

# Zirconium Nitride Derived from Layer-Structured $\beta$ -ZrNCl by Deintercalation of Chlorine Layers

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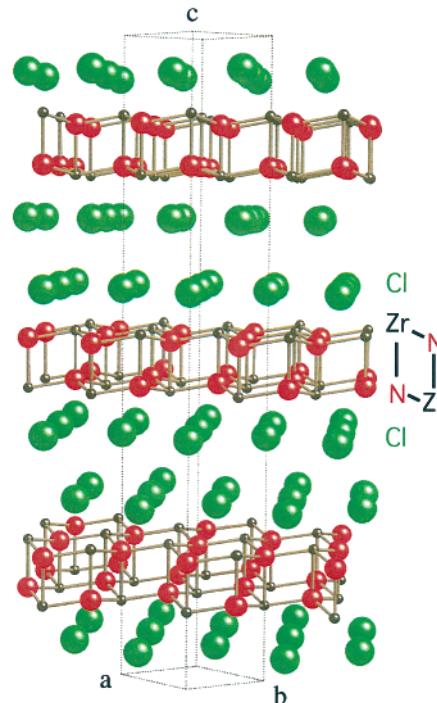
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A highly oriented thin-layered zirconium nitride, ZrN, was derived from layer-structured crystals  $\beta$ -ZrNCl via deintercalation of the chlorine atoms by the reaction with Na metal vapor.  $\beta$ -ZrNCl consists of rhombohedrally stacked [Cl–Zr–N–N–Zr–Cl] slabs, each of which is composed of a honeycomblike double ZrN layer sandwiched between two close-packed chlorine layers. On deintercalation of the chlorine layers, the honeycomblike ZrN layers converted into ZrN(001) layers of the rock salt structure by expanding to the three equivalent directions  $\langle 100 \rangle$  of  $\beta$ -ZrNCl.  $\beta$ -ZrNCl crystals were also thermally decomposed into ZrN at 950 °C under a stream of  $N_2/H_2$  mixed gas. The two types of ZrNs that were obtained had the same stoichiometric composition of 1:1 but showed superconductivity at different transition temperatures ( $T_{cs}$ ) of 6.2 and 10.0 K for the thin-layered and the thermally decomposed structures, respectively.

## 1. Introduction

$\beta$ -Zirconium nitride chloride,  $\beta$ -ZrNCl, consists of strongly bonded six-layered [Cl–Zr–N–N–Zr–Cl] slabs, each of which is composed of a honeycomblike double ZrN layer sandwiched between two close-packed chlorine layers.<sup>1–4</sup> Such slabs stack rhombohedrally as shown in Figure 1. Much attention has been focused on a series of analogues  $\beta$ -MNX (M = Zr, Hf; X = Cl, Br, I) since a new type of superconductivity with relatively high  $T_{cs}$  (transition temperatures) has been found on their alkali metal intercalates. Lithium-intercalated  $\beta$ -ZrNCl showed superconductivity with  $T_c = 13$  K,<sup>5</sup> and the highest  $T_c$  was observed for the cointercalated compound  $Li_{0.48}(THF)_2HfNCl$  (THF = tetrahydrofuran) at  $T_c = 25.5$  K.<sup>6</sup> All possible kinds of combinations of  $\beta$ -MNX show superconductivity on electron doping by the intercalation of alkali metals.<sup>7</sup> Recently, we have determined the crystal structures of  $\beta$ -MNX using single crystals prepared under high-pressure conditions with  $NH_4X$  fluxes.<sup>8,9</sup>

Transition-metal nitrides MN (M = Ti, Zr, Hf, Nb) with the rock salt structure are inherently superconduc-



**Figure 1.** Schematic structural model of  $\beta$ -ZrNCl.

tors with relatively high  $T_{cs}$  at 5.5, 10.7, 8.8, and 18 K, respectively.<sup>10–12</sup>  $\beta$ -MNX are semiconductors having band gaps of 3–4 eV.<sup>1,13</sup> On intercalation of alkali

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metals between the  $[X-M-N-N-M-X]$  slabs, electrons are doped into the double MN layers. The superconductivity occurs within the thin MN layers.<sup>14,15</sup> Note that the  $T_c$ s of the electron-doped thin MN layers of  $\beta$ -MNCl are higher than those of bulk crystals with the rock salt structure.

