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Preparation and Superconductivity of Chlorine-Deintercalated Crystals β-MNCl$_{1-x}$ (M = Zr, Hf)

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The layer structured crystals β-MNCl (M = Zr, Hf) consist of rhombohedrally stacked six-layer [Cl−M−N−N−M−Cl] slabs, each of which is composed of a strongly bonded honeycomb-like double MN layer sandwiched by two close-packed chlorine layers. A part of the chlorine atoms was deintercalated by the reaction with alkali metals (A) formed by the thermal decomposition of the azides AN_3 (A = Na, K, Rb). Upon the partial deintercalation of chlorine atoms, electrons were doped into the MN layers, and the semiconducting β-MNCl changed into superconductors with the transition temperatures (T_c's) of 13−14 and 23−24 K for M = Zr and Hf, respectively. The thermal stability and the structure of the deintercalated phase β-MNCl$_{1-x}$ are discussed.

Introduction

The structure of β-MNCl (M = Zr, Hf) consists of honeycomb-like double MN layers sandwiched by closed-packed chlorine layers as shown in Figure 1.[1−6] β-MNCl can be electron-doped by intercalation of lithium between the layers. The Li intercalation can be carried out using a butyllithium solution in hexane and a lithium naphthalene solution in tetrahydrofuran (THF).[7,8] Upon intercalation, the semiconducting host crystals are changed into superconductors with $T_c = 14$ and 25.5 K for M = Zr and Hf, respectively.[9,10] Other kinds of alkali metals[8] and cobaltocene[11] have been intercalated into these layered crystals using organic reagents. In a recent study, the intercalation of divalent ions such as zinc was carried out by an electrochemical method.[12] We have tried Na metal intercalation into β-ZrNCl using Na vapor in a sealed glass tube at elevated temperatures of about 500 °C.[13] However, Na intercalation did not occur, but chlorine layers were deintercalated, forming ZrN layers topotactically. The resulting ZrN honeycomb layers are stretched along the plane to form ZrN of the rock salt structure.

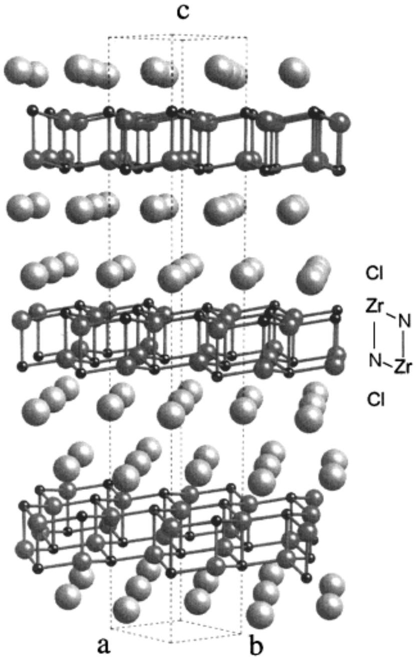

Figure 1. Structure model of β-ZrNCl.

In this study, alkali metal doping has been attempted using alkali metal azides AN_3 (A = Li, Na, K, Rb) at elevated temperatures. Alkali metal azides can be easily purified by recrystallization from ethanol solutions, and the respective pure alkali metals can be produced by thermal decomposition at relatively low temperatures in a dry system.[14] The amount of alkali metals can be controlled by controlling the mixed ratio to β-MNCl.

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[1] Juza, V. R.; Friedrichsen, H. A. *Z. Anorg. Allg. Chem.* **1964**, *332*, 173.

[2] Fuertes, A.; Vlassov, M.; Beltrán-Porter, D.; Alemany, P.; Canadell; Casañ-Pastor, N.; Palacín, M. R. *Chem. Mater.* **1999**, *11*, 203.

[3] Istomin, S. Y.; Kohler, J.; Simon, A. *Physica C* **1999**, *319*, 219.

[4] Yamanaka, S. *Annu. Rev. Mater. Sci.* **2000**, *30*, 53.

[5] Chen, X.; Koiwasaki, T.; Yamanaka, S. *J. Solid State Chem.* **2001**, *159*, 80.

[6] Shamoto, S.; Kato, T.; Ono, Y.; Miyazaki, Ohoyama, K.; Ohashi, M.; Yamaguchi, Y.; Kajitani, T. *Physica C* **1998**, *306*, 7.

[7] Ohashi, M.; Yamanaka, S.; Sumihara, M.; Hattori, M. *J. Inclusion Phenom.* **1984**, *2*, 289.

