and the results obtained are also given in Table I. These analytically determined stoichiometries are used to describe the compounds hereafter.

TABLE I

Annealing treatment	Oxygen stoichiometry	Lattice parameters	
		a (Å)	c (Å)
700°C/5% H_2 in N_2	6.00 ± 0.05	3.892(1)	20.030(4)
Air annealed at 482°C quenched	6.58 ± 0.05	3.874(1)	20.171(6)
482°C O_2 annealed/ slow cooled 20°/min	6.75 ± 0.05	3.868(1)	20.164(4)
500°C O_2 500 atm	7.00 ± 0.05	3.853(1)	20.151(4)

Compounds as prepared at high temperature (1300°C) and quenched to room temperature were found to be extremely sensitive to atmospheric moisture. Decomposition could be observed in the powder X-ray diffraction patterns by the emergence of a peak at 2.19°, corresponding to a c lattice parameter approximately double that of the $Sr_3Fe_2O_{7-y}$ phases, and also by a rapid efflorescence. No sign of a double unit cell as used by Lucchini and Sloccari in their X-ray data analysis was found except in samples that had decomposed (*5*).

Powder neutron diffraction data were collected using two diffractometers. Data from the parent material synthesized in air was collected using D1A at the ILL, Grenoble, while data for the other three oxygen stoichiometries were obtained on HRPD at the Rutherford–Appleton Laboratory. Data collection times ranged from 10–20 h, and final profiles were of excellent quality. Full profile refinements were carried out on the

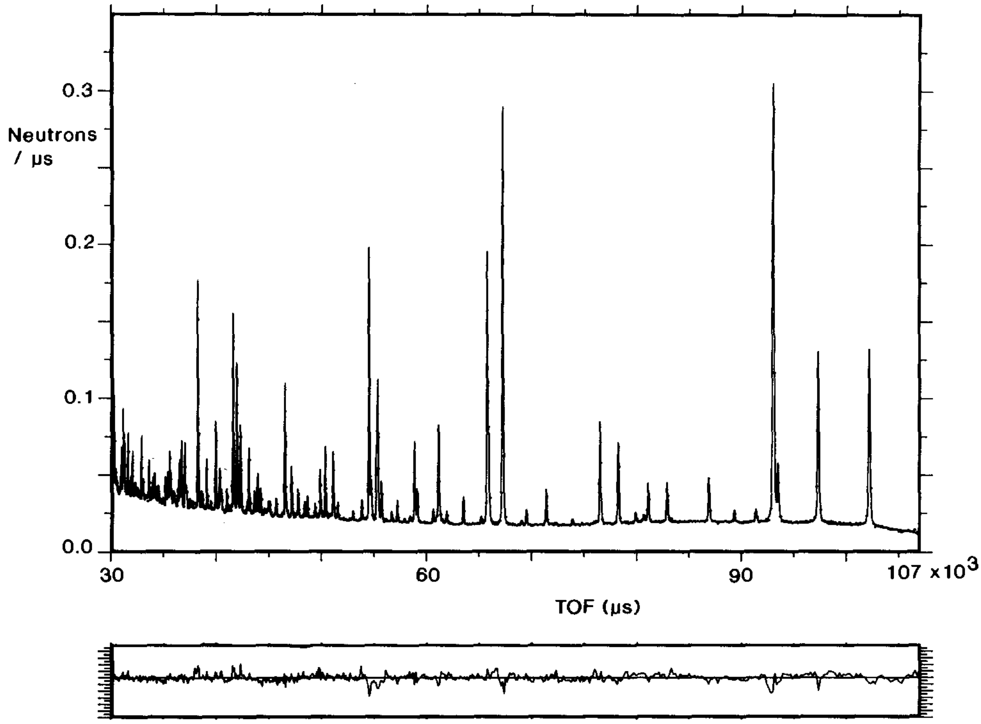

FIG. 1. Final profile fit to the TOF powder neutron diffraction data from $Sr_3Fe_2O_7$. Upper diagram shows observed data (dots) and calculated profile (continuous line). Lower diagram shows a difference plot on a finer scale.

