



The first single-crystal X-ray structural refinement of the superconducting phase $\text{Li}_{0.2(1)}\text{ZrNCl}$ derived by intercalation

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Abstract

The single crystals of the superconducting $\text{Li}_{0.2(1)}\text{ZrNCl}$ have been derived from the single crystals of $\beta\text{-ZrNCl}$ by intercalation of lithium using an *n*-butyllithium solution in hexane. The crystal structure has been refined on the basis of the single-crystal X-ray data: the space group $R\bar{3}m$, $a = 3.591(1)\text{ \AA}$, $c = 27.839(6)\text{ \AA}$, $Z = 6$, $R1 = 0.0749$ for 196 reflections and 12 variables. $\beta\text{-ZrNCl}$ is isotypic with SmSI, while the structure of $\text{Li}_{0.2(1)}\text{ZrNCl}$ can be described as the Li intercalated YOF type, a stacking variant of the SmSI type. The tightly bound slabs with a Cl–Zr–N–N–Zr–Cl sequence of close-packed layers are stacked rhombohedrally along the *c*-axis, with the van der Waals gaps between the chlorine layers hosting Li ions. This is the first single-crystal study on the Li intercalated phase. The structural changes from the pristine single crystals were precisely determined.

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1. Introduction

The layer structured metal nitride halides, $\beta\text{-MNX}$ ($M = \text{Zr, Hf}$; $X = \text{Cl, Br, I}$), have attracted considerable interest, due to the superconductivity of their alkali metal intercalates at relatively high transition temperatures (T_c 's) [1–5]. The Li intercalated $\text{Li}_{0.16}\text{ZrNCl}$ showed a T_c of 14 K [1]. The highest T_c was observed at 25.5 K on the lithium intercalated $\beta\text{-HfNCl}$, $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$, where THF (tetrahydrofuran) molecules were co-intercalated with lithium [3]. $\beta\text{-ZrNCl}$ was first prepared by Juza and Heners [6] in 1964, and Juza and Friedrichsen [7] 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 $[\text{Cl}_A\text{-Zr}_b\text{-N}_C\text{-N}_A\text{-Zr}_b\text{-Cl}_C]$, where the capital letters of the subscripts denote anion sites, and the lower case letters denote cation positions. These slabs were supposed to be stacked in a random manner between the CdCl_2 (ccp) and CdI_2 (hcp) types. After the findings of the superconductivity on the alkali metal intercalated $\beta\text{-MNX}$, the crystal structures of the $\beta\text{-MNX}$ ($M = \text{Zr, Hf}$) host lattices have been redetermined by

several research groups using powder X-ray and neutron diffractions [8–11]. It was revealed that $\beta\text{-ZrNCl}$ and $\beta\text{-HfNCl}$ were isotypic with SmSI, and double $M\text{-N}$ layers were so shifted as to form new $M\text{-N}$ bonds between the layers, such as $[\text{Cl}_A\text{-Zr}_b\text{-N}_C\text{-N}_B\text{-Zr}_c\text{-Cl}_A]$. However, due to the layer-structured nature of the crystals, the powder structural data reported by different authors varied largely.

Recently, we have prepared single crystals of $\beta\text{-ZrNCl}$ and $\beta\text{-HfNCl}$ using NH_4Cl flux at high-temperature and high-pressure conditions (3 GPa, 900–1200°C), and succeeded in the X-ray single-crystal structural analysis [12]. It confirmed the basic structures determined by others using powder patterns. Furthermore, the refined structural data were more accurate with smaller standard deviations. The crystal structures of all possible combinations of $\beta\text{-MNX}$ ($M = \text{Zr, Hf}$; $X = \text{Cl, Br, I}$) have also been determined using single crystals obtained under similar high-temperature and high-pressure conditions with ammonium halides, NH_4X ($X = \text{Cl, Br, I}$) as fluxes [13]. The structural analysis revealed that there were two polymorphs isotypic with SmSI and YOF. $\beta\text{-ZrNCl}$, $\beta\text{-HfNCl}$, and $\beta\text{-ZrNBr}$ are of the SmSI type [14], and $\beta\text{-ZrNI}$, $\beta\text{-HfNI}$ and $\beta\text{-HfNBr}$ are of the YOF type [15]. The two polymorphs are compared in Figs. 1(a) and (b). Both structure

