

High-Pressure Synthesis and Crystal Structures of β -MNCl ($M = \text{Zr}$ and Hf)

Xuean Chen,^{*} Takeshi Koiwasaki,[†] and Shoji Yamanaka^{*†,1}

^{*}CREST, Japan Science and Technology Corporation (JST), Kawaguchi 332-0012, Japan; and [†]Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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The single crystals of two kinds of metal nitride halides, β -ZrNCl and β -HfNCl, have been grown for the first time in the presence of NH_4Cl under a high pressure of 3 GPa at 900°C and 1200°C, respectively. Their crystal structures have been refined on the basis of X-ray four-circle diffractometer data. β -ZrNCl crystallizes in the rhombohedral space group $R\bar{3}m$; $a = 3.6046(4)$ Å, $c = 27.672(4)$ Å, and $Z = 6$; $R1/wR2 = 0.0270/0.0751$ for 447 observed reflections and 11 variables. For the isostructural compound β -HfNCl, $a = 3.5767(8)$ Å, $c = 27.711(7)$ Å; $R1/wR2 = 0.0372/0.0979$ for 454 observed reflections. The compounds are isotypic with SmSI and composed of structural slabs $[\text{Cl}-M-\text{N}-\text{N}-M-\text{Cl}]$ ($M = \text{Zr}, \text{Hf}$) with close-packed anion layers. Three of those slabs are stacked rhombohedrally in the unit cell along the c -axis and held together by Cl...Cl van der Waals interactions. The metal atoms (M) are placed in the octahedral sites between the Cl and N layers, leading to the overall layer sequence of $\text{Cl}_A M_c \text{N}_B \text{N}_c M_b \text{Cl}_A | \text{Cl}_C M_b \text{N}_A \text{N}_B M_a \text{Cl}_C | \text{Cl}_B M_a \text{N}_C \text{N}_A M_c \text{Cl}_B$. This is the first single-crystal study on the layered nitride halides MNX ($M = \text{Zr}, \text{Hf}$; $X = \text{Cl}, \text{Br}, \text{I}$) which recently have gained considerable interest because of the superconductivity caused by alkali metal intercalation. © 2001 Academic Press

INTRODUCTION

β -ZrNCl was first prepared by Juza and Heners in 1964 (1). Juza and Friedrichsen (2) subsequently proposed a layer structure model, in which Cl and N atoms were close-packed and Zr atoms occupied the octahedral interstices to form a slab of $[\text{Cl}_A-\text{Zr}_b-\text{N}_c-\text{N}_a-\text{Zr}_b-\text{Cl}_c]$. These slabs are randomly stacked in a sequence between the CdCl_2 (ccp) and CdI_2 (hcp) types. Ohashi *et al.* (3, 4) developed a new synthetic route for β -ZrNCl and obtained a highly crystalline sample by the chemical transport of the as-prepared sample, the XRD pattern of which could be indexed on the basis of a rhombohedral supercell $\sqrt{3}a \times 3c$ relative to the

average cell of Juza and Friedrichsen. Recently, the layer-structured nitride halides MNX ($M = \text{Zr}, \text{Hf}$; $X = \text{Cl}, \text{Br}, \text{I}$) have attracted much attention because their alkali metal intercalates exhibited superconductivity at pretty high transition temperatures (T_c 's): $\text{Li}_{0.16}\text{ZrNCl}$ and $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$ (THF, tetrahydrofuran) at $T_c = 13$ and 25.5 K, respectively (5–7). The crystal structure of the β -ZrNCl host lattice has been redetermined by several groups using powder X-ray or neutron diffraction (8–11). It was revealed that β -ZrNCl and β -HfNCl were isotypic with SmSI, and the double M -N layers were both shifted so as to form new M -N bonds between the layers. However, because of the layer-structured nature of the crystals, the powder sample showed a very strong preferred orientation, and the structural data reported by different authors varied largely; in particular, the atomic distance Zr-N between the adjacent ZrN layers in the double ZrN layer deviates from 2.14 to 2.49 Å, depending on the different authors. It is evident that any understanding of these materials or band structure calculations would require more accurate atomic parameters. During our investigation of the ternary M -N- X system using the high-pressure technique, we have obtained single crystals of β -ZrNCl and β -HfNCl. In this paper we report their crystal growth and accurate structure determinations.