[8] Ohashi, M.; Uyoeka, K.; Yamanaka, S.; Hattori, *M. Bull. Chem. Soc. Jpn.* **1991**, *64*, 2814.

[9] Yamanaka, S.; Kawaji, H.; Hohetama, K.; Ohashi, M. *Adv. Mater.* **1996**, *8*, 771.

[10] Yamanaka, S.; Hohetama, K.; Kawaji, H. *Nature (London)* **1998**, *392*, 580.

[11] Fogg, A. M.; Green, V. M.; O'hare D. *Chem. Mater.* **1999**, *11*, 216.

[12] Arroyo y de Dompablo, M. E.; Moran, E.; Alario-Franco, M. A.; Drymiotis, F.; Bianchi, A. D.; Fisk, Z. *Int. J. Inorg. Mater.* **2000**, *2*, 581.

[13] Zhu, L.; Ohashi, M.; Yamanaka, S. *Chem. Mater.* **2002**, *14*, 4517.

[14] Fukuoka, H.; Isami, T.; Yamanaka, S. *Chem. Lett.* **1997**, 703.

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Table 1. Decomposition Temperature ($T_{\mathrm{decomp.}}$) of Metal Azides, Reaction Temperature (T_{reaction}) with β-MNCl (M = Zr, Hf), and the First Annealed Temperature ($T_{\mathrm{anneal.}}$)

	$T_{\mathrm{decomp.}}$ (°C)	T_{reaction} (°C)	$T_{\mathrm{anneal.}}$ (°C)
LiN_3	320	270−290	300
NaN_3	380	320−350	350
KN_3	340	260−280	300
RbN_3	300	240−260	260

When small amounts of azides are used, alkali metal atoms are not intercalated between the layers, but instead chlorine atoms are deintercalated by the alkali atoms forming metal chlorides outside the host crystals. Upon deintercalation, electrons are doped into MN layers, and the semiconducting β-MNCl is converted into superconductors. This is a new method for electron doping by deintercalation of chlorine atoms.

Experimental Section

Materials. β-MNCl (M = Zr, Hf) was prepared by the reaction of ZrH_2 (99%) and Hf (99%) powders with NH_4Cl (99.5%) at 650 °C for 30 min.[15] The as-prepared β-MNCl was vacuum-sealed with a small amount of NH_4Cl in a quartz tube and chemically transported from the low-temperature zone to the high-temperature zone in a furnace with a temperature gradient of 750−850 °C as described elsewhere.[16] Metal azides, AN_3 (A = Li, K, Rb) were prepared from NaN_3 (Katayama Chemicals) by ion exchange.[17,18] All the azides were purified by recrystallization from the respective ethanol solutions.

The obtained layer-structured β-MNCl (M = Zr, Hf) were mixed with metal azides AN_3 (A = Li, Na, K, Rb) in different molar ratios. Each mixture was filled in an h-BN cell (7 mm in inner diameter and 8 mm in depth) with a cover, which was placed in an evacuable glass tube. The mixture in the h-BN cell was heated in a vacuum to decompose the azides into the respective alkali metals and nitrogen at temperatures ranging from 240 to 350 °C. The start of the decomposition was monitored as the increase of the pressure due to the evolution of nitrogen gas and the completion of the decomposition was decided by the recovery of the pressure to the starting value. The decomposition temperatures ($T_{\mathrm{decomp.}}$) of azides alone observed in a vacuum and the reaction temperatures ($T_{\mathrm{react.}}$) in the mixtures with β-MNCl are listed in Table 1. $T_{\mathrm{react.}}$'s of the mixtures are lower than the corresponding $T_{\mathrm{decomp.}}$'s without the presence of β-MNCl. This may suggest that the decomposition of alkali metal azides are catalyzed with the presence of β-MNCl. Various molar mixing ratios (0.3−1.0) of azides to β-ZrNCl were examined. After the completion of the azide decomposition, the glass tubes were vacuum-sealed and subjected to further annealing at different temperatures in a range of 300−550 °C. The first annealing was performed at the temperatures ($T_{\mathrm{anneal.}}$'s) shown in Table 1 for 1 day.