In this study, an attempt has been made to derive thin ZrN layers from  $\beta$ -ZrNCl by deintercalation of chlorine layers, and the superconductivity is compared with that of bulk ZrN.  $\beta$ -ZrNCl could be an attractive intermediate compound to prepare thin-layered ZrN if the chlorine layers can be easily removed. ZrN is also a nitride ceramic with considerable technological importance like TiN, owing to their characteristic properties such as the high hardness value, high moduli of elasticity, high melting point, relatively high strengths at elevated temperatures, and chemical stability with respect to most etching solutions.<sup>16–18</sup> ZrN could be used as a hard material and in cutting tools, tool coatings, microelectronics applications, and decorative materials with a golden color.<sup>19,20</sup>

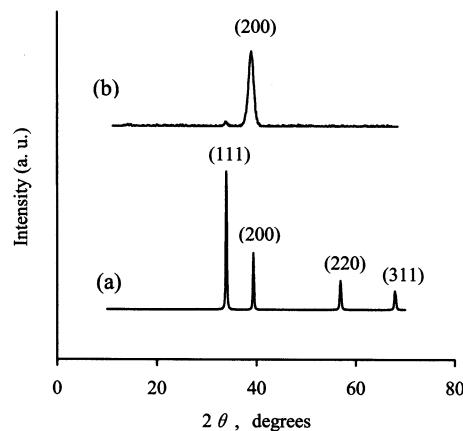
## 2. Experimental Section

**2.1. Synthesis of ZrN.**  $\beta$ -ZrNCl was first prepared by the reaction of  $ZrH_2$  (99%) with  $NH_4Cl$  (99.5%) according to the procedure described elsewhere;<sup>1,21</sup> the as-prepared  $\beta$ -ZrNCl was purified into highly crystalline thin crystals by chemical transport with the aid of  $NH_4Cl$ .<sup>22</sup>  $\beta$ -ZrNCl was converted into ZrN by the following two methods:

**Method 1.** A weighed amount of the chemically transported  $\beta$ -ZrNCl crystals was heated for 1 h at 950 °C in a horizontal furnace under a stream of  $H_2/N_2$  mixed gas. The oxygen contamination in the mixed gas was removed as  $H_2O$  by passing the gas through a Pt-loaded (5%) porous alumina column.<sup>23</sup> The  $H_2O$  that formed was removed by a zeolite 13X column placed at the exit of the alumina column. The gas composition was varied in the range of  $H_2/N_2 = 0.2$  to 3. The weight change of the sample boat was measured after cooling.

**Method 2.** The chemically transported  $\beta$ -ZrNCl was vacuum sealed with Na metal purified by distillation and was placed in a horizontal furnace with two temperature zones. The sample ( $\beta$ -ZrNCl) was placed in the higher-temperature zone of 500 °C, and the Na metal was placed on the other side, at 450 °C. After standing for 3 days, the lower-temperature side (Na) was first cooled to about 100 °C, and then the both sides were cooled to room temperature.

**2.2. Characterization of the Products.** Powder X-ray diffraction (XRD) patterns were measured using graphite-monochromated  $Cu K\alpha$  radiation. The BET surface areas were measured by nitrogen adsorption using the volumetric method. The particle morphologies were measured by scanning electron



**Figure 2.** XRD pattern of the products obtained from  $\beta$ -ZrNCl (a) by reaction 1 with  $H_2/N_2$  mixed gas at 950 °C and (b) by reaction 2 with Na vapor at 500 °C, followed by washing with water.

microscopy (SEM, JEOL 6640F). The transmission electron microscope (TEM) that was used was from Akashi Beam Tech. Co. (EM-002B) with an acceleration voltage of 200 kV; the ZrN powder sample was suspended in alcohol and placed onto a carbon microgrid supported by a Cu mesh. The magnetic susceptibility was measured using a SQUID magnetometer (MPMS-5, Quantum Design).