SAMPLE PREPARATION

The β -ZrNCl and β -HfNCl crystals were grown by a two-step process. First, the powder samples were prepared by the reaction of ZrH_2 (99%) and Hf (99.7%), respectively, with NH_4Cl (99.5%) at 650°C, and then purified by a chemical transport reaction in the temperature gradient of 750 to 850°C as described elsewhere (3, 4). The resulting products were soft and extremely thin platelets, which were easily deformed, and too small and too thin for the single-crystal structural investigations.

The chemically transported β -ZrNCl (0.050 g) was filled in a gold cell (4 mm in inner diameter, 5 mm in depth) with

¹ To whom correspondence should be addressed. Fax: 81-824-24-7740. E-mail: syamana@hiroshima-u.ac.jp.

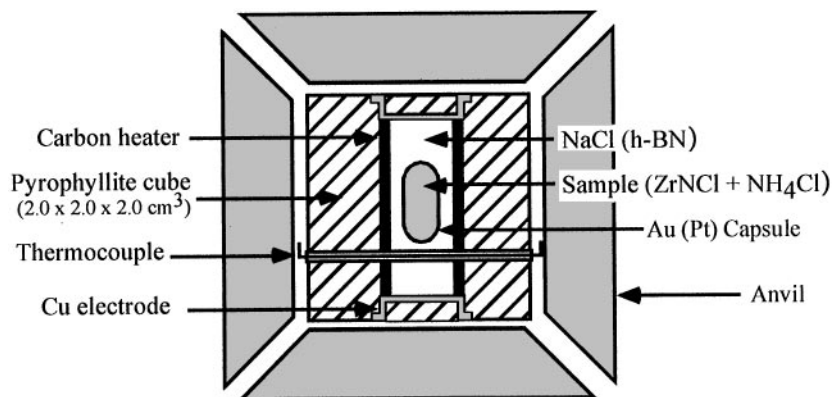


FIG. 1. Schematic view of the cross section of the assembly used for β -ZrNCl single-crystal growth.

0.067 g of NH_4Cl (molar ratio $\text{ZrNCl}/\text{NH}_4\text{Cl} = 1/3.5$) as a reactive flux. The gold cell was surrounded by compressed NaCl powder, which was in turn placed in a carbon tube heater in a pyrophyllite cube ($2.0 \times 2.0 \times 2.0 \text{ cm}^3$) as pressure medium. The reaction temperature was monitored by a thermocouple placed under the Au cell in the cube. The assembly used for the high-pressure synthesis is schematically shown in Fig. 1.

High-pressure synthesis was carried out using a cubic multi-anvil-type press (Riken, model CP-10). Under an applied pressure of 3 GPa, the sample was gradually heated to 900°C , where it was kept for 1 hour, and then cooled to 500°C at a rate of $67^\circ\text{C}/\text{h}$ followed by quenching to room temperature before the pressure was released. Pale yellow-green transparent β -ZrNCl crystals were obtained in about 40% yield. The remaining reaction product was found to be a mixture of NH_4Cl and an amorphous compound giving a diffuse reflection peak at $d = 11 \text{ \AA}$ by powder X-ray diffraction (XRD) measurement using graphite-monochromated $\text{CuK}\alpha$ radiation. The crystals grew on the wall of

the Au cell, and showed a hexagonal platelike habit with the largest dimension of $1.5 \times 1.0 \times 0.10 \text{ mm}^3$. A typical scanning electron micrograph of the obtained crystals is shown in Fig. 2 in comparison with that of the chemically transported sample. As can be seen from the figure, the present crystals are much larger and thicker compared with those obtained from the chemical vapor transport method.