Characterization. After the first annealing, an aliquot of each powder sample was separated into a quartz glass tube in an Ar-filled glovebox to measure the magnetic susceptibility using a SQUID magnetometer (MPMS-5, Quantum Design). The quartz glass tube was vacuum-sealed and subjected to further annealing at higher temperatures up to 550 °C. The magnetic susceptibility was measured after each step of annealing at different temperatures for 1 day. The rest of the powder sample was also thermally treated in a similar manner under vacuum to measure the powder X-ray diffraction (XRD) pattern. The XRD patterns were measured under an Ar atmosphere using a goniometer covered with polyethylene films (MAC Science 18XT). Since the layer-structured β-MNCl was highly preferred oriented with the basal plane parallel to the plane of the glass plate for the XRD measurement, an imaging plate (IP) detector (Rigaku RAPID) was used to measure X-ray diffraction peaks due to *hkl* as well as 00*l* reflections on the sample filled in a glass capillary using graphite monochromated Cu Kα (λ = 1.5418 Å) radiation. The electrical resistivity was measured on the powder sample compressed (1.5 × 7.0 × 0.01 mm^3) under a hydrostatic pressure of 1500 kg/cm^2 using a four-probe dc method for a temperature range of room temperature to 4 K.

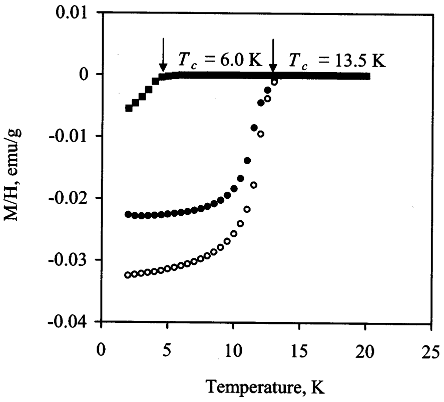

Figure 2. Magnetic susceptibility of the product obtained by the reaction of β-ZrNCl with NaN_3 in a molar ratio of NaN_3/β-ZrNCl = 0.3 and annealed at different temperatures: ●, 350; ○, 450; ■, 550 °C.

Results

1. Reaction of β-ZrNCl with NaN_3. A mixture of NaN_3 and β-ZrNCl in a molar ratio of 0.3:1 was heated at 320 °C until complete decomposition in an h-BN cell placed in a Pyrex glass tube and then it was vacuum-sealed. The azide was decomposed to Na metal and nitrogen gas. Upon decomposition, the color of β-ZrNCl was changed from the starting pale yellow green into black. The magnetic susceptibility measured on the sample after the first annealing at 350 °C is shown in Figure 2. We already reported that β-ZrNCl was changed into a superconductor with T_c = 13−14 K by electron doping via intercalation of alkali metal,[9,10] the basal spacing being increased with the ionic radii of the intercalated alkali metals. As can be seen in Figure 2, a similar superconducting transition was observed at 13.5 K for the sample treated with Na formed by the decomposition of NaN_3. The superconducting fraction was estimated to be ~90% from the diamagnetic value observed in the zero-field-cooling (ZFC) mode at 5 K. The fraction increased on annealing at a higher temperature of 450 °C, but disappeared after the annealing at 550 °C. A small fraction of superconductivity with T_c = 6 K was observed on the sample annealed at 550 °C. Figure 3 shows the resistivity of the sample annealed at 350 °C as a function of temperature. The resistivity curve clearly had a superconducting transition at 13 K (on set), consistent with the transition observed in the magnetic susceptibility curve. The increase of the resistivity observed just before the onset of superconductivity on cooling appears to be due to the presence of grain boundaries in the compressed-powder sample.

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(15) Ohashi, M.; Yamanaka, S.; Sumihara, M.; Hattori, M. *J. Solid State Chem*, **1988**, *75*, 99.

(16) Ohashi, M.; Yamanaka, S.; Hattori, M. *J. Solid State Chem.* **1988**, *77*, 342.

(17) Dion, M.; Piffard, Y.; Tournoux, M. *J. Inorg. Nucl. Chem.* **1978**, *40*, 917.

(18) Andersson, S.; Wedsley, A. D. *Nature (London)* **1960**, *187*, 499.

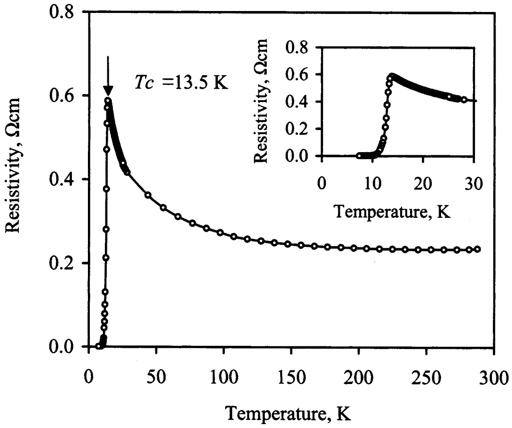

Figure 3. Temperature dependence of the electrical resistivity of β-ZrNCl reacted with NaN_3 in a molar ratio of 1/0.3 and annealed at 350 °C. The inset shows the temperature dependence in a low-temperature range.