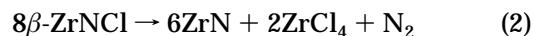
The compositions of the products were determined by chemical analysis. The sample obtained by method 2 was washed with water to remove NaCl and dried by evacuation. The zirconium content was measured by inductively coupled plasma (ICP) spectrometry of the sample dissolved in a mixture of hydrofluoric acid and nitric acid solutions. The nitrogen content was analyzed by the Kjeldahl method.<sup>24</sup>

## 3. Results and Discussion

**3.1. Synthesis of ZrN from  $\beta$ -ZrNCl.** In method 1,  $\beta$ -ZrNCl crystals were thermally decomposed under a stream of  $N_2/H_2$  mixed gas. The crystals began to decompose at about 800 °C and changed to golden color at 950 °C. The XRD pattern showed characteristic peaks for ZrN with the rock salt structure (Figure 2a). The peaks can be indexed on the basis of a cubic unit cell with a lattice parameter of 4.570(8) Å, in good agreement with  $a = 4.5730(5)$  Å reported for  $ZrN_{1.0}$  with the stoichiometric composition.<sup>25</sup> When the hydrogen content of the mixed gas  $H_2/N_2$  was  $>0.2$ , ZrN was obtained quantitatively according to the following reaction:



The yield of ZrN was estimated to be 99.4–101.0% on the basis of the weight change. In a previous study,<sup>26,27</sup> we reported that  $\beta$ -ZrNCl was thermally decomposed into ZrN in vacuum according to the following equation:



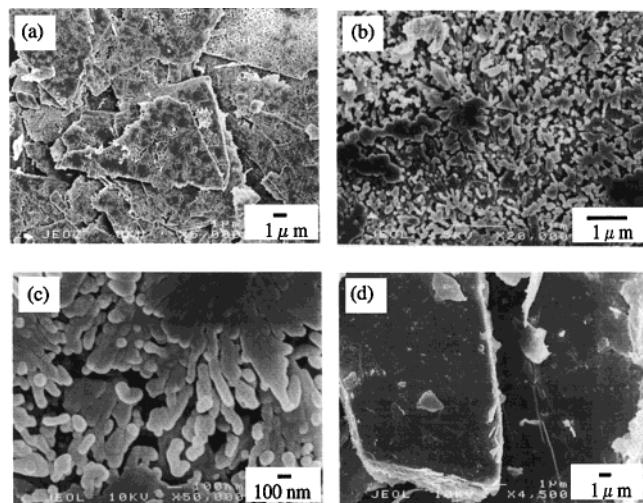
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**Figure 3.** SEM images of the reaction products obtained from  $\beta$ -ZrNCl (a–c) by the reaction with  $H_2/N_2$  mixed gas, observed at different magnifications, and (d) by the reaction with Na vapor.

where the yield of ZrN was only 75% on the basis of the  $\beta$ -ZrNCl formula. When the  $H_2$  content in the mixed gas  $H_2/N_2$  was  $<0.2$ , this type of decomposition was accompanied by the reaction given in eq 1, and the yield of ZrN decreased with the decrease of  $H_2$  content.

The SEM images of the thermally decomposed product under a stream of mixed gas  $H_2/N_2 = 1$  are shown in Figure 3a–c. The picture (Figure 3a) observed at a low magnification indicates that the ZrN that was formed apparently retained the shapes of layer-structured  $\beta$ -ZrNCl. At higher magnifications (Figure 3b and c), however, it was revealed that many holes were formed between the small grains of ZrN. The BET surface area of the thermally decomposed product, which was as high as  $8.3\text{ m}^2/\text{g}$ , was determined using nitrogen adsorption at liquid nitrogen temperature.

In method 2,  $\beta$ -ZrNCl crystals were allowed to react with sodium vapor in a vacuum-sealed glass tube at  $500^\circ\text{C}$  for 3 days. The crystals were converted into a mixture of ZrN and NaCl according to the following equation:

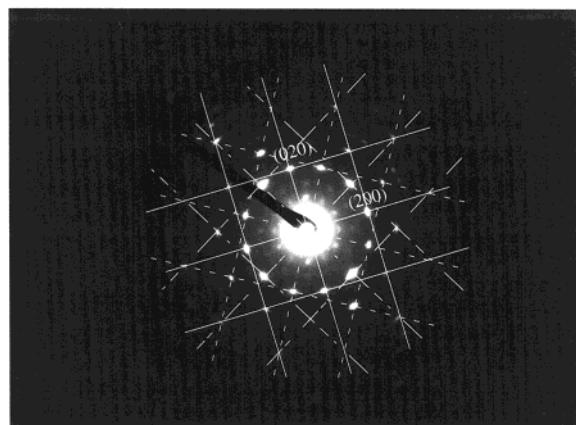


The XRD pattern of the washed product showed that the obtained ZrN crystals were highly oriented with the (001) plane parallel to the plane of the glass sample holder, as shown in Figure 2b; the diffraction peak was fairly broad. This suggested that the crystals were very thin, reflecting the shape of the starting crystals. The thickness was estimated to be about  $60\text{ \AA}$  using Scherrer's equation from the broadening of the ZrN(002) reflection.<sup>28</sup> The BET surface area, which was as high as  $12.9\text{ m}^2/\text{g}$ , was determined using nitrogen adsorption at liquid nitrogen temperature.

The SEM image of the reaction product is shown in Figure 3d. As can be seen, the shape of the  $\beta$ -ZrNCl layered crystals was similarly retained after the removal of the chlorine atoms by Na vapor. However, even at a high magnification, the formation of fine grains and

**Table 1. Chemical Analysis and Superconductivity Data of ZrN Prepared by Different Methods**

	ZrN <sub>calcd</sub>	ZrN (1)	ZrN (2)
reactant		$H_2/N_2$	Na vapor
reaction temperature, $^\circ\text{C}$		950	500
chemical composition			
Zr, %	86.7	86.1	86.4
N, %	13.3	13.5	12.7
total, %	100	99.6	99.1
atomic ratio	ZrN	$\text{ZrN}_{1.02}$	$\text{ZrN}_{0.96}$
surface area, $\text{m}^2/\text{g}$		8.3	12.9
superconductivity			
$T_c$ , K		9.5	6.2
$H_{c2}(0)$ , kOe		8.0	19



**Figure 4.** Selected area diffraction pattern of the product obtained from  $\beta$ -ZrNCl by the reaction with Na vapor. The 12-fold diffraction spots can be explained by the overlap of three  $a^*b^*$  reciprocal planes of ZrN rotated around each other by  $120^\circ$ .

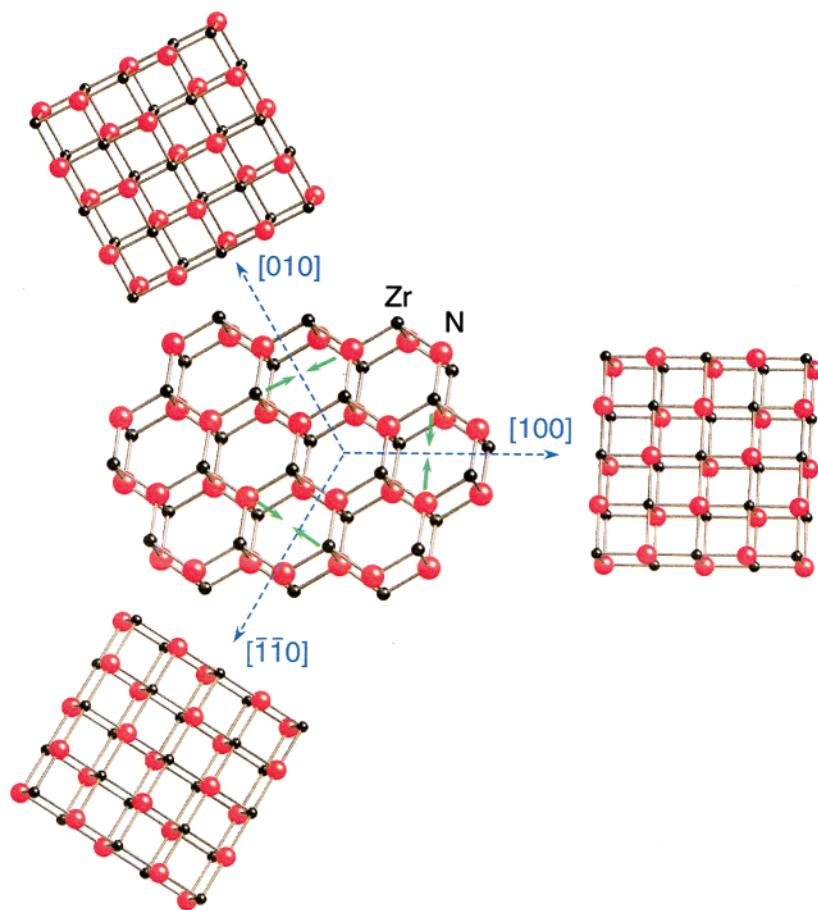
holes such as those found in the ZrN sample obtained by method 1 (Figure 2b and c) was not observed.