Although the elements Hf and Zr have similar electronic configurations and chemical behaviors, it was more difficult to obtain single crystals of β -HfNCl. The same synthesis conditions as those used in the ZrNCl synthesis led to only a white amorphous material. For the crystal growth of β -HfNCl, 0.080 g (0.351 mmol) of chemically transported β -HfNCl powder and 0.040 g (0.748 mmol) of NH_4Cl were introduced into a Pt cell, which was in turn placed in a BN cell, and in a carbon tube heater. Under a pressure of 3 GPa, the sample was heated at 1200°C for 1 hour, and then cooled to 900°C at a rate of $100^\circ\text{C}/\text{h}$ and quenched to room temperature. Colorless transparent platelike crystals of β -HfNCl were obtained in about 30% yield. The by-product

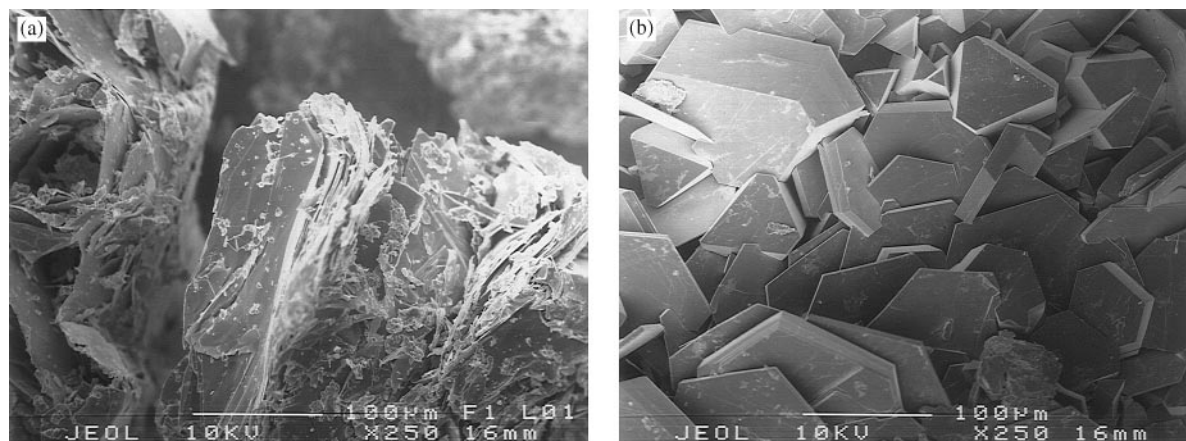


FIG. 2. Scanning electron micrographs of the β -ZrNCl crystals obtained from the chemical vapor transportation method (a) and the high-pressure treatment (b).

accompanying β -HfNCl was again an unknown white amorphous phase. The powder XRD patterns of both kinds of crystals showed narrow and very sharp diffraction peaks characteristic of the β -phases.