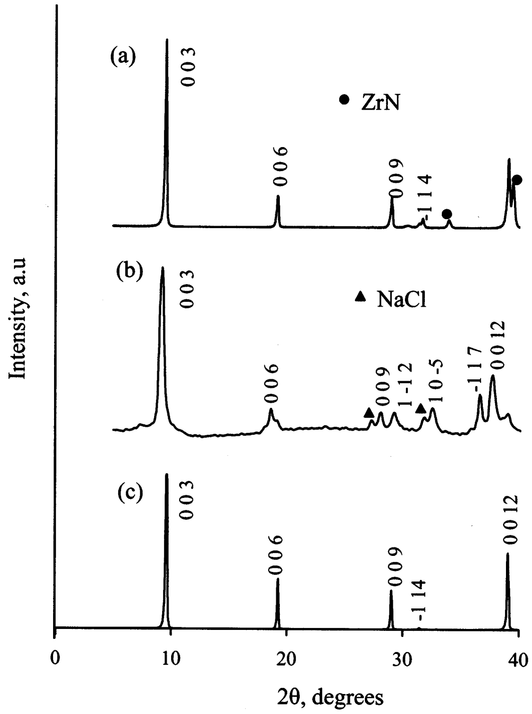

Figure 4. XRD patterns of the pristine β-ZrNCl (a) and the product with NaN_3 in a molar ratio of NaN_3/β-ZrNCl = 0.3 annealed at 350 °C (b) and 800 °C (c) in a vacuum.

Figure 4 compares the XRD patterns of the annealed sample shown in Figure 2, together with that of the pristine β-ZrNCl. Owing to the layered nature, the sample was highly oriented with the basal plane parallel to the glass plate and showed strong peaks due to the basal reflections. The peaks were broadened by the treatment with NaN_3, and the formation of NaCl was detected. The basal spacing was slightly increased to 9.8 Å from 9.2 Å of the pristine β-ZrNCl. In previous studies[8,9] Li- and Na-intercalated β-MNCls were prepared using a *n*-butyllithium solution in hexane and a Na−naphthalene solution in THF, respectively. The basal spacing of the Li-intercalated compound was almost unchanged because the ionic size of Li was small enough to be accommodated in the interstices of chlorine-packed layers. However, the ionic radius of Na was much larger than that of Li, and the spacing increased from 9.2 to 10.4 Å upon intercalation.

It was evident that electrons were doped by the reaction with NaN_3 in this study, but the increase in the spacing was too small for the intercalation of Na ions. On the disappearance of the superconductivity by the annealing at high temperatures, the XRD pattern of the sample reverted to that of pristine β-ZrNCl accompanied by that of ZrN as shown in Figure 4c.

When a higher mixing ratio of 1:1 for NaN_3/ZrNCl was used in the reaction, β-ZrNCl was changed into ZrN at 300 °C. This suggests that the following reaction occurred:

$$\beta\text{-ZrNCl} + \text{NaN}_3 \rightarrow [\beta\text{-ZrNCl} + \text{Na} + {}^3/_2\text{N}_2] \rightarrow \text{ZrN} + \text{NaCl} \quad (1)$$

The resulting ZrN powder showed superconductivity with a transition at $T_c = 6$ K. In a previous study,[13] we reported that ZrN was obtained by the reaction of β-ZrNCl with Na vapor, whose crystal size was comparable with the coherence length of the superconductivity; the T_c of the ZrN fine powder decreased with the decrease of the particle size. The T_c observed (6 K) for this sample was also much lower than 10 K reported for the bulk sample of ZrN,[19−20] which can be interpreted in terms of the small particle size.[21]

2. Reaction of β-ZrNCl with AN_3 (A = Li, K, Rb). Similar reactions were carried out on β-ZrNCl using different kinds of alkali metal azides AN_3 (A = Li, K, Rb). The reaction products with KN_3 and RbN_3 in a molar ratio of AN_3/ZrNCl = 0.3/1 changed into black and green black, respectively, and showed a superconducting transition at 13 K by the SQUID measurement. The superconducting fractions determined on the K- and Rb-reacted samples were again as high as >80%. The reaction of LiN_3 changed the color of β-ZrNCl to gray, but the superconducting fraction was as small as <5%. This suggests that LiN_3 is not so reactive with β-ZrNCl compared with the other azides. It is likely that only the surface of β-ZrNCl crystals was changed. The Rb-reacted sample was prepared by annealing at 300 °C; the superconductivity disappeared on annealing at 320 °C. Note that the thermal stability of the product is dependent on the kinds of alkali metals used. The lattice constants and other characteristics of the reaction products are summarized in Table 2. Note that the basal spacing of K- and Rb-reacted samples were unchanged from the pristine β-ZrNCl, although the ionic size of K and Rb are larger than Na. The XRD patterns of the products showed that the respective metal chlorides (KCl and RbCl) were also formed.

