Determination of the site of incorporation of cobalt in CoZnPO-CZP by multiple-wavelength anomalous-dispersion crystallography

M. Helliwell,[a]* J. R. Helliwell,[a] V. Kaucic,[b,c] N. Zabukovec Logar,[b] L. Barba,[d] E. Busetto[e] and A. Lausi[e]

[a]*Department of Chemistry, University of Manchester, Manchester M13 9PL, England,* [b]*National Institute of Chemistry, 1000 Ljubljana, Slovenia,* [c]*University of Ljubljana, 1000 Ljubljana, Slovenia,* [d]*Istituto di Strutturistica Chimica, CNR, Strada Statale 14, Basovizza, 34102 Trieste, Italy, and* [e]*Sincrotone Trieste, Strada Statale 14, Basovizza, 34102 Trieste, Italy. E-mail: mad@pec6.sc.ch.man.ac.uk*

Abstract

Data were collected from a crystal of CoZnPO-CZP {sodium cobalt–zinc phosphate hydrate, $Na_6[Co_{0.2}Zn_{0.8}-PO_4]_6.6H_2O$} using synchrotron radiation at ELETTRA at the inflection point and 'white line' for both the cobalt and zinc K edges, and at 1.45 Å, a wavelength remote from the K edges of both metals. The data were processed using the programs *DENZO* and *SCALE-PACK*. The *CCP*4 program suite was used for the scaling of data sets and the subsequent calculation of dispersive difference Fourier maps. Optimal scaling was achieved by using a subset of reflections with little or no contribution from the metal atoms (*i.e.* which were essentially wavelength independent in their intensities) and using weights based on the σ's to obtain an overall scale factor in each case. Phases were calculated with *SHELXL*97 based on the refined structure using a much higher resolution and complete Cu $K\alpha$ data set. An occupancy of 100% by zinc at the two metal-atom sites was assumed. The dispersive difference Fourier map calculated for zinc gave two peaks above the background of similar heights at the expected metal-atom sites. The peak height at the Zn1 site was a little higher than at the Zn2 site. The dispersive difference Fourier map calculated for cobalt gave just one peak above the background, at the Zn1 site, and only a small peak at the Zn2 site, thus indicating that incorporation of cobalt takes place mainly at one site. Refinement of the zinc occupancies using *MLPHARE* reinforces this conclusion. The chemical environment of each site is discussed.

1. Introduction

Microporous, phosphate-based molecular sieves have found increasing importance due to their activity as solid acid catalysts (Hong *et al.*, 1996). They have well defined micropore systems and significantly different surface selectivity from that of pure silica molecular sieves or zeolites (Davis, 1991). Although they are catalytically active for many chemical reactions, their acidity is a complicated function of framework charge, structural type and the nature of the metal atoms incorporated into the framework sites, which is not fully understood. The coupling of acidic with redox properties in metal frameworks, due to the ease with which transition metals can change their valence states, is very promising for bifunctional catalysis (Berndt *et al.*, 1996). It is thus vital to study the nature and position of the catalytically active metal sites for a better understanding of the physical-chemical properties, and also with the aim of producing novel materials with desired properties. To determine the site of metal incorporation, the identity of two or more sites (often close together in atomic number), and, in particular, their precise relative occupancies, is a challenging problem, particularly since the crystals of these materials are usually small and weakly diffracting.

The title compound CoZnPO-CZP belongs to a group of small-pore molecular sieves. Its structure was initially determined using a single crystal and data collected using Mo $K\alpha$ radiation (Zabukovec Logar *et al.*, 1995; Rajic *et al.*, 1995). This showed it to have a new and chiral topology, and because of this it has possible applications in enantioselective separations and synthesis, as well as catalytic applications. However, due to the lack of scattering contrast between cobalt and zinc at the Mo $K\alpha$ wavelength, the location of the isomorphously substituted cobalt over the two crystallographically different zinc sites could not be unambiguously determined, although there was an indication from refinement of population parameters that there may be more cobalt at the Zn1 site. We had previously demonstrated the determination of a fully occupied nickel-atom site in the aluminophosphate NiAPO by the calculation of dispersive difference Fourier maps, using synchrotron radiation data collected close to the nickel K edge (Helliwell *et al.*, 1996). In order to determine the site(s) of substitution by cobalt, data were collected on the ELETTRA X-ray diffraction beamline, close to the K absorption edges of zinc and