The chemical analysis data of the products are shown in Table 1. Note that the ZrN powders obtained by both methods 1 and 2 have the stoichiometric composition of 1:1 within the accuracy of the chemical analyses. Oxide contamination and nonstoichiometry were not detected on either ZrN sample.

### 3.2. TEM Study of the Sample Obtained by Method 2.

The electron diffraction pattern of the selected area of the thin ZrN crystal (2) was measured with the electron-beam incidence normal to the plane; this is shown in Figure 4. The pattern indicated that a thin ZrN sheet had a 12-fold symmetry axis rather than an orthogonal lattice of the (001) plane of the rock salt structure. This pattern can be explained in terms of the overlap of the three  $a^*b^*$  reciprocal planes of ZrN with a rotation of  $120^\circ$  with each other, as shown in Figure 4. This finding suggests that the honeycomblike ZrN layers between the chlorine layers are converted into ZrN(001) layers of the rock salt structure by expanding to three equivalent directions  $\langle 100 \rangle$  of  $\beta$ -ZrNCl. This change is schematically shown by the illustration in Figure 5. The appearance of the 12-fold axis indicates that such an expansion of the honeycomblike ZrN layers occurs in the three equivalent directions in a very similar way. Reaction 2 was carried out under a mild heating condition of  $500^\circ\text{C}$  with Na vapor, in contrast to the decomposition condition of reaction 1 at  $950^\circ\text{C}$  under a stream of  $H_2/N_2$  gas.  $\beta$ -ZrNCl is stable under heating at  $800^\circ\text{C}$  in vacuum or in a  $H_2/N_2$  gas atmo-

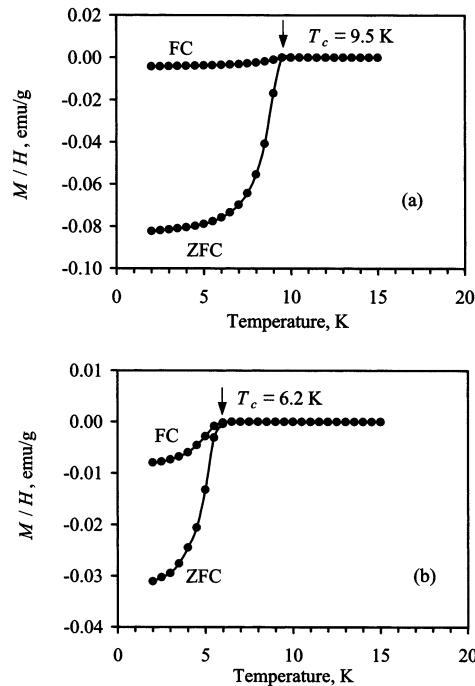
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**Figure 5.** Honeycomblike double ZrN layer of  $\beta$ -ZrNCl is converted to a ZrN(001) plane of the rock salt structure by expanding to the three equivalent directions.

sphere. The expansion of the double ZrN layers to  $\langle 100 \rangle$  directions should occur after the deintercalation of chlorine atoms by Na vapor. The expansion may occur in the same direction over several consecutive [Cl-Zr-N-N-Zr-Cl] slabs so that the resulting ZrN has a thickness of about 60 Å, as estimated from the broadening of the X-ray diffraction peak.

