JOURNAL OF
Materials
CHEMISTRY

Superconducting intercalation compounds of metal nitride halides

Andrew M. Fogg, Victoria M. Green and Dermot O'Hare*

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: dermot.ohare@chem.ox.ac.uk

Received 14th December 1998, Accepted 8th April 1999

The crystal structures of the layered host lattices, β-ZrNBr and β-HfNCl have been determined. They have been found to be isostructural with rhombohedral SmSI. New lithium intercalation compounds (Li_xMNX; M = Zr, Hf; X = Cl, Br, I) have been prepared by treatment of either β-ZrNBr, β-HfNCl, α-ZrNBr or α-ZrNI with an excess of BuLi in hexane. These intercalates are all superconducting and show transition temperatures (T_c) of 12, 20, 11 and 11 K respectively. The lithium intercalates of the host lattices β-ZrNBr, α-ZrNBr and α-ZrNI are the first examples of intercalation into these materials.

Introduction

The intercalation of redox active atomic, organic and organometallic guests in layered materials on many occasions causes dramatic and even unprecedented increases in the electrical conductivity of these new hybrid materials compared to the pristine host lattices. In a few cases metallic and even semiconducting hosts can be transformed into superconducting materials following intercalation of the appropriate atom or molecule. These are normally electron-transfer mediated intercalation reactions and the injected electrons go into the electron band manifold on the host lattice. For example, intercalation of the layered metal disulfides such as 2H-TaS_2 or 2H-$SnSe_2$ with electron-rich metallocene guest molecules produces superconducting materials with T_c values of 2.3 and 8.6 K respectively.[1,2] Controlled intercalation of solid C_{60} with the appropriate amounts of alkali or alkaline earth elements yields superconducting phases with T_c values above 40 K.[3]

Recently, Yamanaka *et al.* have reported that β-ZrNCl intercalated with lithium ions becomes superconducting below 15 K.[4,5] Subsequently, they found that the T_c could be controlled by varying the amount of lithium intercalated between the layers. The highest T_c obtained to date for this system is 25.5 K for $Li_{0.48}(THF)_yHfNCl$.[6] The structure of the host lattice β-ZrNCl was recently reported as being isostructural with rhombohedral SmSI.[7] Here we describe a structural study of β-ZrNBr and β-HfNCl and report their lithium intercalation chemistry. We also report of the first intercalation compounds of the layered hosts α-ZrNX (X = Br, I).

Experimental

Host lattices

Highly crystalline samples of β-ZrNBr and β-HfNCl were synthesised by chemical vapour transport according to the method reported previously for β-ZrNCl.[8,9] α-ZrNBr and α-ZrNI were prepared in a similar manner by sublimation of NH_4X (X = Br, I) over ZrH_2 in a flow of ammonia. In the case of ZrNBr the temperature gradient used in the chemical vapour transport permits control of the polymorph obtained. The experimental conditions are summarised in Table 1.

Table 1 Experimental conditions used in the syntheses of MNX phases

	Synthesis temperature/ °C		Transport temperature[a]/ °C		
Product	Metal	NH_4X	From	To	Colour
β-ZrNBr	650	475	700	800	Pale green crystals
β-HfNCl	750	375	750	850	Cream crystals
α-ZrNBr	650	475	500	600	Yellow–green powder
α-ZrNI	750	570	750	850	Orange crystals

[a] Materials were vapour phase transported 15 cm.

Intercalation

For each of the four host lattices lithium intercalation was achieved by reaction of a suspension of the host lattice with a 2.5 M solution of BuLi in hexane at 60 °C for 1–2 days. In each case the product was black and intercalation was confirmed by the absence of Bragg reflections characteristic of the host lattice in the X-ray diffraction pattern. The guest stoichiometry was determined by atomic absorption elemental analysis.