data using a fixed wavelength version of the Rietveld program running locally (*8*) or a TOF version (*9*) for the Rutherford data. Data were collected in each case at room temperature, $Sr_3Fe_2O_6$ is below its Neél temperature of 298 K at this temperature, and so some contribution to the scattered intensity from the magnetic structure may be expected. However, the maximum *d* spacing data used from HRPD was 2.2 Å, where magnetic scattering is weak and can be neglected. This was confirmed in a separate study of the magnetic structure of the compounds using high *d* spacing data from POLARIS, RAL, which will be published elsewhere. Neutron scattering lengths were taken as 0.954, 0.702, and 0.5805 × 10^{-12} cm for iron, strontium, and oxygen, respectively.

Structure Refinements

Careful scrutiny of all the sets of data in the high *d* spacing range showed no evidence for the double unit cell used by Lucchini, and all peaks could be indexed in the space group *I4/mmm* using the cells given

TABLE IIa

REFINED ATOMIC PARAMETERS FOR $Sr_3Fe_2O_{6.00}$

Atom	Site	x	y	z	B_{eq}	Occupancy
Sr(1)	2*b*	0	0	½	0.11(5)	1.00
Sr(2)	4*e*	0	0	0.3193(1)	0.27(3)	1.00
Fe	4*e*	0	0	0.1022(1)	0.01(2)	1.00
O(1)	8*g*	0	½	0.0843(1)	0.32(3)	1.00
O(2)	4*e*	0	0	0.1963(1)	0.44(4)	1.00
O(3)	—	—	—	—	—	—

Note. $a = 3.8940(1)$, $c = 20.0396(1)$, $R_{wp} = 6.99$, $R_{exp} = 6.15$, $\chi^2 = 1.29$.

TABLE IIb

REFINED ATOMIC PARAMETERS FOR $Sr_3Fe_2O_{6.58}$

Atom	Site	x	y	z	B_{eq}	Occupancy
Sr(1)	$2b$	0	0	$\frac{1}{2}$	0.81(5)	1.00
Sr(2)	$4e$	0	0	0.3176(1)	1.22(2)	1.00
Fe	$4e$	0	0	0.0972(1)	0.75(3)	
O(1)	$8g$	0	$\frac{1}{2}$	0.0911(1)	1.24(4)	1.00
O(2)	$4e$	0	0	0.1950(1)	1.35(5)	1.00
O(3)	$2a$	0	0	0	0.98(4)	0.64(2)

Note. a = 3.8704(1), c = 20.1763(3), R_{wp} = 8.48, R_{exp} = 4.51, χ^2 = 3.53.

TABLE IId

REFINED ATOMIC PARAMETERS FOR $Sr_3Fe_2O_{7.00}$

Atom	Site	x	y	z	B_{eq}	Occupancy
Sr(1)	$2b$	0	0	$\frac{1}{2}$	0.47(5)	1.00
Sr(2)	$4e$	0	0	0.3170(1)	0.31(4)	1.00
Fe	$4e$	0	0	0.0972(1)	0.22(3)	1.00
O(1)	$8g$	0	$\frac{1}{2}$	0.0945(1)	0.55(3)	1.00
O(2)	$4e$	0	0	0.1933(1)	0.63(5)	1.00
O(3)	$2a$	0	0	0	0.61(7)	1.00

Note. a = 3.8526(1), c = 20.1490(1), R_{wp} = 5.41, R_{exp} = 5.22, χ^2 = 1.07.

in Table I. In each case the structural parameters for $Sr_3Ti_2O_7$ were used as a starting model. Initial stages of the refinement included profile parameters such as scale factor, cell parameters, background, and peak shape functions. Atomic positions were then refined. In the case of the materials with oxygen stoichiometries below seven, refinement of oxygen site occupancies rapidly located the vacancies on the O3 site (2*a*; 0, 0, 0) and showed that all other oxide ion sites were fully occupied. Full occupancy of these other sites was maintained throughout the rest of the refinement; in the analysis of the $Sr_3Fe_2O_6$ data the O3 site was removed from the refinement. Final stages of the refinement included isotropic temperature factors for $Sr_3Fe_2O_{6.58}$ and $Sr_3Fe_2O_{6.75}$, but anisotropic temperature factors proved refinable for $Sr_3Fe_2O_6$ and $Sr_3Fe_2O_7$. A typical final fit to the data from HRPD is shown in Fig. 1.