**3.3. Superconductivity of ZrN.** Bulk ZrN is a superconductor with a transition temperature ( $T_c$ ) of 10–10.7 K.<sup>17,29</sup> The magnetic susceptibilities of the ZrN samples prepared by two different methods (1 and 2) were measured using a SQUID magnetometer, and the results are shown in Figure 6a and b, respectively. Sample 1 showed a superconducting transition at  $T_c = 9.5$  K in a magnetic field of 10 Oe, in good agreement with the  $T_c$  of the bulk sample. Sample 2 showed superconductivity with  $T_c = 6.2$  K, which is much lower than that of the bulk sample. It is well known that zirconium nitride forms nonstoichiometric interstitial compounds and that the  $T_c$  varies with the composition; as the composition deviates from the stoichiometry, the  $T_c$  decreases from 10 to 2 K.<sup>30,31</sup> As shown in Table 1, however, both of the ZrN powder samples obtained in this study have the same stoichiometric composition. The low  $T_c$  observed for sample 2 can be attributed to the very small thickness of the particles rather than to



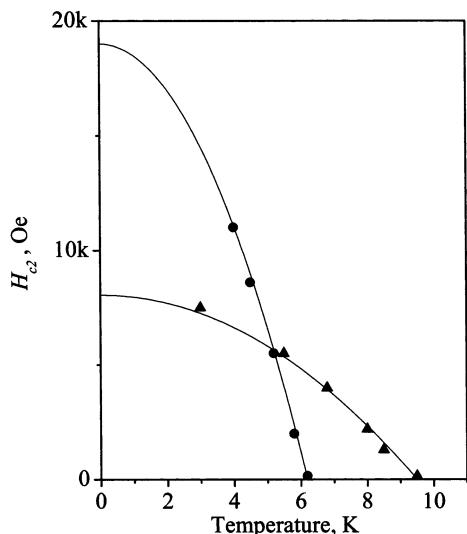
**Figure 6.** Temperature dependence of the magnetic susceptibility of the products obtained from  $\beta$ -ZrNCl (a) by the reaction with  $\text{H}_2/\text{N}_2$  mixed gas and (b) by the reaction with Na vapor. The magnetic field applied was 10 Oe for zero-field-cooling (ZFC) and field-cooling (FC) modes.

the difference in the stoichiometry. It has been reported that the  $T_c$ s of Nb and TiN films are reduced as the

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**Figure 7.** Temperature dependence of the superconducting upper-critical field ( $H_{c2}$ ) of the ZrN samples prepared ( $\blacktriangle$ ) by the reaction with  $H_2/N_2$  mixed gas and ( $\bullet$ ) by the reaction with Na vapor.

film thickness is decreased, when the thickness is comparable to or smaller than the superconducting coherence length.<sup>32–34</sup>

Figure 7 shows the upper-critical magnetic field ( $H_{c2}$ ) measured on the two samples (1 and 2) as a function of temperature. When the particle size of the superconductors is so small that the magnetic field penetration depth  $\lambda$  is comparable to the particle size, the rate of magnetic-field exclusion decreases in volume with the decrease in particle size, and a higher magnetic field

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( $H_{c2}$ ) is required to break the superconductivity.<sup>35</sup> The  $H_{c2}(0)$  value at  $T = 0$  K was determined by fitting the observed data to the following equation:<sup>36, 37</sup>

$$H_{c2}(T) = H_{c2}(0)\{1 - (T/T_c)^2\} \quad (4)$$

Note that sample 2 with the small thickness has a higher  $H_{c2}$  than sample 1, as expected. This finding is also in consistent with the explanation that the lower  $T_c$  of sample 2 can be attributed to the very small thickness of its ZrN (2) particles.

#### 4. Conclusions

Thin-layered ZrN with the rock salt structure was derived from layer-structured crystals of  $\beta$ -ZrNCl by deintercalation of the chlorine layers. The thin layers with a thickness of about 60 Å were highly oriented within the ZrN(001) plane. The electron diffraction studies revealed the formation mechanism of the thin layers of ZrN; the thin layers were formed by expanding the honeycomblike ZrN layers of  $\beta$ -ZrNCl to the three equivalent directions  $\langle 100 \rangle$  upon the deintercalation of the chlorine layers. The thin-layered ZrN had a low  $T_c$  of 6.2 K compared with that of the bulk ZrN at 9.5 K. The low  $T_c$  and high  $H_{c2}(0)$  values observed for ZrN derived from  $\beta$ -ZrNCl by deintercalation can be explained by the thin-crystal effect.

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