Resonant Powder X-Ray Determination of the Cation Distribution in $FeNi_2BO_5$

David A. Perkins and J. Paul Attfield*

Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, UK

The distribution of Fe^{3+} and Ni^{2+} over the four crystallographically distinct octahedral cation sites in $FeNi_2BO_5$ has been precisely determined from a single resonant powder X-ray pattern collected 16 eV below the Fe K absorption edge and is very similar to that in $AlNi_2BO_5$, showing that charge rather than size determines the cation distribution in these borates.

Metal borates are currently of interest for their chemical and physical properties, and resulting applications as catalysts[1,2] and non-linear optical materials.[3] As part of a study of mixed-metal and mixed-valence transition metal borates, we are investigating the structural and magnetic properties of $FeNi_2BO_5$.[4] Like many $M^{3+}(M'^{2+})_2O_2(BO_3)$ borates, this compound adopts the orthorhombic Ludwigite-*I*[5] structure shown in Fig. 1. Edge-sharing MO_6 octahedra form zig-zag chains in the *ab* plane that are linked by BO_3 groups. These planes are stacked up to give infinite chains of octahedra in the *c*-direction. To understand the crystal chemistry and magnetic properties of $FeNi_2BO_5$ it is necessary to know the distribution of Fe^{3+} and Ni^{2+} over the four geometrically similar, but crystallographically distinct, octahedral cation sites in this structure. However, previous X-ray studies of $FeNi_2BO_5$[6,7] have given little indication of the cation distribution as Fe and Ni have very similar normal X-ray scattering factors. Neutron diffraction could not be used to solve this problem as these two elements also have very similar neutron scattering lengths, and the Mössbauer spectrum shows only one unresolved Fe^{3+} signal between 4.2 and 285 K.[8] Hence, this problem provides a good opportunity to test the new technique of resonant X-ray diffraction.

A resonant X-ray diffraction experiment is performed in the same way as an ordinary powder or single crystal X-ray study, except that the wavelength is carefully selected (from a white synchrotron beam) to be very close to an elemental absorption edge. This modifies the atomic X-ray scattering factor of that element through large anomalous dispersion effects,† enabling it to be distinguished from neighbouring elements, and even allows different oxidation states of the resonant element to be contrasted.[9–12] Resonant powder diffraction has recently been used to solve a number of site-ordering problems, often in joint refinements with neutron data,[10] but here we have attempted to solve a more ambitious problem, with cations disordered over four sites, from a single resonant X-ray powder pattern.

$FeNi_2BO_5$ was prepared as a polycrystalline powder‡ and X-ray diffraction data were collected at the Synchrotron

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† The atomic X-ray scattering factor may be written $f^n + f' + if''$, where f^n is the normal scattering which depends upon the electron distribution, and f' and f'' are the wavelength-dependent anomalous scattering terms.

‡ Polycrystalline $FeNi_2BO_5$ was synthesised by dissolving stoichiometric quantities of $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and H_3BO_3 in distilled water and evaporating to dryness. The nitrate mixture was decomposed at 300 °C and sintered at 1050 °C for 12 days in air with frequent regrinding and repelleting. X-Ray powder diffraction revealed $FeNi_2BO_5$ and traces of NiO and α-Fe_2O_3 which were not eliminated by prolonged heating. Analytical electron microscopy[13] of 20 microcrystallites from the final product showed the Fe : Ni ratio to be 1 : 2.05(6).

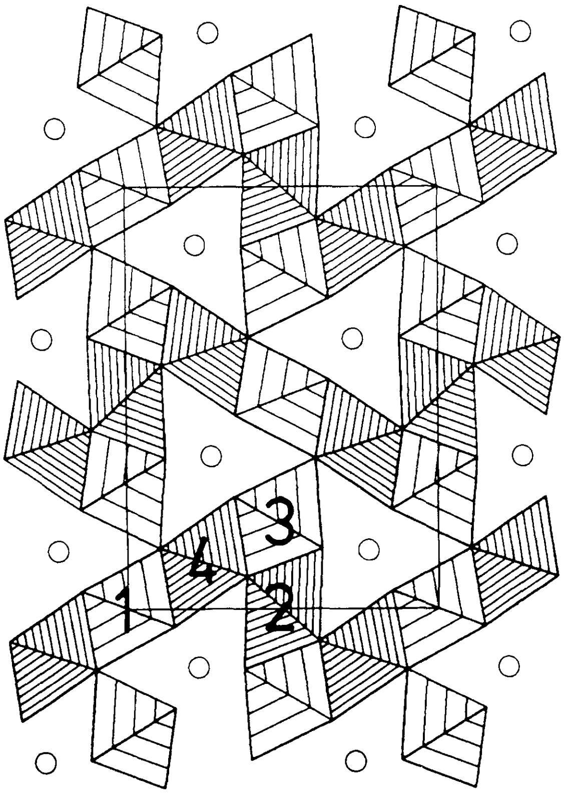

Fig. 1 Polyhedral representation of the Ludwigite-*I* structure projected on (001) with the unit cell marked (*a* horizontal, *b* vertical) and the boron atoms shown as circles. The four crystallographically distinct octahedra are labelled and those centred in the $z = 0/\frac{1}{2}$ planes are lightly/heavily hatched.

