

# Superconductivity of Alkali Metal Intercalated $\beta$ -Zirconium Nitride Chloride, $A_xZrNCl$ ( $A = Li, Na, K$ )

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Alkali metal intercalated compounds  $A_xZrNCl$  ( $A = Li, Na, K$ ) were synthesized by the reaction of  $\beta$ -zirconium nitride chloride with *n*-butyllithium or the respective alkali metal naphthalenes. All of the compounds became superconductors with a transition temperature ( $T_c$ ) of ca. 15 K. Polar solvent molecules such as tetrahydrofuran, dimethylformamide, and propylene carbonate were co-intercalated with the alkali metals, expanding the interlayer spacing. The  $T_c$  was dependent solely on the amount of intercalated alkali metals, or the doping level; the kind of intercalated alkali metals and the interlayer separation were not influential to the  $T_c$ . Although  $\beta$ -ZrNCl is a semiconductor, only a small amount of doping of alkali metals was necessary for the superconductivity. Too much doping with alkali metals resulted in the decrease of  $T_c$  down to ca. 9 K.

## Introduction

In a previous study,<sup>1</sup> we reported a new type of layer structured superconductor, lithium intercalated  $\beta$ -zirconium nitride chloride,  $Li_{0.16}ZrNCl$ .  $\beta$ -ZrNCl adopts the  $CdCl_2$  type layer structure; the Zr–N–N–Zr layers occupy the Cd positions and are sandwiched between the close-packed chloride layers.<sup>2</sup> The layers with a sequence of [Cl–Zr–N–N–Zr–Cl] are stacked with each other by a weak van der Waals interaction. Lithium was intercalated into the van der Waals gap between the chloride layers.<sup>3</sup>  $\beta$ -ZrNCl itself is characterized as a semiconductor with a bandgap of ca. 3 eV. On lithium intercalation, it is changed into a metal with a color change from pale yellow green to black. The electrons are transferred from the intercalated lithium atoms to the ZrN layers through chlorine layers, and the empty  $t_{2g}$  band is partially filled with electrons, giving the metallic behavior. The lithium intercalated compound became a superconductor with a transition temperature ( $T_c$ ) of 12.5 K.<sup>1</sup> This is the first layered nitride superconductor.

The two-dimensional  $\beta$ -ZrNCl has a great flexibility in the modification of the structure: (i) the level of electron doping can be controlled by the intercalation of electron donors without changing the structure,<sup>4</sup> (ii) the kinds of doping metals can be changeable;<sup>5</sup> (iii) the interlayer spacing can also be varied by co-intercalation of organic solvent molecules with the doping metals.<sup>3,5,6</sup> Moreover, we have reported hydrogen uptake by the

nitrogen interlayers of [Cl–Zr–N]<sup>\*</sup>[N–Zr–Cl].<sup>7,8</sup> The concentration of the intercalated hydrogen was determined by <sup>1</sup>H NMR as well as FT-IR spectroscopy.

In this study, the effects of these variables to the superconductivity of  $\beta$ -ZrNCl are investigated.

## Experimental Section

**Materials.**  $\beta$ -ZrNCl was prepared by the reaction of  $ZrH_2$  with  $NH_4Cl$  at 650 °C and purified by a chemical transport according to the method reported elsewhere.<sup>9,10</sup> The as-transported sample contained hydrogen. The hydrogen content was determined to be  $H_{0.23}ZrNCl$  by <sup>1</sup>H NMR spectroscopy with reference to  $NH_4Cl$  as an internal standard. The dehydrogenation was carried out by the treatment with  $KMnO_4$ .<sup>8</sup> The as-transported sample was dispersed in a 0.1 M  $KMnO_4$  solution in 0.5 M  $H_2SO_4$  and refluxed at 373 K for 4 h. The sample was oxidized and most of hydrogen was removed to a level of  $H_{0.04}ZrNCl$ .