STRUCTURE DETERMINATIONS

Intensity data of the title compounds were collected at room temperature (298 K) on a Rigaku AFC7R automatic diffractometer with graphite-monochromated MoK α radiation. Cell dimensions were obtained from a least-squares refinement with 25 automatically centered reflections in the range $35.43^\circ \leq 2\theta \leq 39.95^\circ$ for β -ZrNCl, and $36.95^\circ \leq 2\theta \leq 44.34^\circ$ for β -HfNCl. Three standard reflections were remeasured after every 150 reflections. No decay was observed except the statistic fluctuation in a range of $\pm 0.2\%$ for β -ZrNCl and $\pm 0.1\%$ for β -HfNCl. The raw intensity data were corrected for Lorentz and polarization effects, and for absorption by an empirical method based on ψ -scan data. Patterson interpretation yielded the positions of all atoms, all of which were eventually subjected to the anisotropic refinements. An extinction correction was applied to the calculated structure factors and refined to be 0.002(1) for β -ZrNCl and 0.0003(2) for β -HfNCl. In order to check the deviations from the ideal compositions, occupancy parameters of Zr and N atoms were allowed to vary along with their positional and thermal parameters, while the occupancy parameter of the Cl atom was fixed at 1.0. The resulting occupancies varied between the values of 1.014(7) for Zr and 1.02(2) for N in β -ZrNCl. They are all within one standard deviation of the ideal values. Therefore, in the final least-squares cycles, the ordered model with the ideal atomic occupancies was assumed. For β -ZrNCl, the final full-matrix least-squares refinements on F^2 lead to $R1 = 0.0270$ and $wR2 = 0.0751$ for 447 observed reflections ($I > 2\sigma(I)$) and 11 variables. The reliability factors for compound β -HfNCl converged to $R1 = 0.0372$ and $wR2 = 0.0979$ for 454 observed reflections. The final difference electron density maps showed no features in both cases. Details of crystal parameters, data collection, and structure refinements are given in Table 1. All computations were performed using the SHELX97 program package (12), and crystal structure drawings were produced with ATOMS

TABLE 1
Crystallographic Data for ZrNCl and HfNCl

Formula	ZrNCl	HfNCl
Formula weight	140.68	227.95
Crystal size, mm	$0.20 \times 0.10 \times 0.03$	$0.14 \times 0.12 \times 0.03$
Space group	$R\bar{3}m$ (No. 166)	$R\bar{3}m$ (No.166)
A , Å	3.6046(4)	3.5767(8)
C , Å	27.672(4)	27.711(7)
V , Å ³ , Z	311.38(7), 6	307.01(12), 6
d_{calc} , g/cm ³	4.501	7.398
λ , Å	0.71069	0.71069
μ , mm ⁻¹	6.104	51.786
$2\theta_{\text{max}}$, deg	100	100
Total reflections	2085	2143
Unique reflections	473	471
Observed [$I \geq 2\sigma(I)$]	447	454
No. of variables	11	11
GOF ^a on F_o^2	1.143	1.153
R indices [$I \geq 2\sigma(I)$]	$R1^b = 0.0270$ $wR2^c = 0.0751$	0.0372 0.0979
R indices (all data)	$R1 = 0.0291$ $wR2 = 0.0760$	0.0391 0.0991

^a GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

^b $R1 = (\sum\|F_o\| - |F_c|)/\sum|F_o|$.

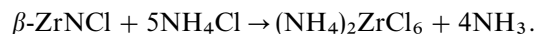
^c $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)\}^{1/2}$.

4.0 (13). The final atomic coordinates and the equivalent isotropic and anisotropic displacement parameters are listed in Tables 2 and 3.

RESULTS AND DISCUSSION

Synthesis

As reported elsewhere (3,4), the as-prepared β -MNCl ($M = \text{Zr, Hf}$) can be chemically transported with the aid of NH_4Cl in a vacuum-sealed glass tube, and purified into highly crystalline crystals, although the transported crystals are very thin. It was also reported that β -ZrNCl reacted with NH_4Cl to form $(\text{NH}_4)_2\text{ZrCl}_6$ and ammonia:



The hexachloride is vaporized into 5 moles of gaseous mixtures at elevated temperatures as follows:



TABLE 2
Atomic Coordinates, and Equivalent Isotropic and Anisotropic Temperature Factors (Å²) for ZrNCl

Atoms	x	y	z	$U_{11} = U_{22}$	U_{33}	$U_{23} = U_{13}$	U_{12}	U_{eq}
Zr	0	0	0.11924(1)	0.0106(1)	0.0108(1)	0	0.0053(1)	0.0107(1)
Cl	0	0	0.38780(3)	0.0164(2)	0.0124(2)	0	0.0082(1)	0.0151(1)
N	0	0	0.19771(8)	0.0130(4)	0.0108(6)	0	0.0065(2)	0.0123(3)

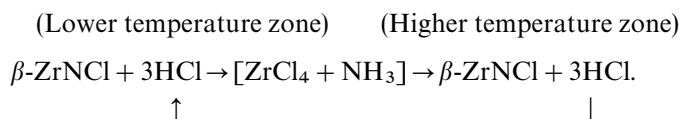
Note. U_{eq} is defined as one-third of the trace of the orthogonalized \mathbf{U} tensor.