Radiation Source, Daresbury, UK.§ The X-ray energy (7103.9 eV) was chosen to be below both the Fe K edge, which is at 7120 eV for α-Fe_2O_3, and the *ca.* 10 eV pre-edge region that may contain XANES features.[17] At such energies the sample absorption is low, the imaginary anomalous dispersion correction, f'', is small and calculable, but the real anomalous term, f', is large and negative giving good elemental contrast. The value of f' may differ from calculated values as it is influenced by the valence shift and near-edge structure in the absorption edge, and so data from α-Fe_2O_3 were used to refine f'(Fe), as the iron is in the same oxidation state and coordination geometrty as those in $FeNi_2BO_5$. Starting with published coordinates[18] and calculated anomalous terms,[19] the refinement converged successfully¶ giving f'(Fe) = −6.94(3) electrons/atom which differs slightly from the calculated value of −6.61 e/atom.

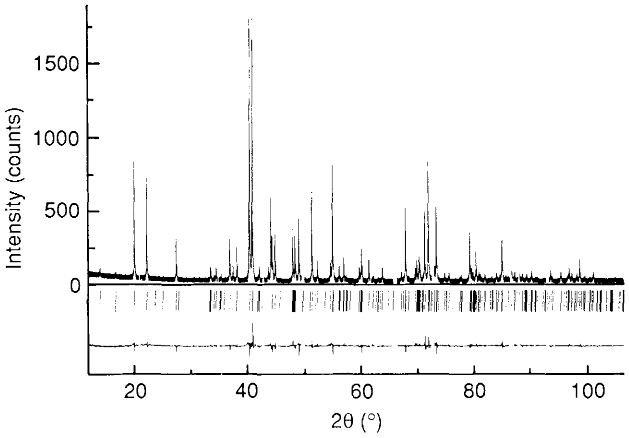

Fig. 2 Observed (dashes), calculated (full line) and difference resonant X-ray diffraction profiles for $FeNi_2BO_5$ with the reflection positions marked

The $FeNi_2BO_5$ profile was then fitted using calculated anomalous scattering terms,[19] except for f'(Fe) which was taken from the α-Fe_2O_3 refinement, with regions containing Bragg peaks from the NiO and α-Fe_2O_3 impurities excluded. The initial refinement in which the site occupancies were fixed at statistically expected values gave a poor fit with R_{WP} (weighted profile *R*-factor) = 17.1%. The occupancies of the four metal sites were then refined independently, subject only to the constraint that the correct overall ratio of 1Fe : 2Ni be preserved, which greatly improved the fit to R_{WP} = 12.6%. Results of this refinement|| are given in Table 1 and Fig. 2. Further refinements in which the stoichiometry was also varied produced no significant improvements to this fit.

The sensitivity of this resonant X-ray refinement of $FeNi_2BO_5$ to the Fe/Ni distribution is evident from the improvement in the fit on refining the occupation factors and their calculated estimated standard deviations (esds). This precision results from the f'(Fe) value of −7 e/atom which drastically reduces the Fe scattering power, making it comparable to the normal scattering of K. The accuracy of the refined occupation factors is not independently verifiable, but the marked similarity of the values to those from conventional single crystal X-ray studies of $AlNi_2BO_5$[20] (Table 1), and the near-stoichiometric Ludwigites $Al_{0.9}Co_{2.1}BO_5$[20] and $Mn_{1.07}Mg_{1.93}BO_5$[21] suggests that they are reliable. The fact that the mean M–O distances around the M(2)[2.047(5) Å] and M(4)[2.058(4) Å] sites are slightly smaller than those around M(1) [2.070(4) Å] and M(3)[2.073(5) Å] also suggests a greater concentration of Fe^{3+} at these positions, but the

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§ Synchrotron X-ray data were collected on SRS powder diffractometer 8.3. The wavelength of 1.74530(3) Å (7130.9 eV) was selected with an Si(111) channel-cut monochromator and calibrated using an NBS silicon powder standard [*a* = 5.430940(35) Å]. The diffraction patterns of α-Fe_2O_3 in the range 2θ = 26–80° and $FeNi_2BO_5$ in the range 2θ = 12–106.8° were collected from flat-plate samples in θ/2θ geometry, counting for 2 s per 0.01° step. The data were corrected for variations in the incident beam intensity and scaled to counts s^{-1} 100 mA^{-1} ring current. Rietveld profile refinements[14] were performed using the GSAS[15] and Brookhaven PROFPV[16] programs with neutral atom X-ray scattering factors.