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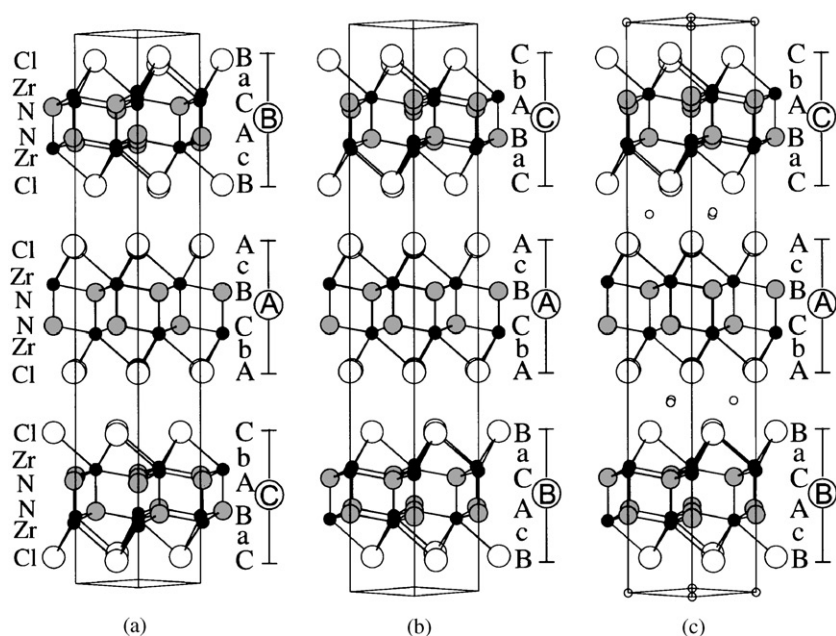


Fig. 1. Perspective view of the structures of MNX isotypic with (a) SmSI and (b) YOF along [110]. The stacking sequences and unit cells are outlined (the capital letters (A, B, C) denote anions (X and N)); the lower case letters denote metal ions (M): large open circles, X ; medium gray circles, N; small black circles, M . Perspective view of the structure of $Li_{0.2(1)}ZrNCl$ is compared in (c): small open circles, Li.

variants are composed of the same structural slabs $[X-M-N-N-M-X]$ stacked together by $X \cdots X$ van der Waals forces, but the layer stacking sequence are different; the slabs repeat in two different sequences of ABC and ACB for the SmSI and the YOF types, respectively.

In this study, we have performed Li-intercalation into the single crystals of β -ZrNCl, and determined the structural changes of the slabs upon the intercalation. This is the first single crystal X-ray structural refinement of the intercalated phase Li_xZrNCl .

2. Experimental

2.1. Preparation of lithium intercalated β -ZrNCl single crystals

The single crystals of β -ZrNCl with sub-millimeter sizes were prepared using NH_4Cl flux at 3 GPa, $1000^\circ C$ as described elsewhere [12]. The lithium intercalation was carried out by keeping the β -ZrNCl crystals in a 15% *n*-butyllithium solution in hexane (BuLi) in an Ar-filled glove box at room temperature for about 4 months. The color of the crystals changed from pale yellow green to black by Li-intercalation. The resulting crystals were air-sensitive, and therefore they were loaded and sealed into 0.3 mm thin-walled glass capillaries for the structural investigation. The Li content was obtained from the structural refinements to be $Li_{0.2(1)}ZrNCl$. The value is, within the experi-

mental error, close to that (0.16) obtained previously for the Li-intercalated powder sample [2]; this was the largest Li content when BuLi was used as the lithiation reagent at room temperature [16].