Measurements

X-Ray powder diffraction patterns of both the host lattices and their intercalation compounds were recorded in transmission geometry on a Siemens D5000 diffractometer equipped with linear position sensitive detector using Cu Kα_1 radiation on samples sealed in 0.3 mm capillaries under an atmosphere of nitrogen. Structural refinements of the host lattices β-ZrNBr and β-HfNCl were performed using the GSAS suite.[10] The magnetic susceptibility of the intercalation compounds was recorded on a Quantum Design MPMS-5 SQUID magnetometer. The temperature dependence of the susceptibility was recorded in a magnetic field of 40 G on samples cooled in both the presence (FC) and absence of the field (ZFC). Critical field values were determined from measurement of the field dependence of the susceptibility below the transition temperature.

Results and discussion

The metal nitride halides, MNX, (M = Ti, Zr; X = Cl, Br, I) were first reported by Juza and Heners in 1964 along with a high temperature β-polymorph for ZrNCl and ZrNBr.[11] The low temperature α-polymorph, α-MNX (M = Ti, Zr; X = Cl, Br, I), adopts the orthorhombic FeOCl-type layered structure, containing zirconium nitride double layers between planes of halide ions.[11] The synthesis of β-ZrNCl and β-ZrNBr by chemical vapour transport yields more highly crystalline samples of these compounds than were previously available.[8,9] We have recently shown that β-ZrNCl is in fact isostructural with rhombohedral SmSI.[7]

Structural study of β-ZrNBr and β-HfNCl

A least squares refinement of the unit cell dimensions from the X-ray powder pattern of both β-ZrNBr and β-HfNCl suggested that they were isostructural with β-ZrNCl. Therefore in each case the powder XRD pattern was refined from the structural model based on our recently reported structure of β-ZrNCl.

In the case of β-ZrNBr the starting model consisted of a three layer unit cell with $a=3.60$ and $c=29.25$ Å in the space group $R\bar{3}m$. The final refinement of the capillary X-ray data consisted of 28 parameters (7 structural and 21 instrumental and background) with 3750 data points (49 reflections). 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. Final convergence was achieved at $\chi^2=2.47$, $R_{wp}=3.43\%$ and $R_{F^2}=14.18\%$ for a rhombohedral cell with $a=3.6382(2)$, $c=29.2596(17)$ Å. As a consequence of the hexagonal platelet morphology of the microcrystalline sample it was necessary to apply a preferred orientation term on the [001] direction using the March–Dollase model which refined to 0.67(1).[12,13] This value is comparable to that obtained for β-ZrNCl. The final Rietveld fit showing the observed, calculated and difference profiles is given in Fig. 1. Bond valence calculations gave values of 4.42 for Zr, 3.26 for N and 1.15 for Br.[14,15]

The structure of β-HfNCl was refined in an analogous manner from an initial three layer unit cell with $a=3.60$ and $c=27.75$ Å in the space group $R\bar{3}m$. The final refinement of the capillary X-ray data consisted of 28 parameters (7 structural and 21 instrumental and background) with 1460 data points (34 reflections). Final convergence was achieved at $\chi^2=0.67$, $R_{wp}=1.89$ and $R_{F^2}=18.07$ for a rhombohedral cell with $a=3.5725(4)$, $c=27.736(2)$ Å. The preferred orientation parameter on the [001] direction refined to 0.64(1) indicating a similar degree of preferred orientation to the zirconium analogues. The final Rietveld fit showing the observed, calculated and difference profiles is given in Fig. 2. Bond valence calculations gave values of 4.41 for Hf, 3.49 for N and 0.92 for Cl.[14,15]

The crystallographic data for both refinements is summarised in Table 2 and the atomic parameters presented in Tables 3 and 5. The crystallographic data for β-ZrNCl are included in Table 2 for comparison though full details of the refinement have been published elsewhere.[7]

β-ZrNBr and β-HfNCl adopt the SmSI structure[16,17] in which each M atom is seven coordinate in a distorted monocapped octahedral arrangement with three halide atoms and three N atoms in a *fac*-arrangement with a fourth capping nitrogen above the N_3 face. These monocapped octahedral units are arranged in an edge sharing manner forming the XMNNMX layer structure. The structure of β-ZrNBr is shown in Fig. 3 and interatomic distances and angles of all three metal nitride halides are summarised in Table 4.

