

Crystal structure of β -MNX (M = Zr, Hf; X = Cl, Br)

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Superconductivity with critical temperatures of up to 25.5 K has recently been reported for alkali metal intercalates of β -MNX (M = Zr, Hf; X = Cl, Br); we have investigated the structures of these host lattices and found that they are not as reported in the literature but are isostructural with rhombohedral SmSI.

β -ZrNX (X = Cl, Br) was first prepared by Juza and Heners.¹ The crystal structures were reported by Juza and Friedrichsen to consist of a random stacking sequence of hexagonal XZrNNZrX layers leading to cell parameters of $a = b = 2.08$ Å, $c = 9.22$ Å ($a = 3.60$ Å using conventional axes).² A second synthetic route to β -ZrNCl *via* chemical vapour transport was reported by Ohashi *et al.* who demonstrated that a supercell with $\sqrt{3}a$ and $3c$ relative to the previous study was required to index their diffraction data though no further structural details were reported.³

The intercalation of lithium into β -ZrNCl was first reported by Yamanaka *et al.* in 1984.^{4,5} It was subsequently shown that these and other alkali metal intercalates become superconducting below 15 K for doping levels of up to 0.4 mol alkali metal per ZrNCl.^{6,7} These compounds represent the first examples of superconducting layered metal nitrides. More recently, β -Li_{0.48}(THF)_yHfNCl was shown to undergo a superconducting transition at 25.5 K, the highest of any nitride.⁸ Any understanding of these materials will require a correct structural model of both the host lattice and its intercalation compounds. We have thus redetermined the structure of the β -MNX (M = Zr, Hf; X = Cl, Br) host lattices and find the true structure to be different from that generally accepted.

β -MNX (M = Zr, Hf; X = Cl, Br) were synthesised by the reaction of ZrH₂ or Hf with NH₄X followed by crystal growth *via* vapour transport under conditions reported previously.^{3,9} Powder X-ray diffraction data for β -ZrNCl, β -ZrNBr and β -HfNCl indicated that in each case the three layer supercell proposed previously was necessary to index the diffraction patterns. Structural studies on β -ZrNCl are complicated by a number of factors relating to its crystal morphology. Firstly, the prevalence of stacking faults along the *c*-axis makes single crystal analysis extremely difficult. These stacking faults are presumably related to the disordered hexagonal cell reported previously.² Secondly, the plate-like morphology of the crystals causes preferred orientation to be extreme in microcrystalline samples. Indeed in conventional Bragg–Brentano geometry the preferred orientation is so great that the 00*l* class of reflections are frequently the only ones observed. Attempts to alleviate this problem by grinding and subsequent annealing of the sample resulted in significant loss of crystallinity. In order to obtain suitable data for structural analysis diffraction data were collected in two distinct geometries. The microcrystalline samples were sieved to less than 90 μ m and either loaded into a 0.3 mm glass capillary or sprinkled onto a thin Mylar sheet and recorded in transmission geometry on a Siemens D5000 diffractometer using Cu-K α radiation and a Braun linear position sensitive detector. In this manner data sets were obtained showing either artificially enhanced or diminished 00*l* intensity. The capillary data together with a calculated diffraction pattern based on the reported structural coordinates of the

original structure are shown in Fig. 1. The calculated diffraction pattern was produced for a rhombohedral stacking sequence of layers with the layer structure suggested by Juza *et al.* The poor agreement is apparent.

The structure was solved by constructing trial solutions based on ClZrNNZrCl layers with differing stacking sequences and calculating their diffraction patterns within the InsightII software package.¹⁰ The structure showing the closest agreement between the observed and calculated diffraction patterns was found to have rhombohedral symmetry (space group $R\bar{3}m$) and was used as the starting point for a combined Rietveld refinement of both sets of data within the GSAS software suite.¹¹ The final refinement consisted of 52 parameters (7 structural and 45 instrumental and background) with 3549 data points (9–80° 2 θ , step = 0.02°, 46 reflections) for the capillary data and 4098 data points (8–90° 2 θ , step = 0.02°, 59 reflections) for the flat plate data. Isotropic temperature factors for the Zr and N atoms were constrained to be equal. A refinement in which all the temperature factors were allowed to refine freely led to no improvement in the agreement factors. Convergence was achieved at $\chi^2 = 2.07$, $R_{wp} = 2.40\%$ (capillary), $R_{wp} = 6.40\%$ (flat plate), $R_{wp} = 3.81$ (combined), $R_F^2 = 16.4$ (capillary) and $R_F^2 = 16.3\%$ (flat plate) for a rhombohedral cell with $a = 3.6052(1)$, $c = 27.6716(7)$ Å. Whilst these agreement factors are higher than those normally reported, we believe our model to be essentially correct. The diffraction data shown in Fig. 2 illustrate the dramatic effect which preferred orientation can have on the intensities of Bragg reflections of this phase. The structural model reported simultaneously provides a satisfactory fit to both data sets with only a simple March–Dollase type preferred orientation correction.^{12,13} For the capillary data, the preferred orientation parameter for the 001 direction is 0.72 and for the flat plate data is 2.14. The atomic coordinates of β -ZrNCl are given in Table 1 and the final Rietveld fits of both sets of data are shown in Fig. 2. Bond valence calculations gave values of 4.51 for Zr, 3.56 for N and 0.96 for Cl.^{14,15}