2.2. Structure determination

X-ray data collection was performed at room temperature (298 K) on a Rigaku RAXIS diffractometer with an imaging plate area detector and graphite monochromated $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) operated at 50 kV and 40 mA. A total of 22 oscillation images were recorded using ω scans (width of 15° and exposure time of 1800 s per frame). Indexing all of 22 images produces a trigonal cell with $a \approx 9.51 \text{ \AA}$, $\alpha \approx 21.8^\circ$ ($a \approx 3.6 \text{ \AA}$, $c \approx 27.8 \text{ \AA}$ in hexagonal setting) in an accuracy of about 83%. After the data reduction 899 reflections were obtained, all of which satisfy the condition of $-h + k + l = 3n$. No reflections that violate the systematic absences were obtained. An attempt to refine the structure in a rhombohedral obverse-reverse twinning model failed.

The raw intensity data were corrected for Lorentz and polarization effects, and for absorption by a Gaussian numerical integration using the measured dimensions of the crystal. The structure was solved by Patterson methods in SHELX-97 system [17] and standardized by the program STRUCTURE TIDY [18]. Once the heavy atoms Zr, N, Cl were defined at the Wyckoff $6c$ sites, refinements of their positional and anisotropic displacement parameters lead to a reliability factor of

$R1=0.0768$. At this stage, an examination of the difference Fourier map revealed that the highest peak with an electron density of $2.72\text{ e}\text{\AA}^{-3}$ was located at 1.07 \AA apart from the Zr site, and the second highest peak ($2.67\text{ e}\text{\AA}^{-3}$) was at the $3a$ site, 2.58 \AA apart from the Cl position. There were some other peaks ($< 2.52\text{ e}\text{\AA}^{-3}$) located at positions too close to Zr ($< 1.0\text{ \AA}$) and Cl ($< 2.14\text{ \AA}$). Considered the sum of the Li and Cl ionic radii (2.57 \AA), only the $3a$ site was assigned to Li. In the subsequent least-squares cycles, occupancy parameter of the Li atom was allowed to vary along with its thermal parameter, while the occupancy parameters of other atoms were fixed at 1.0. The resulting occupancy of 0.3(2) for Li gives a formula of $\text{Li}_{0.2(1)}\text{ZrNCl}$, which is consistent with the literature results for the powder sample [2,8,16]. The refinement of 12 variables converged to $R1/wR2=0.0749/0.1668$ for 196 observed reflections

$[I \geq 2\sigma(I)]$. The final difference electron density maps showed no features, with the highest electron density of $2.62\text{ e}\text{\AA}^{-3}$ very close to the heavy atom sites. As a further test of this model (YOF-type), the present single-crystal data were alternatively refined using the atomic positions of the parent $\beta\text{-ZrNCl}$ structure (SmSI-type). These refinements led to irregular behavior of the atomic displacement factors and poor convergence with $R1/wR2 \approx 0.603/0.853$. Thus, the YOF model is in good agreement with the diffraction data, and gives results that appear physically reasonable. Details of crystal parameters, data collection and structure refinements are given in Table 1 and the atomic coordinates and the equivalent isotropic and anisotropic displacement parameters are summarized in Table 2, together with those of the pristine $\beta\text{-ZrNCl}$ for comparison. Note that the Cl positions remain basically unchanged, while the z coordinates of Zr and N atoms are exchanged with each other after Li intercalation.