TABLE 3
Atomic Coordinates, and Equivalent Isotropic and Anisotropic Temperature Factors (\AA^2) for HfNCl

Atoms	x	y	z	$U_{11} = U_{22}$	U_{33}	$U_{23} = U_{13}$	U_{12}	U_{eq}
Hf	0	0	0.11950(1)	0.0089(1)	0.0090(1)	0	0.0044(1)	0.0089(1)
Cl	0	0	0.38795(8)	0.0127(5)	0.0111(5)	0	0.0064(2)	0.0122(3)
N	0	0	0.1976(2)	0.014(2)	0.008(2)	0	0.0067(8)	0.012(1)

Note. U_{eq} is defined as one-third of the trace of the orthogonalized \mathbf{U} tensor.

The net vapor transport reaction can be simply written by the following equation:



The transport reaction occurs to the higher-temperature zone.

In the high-pressure treatment of β -ZrNCl with NH_4Cl in this study, a much larger amount of NH_4Cl was mixed with β -ZrNCl compared with the amount used in the reaction in the chemical vapor transport. It was very likely that all of the β -ZrNCl crystals were decomposed into the gaseous mixtures by reaction with a large amount of NH_4Cl in a temperature range of 900–1200°C, and then recrystallized from the surface contacting with the gold cell. The high pressure was required to confine the gaseous mixtures in the gold cell at high temperatures. When the cell was cooled to room temperature rapidly, the uncrystallized part was supposedly quenched into an amorphous phase containing NH_4Cl . β -ZrNCl single crystals were also obtained from a mixture of ZrN and NH_4Cl by a similar high-pressure treatment. This is because ZrN also gives ZrCl_4 by the reaction with NH_4Cl . Single crystals of β -HfNCl were also similarly grown under high-temperature and high-pressure conditions, but a much higher temperature of 1200°C was necessary as compared to that used in the synthesis of β -ZrNCl; a platinum high-temperature cell was used instead of a gold cell. Although we have succeeded in obtaining single crystals suitable for the structural analysis, the details of the reactions occurring under high pressure are not clear.

Structure Description

Our present single-crystal studies have fully confirmed the recent structural model proposed by Fogg *et al.* (8), Shamoto *et al.* (9), Fuertes *et al.* (10), and Istomin *et al.* (11) by powder X-ray and neutron Rietveld analyses. The single-crystal analysis data are more accurate owing to the larger reflection number/parameter number ratio (> 40). β -ZrNCl is isostructural with SmSI (14). It is a typical layered structure (Fig. 3) and is composed of structural slabs

[Cl–Zr–N–N–Zr–Cl] with close-packed anion layers; the Zr atoms are placed in the octahedral sites between the Cl and N layers. Three such slabs are stacked rhombohedrally along the c -axis to build the unit cell and are held together by weak Cl...Cl van der Waals interactions (Cl...Cl distance = 3.663(1) Å). This is also reflected by the fact that the crystals have a highly perfect (001) cleavage characteristic. Figure 4 depicts a schematic structural model of a double Zr–N layer between the close-packed chloride layers. Note that the double Zr–N layer forms a honeycomb lattice almost planar with the N–Zr–N bond angle of 115.60(4)°. Each Zr atom is coordinated to three Cl and four N atoms