Table 1. *Experimental details for the Cu Kα data*

Crystal data

Chemical formula	$Na_6[Co_{0.2}Zn_{0.8}PO_4]_6\cdot$ $6H_2O$
Chemical formula weight	200.06
Cell setting	Hexagonal
Space group	$P6_522$
a (Å)	10.464 (4)
c (Å)	15.056 (4)
V (Å^3)	1427.6 (6)
Z	12
D_x (Mg m^{-3})	2.792
Radiation type	Cu $K\alpha$
Wavelength (Å)	1.5418
No. of reflections for cell parameters	14
θ range ($^\circ$)	15.6–26.1
μ (mm^{-1})	15.007
Temperature (K)	294 (2)
Crystal form	Prismatic
Crystal size (mm)	$0.05 \times 0.02 \times 0.02$
Crystal colour	Blue

Data collection

Diffractometer	Rigaku AFC-5R four-circle
Data collection method	ω–2θ scans
Absorption correction	ψ scans (North *et al.*, 1968)
T_{min}	0.592
T_{max}	0.741
No. of measured reflections	1733
No. of independent reflections	713
No. of observed reflections	637
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0587
θ_{max} ($^\circ$)	59.87
Range of h, k, l	$-10 \rightarrow h \rightarrow 10$
	$-10 \rightarrow k \rightarrow 10$
	$-16 \rightarrow l \rightarrow 16$
No. of standard reflections	3
Frequency of standard reflections	Every 150 reflections
Intensity decay (%)	1.01

Refinement

Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0513
$wR(F^2)$	0.1252
S	1.081
No. of reflections used in refinement	713
No. of parameters used	72
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 20.8883P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000
$\Delta\rho_{max}$ (e Å^{-3})	0.624
$\Delta\rho_{min}$ (e Å^{-3})	-0.466
Extinction method	*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient	0.0020 (2)
Absolute structure	Flack (1983)
Flack parameter	0.00 (18)
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Computer programs

Data collection	*MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989)

Table 1 (*cont.*)

Cell refinement	*MSC/AFC Diffractometer Control Software*
Data reduction	*TEXSAN* (Molecular Structure Corporation, 1995)
Structure solution	Zabukovec Logar *et al.* (1995); Rajic *et al.* (1995)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)
Preparation of material for publication	*TEXSAN*

cobalt, and at a wavelength of 1.45 Å, using a MAR online image-plate detector. The subsequent calculation of f' difference Fourier maps allowed the pin-pointing of both the zinc and cobalt positions.

2. Experimental

The same crystal of CoZnPO-CZP was used for all collections of diffraction data described below.†

2.1. *Cu Kα data collection*

Data collection was carried out using Cu $K\alpha$ radiation and a 12 kW rotating-anode AFC-5R diffractometer. Details of the data collection and refinement are summarized in Table 1. Previously, the structure had been reported in the space group $P6_1$ (Zabukovec Logar *et al.*, 1995; Rajic *et al.*, 1995), so two Friedel equivalents of data were collected, assuming a Laue symmetry of $6/m$. However, it soon became clear that the Laue symmetry was in fact $6/mmm$; the merging R values in each case were similar ($R_{int} = 0.0559$ for $6/m$ and 0.0587 for $6/mmm$); refinement was more satisfactory assuming the space group $P6_122$ or $P6_522$ rather than $P6_1$ or $P6_5$, with the conventional R value improved by about 2% in the higher symmetry. Moreover, the disordered regions of the structure were not resolved in the lower-symmetry space groups. Having identified the Laue symmetry as $6/mmm$, the final space-group selection was decided by refinement of the Flack parameter (Flack, 1983), which clearly indicated that the space group was in fact $P6_522$.