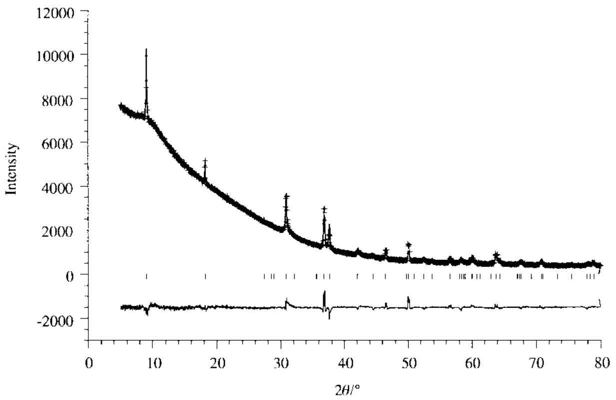

Fig. 1 Final Rietveld fit for β-ZrNBr: crosses represent the observed data, the solid line is the calculated pattern and the allowed reflection positions and difference profile are shown underneath.

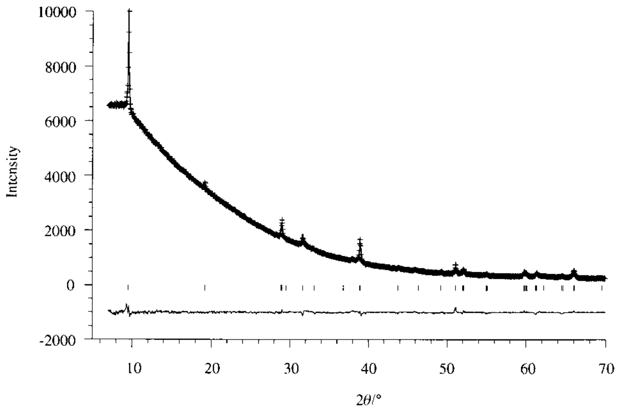

Fig. 2 Final Rietveld fit for β-HfNCl: crosses represent the observed data, the solid line is the calculated pattern and the allowed reflection positions and difference profile are shown underneath.

Table 2 Summary of crystallographic data for structurally characterised β-MNX (M=Zr, Hf; X=Cl, Br) (esds in parentheses)

	β-ZrNCl[7]	β-ZrNBr	β-HfNCl
a/Å	3.6052(1)	3.6382(2)	3.5725(4)
c/Å	27.6716(7)	29.2596(17)	27.7362(24)
V/Å^3	311.48(1)	335.41(4)	306.56(5)
Space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
D_c/g cm^{-3}	4.50	5.50	7.41
No. parameters refined	30	28	28
No. of data points	3549	3750	1460
No. of reflections	46	49	34
Zero point correction	−0.43	−0.20	0.69
Preferred orientation	0.72(1)	0.67(1)	0.64(1)
R_{wp} (%)	2.40	3.43	1.89
R_{F^2} (%)	16.40	14.18	18.07
χ^2	2.07	2.47	0.67

Table 3 Fractional atomic coordinates and thermal parameters for β-ZrNBr (esds in parentheses)

Atom	x	y	z	U/Å^2
Zr	2/3	1/3	0.7106(2)	0.0051(11)
N	2/3	1/3	0.0395(9)	0.0051(11)
Br	2/3	1/3	0.4452(1)	0.0029(9)

Comparison of the geometric parameters around the metal ions in β-ZrNCl and β-HfNCl structures suggests that the M–N$_{cap}$ is the most sensitive to the change from Zr to Hf, varying from 2.492(1) to 2.57(7) Å. There is no significant change in the terminal M–N bond lengths between the two structures. Between β-ZrNCl and β-ZrNBr the M–N distance is the most sensitive to the change in the halide ion, varying from 2.086(1) to 2.105(1) Å for the chloride and bromide derivatives respectively.