Table 1
Crystallographic data for $\text{Li}_{0.2(1)}\text{ZrNCl}$

Formula	$\text{Li}_{0.2(1)}\text{ZrNCl}$
Formula weight	141.73
Crystal size (mm)	$0.15 \times 0.15 \times 0.04$
Space group	$R\bar{3}m$ (No. 166)
a (\AA)	3.591(1)
c (\AA)	27.839(6)
V (\AA^3), Z	310.9(1), 6
D_{calc} , (g/cm^3)	4.542
μ (mm^{-1})	6.114
$2\theta_{\text{max}}$, (deg)	70
Total reflections	899
Unique reflection	219
Observed [$I \geq 2\sigma(I)$]	196
No. of variables	12
GOF on F^2	1.149
R indices [$I \geq 2\sigma(I)$]	$R1 = 0.0749$ $wR2 = 0.1668$
R indices (all data)	$R1 = 0.0827$ $wR2 = 0.1755$

3. Results and discussion

It is a challenging subject in intercalation chemistry to determine the structures of host crystals before and after the intercalation reactions using single crystals, since such structural data enable us to understand the effect of the charge transfer from the guest species to the host layers in relation to the structural changes. Although intercalation reactions can maintain the layered structures of the crystals, the interlayer spacings are expanded by insertion of guest molecules and ions between the layers. This often results in the loss of crystallinity and periodicity of the crystals along the direction normal to the layers, and thus makes the X-ray single-crystal structural analysis very difficult. We have attempted to prepare the intercalation compound $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$ with the highest T_c (25.5 K) in this series, but it was found to be very difficult to derive

Table 2
Atomic coordinates, equivalent isotropic and anisotropic temperature factors (\AA^2) for $\text{Li}_{0.2(1)}\text{ZrNCl}$ in comparison with those for the host lattice $\beta\text{-ZrNCl}$

Atoms	x	y	z	$U_{11} = U_{22}$	U_{33}	$U_{23} = U_{13}$	U_{12}	U_{eq}
$\beta\text{-ZrNCl}^a$: $a = 3.6046(4)\text{ \AA}$, $c = 27.672(4)\text{ \AA}$								
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)
$\text{Li}_{0.2(1)}\text{ZrNCl}$: $a = 3.591(1)\text{ \AA}$, $c = 27.839(6)\text{ \AA}$								
N	0	0	0.1362(5)	0.014(3)	0.023(5)	0	0.007(2)	0.017(2)
Cl	0	0	0.3885(2)	0.024(1)	0.024(2)	0	0.0122(6)	0.0241(9)
Zr	0	0	0.21263(6)	0.0165(6)	0.0238(8)	0	0.0083(3)	0.0189(5)
Li	0	0	0					0.02(3)

^aData taken from Ref. [12].

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U tensor. Occupation factor of Li was refined to be 0.3(2).

single crystals with an expanded spacing of about 18 Å due to the co-intercalation of THF molecules. Dompa-blo et al. [19] prepared Zn intercalated β -ZrNX ($X = \text{Cl}, \text{Br}$) by an electrochemical method. They reported that the intercalation reaction resulted in significant loss of crystallinity of the sample as judged from the diffusive rings of the electron diffraction patterns and the broadening of the peaks of the XRD