The coordinates of the framework atoms were taken from the previous determination, suitably adjusted to take into account the higher Laue symmetry. The non-framework atoms were found by successive rounds of refinement and difference Fourier calculations. Zn1 and Zn2 are located on a twofold axis and Na1 is disordered over two sites related by the twofold axis. The non-framework atoms Na2 and O5 are resolved into two disordered sites each (*A* and *B*), with the refined occupancies constrained to sum to 0.5 and 1.0, respectively. The displacement factor of Zn1 is a little higher than

---

that of Zn2 [U_{eq} = 0.0160 (6) and 0.0145 (6) Å^2, respectively] suggesting that incorporation of cobalt may have taken place preferentially at Zn1. Accordingly, refinement was carried out including Co1 at an occupancy of *x* and Co2 at an occupancy of *y* at the Zn1 and Zn2 sites, respectively, and with the populations of Zn1 set to 1 − *x* and Zn2 to 1 − *y*. Fixing the anisotropic displacement parameters for Co1, Co2, Zn1 and Zn2 to be equal again indicates the presence of a larger amount of cobalt at the Zn1 site. [Co1 occupancy 19 (3)%, Co2 occupancy 12 (3)%]. However, since the occupancies are not significantly different from one another, populations of 100% zinc at these two sites were assumed for the final rounds of refinement. The atomic coordinates are presented in Table 2 and Fig. 1 shows a plot of a portion of the framework structure.

2.2. *ELETTRA data collection*

The exact positions of the *K* edges for zinc and cobalt in the sample were determined from fluorescence scans, measured directly from the crystal used for the subsequent data collection (Fig. 2). For zinc (Fig. 2*a*), the position of the '*f′* dip' was found to be at 1.2846 Å (9.652 keV), whilst the position of the *f″* maximum, at the top of the white line, was determined to be 1.2840 Å (9.656 keV). Similarly, the edge scan for cobalt showed the *f′* dip and *f″* maximum to occur at 1.6083 (7.709 keV) and 1.6073 Å (7.714 keV), respectively (see Fig. 2*b*). Data collection at these four wavelengths, together with the collection of an additional data set at 1.45 Å (*i.e.* the remote wavelength, serving equally well for each edge), was then carried out using the on-line MAR image-plate detector (diameter 180 mm). The constant-dose method, involving setting the exposure time according to accumulated counts, was used in each case to collect a little more than 180° of data using 6 or 7° oscillations, depending on the wavelength (see Table 3). The detector was moved as close as possible to the crystal (about 70 mm) in order to maximize the recordable resolution. Even so, due to the long wavelengths and small aperture of the MAR detector, the
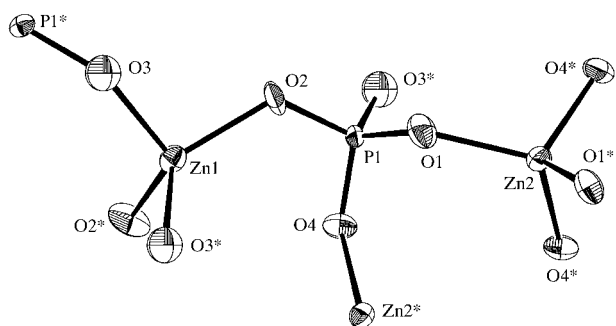
resolution limits are only 1.44 Å for the two data sets collected at the zinc *K* edge, 1.62 Å for the data set collected at a wavelength of 1.45 Å and 1.8 Å for the two data sets collected at the cobalt *K* edge (see Table 3).

2.3. *Data processing of ELETTRA data*

The five data sets were processed using *DENZO* and *SCALEPACK* (Otwinowski, 1988), keeping the Bijvoet pairs separate. There was a small number of overloaded reflections and it was found that exclusion of these from the scaling led to improved merging *R* values. Other details of the data processing are summarized in Table 3.