3. Reaction of β-HfNCl with KN_3. β-HfNCl was subjected to reaction with KN_3 in a molar ratio of KN_3/HfNCl = 0.3/1 and annealed at different temperatures in a similar manner as that used in the reaction of β-ZrNCl. Figure 5 shows the magnetic susceptibility of the reaction product annealed at different temperatures. The samples annealed at temperatures ranging between

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(19) Liang, C. L.; Cheung, N. W. *J. Vac. Sci. Technol., B* **1987**, *5*, 1716.

(20) Pesall, N.; Gold, R. E.; Johansen, H. A. *J. Phys. Chem. Solids* **1968**, *29*, 19.

(21) Zhu L.; Ohashi M.; Yamanaka S. *Mater. Res. Bull.* **2002**, *37*, 475.

Table 2. Crystal Structural Data and T_c's of β-ZrNCl, β-HfNCl, and Their Reaction Products with Metal Azides[a]

	β-ZrNCl				β-HfNCl			
RN_3:	–	NaN_3	KN_3	RbN_3	–	NaN_3	KN_3	RbN_3
structure	SmSI	YOF	SmSI	SmSI	SmSI	–	SmSI	SmSI
a, Å	3.6046(4)	3.614(2)	3.596(9)	3.602(2)	3.5767(8)	–	3.567(3)	3.572(2)
c, Å	27.672(4)	29.50(2)	27.70(7)	27.70(2)	27.711(7)	–	27.66(3)	27.74(3)
T_c, K	–	13.5	13.0	14.0	–	–	24	24.5
$T_{\text{anneal.}}$, °C	–	350	350	260	–	–	300	260
$T_{\text{disprop.}}$, °C	–	550	550	320	–	–	500	320

[a] The basal spacing $d = c/3$.

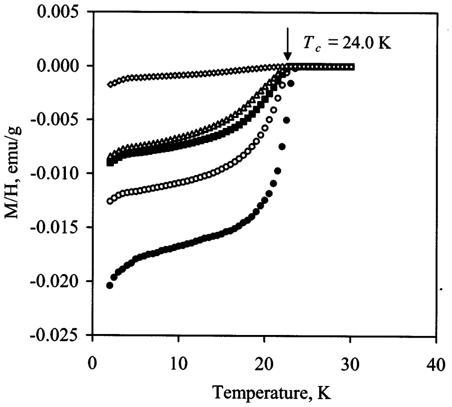

Figure 5. Magnetic susceptibility of the product obtained by the reaction of β-HfNCl with KN_3 in a molar ratio of KN_3/β-HfNCl = 0.3 and annealed at temperatures of (●) 300, (○) 320, (■) 350, (△) 400, and (◇) 500 °C.

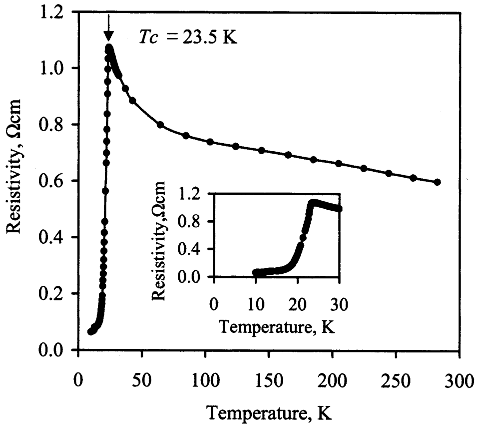

Figure 6. Temperature dependece of the electrical resisitivity of β-HfNCl reacted with KN_3 in a molar ratio of 1/0.3 and annealed at 350 °C. The inset shows the temperature dependence in a low-temperature range.

