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Preparation and Superconductivity of New Stage and Polytypic Phases in Potassium-Intercalated Zirconium Nitride Chloride (K_xZrNCl)

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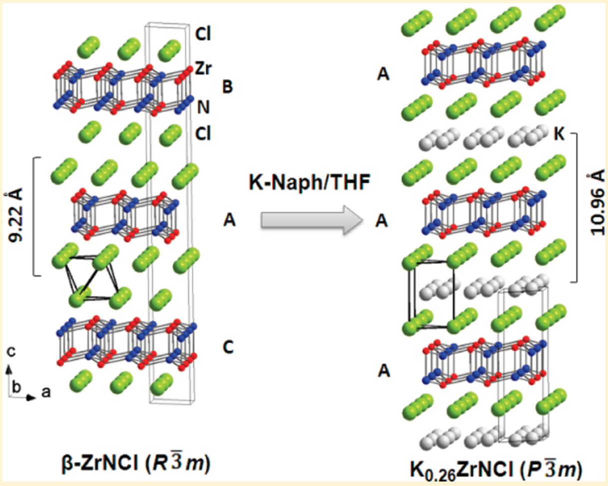
S *Supporting Information*

ABSTRACT: Potassium was intercalated into β-ZrNCl layer structured crystals using a K-naphthalene solution in tetrahydrofuran (THF), and a direct reaction with potassium metal. New polytypic and intermediate-stage intercalation compounds have been obtained with different amounts of potassium and the co-intercalation of THF. The structure and the formation mechanism have been discussed. The intercalation compounds showed superconductivity with the transition temperatures of 11.5−15.0 K. The higher critical temperature (T_c) values of the lower K-doped and co-intercalated phases can be interpreted in terms of the unconventional superconductivity of the present system.

KEYWORDS: superconductors, intercalation compounds, β-ZrNCl, X-ray structural characterization



INTRODUCTION

β-ZrNCl has a layered structure consisting of [Cl−Zr−N−N−Zr−Cl] slabs, each of which is composed of a honeycomb-like double ZrN layer sandwiched between two close-packed Cl layers. Such slabs are separated by a van der Waals gap with a rhombohedral stacking sequence in the space group $R\bar{3}m$.[1−6] Upon intercalation of alkali metals into the van der Waals gap (interlayer space) between Cl layers, β-ZrNCl becomes superconductors with transition temperatures (T_c) ranging from 11.5 K to 15.5 K.[7,8] Fogg et al. has intercalated organometallics (cobaltocene, 1,1′-dimethylcobaltocene, and decamethylcobaltocene) into β-ZrNCl showing a similar T_c at 14 K.[9] β-ZrNCl co-intercalated with magnesium and propylene carbonate (PC) showed a superconductivity of $T_c \approx 15$ K.[10] The hafnium analog, β-HfNCl, which is isotypic with β-ZrNCl, forms a Li- and THF-co-intercalated compound $Li_{0.48}(THF)_yHfNCl$ with a basal spacing of 18.7 Å, which exhibits superconductivity with T_c = 25.5 K, which is a remarkably high transition temperature for noncuprate compounds.[11] Note that most of the high-T_c superconductors have been found in layer structured compounds such as cuprates,[12] MgB_2,[13] recently found iron pnictides,[14] and the present electron-doped MNCl (M = Ti, Zr, Hf). The pristine β-MNCl (M = Zr, Hf) are semiconductors having an optical band gap of 3−4 eV, which are changed into superconductors by electron doping via intercalation of electron dopants.[15,16] The advantages of the layer structured superconductors derived by intercalation are as follows:

(i) the doping can be done without substitutional modification in the superconducting layers;
(ii) a variety of dopants can be used such as alkali, alkaline-earth metals, and organic Lewis bases, and the amount of doping can be controlled; and
(iii) the interlayer separation of the superconducting layers can be controlled by expanding the interlayer space by co-intercalation of polar solvents.