2.4. *Calculation of f′ difference Fourier maps*

Intensities generated by *SCALEPACK* were converted to |*F*|'s using a version of the program *TRUNCATE* [Collaborative Computational Project No. 4 (CCP4), 1994] modified for use with the small number of reflections in each data set. All further calculations were also performed using the CCP4 program suite. The
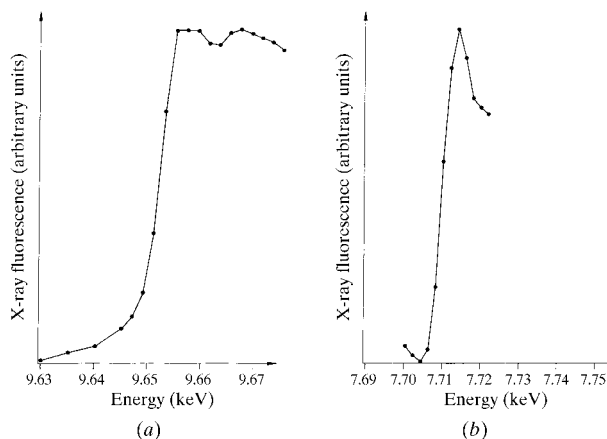
Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the Cu Kα data*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Zn1	−0.49273 (11)	−0.50727 (11)	0.0833	0.0160 (6)
Zn2	0.15823 (11)	−0.15823 (11)	0.0833	0.0145 (6)
P1	−0.1691 (3)	−0.4097 (3)	0.05934 (18)	0.0123 (7)
Na1	−0.6343 (11)	−0.2974 (11)	0.0765 (9)	0.044 (3)
O1	−0.0491 (8)	−0.2469 (8)	0.0535 (5)	0.023 (2)
O2	−0.3112 (8)	−0.4286 (10)	0.0181 (5)	0.027 (2)
O3	−0.6162 (9)	−0.4919 (9)	−0.0088 (6)	0.028 (2)
O4	−0.1966 (8)	−0.4612 (8)	0.1553 (5)	0.0200 (19)
Na2*A*	−0.091 (4)	−0.018 (5)	−0.038 (2)	0.137 (12)
Na2*B*	−0.212 (7)	−0.185 (8)	−0.049 (4)	0.137 (12)
O5*A*	−0.414 (4)	−0.312 (5)	−0.157 (3)	0.168 (14)
O5*B*	−0.416 (7)	−0.173 (10)	−0.064 (8)	0.168 (14)

Fig. 1. An *ORTEP* (Johnson, 1965) plot of CoZnPO-CZP with 60% probability ellipsoids showing a portion of the framework. The non-framework atoms have been omitted for clarity.

Fig. 2. Edge scans measured from the crystal of CoZnPO-CZP at ELETTRA. (*a*) At the zinc *K* edge. (*b*) At the cobalt *K* edge.

Table 3. *Summary of the data processing of ELETTRA data*

Data set	Znf'	Znf''	1.45 Å	Cof'	Cof''
Wavelength (Å)	1.2846	1.2840	1.4500	1.6083	1.6073
Oscillation angle (°), No. of images, total angle of data collection (°)	6, 31, 186	6, 31, 186	6, 31, 186	7, 27, 189	7, 26, 182
Resolution limit (Å)	1.44	1.44	1.62	1.80	1.80
Total No. of reflections	2008	2014	1347	970	957
No. of unique reflections (Bijvoets separate and overloaded reflections removed)	170	175	119	84	85
No. of overloaded reflections excluded	9	5	10	8	7
R_{merge} (F)	0.082	0.159	0.065	0.062	0.079

data sets were sorted and combined, and then scaling of the f' data for zinc and cobalt to the 1.45 Å data was carried out using *SCALEIT*. After a number of computational trials, it was found that the optimum scaling was obtained by using an overall scale factor determined from a small subset of reflections, the intensities of which were essentially independent of the wavelength, and applying weights according to the standard deviations of the measurements. The wavelength-independent reflections were determined using the program *SFALL* by the generation of three lists of calculated structure factors: the first was calculated for Zn1 only, the second was calculated on the basis of Zn2 only and a third set was calculated for Zn1 with Zn2 only. The lists were then inspected for structure factors of zero or close to zero in all three data sets, since these reflections had little or no contribution from the zinc atoms and were therefore essentially wavelength independent. Six such reflections were found and were used to calculate the overall scale factors. The use of wavelength-independent reflections to determine overall scale factors was particularly important for scaling the zinc f' data to the 1.45 Å data, since the dispersive effect on the reflection intensities of the former set, as expected, is large; the r.m.s. isomorphous difference for the zinc f' data to the 1.45 Å data is 22.15, whilst for the cobalt f' data it is 2.67. Phases were calculated by refinement of the structure using the much higher resolution data set collected previously (from the same crystal) using Cu $K\alpha$ radiation, see §2.1 and Table 1. An occupancy of 100% zinc at the metal-atom sites was assumed (phase set A). A second phase set (phase set B) was generated, using the same data set but substituting phosphorus for zinc at the two independent sites. Refinement of the structure using fixed isotropic displacement parameters for these positions, and fixing the Na2A, Na2B, O5A and O5B positions, gave the desired phase set, with an R value of 0.1550. Both phase sets were combined with the scaled data sets. Finally, dispersive difference Fourier maps were calculated using the program *FFT*. The results are summarized in Table 4. Using either phase set, the maps calculated using the coefficients $|F_{1.45\ \text{Å}} - F_{Znf'}|$ (where $F_{Znf'}$ are the data measured at the zinc f' dip) give two peaks of similar height above the background, which are close to the Zn1