350 and 500 °C showed a superconducting diamagnetic transition at 24 K; the superconducting fraction decreased with the increase of the annealing temperature. Figure 6 shows the electric resistivity of the β-HfNCl sample annealed at 300 °C after the reaction with KN_3. Although zero resistivity was not attained down to 4 K, the superconducting transition was clearly observed at $T_c = 24$ K (onset). The T_c is in good agreement with the value determined by the magnetic measurement (Figure 5) and comparable with those found for alkali metal doped HfNCls prepared using alkali metal naphthalene solutions in THF.[10]

The XRD diffraction peaks of the annealed β-HfNCl after the reaction with KN_3 were slightly broadened, but the interlayer spacing was kept unchanged at 9.2 Å from the pristine β-HfNCl. The formation of KCl was also detected by the XRD measurement. The XRD pattern was measured using an IP detector, and the lattice constants were determined to be as listed in Table 2. It was also found that when a larger amount of KN_3 was used in a molar ratio of 1:1 with β-HfNCl, β-HfNCl was converted into HfN according to the equation

$$\beta\text{-HfNCl} + KN_3 \rightarrow HfN + KCl + {}^3/_2N_2 \qquad (2)$$

The obtained HfN powder sample showed superconductivity with $T_c = 4.5$ K, which was much lower than the T_c of 8.5 K for bulk HfN. This is due to the small particle size comparable with the coherence length.[22–24] In all the magnetic susceptibility curves shown in Figure 5 for the β-HfNCl sample annealed at different temperatures after the reaction with KN_3, a diamagnetic drop was observed at about 4.5 K. This probably suggests the coexistence of HfN formed on the edge of the crystals.

4. Reaction of β-HfNCl with AN_3 (A = Li, Na, Rb). It was found that Li and Na azides were not reactive with β-HfNCl. The gray color products were obtained, but showed a superconducting shielding volume fraction of <1%. RbN_3 was reactive with β-HfNCl to form a superconductor with $T_c = 24.5$ K and a bulk superconducting fraction of 35%. The formation of RbCl was detected by the XRD measurement. The superconducting compound was prepared by annealing at 300 °C. On annealing at 320 °C, the superconductivity disappeared. The crystal structural data and superconducting characteristics of the reaction products are listed in Table 2.

5. Polytypes. To avoid the preferred orientation of the layer-structured sample, X-ray oscillation photographs of the powder samples were measured using an IP detector. The data of the photograph was converted into the powder pattern using the $I-2\theta$ conversion program. Figure 7a shows the powder pattern thus obtained on the starting β-ZrNCl and that of the sample treated with Na azide and annealed at 350 °C. It should be noted that an intense diffraction peak of (-1 1 4) of β-ZrNCl disappeared, and instead an intense peak (1 0 -5) appeared in the powder diffraction pattern of the reaction product, although the spacing was almost unchanged (Figure 7b).

It is known that β-MNX has two kinds of polytypes, the SmSI and the YOF types.[25–27] The two polytypes

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(22) Minhaj, M. S. M.; Meepagala, S.; Chen, J. T.; Wegner, L. E. *Phys. Rev. B* **1994**, *49*, 15235.

(23) Wolf, S. A.; Kennedy, J. J.; Nisenoff, M. *J. Vac. Technol.* **1976**, *13*, 145.

(24) Lefloch, F.; Hoffmann, C.; Demolliens, O. *Physica C* **1999**, *39*, 258.

(25) Beck, H. P.; Strobel, C. *Z. Anorg. Allg. Chem.* **1986**, *535*, 229.

(26) Mann, A. W.; Bevan, D. J. M. *Acta Crystallogr.* **1970**, *B26*, 2129.

(27) Chen, X.; Fukuoka, H.; Yamanaka, S. *J. Solid State Chem.* **2002**, *163*, 77.

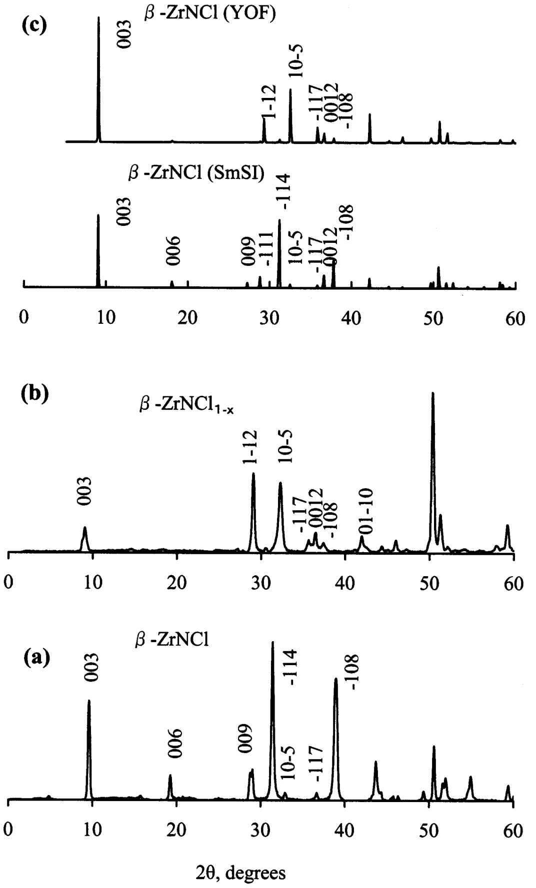

Figure 7. XRD pattern measured by an imaging plate detector for the product from the reaction of β-ZrNCl with NaN$_3$ (a) as compared to that of starting β-ZrNCl crystal (b) and the calculated XRD patterns of β-ZrNCl on the basis of SmSI and YOF polytypes (c).