In the intercalation of alkali metals into β-ZrNCl, the types of alkali metals do not influence the T_c value, and the increase of the doping level rather decreases the T_c value.[17] Taguchi et al. studied the effect of the amount of lithium doping on β-ZrNCl, and they found that the T_c value increases from 11.5 K to 15.5 K as the amount of doping decreases from $x = 0.32$ to $x = 0.06$ in Li_xZrNCl.[8] The Li_xZrNCl compound suddenly changed to a semiconductor at $x \leq 0.05$. The interlayer separation of alkali-metal-intercalated β-ZrNCl increased upon the co-intercalation of organic solvent molecules such as THF and PC, up to ∼30 Å.[18−20] The increase in spacing should be considered to decrease the coupling between the layers; nevertheless, the T_c value increases

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by ~2 K as the spacing increases. These behaviors cannot be understood in the framework of the Bardeen, Cooper, and Schrieffer (BCS) mechanism. The electron-doped β-ZrNCl and β-HfNCl are considered to be unconventional superconductors; these have attracted much attention from theoretical as well as experimental physicists.[8,18,19,21−29]

The formation of stage compounds is often observed in graphite and layer-structured chalcogenide intercalation compounds.[30,31] In graphite intercalation compounds (GICs), when all the intervals between carbon layers are occupied by an intercalant layer, the compound is said to be "first stage". In the *n*-stage compounds, the intervals are partially occupied by the intercalated layers, and the intercalant layers are separated by *n* graphite layers. Staging influences the physical properties of GICs. It would be interesting to prepare stage compounds in the intercalated β-ZrNCl system to measure the influence on superconductivity. Oro-Sole et al.[32,33] prepared intermediate-stage compounds of Na-doped β-HfNCl, where intercalated and nonintercalated layers are randomly stacked, having an intermediate basal spacing between the nonintercalated and first-stage compounds. The intermediate phase had a T_c value of 20 K, which is lower than that of the first-stage compound $Na_{0.29}HfNCl$ (24 K). In this study, an attempt has been made to prepare K-doped β-ZrNCl, and new K-intercalated polytypic phases have been found; the THF-co-intercalated compound is changed to a new stage phase upon evacuation. The structural change and superconductivity of the new compounds will be discussed.

EXPERIMENTAL SECTION

β-ZrNCl Preparation and Intercalation. β-ZrNCl was prepared by flowing NH_4Cl vapor over ZrH_2 in a N_2 stream at 650 °C, and then recrystallized by chemical transport with the aid of NH_4Cl in a vacuum-sealed fused-silica tube placed horizontally in a two-zone furnace (750−850 °C), as described elsewhere.[34,35] The intercalation of potassium was performed using a 0.1 M K-naphthalene solution in THF (K-Naph/THF).[20] β-ZrNCl was dispersed in the solution in such a way that the K/ZrNCl molar ratios in the reactant ranged from 0.1 to 0.5 under stirring for 12 h at room temperature. In another K-intercalation process, β-ZrNCl was mixed with potassium metal directly in a K/ZrNCl molar ratio of 0.5 in a vacuum-sealed Pyrex glass tube, and heated at temperatures ranging from 75 °C to 150 °C. The completion of the reaction could be monitored by the disappearance of the metal, accompanied by a color change of β-ZrNCl from pale yellow green to a golden color. All the manipulations of the samples were carried out in an argon-gas-filled glovebox (mBRAUN), to prevent the contact with moisture and oxygen.