and Zn2 sites (see Fig. 3a). The peak at the Zn1 site is slightly higher than that at Zn2. The maps calculated using the coefficients $|F_{1.45\ \text{Å}} - F_{Cof'}|$ (where $F_{Cof'}$ are the data measured at the cobalt f' dip) give only one peak above the background, close to the Zn1 site (Fig. 3b). There is a small peak at the Zn2 site, but this is at the noise level, since it is less than three r.m.s. high and is in fact the fifth highest peak overall. Elsewhere, there is no evidence for the presence of cobalt. Thus there is an ambiguity, since if cobalt is incorporated mainly at the Zn1 site the dispersive difference Fourier map calculated using the zinc f' data should give a higher peak at the Zn2 site.

Accordingly, refinement of the zinc-site occupancies was carried out using the program *MLPHARE*. The native data set was defined as that collected at the zinc f' minimum, using the zinc positions and B factors taken from the refinement carried out using the Cu $K\alpha$ data set. Refinement of the occupancies of the zinc sites was then performed, using the four other data sets (at wavelengths of 1.2840, 1.45, 1.6083 and 1.6073 Å) as derivatives, *i.e.* the refinement was carried out against $|F_{derivative} - F_{Znf'}|$. In each case, the occupancy at Zn2 refined to a higher value than that at Zn1, with the relative size of the occupancies approximately reflecting the f' differences between the wavelength pairs (see Table 5). Similar attempts were made to refine the cobalt occupancies at the two sites, but the refinement was unstable and tended to give negative values, indicating that the cobalt signal was not sufficient to allow refinement of the occupancy.

3. Discussion

The calculation of dispersive difference Fourier maps using the 1.45 Å Cof' data with two different phase sets gave rise to a peak, in each case, at the Zn1 site, but much less indication of incorporation of Co at the Zn2 site. This result confirms what was suspected in the earlier study (Zabukovec Logar *et al.*, 1995; Rajic *et al.*, 1995) when it was found that the minimum peak on the final difference map was located in the vicinity of Zn1, indicating that the partial replacement of zinc by the lighter cobalt atom takes place preferentially at this site. In addition, refinement of the population parameters for

Table 4. *Results from FFT*

Data	Height of peak 1, height/r.m.s	Height of peak 2, height/r.m.s	R.m.s.	Position of peak 1, distance from Zn1 site (Å)	Position of peak 2, distance from Zn2 site (Å)
1.45 Å − Znf', phase set A	4.38, 7.89	4.00, 7.20	0.56	(0.5132, 0.4867, 0.0833), 0.107	(0.1536, 0.8464, 0.0833), 0.084
1.45 Å − Znf', phase set B	4.51, 8.12	4.19, 7.54	0.56	(0.5088, 0.4912, 0.0833), 0.028	(0.1558, 0.8442, 0.0833), 0.044
1.45 Å − Cof', phase set A	0.41, 6.88	0.16, 2.75	0.06	(0.5128, 0.4872, 0.0833), 0.100	(0.1525, 0.8302, 0.0857), 0.104
1.45 Å − Cof', phase set B	0.38, 6.32	0.17, 2.85	0.06	(0.5131, 0.4869, 0.0833), 0.106	(0.1596, 0.8404, 0.833), 0.025