differ in the stacking sequence of the six-layer [X−M−N−N−M−X] slabs. The slabs repeat in two different sequences of ABC and ACB for the SmSI and the YOF types, respectively. Our previous structural analysis[5,27] on the single crystals of all the combinations of β-MNX (M = Zr, Hf; X = Cl, Br, I) revealed that ZrNCl, HfNCl, and ZrNBr have the former polytype and ZrNI, HfNI, and HfNBr have the other polytype. We have also reported that β-ZrNCl with the SmSI structure was converted into the YOF type on intercalation of Li ions between the chlorine layers.[28] Similar changes were reported on the alkali metal intercalated β-ZrNCl and β-HfNCl powder samples using neutron diffraction by Shamoto et al.[6] The change of the stacking sequence on intercalation suggests the occurrence of a systematic shift of the six-layer slabs from the ABC to the ACB stacking. The X-ray diffraction patterns of β-ZrNCl calculated on the basis of the SmSI and the YOF polytypes are shown in Figure 7c. There are several characteristic reflections, (1 −1 2), (−1 1 4), (1 0 −5), (−1 1 7), and (−1 0 8). These peaks are very strong in only one polytype, while very weak in the other polytype. The intense reflection of (1 0 −5) was observed in the XRD pattern of the reaction product with Na azide, but the reflection for (−1 1 4) of β-ZrNCl disappeared. Similar comparisons on the characteristic reflections between the two powder diffraction patterns (Figure 7a,b) indicate that the layer structure is changed from the SmSI to the YOF type by the reaction with NaN$_3$.

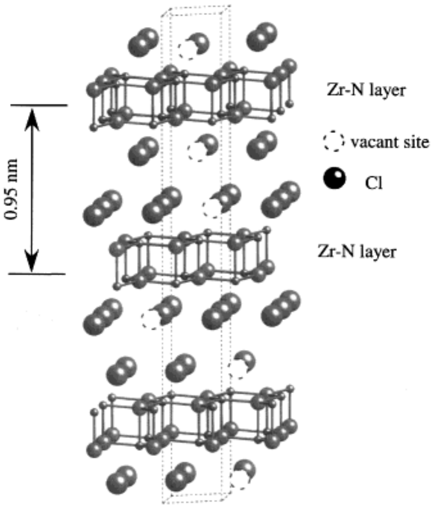

Figure 8. Schematic structural model of chlorine-deintercalated β-ZrNCl$_{1-x}$.

A similar study was performed on all of the reaction products, and the lattice constants and the polytype were determined, which are listed in Table 2. Only the reaction product of β-ZrNCl with NaN$_3$ changed into the YOF type. All the other products remained as the SmSI structure.

Discussion

In the reaction of β-ZrNCl with NaN$_3$, it is evident that the ZrN layers sandwiched by chlorine layers are electron-doped in a manner very similar to the alkali metal intercalation. However, the basal spacing of the crystals was kept essentially unchanged, and NaCl was formed outside the crystals. These findings suggest that the crystals are electron-doped according to the following reaction:

$$\beta\text{-ZrNCl} + x\text{NaN}_3 \rightarrow \text{ZrNCl}_{1-x} + x\text{NaCl} + (3x/2)\text{N}_2 \quad (3)$$

This reaction is not intercalation, but the chlorine ions are partially removed, or *deintercalated* by the reaction with Na to form NaCl. A schematic structural model of the chlorine-deintercalated compound is shown in Figure 8. It was apparent that a similar deintercalation of chlorine atoms occurred in the reaction of the other alkali azides with β-ZrNCl and β-HfNCl.