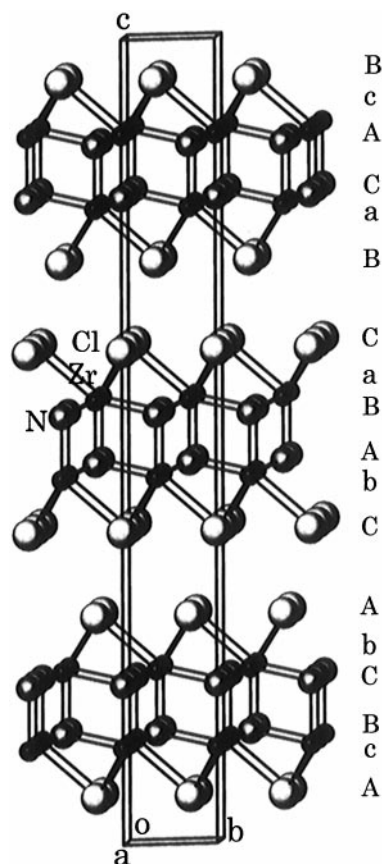


FIG. 3. View of the β -ZrNCl structure approximately along the a -axis. Large light balls, Cl; medium balls, N; small dark balls, Zr atoms.

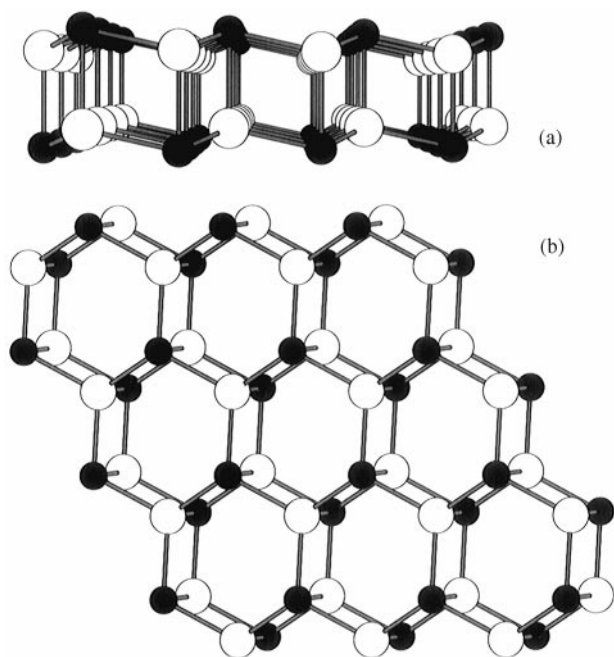


FIG. 4. Schematic illustration of the double Zr–N layer of a honeycomb-like two-dimensional structure, where large open circles and small solid circles are N and Zr atoms, respectively. The upper plot (a) is the projection along the a -axis, and the lower plot (b) is the projection along the c -axis.

in a highly distorted monocapped octahedral geometry, as depicted in the ORTEP plot of Fig. 5. The Zr–N bond distances for the capping N atom and the octahedral vertex N atoms are 2.172(2) and 2.1299(5) Å, respectively, which are considerably shorter than the Zr–N bond distance of 2.289(1) Å of ZrN of the rock salt type (15).

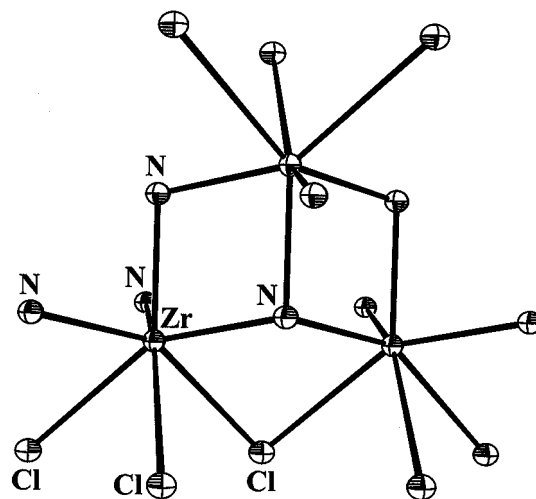


FIG. 5. An ORTEP representation of the local coordination geometry of Zr in β -ZrNCl. Displacement ellipsoids are drawn at the 50% probability level.