TABLE IIc

REFINED ATOMIC PARAMETERS FOR $Sr_3Fe_2O_{6.75}$

Atom	Site	x	y	z	B_{eq}	Occupancy
Sr(1)	$2b$	0	0	$\frac{1}{2}$	0.41(2)	1.00
Sr(2)	$4e$	0	0	0.3175(1)	0.14(1)	1.00
Fe	$4e$	0	0	0.0984(1)	0.00(1)	1.00
O(1)	$8g$	0	$\frac{1}{2}$	0.0922(1)	0.51(1)	1.00
O(2)	$4e$	0	0	0.1942(1)	0.43(2)	1.00
O(3)	$2a$	0	0	0	0.15(6)	0.740(9)

Note. a = 3.8642(1), c = 20.1569(1), R_{wp} = 6.56, R_{exp} = 3.61, χ^2 = 3.30.

Tables II a–d contain the final refined parameters for all four compounds together with their e.s.d.'s given in parentheses and final profile fit factors. For compounds where anisotropic temperature factors refined $B_{equivalent}$ values are given in the tables. Calculated bond distances are summarized in Table III. In the mixed valence materials $Sr_3Fe_2O_{6.58}$ and $Sr_3Fe_2O_{6.75}$ the refined oxygen stoichiometries were close to the chemically analyzed values at 6.64(2) and 6.74(1), respectively.

Discussion

Figure 2 shows the variations in the lattice parameters in this system as a function of stoichiometry. The very accurate values obtained from the neutron work were in excel-

TABLE III

IMPORTANT BOND LENGTHS AND ANGLES FOR $Sr_3Fe_2O_{7-y}$

	$Sr_3Fe_2O_{6.00}$	$Sr_3Fe_2O_{6.58}$	$Sr_3Fe_2O_{6.75}$	$Sr_3Fe_2O_7$
Sr1–O1	2.578(1) × 8	2.669(1) × 8	2.681(1) × 8	2.709(2) × 8
Sr1–O3	—	2.737(–) × 4[a]	2.732(–) × 4[a]	2.724(–) × 4
Sr2–O1	2.743(3) × 4	2.672(2) × 4	2.655(2) × 4	2.625(3) × 4
Sr2–O2	2.464(4) × 1	2.473(3) × 1	2.485(4) × 1	2.493(3) × 1
Sr2–O2	2.771(1) × 4	2.748(1) × 4	2.743(1) × 4	2.732(1) × 4
Fe–O1	1.980(1) × 4	1.942(1) × 4	1.936(1) × 4	1.927(1) × 4
Fe–O2	1.886(4) × 1	1.933(2) × 1	1.932(4) × 1	1.936(4) × 1
Fe–O3	—	2.002(2) × 1[a]	1.983(2) × 1[a]	1.958(2) × 1

[a] Partially filled site.