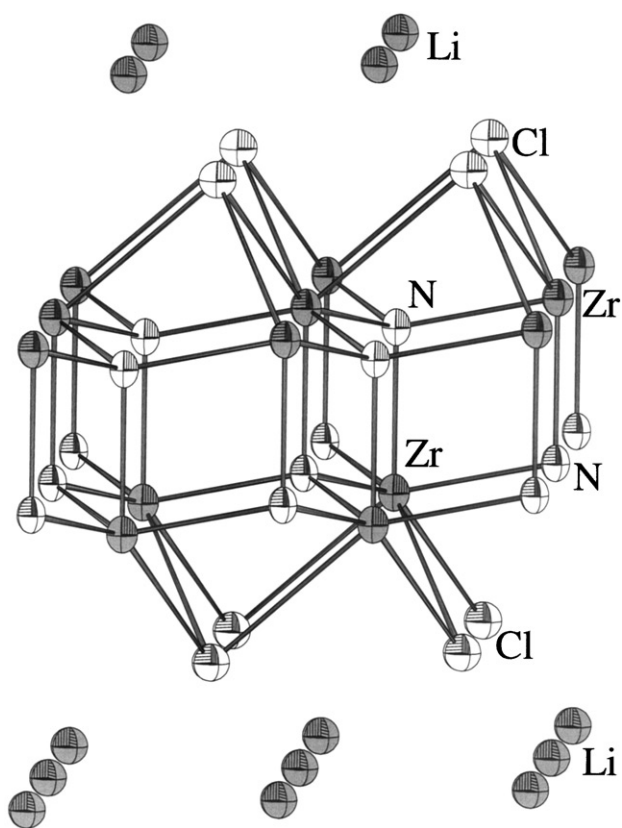


Fig. 2. An ORTEP representation of the partial structure of $\text{Li}_{0.2(1)}\text{ZrNCl}$ to show the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

patterns. In the Li-intercalation reaction of β -ZrNCl using BuLi, the basal spacing only slightly changed from 9.224 to 9.280 Å, where the use of non-polar solvent, hexane, can avoid the further expansion of the interlayer spacing without forming co-intercalation complexes.

$\text{Li}_{0.2(1)}\text{ZrNCl}$ crystallizes in a Li-filled YOF-type. In the a - b plane, Zr and N atoms are arranged to form h-BN-like layers. Two inversion-center-related Zr-N layers are condensed via the interlayer Zr-N bonds to generate a honeycomb-like bilayer, which is sandwiched by chlorine layers to produce the structural slab of $[\text{Cl}-\text{Zr}-\text{N}-\text{N}-\text{Zr}-\text{Cl}]$ as shown in the ORTEP plot of Fig. 2. Three such slabs are stacked rhombohedrally in the unit cell along the c -axis, and bridged by the Li^+ ions intercalated in the octahedral interstices of the chloride layers. Fig. 1(c) shows a perspective view of the $\text{Li}_{0.2(1)}\text{ZrNCl}$ structure. If the tightly bound six-layer slabs $[\text{Cl}_A-\text{Zr}_b-\text{N}_C-\text{N}_B-\text{Zr}_c-\text{Cl}_A]$, $[\text{Cl}_B-\text{Zr}_c-\text{N}_A-\text{N}_C-\text{Zr}_a-\text{Cl}_B]$, and $[\text{Cl}_C-\text{Zr}_a-\text{N}_B-\text{N}_A-\text{Zr}_b-\text{Cl}_C]$ are defined as A, B, and C, respectively, these slabs are stacked in the sequence of ABC... in β -ZrNCl, and in ACB... in $\text{Li}_{0.2(1)}\text{ZrNCl}$, ignoring Li atoms. In this sense, the host structure of $\text{Li}_{0.2(1)}\text{ZrNCl}$ can be viewed as the YOF type, a stacking variant of β -ZrNCl of the SmSI type. It is interesting to note that the slabs of the host structure should be shifted each other within the plane in such a manner that the stacking sequence is changed from ABC to ACB upon the intercalation of lithium.

The selected bond lengths and angles of β -ZrNCl determined on the single crystals before and after the Li-intercalation are compared in Table 3. In $\text{Li}_{0.2(1)}\text{ZrNCl}$, each Zr atom is coordinated to three Cl and four N atoms in a highly distorted monocapped octahedral geometry (Fig. 2). The Zr atoms are displaced from the center of the octahedron toward the capped N_3 face by 0.495 Å, resulting in an almost planar Zr-N double layers with the N-Zr-N bond angle of $116.0(2)^\circ$. The Zr-N bond distance for the capping N atom is about 0.012(12) Å larger than that for the octahedral vertex N

Table 3

Selected bond lengths (Å) and angles ($^\circ$) for $A_x\text{MNCl}$ ($A = \text{Li}, \text{Na}$; $M = \text{Zr}, \text{Hf}$) compared with those in β - MNCl ($M = \text{Zr}, \text{Hf}$)