the zinc positions gave values of 0.95 (2) and 0.99 (2) for Zn1 and Zn2, respectively. In this study, refinement was carried out using the Cu $K\alpha$ data, including Co1 at an occupancy of x and Co2 at an occupancy of y at the Zn1 and Zn2 sites, respectively, and with the populations of Zn1 set to $1 - x$ and Zn2 to $1 - y$. Fixing the anisotropic displacement parameters for Co1, Co2, Zn1 and Zn2 to be equal again indicated the presence of a larger amount of cobalt at the Zn1 site [Co1 occupancy 19 (3)% and Co2 occupancy 12 (3)%]. A possible explanation for the preferential substitution of cobalt at the Zn1 site was suggested by Rajic *et al.* (1995), when it was found that the hopeite phase is a precursor of the CoZnPO-CZP phase. Hopeite consists of ZnO$_4$ tetrahedra and ZnO$_2$(H$_2$O)$_4$ octahedra, and it was suggested that Co^{II} partially replaces the octahedrally coordinated fraction of zinc in the zincophosphate lattice.

The calculation of f' difference Fourier maps using the 1.45 Å − Znf' data with the two phase sets gave two peaks which were close to the refined positions (from the Cu $K\alpha$ refinement) for the Zn1 and Zn2 sites. The peak heights were very similar, but that at Zn1 was slightly higher (see Table 4). Thus, there remains an ambiguity, since if Co replaces Zn at the Zn1 site the order of the peak heights in the dispersive difference Fourier map should be reversed. In order to obtain a better estimate of the zinc occupancy at each site, refinement of the occupancies was carried out using the program *MLPHARE*, with the data measured at the f' dip as the 'native' (1.2846 Å), and the data measured at the other four wavelengths as the 'derivatives'. The results (Table 5) indicate a higher population of zinc at the Zn2 site, with the ratio of the populations of Zn1/Zn2 varying from 0.77 to 0.91. Thus, refinement of the population parameters leads to results in keeping with the expected occupancies of zinc at the two sites, *i.e.* that there is less zinc at the Zn1 site, due to incorporation of a greater proportion of cobalt at this site. A very likely explanation for the reversing of the expected peak heights in the maps using the coefficients $|F_{1.45\,Å} - F_{Znf'}|$ is that the maps were calculated with data to only limited resolution, due to the long wavelengths of the data sets

and the small aperture of the MAR image-plate detector.

Two phase sets were used in the generation of the f' difference Fourier maps: the first (phase set A) was calculated using the refinement of the model with 100% zinc incorporated at the two metal sites, whilst the second (phase set B) used phosphorus incorporated at these two sites. Although the latter model is considerably less accurate (as indicated by the much higher R value), the maps produced using either phase set were remarkably similar, both in peak heights and coordinate accuracy of the peaks. A further phase set was tested, with no atoms at the two metal-atom positions and with the other atoms fixed. In this case the maps became noisy, with no obvious peaks, indicating that with such a large proportion of the scattering power missing from the model the resulting phases were too inaccurate to give meaningful results.

The most sensitive method for detecting the metal at lower concentration, *i.e.* cobalt, is by the generation of the difference Fourier map using the coefficients
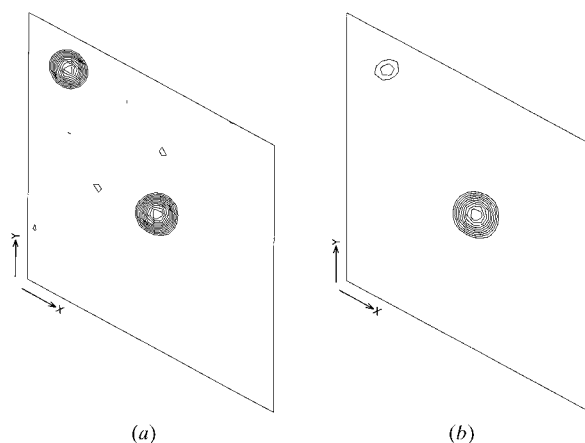

Fig. 3. Dispersive difference Fourier maps using phases calculated assuming 100% occupancy of zinc at sites 1 and 2 (phase set A): (*a*) using the coefficients $|F_{1.45\,Å} - F_{Znf'}|$, (*b*) using the coefficients $|F_{1.45\,Å} - F_{Cof'}|$.