The structure of β -ZrNCl is shown in Fig. 3(a) and it is isostructural with SmSI.^{16,17} This structure is known to support intercalation as shown, for example, by the insertion of pyridine into YbOCl.¹⁸ In this structure each Zr atom is seven coordinate in a distorted monocapped octahedral arrangement with three Cl

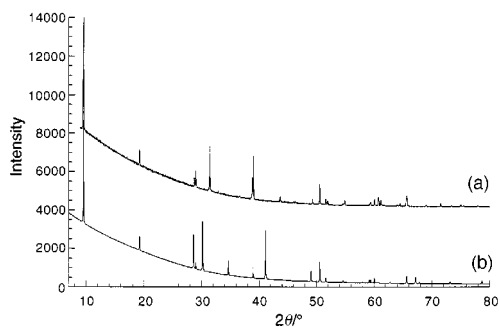


Fig. 1 (a) Powder X-ray diffraction pattern of β -ZrNCl and (b) calculated diffraction pattern based on the fractional coordinates of the original structure

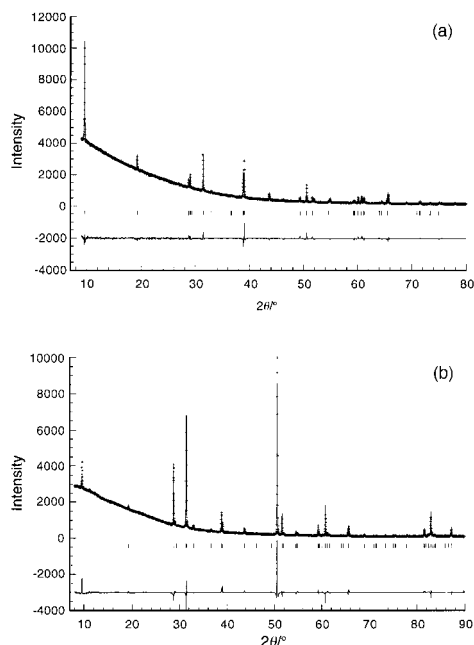


Fig. 2 Final Rietveld fit for β -ZrNCl: (a) capillary data (b) flat plate data; crosses represent the observed data, the solid line is the calculated pattern and the allowed reflection positions and difference profile are shown underneath

Table 1 Fractional atomic coordinates and isotropic thermal parameters for β -ZrNCl (esds in parentheses)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> /Å ²
Zr	2/3	1/3	0.7142(1)	0.0080(7)
N	2/3	1/3	0.0425(5)	0.0080(7)
Cl	2/3	1/3	0.4460(2)	0.0117(11)

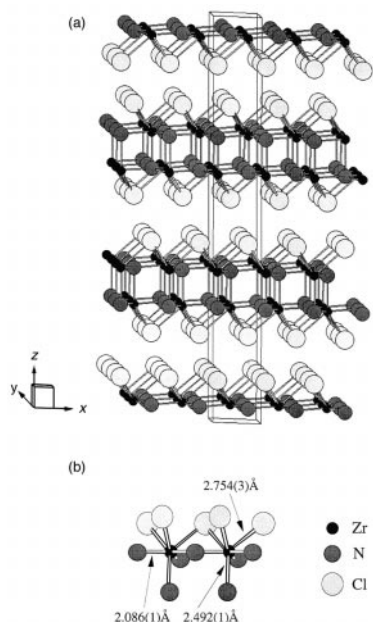


Fig. 3 (a) Structure of β -ZrNCl and (b) local coordination geometry of Zr in β -ZrNCl

atoms at 2.754(3) Å and three N atoms at 2.086(1) Å in a *fac*-arrangement with a fourth capping nitrogen at 2.492(1) Å as shown in Fig. 3(b). The octahedra are distorted by the displacement of the Zr atom from the centre towards the capped N₃ face to such an extent that the Zr and N atoms become

essentially coplanar. These monocapped octahedral units are arranged in an edge sharing manner forming the ClZrNNZrCl layer structure. The ClZrNNZrCl layers are held together by van der Waals interactions. Alternatively the structure can be viewed as originating from the NaCl structure in a rhombohedral setting. Removal of alternate layers of cations and replacement of one half of the chloride layers in the sequence ClNNCl gives the β -ZrNCl structure. The vacant Zr layers can then collapse down so that one face of the *fac*-ZrN₃Cl₃ octahedron is capped by an additional N atom. The close relationship between the ZrN slabs in β -ZrNCl and the rock salt structure adopted by ZrN is perhaps of relevance to the superconductivity in the intercalates of β -MNX as the binary nitrides themselves undergo superconducting transitions at 9.05 K (ZrN) and 8.3 K (HfN).^{19,20} Perhaps the most significant difference between this structure and the one originally reported is the absence of a short Zr–Zr distance which is instead replaced by the fourth capping N atom.^{2,21,22} This Zr–Zr interaction had been thought to play an important role in the superconducting intercalates.

Further confirmation that this is the correct structure can be sought by simulating a structure in DIFFaX in which there is random stacking of the layers.²³ If this model is correct then it should be able to reproduce the data reported by Juza *et al.* This is found to be the case, suggesting that the chemical transport synthesis of Ohashi *et al.* produces a material with the same constituent layers as that produced by Juza, but with significantly enhanced ordering of layer stacking.

Refinement of the structures of β -ZrNBr and β -HfNCl using the same structural model showed that these compounds are indeed isostructural with β -ZrNCl as reported here. Full details of these refinements, the metallocene intercalation chemistry of β -ZrNCl and intercalation of β -ZrNBr will be published elsewhere.

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