Structure type	β -ZrNCl	$\text{Li}_{0.2(1)}\text{ZrNCl}$	Difference	β -ZrNCl	$\text{Li}_{0.16}\text{ZrNCl}$	Difference	β -HfNCl	$\text{Na}_{0.29}\text{HfNCl}$	Difference
Reference	SmSI	YOF-like		SmSI	YOF-like		SmSI	YOF-like	
Radiation	[12]	This work		[11]	[11]		[12]	[23]	
Temperature	X-rays	X-rays		Neutrons	Neutrons		X-rays	Neutrons	
	298 K	298 K		4 K	4 K		298 K	4 K	
$M-\text{N} \times 3$	2.1299(5)	2.117(3)	-0.013	2.1133(8)	2.0831(8)	-0.030	2.114(2)	2.103(3)	-0.011
$M-\text{N}_{\text{cap}} \times 1$	2.172(2)	2.129(12)	-0.043	2.136(5)	2.045(1)	-0.091	2.163(7)	2.13(2)	-0.03
$M-\text{Cl} \times 3$	2.7465(6)	2.762(3)	+0.016	2.769(2)	2.909(8)	+0.140	2.738(2)	2.81(1)	+0.07
$M-M^* \times 3$	3.3498(5)	3.294(3)	-0.056	3.272(5)	3.100(1)	-0.172	3.3313(7)	3.24(2)	-0.09
$\text{Cl} \cdots \text{Cl}^* \times 3$	3.663(1)	3.706(7)	+0.043	3.640(3)	3.686(7)	+0.046	3.664(4)	4.18(2)	+0.52
$A-\text{Cl} \times 6$		2.580(3)			2.577(3)			2.755(8)	
$\text{N}-M-\text{N} \times 3$	115.60(4)	116.0(2)	+0.4	116.69(5)	119.56(6)	+2.87	115.6(1)	117.3(3)	+1.7

Note. * Represents interlayer distances. Difference: bond lengths and angles in $A_x\text{MNCl}$ —those in β - MNCl .

atom (2.117(3) Å) and both are considerably shorter than the Zr–N bond distance of 2.289(1) Å in the superconducting mononitride ZrN of the rock salt type.¹ The shorter Zr–N bond distances, i.e., the stronger bonding in the Zr–N network of Li_{0.2(1)}ZrNCl may be related to its higher *T_c* value (14 K) relative to that of ZrN (10.7 K) [20]. The Zr–Cl distance increases slightly on Li-intercalation. The Cl⋯Cl van der Waals gap is also slightly opened to accommodate lithium, as seen from somewhat enlarged interlayer Cl⋯Cl contacts (3.706(7) Å) compared with 3.663(1) Å for the host. The Li⁺ ion occupies about 1/3 of the octahedral interstices between the double chloride layers with an Li–Cl distance of 2.580(3) Å, which is close to Shannon's crystal radius sum, 2.57 Å [21]. On Li-intercalation, electrons are doped into the double Zr–N layers through the bonding Zr–Zr orbitals at the bottom of the conduction band [10]. This will strengthen the Zr–Zr interactions, shortening the Zr–Zr bond distances. The increased repulsion between the electron doped Zr–N layers and Cl ions will increase the Zr–Cl distances accompanied by a shortening of the Zr–N distances as shown in Table 3.

Shamoto et al. studied similar structural changes of β-ZrNCl on the Li-intercalation using BuLi on the basis of the powder neutron diffraction data [11], which are compared in Table 3, together with those of the single-crystal data. Very similar trends in the changes of the bond lengths and angles were found, but the order of the changes are much larger than those determined on the single-crystal data in the present study. We have collected X-ray data using two different crystals, but the obtained bond lengths and angles for both data sets were practically identical within the experimental error, further confirming the results presented here.