Three kinds of 0.1 M alkali metal naphthalene solutions (Naph-A,  $A = Li, Na, K$ ) in tetrahydrofuran (THF) were prepared by dissolving equimolar amounts of naphthalene and the respective alkali metals into THF purified by distillation. Butyllithium (Bu–Li) used was a 15% solution in *n*-hexane.

**Intercalation.** Lithium intercalation was carried out by dispersing  $\beta$ -ZrNCl into the Bu–Li solution in an argon-filled drybox. The sample was separated after standing for 1 day and washed with hexane. The sample was changed into a lithium intercalated phase, which was then soaked into propylene carbonate (PC) and dimethylformamide (DMF) in order to obtain the respective co-intercalation phases. The co-intercalated phases were separated by filtration using a Teflon filter in the argon-filled drybox. The amounts of alkali metal intercalated were varied by using different concentrations of Naph-A solutions in THF ( $A = Li, Na, K$ ), followed by washing with THF on a Teflon filter according to the procedure reported in a previous paper.<sup>5</sup>

**Analyses.** The X-ray powder diffraction (XRD) patterns of the intercalated samples were recorded under an argon

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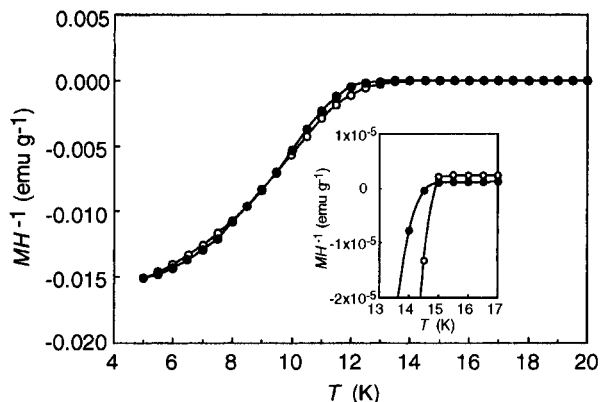
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**Figure 1.** Temperature dependences of the magnetization of the lithiated phases,  $\text{Li}_{0.16}\text{H}_x\text{ZrNCl}$  derived from as-transported  $\text{H}_{0.23}\text{ZrNCl}$  (●) and dehydrogenated  $\text{H}_{0.04}\text{ZrNCl}$  (○).

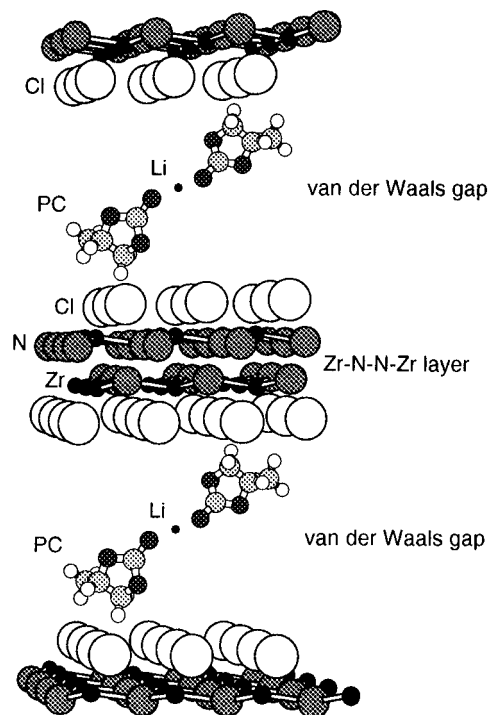
atmosphere in a cylindrical cover with polyethylene windows by using graphite monochromatized  $\text{Cu K}\alpha$  radiation. The amount of alkali metal intercalated was determined by an inductively coupled plasma (ICP) spectrometer (Perkin-Elmer, Optima 3000) on the sample dissolved in a mixture of hydrofluoric and sulfuric acid. Broad-line  $^1\text{H}$  NMR spectra were measured by a Bruker AMX-400 spectrometer. The magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design, MPMS-5). The sample sealed in a gelatin capsule was cooled to 5 K in a zero magnetic field (ZFC), and then the susceptibility was recorded up to 20 K in a magnetic field of ca. 50 Oe.