Intercalation reactions

The intercalation of lithium in β-ZrNCl was first reported in 1984 and subsequent studies showed that other alkali metals could also be intercalated into this lattice.[18,19] Intercalation of other materials that adopt the rhombohedral SmSI structure has also been observed previously. For example, intercalation of pyridine in YbOCl has been reported by Odink *et al.*[20] We have recently reported that intercalation of alkyl substituted cobaltocenes in β-ZrNCl produces new superconducting materials with T_c values of *ca.* 14 K.[21]

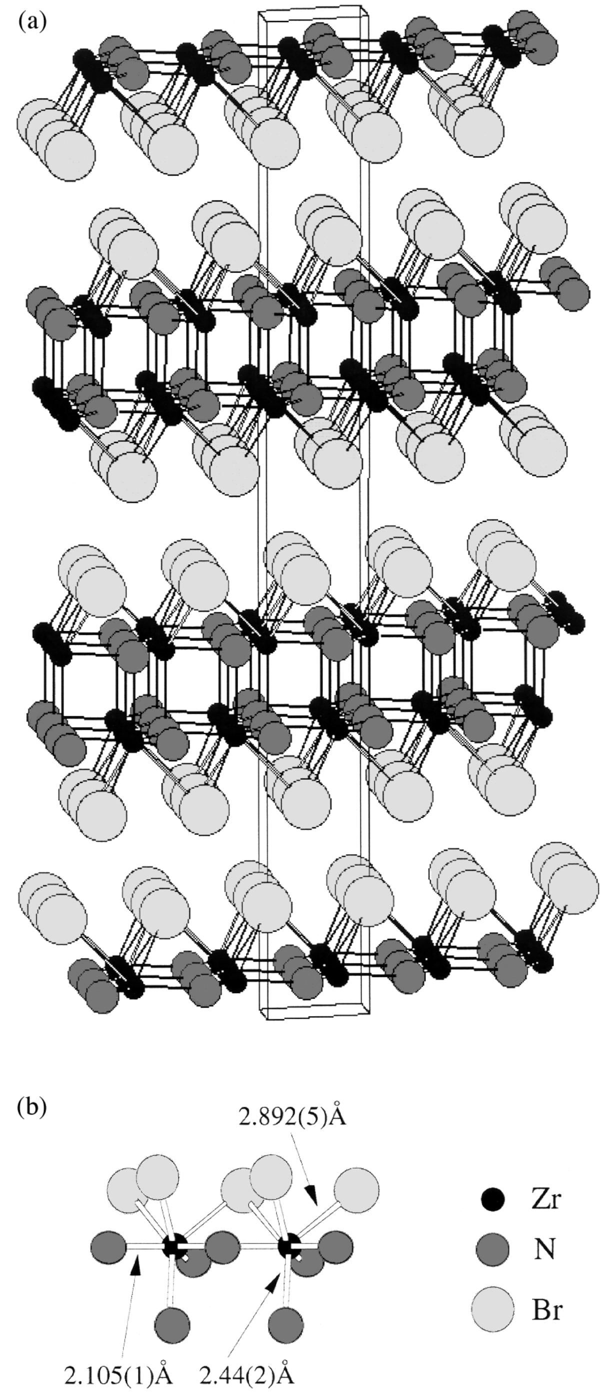

Fig. 3 (a) Structure of β-ZrNBr; (b) local coordination geometry of Zr in β-ZrNBr.