¶ Refinement in space group $R\bar{3}c$ (No. 167) gave R_{WP} = 10.3, R_P = 7.4, R_F = 3.1, R_{Ex} = 7.9%; cell parameters (Å): *a* = 5.03521(5), *c* = 13.7508(2); coordinates: Fe: [0,0,0.35517(6)], O: [0.6950(3),0,1/4]; overall isotropic *B* = 0.12(3) $Å^2$.

|| Rietveld refinement of $FeNi_2BO_5$ in orthorhombic space group *Pbam* (No. 55) using 9062 points with 189 contributing Bragg reflections gave R_{WP} = 12.6, R_P = 9.5, R_I = 4.8, R_{Ex} = 8.3%; cell parameters (Å): *a* = 9.21048(7), *b* = 12.23794(9), *c* = 3.00620(2); isotropic atomic temperature factors ($Å^2$): B_M = 0.13(3), B_B = 0.3(2), B_O = 0.13(4); fractional coordinates:

Site	Symmetry position	*x*	*y*	*z*
M(1)	2(*a*)	0	0	0
M(2)	2(*d*)	1/2	0	1/2
M(3)	4(*g*)	−0.0001(2)	0.2814(4)	0
M(4)	4(*h*)	0.7378(2)	0.3848(1)	1/2
B(1)	4(*h*)	0.274(1)	0.3602(9)	1/2
O(1)	4(*h*)	0.8516(5)	0.0438(4)	1/2
O(2)	4(*g*)	0.3910(5)	0.0763(4)	0
O(3)	4(*h*)	0.6276(5)	0.1394(5)	1/2
O(4)	4(*g*)	0.1038(6)	0.1444(5)	0
O(5)	4(*h*)	0.8497(6)	0.2395(4)	1/2

Table 1 Site occupancies for the four cation sites in $FeNi_2BO_5$ from the resonant powder X-ray diffraction study, together with the occupancies and calculated site potentials in $AlNi_2BO_5$[20] and the connectivities of the six oxygens around each site; O_{4M} coordinated to four cations, O_{5M} coordinated to five cations, O_B bonded to boron (and three cations). The ionic radii[22] for Fe^{3+}, Al^{3+} and Ni^{2+} are also given.

	Occupation factors (%)							
	$FeNi_2BO_5$		$AlNi_2BO_5$			Oxygen connectivity		
Site	Fe	Ni	Al	Ni	Potential in $AlNi_2BO_5$	O_{4M}	O_{5M}	O_B
M(1)	8.8(6)	91.2(6)	14.8(4)	85.2(4)	−2.17	2	0	4
M(2)	38.5(6)	61.5(6)	34.8(4)	65.2(4)	−2.29	0	4	2
M(3)	14.4(5)	85.6(5)	11.0(4)	89.0(4)	−2.18	1	1	4
M(4)	61.9(4)	38.1(4)	64.2(4)	35.8(4)	−2.37	2	2	2
$r_{ionic}/Å$	0.645	0.690	0.535	0.690				

differences are too small to be used to derive reliable occupation factors.

The cation distribution in $FeNi_2BO_5$ is significantly non-random, but does not correspond very closely to the simple ordering scheme previously suggested in which Ni^{2+} occupied sites M(1)–M(3) and Fe^{3+} was only on M(4).[6,7] In both $FeNi_2BO_5$ and $AlNi_2BO_5$,[20] Ni^{2+} tends to occupy the M(1) and M(3) sites while Fe^{3+}/Al^{3+} exhibit a slight preference for M(2) and a strong preference for the M(4) position. The similarity of these distributions despite the fact that the discrepency between the ionic radii[22] of Al^{3+} (0.535 Å) and Ni^{2+} (0.690 Å) is much greater than that between the radii of Fe^{3+} (0.645 Å) and Ni^{2+} suggests that the cation distributions in these borates are determined by charge rather than size factors. Both ionic and covalent considerations apply; the ionic contribution may be illustrated with the previously calculated site-potentials for $AlNi_2BO_5$[20] in Table 1 which show that the expected order of site preferences for the more highly charged Fe^{3+}/Al^{3+} cations is $M(4) > M(2) > M(3) = M(1)$. There is also a covalent contribution as the amount of oxygen electron density available per cation decreases when the oxygen is coordinated by five cations rather than four, and is still further reduced when oxygen is covalently bonded to boron. The connectivities of the coordinating oxygens at each cation site in Table 1 show that expected order of preferences for Fe^{3+}/Al^{3+} should be $M(4) > M(2) > M(1) = M(3)$. Hence, both the ionic and covalent arguments support the observed cation distributions qualitatively.

Another important feature of this work is that the derived structural information is as good as would be expected from a non-resonant powder X-ray determination, and even the boron and the oxygen atoms are located with greater precision than that of a recent single crystal study.[7] In addition to these structural data, the extra effort of selecting a resonant wavelength results in site occupancy information unavailable from an ordinary X-ray refinement. By collecting data over as wide a $\sin\theta/\lambda$ range as posssible, correlations between the occupancies, temperature factors and the scale factor are minimised enabling them to be refined simultaneously without the need for additional data sets. This is the most complex site occupancy problem yet solved using resonant powder X-ray diffraction, and shows that the limitations of this technique have not yet been reached.

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