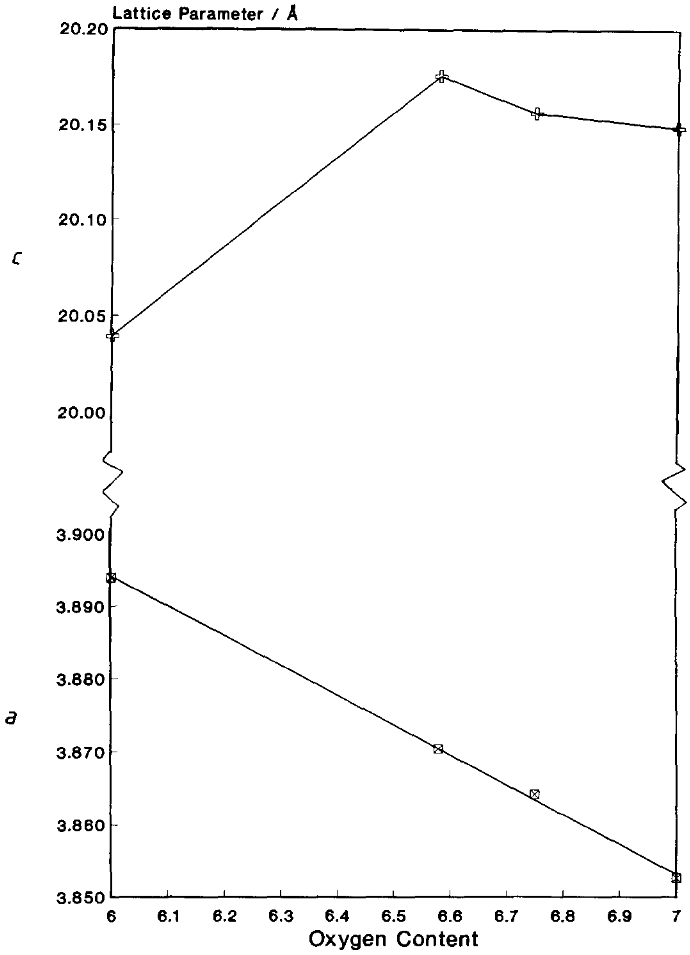

FIG. 2. Variation of a and c lattice parameters with oxygen stoichiometry in $Sr_3Fe_2O_{7-y}$.

lent agreement with those from the powder X-ray results. The a lattice parameter shows a monotonic decrease with diminishing y in $Sr_3Fe_2O_{7-y}$, as would be expected from the higher level of the smaller Fe^{4+} ion in these compounds. The a parameter is controlled only by the Fe–O–Fe distance between the corner-sharing octahedra. The c lattice parameter behavior as a function of oxygen content is more complex. As the oxygen content rises above six, a rapid increase in the c parameter occurs and a maximum value is found with $y \approx 0.5$; beyond this value, c contracts though more slowly as a function of the oxygen stoichiometry. This variation of c with oxygen stoichiometry is similar to that observed by McChesney and co-workers (*7*), though our values are in general slightly higher. This behavior can be explained in terms of the site occupied by the additional oxygen. Figure 3 presents a STRUPLO (*10*) plot of $Sr_3Fe_2O_7$ showing the FeO_6 octahedra; in $Sr_3Fe_2O_6$ the oxygen atom linking the octahedra pairs in the c direction is absent. This gives rise in $Sr_3Fe_2O_6$ to a square pyramidal iron coordi-

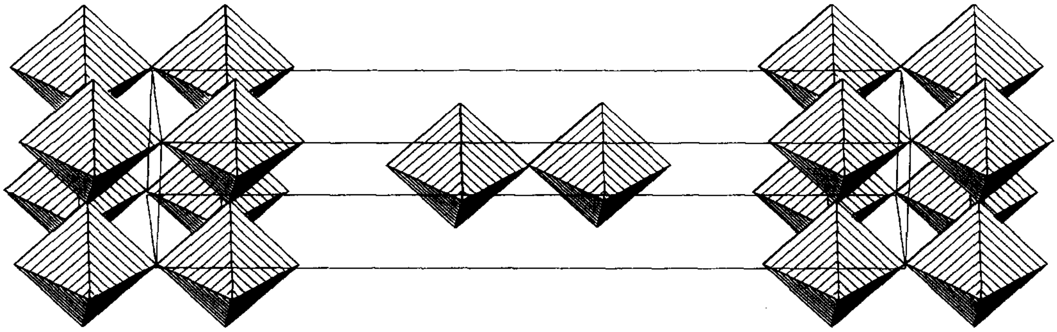

FIG. 3. STRUPLO (10) plot of $Sr_3Fe_2O_7$ showing the FeO_6 octahedra.

nation geometry, and the distance between the faces of these square pyramids is 3.38 Å, which is considerably less than twice a typical Fe^{3+}–O (1.95 Å) or Fe^{4+}–O (1.90 Å) distance. Addition of oxygen to the O3 site between the two pyramids therefore requires a considerable expansion along *c* together with displacements of the iron and O3 positions to form a more regular geometry around the metal atom.