## Results

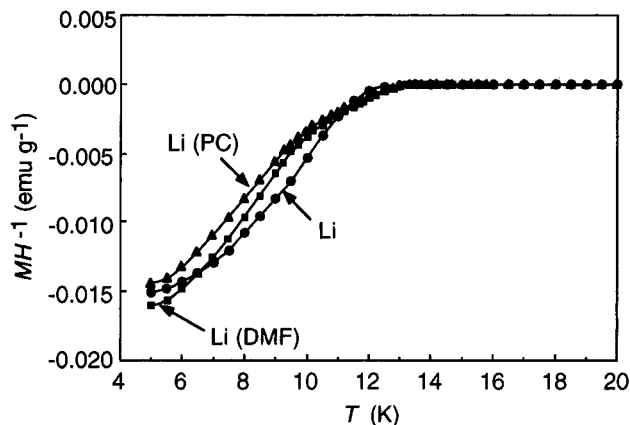
**Effect of Hydrogen Intercalation.** Lithium intercalation was carried on into as-transported and dehydrogenated samples with compositions of  $\text{H}_{0.23}\text{ZrNCl}$  and  $\text{H}_{0.04}\text{ZrNCl}$ , respectively. Both samples took up lithium up to 0.16  $\text{Li}/\text{ZrNCl}$ , and the basal spacing increased slightly from 0.92 to 0.93 nm. Figure 1 shows the temperature dependence of the magnetization of the two samples. The  $T_c$  was determined to be 15 K for both samples. In a previous study,<sup>1</sup> the  $T_c$  was 12.5 K, which was determined from the temperature at which the magnetization began to decrease from  $10^{-3}$  of the perfect diamagnetism. In this study, the  $T_c$  was determined from the point where the diamagnetic susceptibility began to exceed  $10^{-5}$  of the perfect diamagnetism ( $-1/4\pi$ ). The  $T_c$  of 12.5 K is corresponding to 15 K determined from this standard.

It is interesting to note that the hydrogen intercalation does not influence the superconducting behavior of  $\beta$ - $\text{ZrNCl}$ . The magnetic behaviors shown in Figure 1 for the samples with different hydrogen contents almost overlap with each other. Although the influence of the hydrogen located between the nitrogen layers is not clear, further study was made on the as-transported sample without dehydrogenation.

**Effect of Co-intercalation of Solvent Molecules.** DMF and PC molecules were co-intercalated with lithium when the lithium intercalated  $\beta$ - $\text{ZrNCl}$  with  $\text{Bu-Li}$ ,  $\text{Li}_{0.16}\text{ZrNCl}$ , was soaked into the respective liquids at room temperature. The basal spacings increased from 0.93 to 1.98 and 2.24 nm, respectively. The interlayer arrangement of the PC molecules co-intercalated with Li atoms between the layers was estimated in a previous study<sup>6</sup> on the basis of the one-dimensional Fourier analysis of the XRD data. A schematic structural model of the arrangement is drawn in Figure 2.



**Figure 2.** Schematic illustration of the crystal structure of propylene carbonate (PC) co-intercalated  $\text{Li}_x\text{ZrNCl}$ .



**Figure 3.** Temperature dependences of the magnetization of  $\text{Li}_{0.16}\text{ZrNCl}$  (●), and solvent co-intercalated phases,  $\text{Li}_{0.16}(\text{DMF})_y\text{ZrNCl}$  (■) and  $\text{Li}_{0.16}(\text{PC})_y\text{ZrNCl}$  (▲).

It is likely that DMF co-intercalated compound also has a similar structure with double adsorbed layers.