Table 4 Summary of the interatomic distances (Å) and angles (°) in β-MNX (M = Zr, Hf; X = Cl, Br) (esds in parentheses)

	β-ZrNCl[7]	β-ZrNBr	β-HfNCl
M–N	2.086(1)	2.105(1)	2.064(2)
M–N_{cap}	2.492(1)	2.44(2)	2.57(7)
M–X	2.754(3)	2.892(5)	2.738(13)
N–M–N	119.6(1)	119.6(2)	119.9(2)

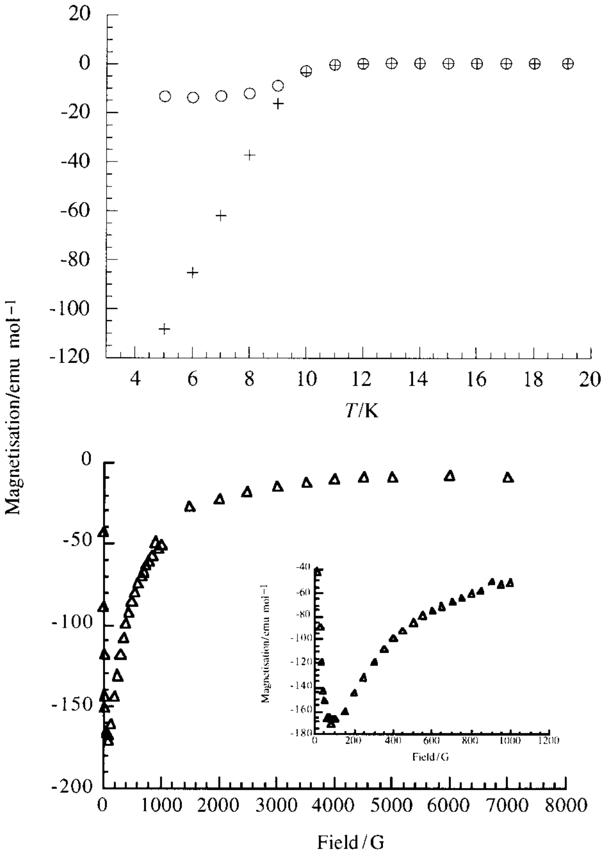

Fig. 4 (a) Temperature dependence of the magnetisation of $Li_{0.15}ZrNBr$ in a field of 40 G (+ = ZFC, ○ = FC); (b) field dependence of the magnetisation at 3 K.

Intercalation of β-ZrNBr

Intercalation of lithium into β-ZrNBr was achieved by reaction of a suspension of the host lattice with BuLi in hexane yielding a black crystalline solid. Elemental microanalysis data gave the stoichiometry as $Li_{0.15}ZrNBr$. The interlayer separation of the intercalate is 9.88 Å compared with 9.76 Å for the host. This is the first example of intercalation into this host lattice. The temperature dependence of the magnetisation of $Li_{0.15}ZrNBr$ was recorded and the data indicated a superconducting transition at 12 K. The field dependence of the magnetisation was measured at 3 K. The magnetisation data show that $Li_{0.15}ZrNBr$ is a type II superconductor. The magnetic data are shown in Fig. 4.

The field dependence measurements yield lower and upper critical fields of $H_{c1} = 80$ G and $H_{c2} \approx 9000$ G respectively. The shielding fraction can be estimated as being 80% indicating that $Li_{0.15}ZrNBr$ is a bulk superconductor. From the data it is apparent that the behaviour of $Li_{0.15}ZrNBr$ is very similar to the intercalation compounds of β-ZrNCl.