On heating to a higher temperature above 550 °C, the compound was decomposed, or disproportionated to β-ZrNCl and ZrN, according to eq 4. The disproportionation temperature ($T_{\text{disprop.}}$) is shown in Table 2 for each deintercalated compound. If it is a simple chlorine deintercalation, all the products should be very similar irrespective of the kinds of alkali metal azides used. However, as shown in the table, the product by the reaction with Na azide was most stable against heating, while the product by the reaction with Rb azide was only stable in a very narrow temperature range of heating

$$\text{ZrNCl}_{1-x} \rightarrow (1-x)\beta\text{-ZrNCl} + x\text{ZrN} \quad (4)$$

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[28] Chen, X.; Zhu, L.; Yamanaka, S. *J. Solid State Chem.* **2002**, *169*, 149.

and underwent the disproportionation at temperatures above 320 °C. The difference in the thermal stability could be explained in terms of the difference in the arrangement of the atoms of the interlayer surfaces as follows: Na and K ions are small enough to be encapsulated into the vacant sites left by the deintercalated chlorine ions, whereas Rb ions are too large in size to be placed in the vacant sites. The reaction with Na and K azides can be written as follows:

$$\beta\text{-MNCl} + (x + y)\text{AN}_3 \rightarrow \text{MN(Cl}_{1-x}\text{A}_y) + x\text{ACl (A} = \text{Na, K)} + {}^3/_2(x + y)\text{N}_2 \quad (5)$$

The reaction with RbN_3 should be a simple deintercalation like eq 3; the interlayer surface of the compound has more vacant sites in the chlorine layers, and the compound could be easily disproportionated according to eq 4. In the compounds derived by the reaction with Na and K azides, the defects of the chlorine layers are partially filled with the alkali metal ions and should be more stable against the disproportionation up to higher temperatures. It is strange that the basal spacing β-ZrNCl deintercalated by the reaction with NaN_3 was 9.8 Å, which was larger than 9.2 Å for the pristine β-ZrNCl, but smaller than 10.4 Å for the Na-intercalated one. The reason is not clear, but it is likely that it could be a mixed layer compound between the 9.2- and 10.4-Å phases, having an average spacing.[29]

When the reactions were carried out using sufficient amounts of azides to remove all of the chlorine layers, the crystals were converted into MN (eqs 1 and 2). This reaction occurs topotactically as studied in a previous paper.[13] The resulting nitrides were very thin, and the T_c was found to be very low, compared with those of the bulk samples. It is reasonable to assume that HfN was also formed in the reaction, even with a small amount of alkali metal azides on the surface of the crystals. In the measurement of the magnetic susceptibility of the reaction product of β-HfNCl (Figure 5), we have observed drops of the susceptibility at 24 and 4.5 K, which can be attributed to the superconducting transitions due to the electron-doped β-HNCl$_{1-x}$ and HfN, respectively.

The reaction of LiN_3 with β-ZrNCl and β-HfNCl occurred only on the surface of the crystals. Na azide did not react with β-HfNCl either. These products did not show superconductivity. On the other hand, heavy alkali metals reacted with β-MNCl, forming the chlorine-deintercalated superconductors as described above. The reactivity is in the order of $LiN_3 < NaN_3 < KN_3 < RbN_3$. This is the order of decreasing the first ionization energy of alkali metals, 520.3 (Li) > 495.8 (Na) > 418.9 (K) > 403.0 (Rb) kJ/mol.[30] The reaction should be initiated by a catalytic decomposition of alkali metal azides on the surface of β-MNCl crystals, and electrons are transferred from the alkali metal to β-MNCl. Alkali metal chloride is formed on the surface of the crystals, leaving the electrons in the ZrN layers. The formation of metal chloride will be preferable for the reaction. The smaller alkali ions will be energetically preferred for the formation of the chloride, but the first step of the electron transfer appears to be most important in this reaction. This is a dry reaction system. The reaction mechanism of intercalation of alkali metals using organic reagents such as butyllithium and naphthalene solutions will be different.

Conclusions

β-ZrNCl and β-HfNCl layer-structured crystals can be electron-doped by the partial deintercalation of chlorine atoms via the reaction of metal azides at elevated temperatures. The deintercalated compounds showed superconductivity very similar to that found on the corresponding compounds prepared by the reaction with metal−organic reagents. The change of the stacking sequence from the SmSI to the YOF type was observed on the Na-reacted compound. Since the chlorine-deintercalated compounds are more stable in air than the alkali metal intercalated compounds, the handling of the samples will be easier for the detailed study on the superconductivity. There are a variety of layer-structured halides. A similar electron doping to the crystals by deintercalation of halogen atoms will be widely applicable.

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(29) Drits, V. A.; Tchoubar, C. *X-ray Diffraction by Disordered Lamellar Structures*; Springer-Verlag: New York, 1990.

(30) Emsley, J. *The Elements*, 3rd ed.; Oxford: New York, 1997.