As can be seen from Table 4, the geometrical parameters of β -ZrNCl determined at room temperature vary in the literature, especially for the Zr–N_{cap} distance; Istomin *et al.* (11) and Fogg *et al.* (8) gave 2.339(9) and 2.492(1) Å, respectively, while Fuertes *et al.* (10) reported a smaller value of 2.17(3) Å. Our present refinements are in good agreement with the latter, with more than 10 times smaller standard deviations. The better agreement of the data obtained by Fuertes *et al.* is probably attributed to their XRD patterns obtained from randomly oriented powder samples. A similar good agreement was also found in the data obtained by neutron analysis of randomly oriented powder samples (9).

TABLE 4
Selected Bond Lengths (Å) and Angles (°) for ZrNCl and HfNCl

	β -ZrNCl(I)	β -HfNCl(II)	β -ZrNCl	β -ZrNCl	β -ZrNCl	β -ZrNCl	β -HfNCl
Reference	This work	This work	(10)	(8)	(11)	(9)	(10)
Radiation	X-rays	X-rays	X-rays	X-rays	X-rays	Neutrons	X-rays
Temperature	298 K	298 K	298 K	298 K	298 K	4 K	298 K
$M-N \times 3$	2.1299(5)	2.114(2)	2.125(6)	2.086(1)	2.099(1)	2.1133(8)	2.11(1)
$M-N_{\text{cap}} \times 1$	2.172(2)	2.163(7)	2.17(3)	2.492(1)	2.339(9)	2.136(5)	2.20(6)
$M-Cl \times 3$	2.7465(6)	2.738(2)	2.755(4)	2.754(3)	2.766(2)	2.769(2)	2.722(7)
$M-M^* \times 3$	3.3498(5)	3.3313(7)	3.351(4)	3.355(3)	3.342(3)	3.272(5)	3.335(3)
$Cl \dots Cl^* \times 3$	3.663(1)	3.664(4)	3.663(6)	3.642(6)	3.617(3)	3.640(3)	3.70(1)
$N-M-N \times 3$	115.60(4)	115.6(1)	116.7(3)	119.56(6)	118.29(8)	116.69(5)	116.4(7)
$N-M-N_{\text{cap}} \times 3$	77.71(6)	77.7(2)	79.4(7)	86.2(4)	82.4(2)	79.4(1)	79(2)
$N-M-Cl \times 3$	151.55(6)	151.3(2)	149.9(7)	142.9(4)	146.3(3)	149.2(1)	151(2)
$N-M-Cl \times 3$	76.63(5)	76.8(1)	75.4(5)	70.5(3)	73.4(2)	75.72(7)	76(1)
$N_{\text{cap}}-M-Cl \times 3$	130.74(1)	131.05(4)	130.7(1)	130.9(1)	131.24(6)	131.43(6)	130.7(2)
$Cl-M-Cl \times 3$	82.02(2)	81.55(6)	82.1(1)	81.8(1)	81.26(8)	80.99(8)	82.1(2)

Note. *represents interlayer distance.

TABLE 5
Structural Parameters of the Nitrides

	β -ZrNCl	β -HfNCl	ZrN	HfN
Structure type	SmSI	SmSI	NaCl	NaCl
Bond length (Å)				
M -N	2.1299(5)	2.114(2)	2.289(1)	2.263(1)
M -N _{cap}	2.172(2)	2.163(7)		
Bond angle (°)				
N-M-N	115.60(4)	115.6(1)	90	90
T_c (K)	13.0 ^a	25.5 ^a	10.7 ^b	8.8 ^b

^a T_c for the lithium intercalated phases.

^b Reference (16).

The smaller bond distances obtained by the neutron study were due to the low measurement temperature of 4 K. It is also clear from Table 4 that the bond distances around the Hf atom in β -HfNCl are all smaller than the corresponding distances for the Zr atom in β -ZrNCl, while the interlayer van der Waals gap is slightly larger in the former compound (3.027(5) vs 3.015(2) Å, also see c -parameters of both compounds).