Intercalation of β-HfNCl

Intercalation of lithium into β-HfNCl was achieved by treatment of a suspension of the host with a hexane solution of BuLi for 2 days. A black solid was obtained with the stoichiometry $Li_{0.11}HfNCl$. The interlayer separation of the intercalate is 9.37 Å compared with 9.24 Å for the host. Yamanaka *et al.* have reported materials with significantly higher loading of lithium. For example, treatment of β-HfNCl with lithium naphthalide gives $Li_{0.48}(THF)_yHfNCl$.[4,6]

The temperature dependence of the magnetisation of $Li_{0.11}HfNCl$ was measured and the data clearly show the onset of superconductivity at 20 K. The field dependence of the magnetisation was measured at 3 K. The magnetisation data indicate that it is a type II superconductor (Fig. 5). From the field dependence measurements the lower and upper critical fields can be estimated as being $H_{c1} = 200$ G and $H_{c2} \approx 5000$ G respectively. The shielding fraction is estimated to be 20%. We believe the relatively low value of the shielding fraction for $Li_{0.11}HfNCl$ is a result of some decomposition due to the extreme air sensitivity of the sample.

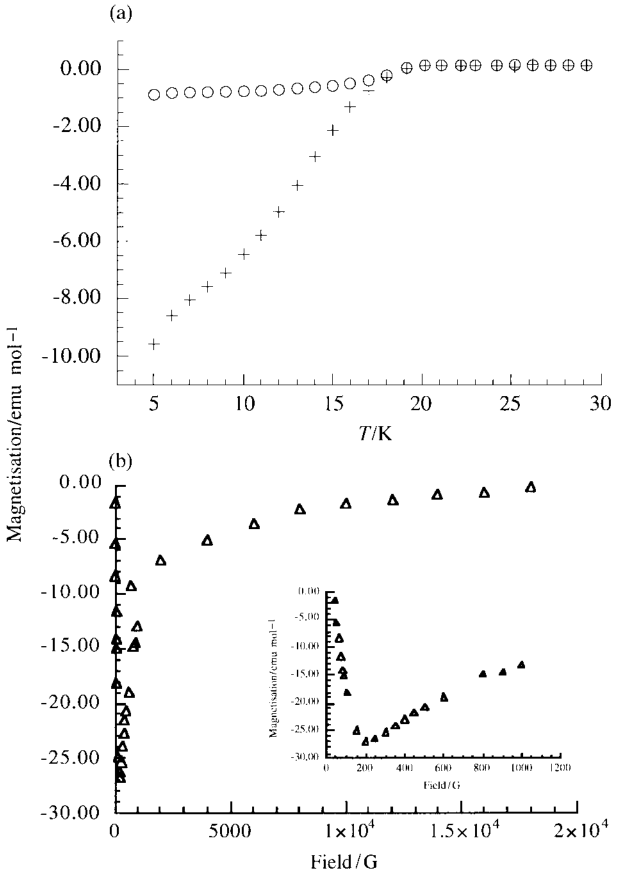

Fig. 5 (a) Temperature dependence of the magnetisation of $Li_{0.11}HfNCl$ in a field of 40 G (+ = ZFC, ○ = FC); (b) field dependence of the magnetisation at 3 K.

Table 5 Fractional atomic coordinates and thermal parameters for β-HfNCl (esds in parentheses)

Atom	x	y	z	$U/\text{Å}^2$
Hf	2/3	1/3	0.7142(2)	0.017(3)
N	2/3	1/3	0.0452(3)	0.017(3)
Cl	2/3	1/3	0.4458(8)	0.0010(8)

Discussion of β-MNX intercalation compounds

It has proved possible to synthesise the first intercalation compound of β-ZrNBr and a new intercalate of β-HfNCl. These lithium intercalates show superconducting transition temperatures of 12 and 20 K, respectively. In the case of $Li_{0.15}ZrNBr$ the transition temperature is similar to those observed in intercalation compounds of β-ZrNCl with a comparable doping level.[4,5,21] The observation that the transition temperatures are relatively independent of the halide layer coupled with the fact that the nature of the guest has no effect on the T_c indicates that the superconductivity is largely confined to the thin ZrN layers. The existence of superconductivity in these compounds is perhaps not surprising given the structural similarities between the ZrN layers and zirconium nitride which is itself a superconductor below 9.05 K.[7,22]