Table 5. *Results of the refinement of the zinc occupancies using MLPHARE*

The 'native' data set in all cases was that measured at the zinc f' dip, with a wavelength of 1.2846 Å and f', f'' values of -11.519, 0.486 e, respectively. $\Delta f'$ is $[f'_{\text{derivative}} - f'_{\text{1.2846 Å}}]$. The refinement of the occupancy was against $|F_{\text{derivative}} - F_{\text{Zn}f'}|$.

Wavelength of 'derivative' (Å)	f', f'' for zinc (e)†	$\Delta f'$ (e)	Refined Zn occupancy at Zn1 site	Refined Zn occupancy at Zn2 site	Ratio of Zn1/Zn2 occupancies
1.2840	-7.721, 3.894	3.798	0.067	0.078	0.86
1.45	-1.934, 0.608	9.585	0.164	0.181	0.91
1.6083	-1.311, 0.792	10.208	0.138	0.154	0.90
1.6073	-1.329, 0.783	10.190	0.130	0.169	0.77

† Sasaki, 1989.

$|F_{\text{1.45 Å}} - F_{\text{Co}f'}|$, which gives clear evidence that incorporation of cobalt had taken place mainly at site 1, with much lower incorporation at site 2. From the elemental analysis the Zn:Co ratio is 0.8:0.2, so if all the cobalt were incorporated at site 1, cobalt would represent 40% of this site. The refinement of the zinc occupancies using *MLPHARE* indicates an upper limit for the cobalt substitution at site 1 of 30% and a lower limit of 24%, suggesting that incorporation of cobalt at site 2 takes place to an extent of 10 to 16%. From the small size of the cobalt peak at site 2 in the cobalt f' difference Fourier map, it is probable that the concentration is in fact closer to the lower limit of 10%. This gives an indication of the limits of the method in terms of the partial occupancy discernible, since an occupancy of between 24–30% of cobalt gives rise to a peak height of between six and seven times the r.m.s. value, suggesting that a lower limit for detection would be about half this concentration, *i.e.* 12–15%. It is probable, however, that the sensitivity would improve significantly if there were more coefficients for the maps, and for the *MLPHARE* refinements, again suggesting the need for data measured to higher resolution.

In order to improve the resolution limits of the required data sets, a cylindrical image-plate geometry could be used (Snell *et al.*, 1995). Alternatively it would be necessary to collect data at each wavelength from a four-circle diffractometer. Previously, in the determination of the site of nickel incorporation in the aluminophosphate NiAPO at the NSLS, wavelength and sample stability were found to be a problem with the longer data collection times required (Helliwell *et al.*, 1996). So far, however, the crystal of CoZnPO-CZP which has been used throughout the experiments described herein has shown no signs of decay, and the wavelength remained stable at ELETTRA.

References

Berndt, H., Martin, A. & Zhang, Y. (1996). *Microporous Mater.* **6**, 1–12.

Collaborative Computational Project, Number 4 (1994). *Acta Cryst.* D**50**, 760–763.

Davis, M. E. (1991). *Ind. Eng. Chem. Res.* **30**, 1675–1683.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Helliwell, M., Helliwell, J. R., Cassetta, A., Hanson, J. C., Ericsson, T., Kvick, A., Kaucic, V. & Frampton, C. (1996). *Acta Cryst.* B**52**, 479–486.

Hong, S. B., Kim, S. J. & Uh, Y. S. (1996). *J. Am. Chem. Soc.* **118**, 8102–8110.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1989). *MSC/AFC Diffractometer Control Software*. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Otwinowski, Z. (1988). *DENZO. A Program for Automatic Evaluation of Film Densities*. Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, Connecticut, USA.

Rajic, N., Zabukovec Logar, N. & Kaucic, V. (1995). *Zeolites*, **17**, 304–309.

Sasaki, S. (1989). KEK Report 88-14. National Laboratory for High Energy Physics, Tsukuba, Japan.

Sheldrick, G. M. (1997). *SHELXL*97. *Program for Crystal Structure Refinement*. University of Göttingen, Germany.

Snell, E., Habash, J., Helliwell, M., Helliwell, J. R., Raftery, J., Kaucic, V. & Campbell, J. W. (1995). *J. Synchrotron Rad.* **2**, 22–26.

Zabukovec Logar, N., Rajic, N., Kaucic, V. & Golic, L. (1995). *J. Chem. Soc. Chem. Commun.* pp. 1681–1682.