Some important structural data of the double M -N layers (Fig. 4) in β -MNCl ($M = \text{Zr}$ and Hf) are compared with those of the corresponding metal mononitrides with the rock salt structure (16) in Table 5. The Hf-N distances in the double Hf-N layer are again much shorter than the bond distance of 2.263(1) Å of HfN of the rock salt type (17); the double Hf-N layers are almost coplanar with the bond angle N-Hf-N of 115.6(1)°. On alkali metal intercalation, electrons are doped into the MN double layers. Some reasons for the remarkably high T_c 's observed for the electron-doped β -MNCl could be found in the shorter M -N bond distances, or the stronger covalent bonds, compared with those of the corresponding mononitrides with the rock salt structure, and in the coplanarity of the double M -N layers as shown in Fig. 4.

Alternatively, the structural slab of ClZrNNZrCl can also be considered as being built from two sheets of edge-sharing octahedra. They are condensed in such a way that the capping site of one monocapped octahedral unit from one sheet is the octahedral vertex of its neighbor in another sheet. Referring to the widely studied ZnIn₂S₄ polytype family (18), the overall layer sequence of the β -ZrNCl structure can be represented as Cl_AZr_cN_BN_CZr_bCl_A|Cl_CZr_bN_AN_BZr_aCl_CCl_BZr_aN_CN_AZr_cCl_B. Here the anions are stacked in (hcch)₃ type, with the Cl atoms in hexagonal sequence and the N atoms in a cubic manner.

The crystal structure of β -ZrNCl is closely related to those of ZrCl (19) and $Ln_2C_2X_2$ ($Ln = \text{La}, \text{Y}, \text{Lu}; X = \text{Br}, \text{I}$) (20), and it may be described as a filled-up version of the ZrCl-type structure. The monohalides MX ($M = \text{Sc}, \text{Zr}, \text{Hf}, \text{Y}, \text{Ln}; X = \text{Cl}, \text{Br}$) are layer-structured compounds com-

posed of cubic close-packed layers of metal and halide atoms that stack in the sequence $X_A M_c M_b X_A | X_C M_b M_a X_C | X_B M_a M_c X_B$. The insertion of the nitrogen atoms in all of the tetrahedral holes between the double metal layers will give the β -ZrNCl-type structure, whereas the filling of the octahedral interstitial voids with C_2 pairs will result in $Ln_2C_2X_2$ families of compounds which represent another class of superconductors. In fact, the β -ZrNCl and ZrCl phases crystallize in the same space group with similar lattice constants. The space group $C2/m$ of $Ln_2C_2X_2$ is a maximal nonisomorphic subgroup (index 3) of the group $R-3m$ adopted by β -ZrNCl and ZrCl. The symmetry reduction represents a step which is "translationengleich."

CONCLUSIONS

So far the structural data of β -MNCl ($M = \text{Zr}, \text{Hf}; X = \text{Cl}, \text{Br}, \text{I}$) have all been based on the powder results due to the difficulty in obtaining their single crystals. This is the first time that structural refinements of β -ZrNCl and β -HfNCl could be performed based on X-ray four-circle diffractometer data. The successful syntheses of single crystals of the title compounds indicated that the high-pressure conditions suppress the crystal growth in the a - b plane, enhance the ordering of the layer stacking along the c -axis, and allow the large and thick crystals to be available. It is believed that the synthetic route is still promising for the preparation of more different kinds of layer-structured nitrides β -MNCl ($M = \text{Zr}, \text{Hf}; X = \text{Cl}, \text{Br}, \text{I}$).

We are now deriving alkali metal intercalation compounds of β -MNCl ($M = \text{Zr}, \text{Hf}$) from the single crystals obtained in this study. The precise determination of the structural changes on intercalation is the next subject of great interest toward the better understanding of the mechanism of superconductivity.

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