Magnetic susceptibilities of the two kinds of co-intercalated compounds were measured in a magnetic field of 50 Oe by a zero-field-cooled mode (ZFC) and are shown in Figure 3, together with that of  $\text{Li}_{0.16}\text{ZrNCl}$  without solvent co-intercalation. All of the magnetization curves showed a similar diamagnetism, indicating that the large expansion of the basal spacing by the co-intercalation of the solvent molecules does not influence the superconducting characteristics of  $\text{ZrNCl}$  layers. This finding suggests that the interaction between the layers is very weak from the beginning even without co-intercalation, and the superconductivity occurs within the  $\text{Zr-N}$  layers separated by chloride layers. Similar insensitiveness of the superconducting properties against the separation of the layers has been reported on the intercalation compounds of transition metal chalcogenides such as  $\text{TaS}_2$ .<sup>11</sup>

**Table 1. Basal Spacings and Compositions of Alkali Metal Intercalated Compounds.**

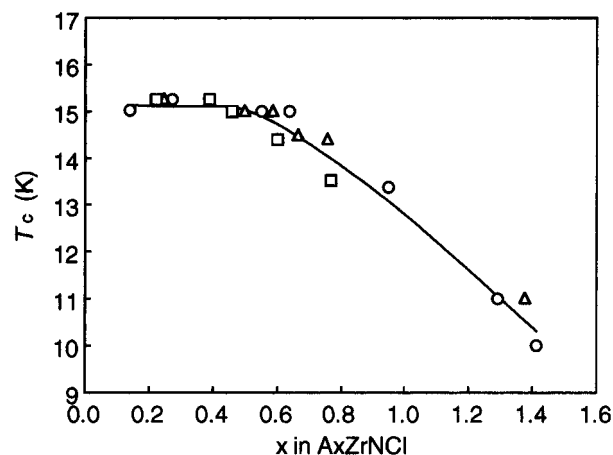
reagent	basal spacing (d) (nm)	interlayer composition/ZrNCl
Bu-Li	0.93	0.16Li
Naph-Li	1.35, 1.85	0.27Li + yTHF
	1.01, 1.59, 1.85	0.55Li + yTHF
	1.01, 1.59, 1.85	0.64Li + yTHF
	1.08, 1.85, 2.00	0.95Li + yTHF
	1.08, 1.65	1.29Li + yTHF
	1.08, 1.65	1.41Li + yTHF
Naph-Na	0.99	0.27Na
	1.06	0.59Na
	1.06	0.67Na
	1.06	0.76Na
	1.06	1.38Na
Naph-K	1.10, 1.30	0.39K + yTHF
	1.10, 1.30, 1.47	0.39K + yTHF
	1.10, 1.47	0.46K + yTHF
	1.10, 1.79	0.60K + yTHF
	1.10, 1.90	0.75K + yTHF

**Alkali Metal Intercalation Other Than Li.** The alkali metal intercalated compounds with different degrees of doping were prepared by varying the amounts of Naph-A (A = Li, Na, K) used for the reaction. Naph-Li is a stronger reducing agent than Bu-Li, and a deeper doping with Li can be made with THF solvent molecules co-intercalated. Mixtures of co-intercalation phases with different spacings were obtained, depending on the doping level. In the case of the reaction with Naph-Na, THF molecules were not co-intercalated with Na as found in a previous study.<sup>5</sup> Naph-K formed co-intercalation phases with different spacings depending on the doping level of K. Spacings found for the intercalation compound with different levels of doping are listed in Table 1.

The  $T_c$ 's of alkali metal intercalated phases were determined on the basis of the magnetic susceptibility study and are plotted in Figure 4 as a function of nominal composition of the respective alkali metals. The contents of alkali metals are nominal since some samples are mixtures of different spacings and different doping levels as shown in Table 1. However, it is interesting to note that the  $T_c$  is almost constant at ca. 15 K up to the doping of 0.4 mol of alkali metal/ZrNCl, irrespective of the kind of alkali metals, and then decreases gradually with the increase of the doping level. It appears that the  $T_c$  varies only as a function of the doping level; it does not depend on either the kind of alkali metals nor the spacings.