The change in the iron coordination geometry as the oxygen level increases is quite marked. In $Sr_3Fe_2O_6$ the trivalent iron atom has a square-based pyramidal coordination, which is rather rare for this ion in oxides, though it is reasonably well known in iron coordination complexes. The Fe–O distances for the four basal plane oxygens are typical for Fe^{3+}, while the apical iron oxygen distance is very short. Bond valence calculation (11) on this site using the parameters for Fe^{3+} gave a reasonable calculated iron valence of 2.91. Introduction of oxygen onto the O3 site obviously occurs randomly throughout the structure, and therefore the refined coordinates in the mixed valence materials represent an average over the bulk. For iron this means an average of Fe^{3+} coordinated to five oxygens and Fe^{4+} coordinated to six oxygens is observed. This is reflected as a gradual increase in the iron-to-apical-oxygen distance as the proportion of higher coordinate iron rises. On reaching $Sr_3Fe_2O_7$ the iron coordination geometry becomes an almost regular octahedron with a slight axial distortion similar to that found in Sr_2FeO_4.

The structural behavior of this system as a function of oxygen content shows similar aspects to that seen in the $La_2SrCu_2O_{6+y}$ systems but extends over a much larger stoichiometry range. In the $Sr_3Fe_2O_{7-y}$ system, as the level of oxygen increases the coordination geometry of Sr(1) increases from 8 to 12, though the average Sr–O distance naturally increases. This shows that with strontium (or indeed the similar sized La^{3+}) on an inter-$(MO)_n$-layer site incorporation of oxygen between these planes with oxidation is facile. This is the likely reason why compounds which contain moderately large ions between copper oxygen planes are not superconducting or show degraded superconducting behavior, e.g., $La_2SrCu_2O_6$, $NdBa_2Cu_4O_8$, $LaBa_2Cu_3O_7$.

Bond valence parameters have been widely used to characterize oxidation states of transition metals in complex oxides. These are well known for metals in common oxidation states; however, no parameters exist for Fe^{4+}. Using the structural data from $SrFeO_3$, Sr_2FeO_4, and $Sr_3Fe_2O_7$ a value for R_0 for Fe^{4+} can be derived as 1.788 ± 0.002. However, given the paucity of data and the constrained nature of the structures this value should be treated with some caution. Application of this value to iron doped onto copper sites in superconductors may allow the unequivocal assignment of the iron oxidation state on different sites in these doped materials.

Acknowledgments

We thank the SERC for grants in support of this work and a studentship for SED.

References

1. T. Takeda, Y. Yamagughi, and H. Watanabe, *J. Phys. Soc. Jpn.* **33,** 967 (1972).
2. M. Shimada, Y. Takeda, H. Taguchi, F. Kanamaru, and M. Koizumi, *J. Cryst. Growth* **29,** 75 (1975).
3. S. E. Dann, M. T. Weller, and D. B. Currie, *J. Solid State Chem.* **92,** 237 (1991).
4. J. B. McChesney, R. C. Sherwood, and J. F. Potter, *J. Chem. Phys.* **43,** 1908 (1965).
5. E. Lucchini, D. Minichelli, and G. Sloccari, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **29,** 2356 (1973).
6. D. B. Currie, M. T. Weller, S. Rowles, and D. H. Gregory, *Mater. Res. Bull.* **25,** 1279 (1990).
7. P. K. Gallagher, J. B. McChesney, and D. N. E. Buchanan, *J. Chem. Phys.* **45,** 2466 (1966).
8. H. M. Rietveld, *Acta Crystallogr.* **2,** 65 (1969).
9. M. W. Johnson and W. I. F. David, Rutherford–Appleton Lab. Report. No. 85/112 (1985).
10. R. Fischer, *J. Appl. Crystallogr.* **18,** 258 (1985).
11. I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.* **41,** 244 (1985).