Table 6 Summary of analytical and electronic data for intercalation compounds

Host	Intercalation compound	Intercalate interlayer separation, c/Å	Interlayer expansion, Δc/Å	T_c/K
β-ZrNBr	$Li_{0.15}ZrNBr$	9.88	0.12	12
β-HfNCl	$Li_{0.11}HfNCl$	9.37	0.13	20
α-ZrNBr	$Li_{0.9}ZrNBr$	8.72	0	11
α-ZrNI	$Li_{0.7}ZrNI$	9.44	0	11

The lithium intercalation compound of β-HfNCl described above differs from that recently reported by Yamanaka *et al.*[6] in that it has a different stoichiometry and contains no co-intercalated solvent. As the transition temperature in the zirconium system has been shown to be independent of the interlayer separation for a fixed doping level but to vary as a function of the doping level it is likely, therefore, that the latter factor is the main cause of the difference in the observed transition temperatures.[4,5,21] As β-HfNCl is isostructural with β-ZrNX (X = Cl, Br) the superconductivity is likely to occur in the HfN layers which is reasonable given the structural similarities with hafnium nitride which is superconducting below 8.8 K.[23] What is less obvious however is why the intercalates of β-HfNCl have higher transition temperatures than their zirconium analogues when in the binary nitrides the zirconium compound displays the higher T_c. This may be related to the shorter M–N bond lengths in β-MNX as compared to MN, the different N–M–N bond angles (119.6° in MNX and 90° in MN), the absence of alternate layers of M atoms or a combination of these factors. It is hoped that future band structure calculations will provide an insight into the origin of the superconductivity in these compounds.

Intercalation of α-ZrNX (X = Br, I)

The reaction of a hexane solution of BuLi with a suspension of α-ZrNX (X = Br, I) yielded black intercalation compounds with compositions $Li_{0.9}ZrNBr$ and $Li_{0.7}ZrNI$. X-Ray powder diffraction patterns of these materials showed that the lithium is intercalated into these hosts with no apparent increase in the interlayer separation. In fact they could both be indexed on the same cell as their respective host lattices. No evidence for the formation of any other phases was observed. These are the first reported intercalation compounds of these host lattices. The intercalation of lithium ions into the isostructural host FeOCl has also been observed to occur with no change in interlayer separation.[24] It was proposed that for doping levels of less than one Li per FeOCl that the Li atoms can occupy octahedral holes, in which they are surrounded by five chlorine atoms and one oxygen atom, without perturbing the structure.

The temperature dependence of the magnetisation for both $Li_{0.9}ZrNBr$ and $Li_{0.7}ZrNI$ was measured following cooling in zero field (ZFC) and in a magnetic field of 40 G. The magnetisation data for $Li_{0.9}ZrNBr$ are shown in Fig. 6 and a superconducting transition is observed below 11 K. $Li_{0.7}ZrNI$ also exhibits a superconducting transition at 11 K. The field dependence of magnetisation was measured at 3 K for both intercalates and the data are indicative of type II superconductors. The similarity of the transition temperatures between the

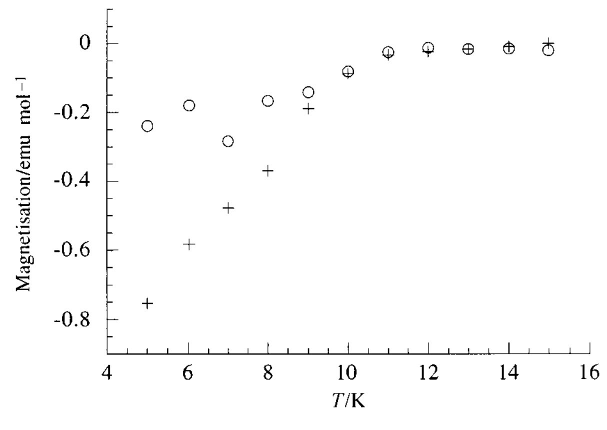

Fig. 6 Temperature dependence of the magnetisation of $Li_{0.9}ZrNBr$ in a field of 40 G (+ = ZFC and ○ = FC).

two compounds suggests that the superconductivity may be largely confined to the two-dimensional ZrN double layers.