### Discussion

$\beta$ -ZrNCl is a unique two-dimensional framework for superconductivity. On intercalation or doping with alkali metals as electron donors, it is changed into a two-dimensional superconductor. The superconductivity occurs within Zr-N double layers of a molecular thickness. The ZrN layers are separated from each other by chloride layers and the co-intercalated organic molecules. Owing to the two-dimensional characteristics, the separation of the layers does not influence the superconducting behavior. It appears that alkali metals are completely ionized between the layers; the superconducting behavior depends not on the kind of the metals but solely on the amount of doping.



**Figure 4.**  $T_c$  versus alkali metal content of  $\text{Li}_x\text{ZrNCl}$  (○),  $\text{Na}_x\text{ZrNCl}$  (△), and  $\text{K}_x\text{ZrNCl}$  (□).

According to the BCS (Bardeen-Cooper-Schrieffer) theory for phonon-mediated superconductivity, the  $T_c$  is determined by two factors: the Debye frequency and the electron-phonon coupling constant. The transition metal nitrides are generally very hard and have high Debye frequencies, which are favorable as a framework for high  $T_c$  superconductivity. Some nitrides with the rock salt structure such as TiN, ZrN, and NbN, are superconductors with  $T_c$  at 5.5, 10.7, and 16.0 K, respectively.<sup>12</sup> The structure of  $\beta$ -ZrNCl consists of ZrN double layers sliced from a ZrN crystal parallel to the (111) plane, each layer being sandwiched between two chloride layers. Such ZrN layers should also be a good framework for superconductivity. The electron-phonon coupling constant is the product of  $N(E_f)$  and  $V$ , where  $N(E_f)$  is the density of electron states at the Fermi level, and  $V$  is the average electron pairing interaction. The increase in the amount of doping may increase  $N(E_f)$ , which is favorable for higher  $T_c$ . However, the  $T_c$  of  $A_x\text{ZrNCl}$  decreased with the increase of the doping level. Although  $\beta$ -ZrNCl is a semiconductor with a bandgap of ca. 3 eV, only a small amount of doping was sufficient for the superconductivity. Too much increase in the concentration of doping decreased the  $T_c$ . Too much doping may screen the phonon-electron interaction, and decrease the average electron pairing interaction ( $V$ ) for the formation of Cooper pairs. A similar overdoping behavior was reported in a bronze system,  $\text{Na}_x\text{WO}_3$ .<sup>13</sup> The highest  $T_c$  of the  $\text{Na}_x\text{WO}_3$  system is about 3 K, and the  $T_c$  decreased with the increase of the Na content. This was also explained in terms of the increase of screening effect.<sup>14</sup>

It is interesting to note that the  $T_c$  of the  $A_x\text{ZrNCl}$  (A = Li, Na, K) system approached 9 K for the  $T_c$  of ZrN with the increase of doping. In the context of doping, the electron state of ZrN of the rock salt structure is corresponding to  $x = 1$  of  $A_x\text{ZrNCl}$ , and it should be in a state of too much doping for superconductivity. In case of the three-dimensional crystal, it is difficult to control the doping level by chemical modification.

### Conclusions

A new type of layer structured nitride superconductors,  $A_x\text{ZrNCl}$  (A = alkali metals) are modified in a

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variety of ways; doping level, interlayer spacing, and the kind of alkali metals. The characterization of these superconductors showed that they were two-dimensional superconductors and conductivity occurred within the individual thin crystalline layers. For the superconductivity only a small amount of doping is sufficient. Overdoping decreases the  $T_c$ , which is explained in terms of screening effect.

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