β-ZrNCl formed Na-intercalation compounds without co-intercalation of THF even if Na-naphthalene in THF solutions were used as the reaction reagent [22]. This is a strong contrast to the formation of the Li co-intercalation compounds co-intercalated with THF under a similar condition using Li-naphthalene. This can be interpreted in terms of a smaller polarizing power of Na ions than Li ions; THF molecules are not co-intercalated with Na ions. In this context, Shamoto et al. [23] prepared Na intercalated β-HfNCl without containing THF molecules using Na-naphthalene solutions in THF. They determined the structure of the Na_{0.29}HfNCl using the powder neutron diffraction data. The results are also compared in Table 3. It was clearly shown that β-HfNCl with the SmSI-type stacking sequence changed into the YOF type on Na-intercalation. It can be seen that there are again general trends in the changes of the bond lengths and bond angles. The bond lengths of Hf–N and Hf–Hf are shortened,

Table 4

Two types of layer stackings found in layer structured compounds having the space group *R-3m*

[ABC]	<i>R_x</i> [ABC]	[ACB]	<i>R_x</i> [ACB]	Reference
SmSI		YOF		[14,15]
		YCIO	Na _{0.08} YCIO	[26]
β-ZrNCl			Li _{0.2(1)} ZrNCl	This work
β-HfNCl			Na _{0.29} HfNCl	[12,23]
β-ZrNBr				[13]
		β-ZrNI		[13]
		β-HfNI		[13]
		β-HfNBr		[13]
ZrCl		ZrBr		[24,25]

and the bond angles N–Hf–N are enlarged. The Hf–Cl bond distances are increased. These changes can also be interpreted in terms of electron doping to the Hf–N layers as discussed in the preceding paragraphs.

The crystal structure of β-ZrNCl isotypic with SmSI can be described as the filled-up version of ZrCl [24]. ZrCl crystallizes in the trigonal space group *R-3m*, and the strongly bonded slabs *X–Zr–Zr–X* (*X* = Cl) are stacked along the *c* direction with a sequence of ABC (following the position of the *X* layers). The insertion of the nitrogen atoms in all the tetrahedral-like interstices between the double-metal layers of ZrCl will give β-ZrNCl. ZrBr also crystallizes in the same trigonal space group *R-3m*, and consists of the same four-layer slabs *X–Zr–Zr–X* (*X* = Br) but with an alternate stacking sequence of ACB rather than ABC [25]. Li_{0.2(1)}ZrNCl isotypic with YOF is the filled-up version of the ZrBr-type layered compounds.

Layer structured compounds with the space group *R-3m* can have either of ABC or ACB stacking sequence. Some examples are listed in Table 4, which clearly suggests the preference of the ZrBr or ACB arrangement for the intercalated phases. This can be explained in terms of the minimization of the repulsive interactions between the intercalated metals and their second-nearest neighbors [26]: in the ZrCl-type structure, each octahedral site in the van der Waals gap is coordinated by two metal atoms (Zr) along the *c*-axis as second-nearest neighbors, while in the ZrBr arrangement, these metal neighbors can be situated at a longer distance.

4. Conclusions

The single crystals of Li intercalated β-ZrNCl were derived from the single crystals of β-ZrNCl by Li-intercalation. The X-ray single-crystal analysis of the intercalated phase revealed that the stacking of the tightly bound slabs [Cl–Zr–N–N–Zr–Cl] of the SmSI or ZrCl type was changed into that of the YOF or ZrBr

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type upon Li-intercalation. This indicates that the slabs are shifted each other in the plane in such a manner that the stacking of the slabs is systematically changed from ABC to ACB. This shift is preferred because the electrostatic repulsion between the intercalated Li ions and the Zr ions of the slabs can be reduced by increasing the separation between the two kinds of ions. The changes in bond distances and bond angles upon Li-intercalation were precisely determined.

Acknowledgments

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