Band structure calculations have been performed for all the α-MNX compounds.[25] These crystal orbital overlap population calculations suggest that the largely metal based conduction band is predominantly M–N bonding and M–X antibonding in nature with a small degree of M–M bonding character. These calculations can be used to rationalise why the same transition temperature is observed regardless of the halide in the host lattice.

References

1 A. H. Thompson and F. R. Gamble, *Bull. Am. Phys. Soc.*, 1975, 289.

2 C. A. Formstone, E. T. Fitzgerald, D. O'Hare, P. A. Cox, M. Kurmoo, J. W. Hodby, D. Lillicrap and M. Goss-Custard, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 501.

3 M. J. Rosseinsky, *J. Mater. Chem.*, 1995, **5**, 1497.

4 S. Yamanaka, H. Kawaji, K. Hotehama and M. Ohashi, *Adv. Mater.*, 1996, **8**, 771.

5 H. Kawaji, K. Hotehama and S. Yamanaka, *Chem. Mater.*, 1997, **9**, 2127.

6 S. Yamanaka, K. Hotehama and H. Kawaji, *Nature*, 1998, **392**, 580.

7 A. M. Fogg, J. S. O. Evans and D. O'Hare, *Chem. Commun.*, 1998, 2269.

8 M. Ohashi, S. Yamanaka and M. Hattori, *J. Solid State Chem.*, 1988, **77**, 342.

9 M. Ohashi, S. Yamanaka, M. Sumihara and M. Hattori, *J. Solid State Chem.*, 1988, **75**, 99.

10 A. C. Larson and R. B. von Dreele, *GSAS—Generalised Structure Analysis System*, LA-UR-86–748, Los Alamos National Laboratory, CA, 1987.

11 R. Juza and J. Heners, *Z. Anorg. Allg. Chem.*, 1964, **332**, 159.

12 A. March, *Z. Kristallogr.*, 1938, **81**, 285.

13 W. A. Dollase, *J. Appl. Crystallogr.*, 1986, **19**, 267.

14 I. D. Brown and D. Altermatt, *Acta Crystallogr.*, *Sect. B*, 1985, **41**, 244.

15 N. E. Brese and M. O'Keefe, *Acta Crystallogr.*, *Sect. B*, 1991, **47**, 192.

16 N. Savigny, P. Laurelle and J. Flahaut, *Acta Crystallogr.*, *Sect. B*, 1973, **29**, 345.

17 H. P. Beck and C. Strobel, *Z. Anorg. Allg. Chem.*, 1986, **535**, 229.

18 M. Ohashi, S. Yamanaka, M. Sumihara and M. Hattori, *J. Inclusion Phenom.*, 1984, **2**, 289.

19 M. Ohashi, K. Uyoeka, S. Yamanaka and M. Hattori, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2814.

20 D. A. Odink, K. Song and S. M. Kauzlarich, *Chem. Mater.*, 1992, **4**, 906.

21 A. M. Fogg, V. M. Green and D. O'Hare, *Chem. Mater.*, 1999, **11**, 216.

22 B. T. Matthias and J. K. Hulm, *Phys. Rev.*, 1952, **87**, 799.

23 B. W. Roberts, *J. Phys. Chem. Ref. Data*, 1976, **5**, 581.

24 P. Palvadeau, L. Coic, J. Rouxel and J. Portier, *Mater. Res. Bull.*, 1978, **13**, 221.

25 P. M. Woodward and T. Vogt, *J. Solid State Chem.*, 1998, **138**, 207.

Paper 8/09735F