Analyses and Characterization. The powder X-ray diffraction (XRD) patterns of β-ZrNCl and the intercalated samples were measured using an imaging plate (IP) Guinier camera (Huber G670) with monochromated Cu Kα_1 (λ = 1.540596 Å) or Mo Kα_1 (λ = 0.709260 Å) radiation. The sample for XRD measurement was sealed in a thin Pyrex glass capillary with a diameter of ~0.3 mm. The intercalated samples were very air-sensitive. The use of a glass capillary can protect the samples from being exposed to humid air, and the use of rotating goniometer for the capillary also can avoid the preferred orientation of the layered-structure sample. The XRD data thus obtained made it possible to determine the polytypic changes of the layered crystals. The XRD patterns were analyzed by the Rietveld refinement, using the TOPAS-Academic program.[36] The amount of potassium intercalated was determined on the basis of zirconium content by inductively coupled plasma (ICP, iCAP 6000 series, Thermo Scientific) after dissolving the sample in a HF-HNO_3 mixed-acid solution. The magnetic susceptibility was measured on a SQUID magnetometer under zero-field-cooled (ZFC) and field-cooled (FC) conditions, subjected to a magnetic field strength of 20 Oe in a temperature range of 2−20 K. The samples were sealed in Pyrex glass tubes to prevent the presence of moisture during the measurement.

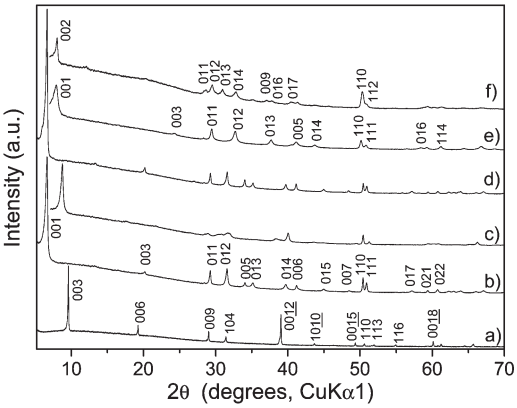


Figure 1. XRD patterns measured using a Guinier camera with Cu Kα_1 radiation: (a) pristine β-ZrNCl; (b) $K_{0.08}(THF)_yZrNCl$; (c) $K_{0.08}ZrNCl$ prepared by removing THF by evacuation from the sample described in panel b; (d) $K_{0.08}(THF)_yZrNCl$ obtained by immersing the sample described in panel c into THF; (e) $K_{0.26}ZrNCl$; and (f) $K_{0.26}(PC)_yZrNCl$.

RESULTS AND DISCUSSION

Potassium Intercalation from K-Naph/THF Solution and XRD Study. The intercalation behavior is strongly influenced by the molar ratio K/ZrNCl used for the reaction of K-Naph/THF solution (0.1 M) with β-ZrNCl. When the K/ZrNC(*l*) molar ratio was < 0.3, the basal spacing of the product increased to 13.14 Å from 9.22 Å of the pristine sample. When the K/ZrNC(*l*) molar ratio was ≥ 0.3, the spacing only increased to 10.96 Å. The small basal spacing phase implies that only K atoms are intercalated, whereas the larger basal spacing suggests that THF molecules are co-intercalated with K. The color disappearance of K-Naph/THF solution after intercalation reaction indicates that almost all of the potassium in the solutions was intercalated. This is also proved by ICP analysis of the two samples obtained with a K/ZrNCl molar ratio of 0.1 and 0.3, which shows the K/Zr atomic ratios were 0.08 and 0.26, respectively. Therefore, the chemical formula of these two samples can be written as $K_{0.08}(THF)_yZrNCl$ and $K_{0.26}ZrNCl$. It is very likely that the higher K/ZrNCl molar ratio of the reactant yielded the intercalation compound with the high K occupation, which would make co-intercalation of the THF difficult. Figure 1 shows the XRD patterns of two products, $K_{0.08}(THF)_yZrNCl$ and $K_{0.26}ZrNCl$, in comparison with that of the pristine β-ZrNCl. The XRD patterns for $K_{0.08}(THF)_yZrNCl$ (Figure 1b) and $K_{0.26}ZrNCl$ (Figure 1e) can be indexed based on the lattice parameters and the space groups shown in Table 1. The Rietveld analysis was performed on the $K_{0.26}ZrNCl$ sample, and the results are shown in Table 1 and Figure 2. Note that the lattice parameters in the *ab* plane are essentially unchanged upon intercalation, but the stacking pattern of the layers is changed, leading to the change in the polytype from $R\bar{3}m$ to $P\bar{3}m$. The refinement result of the pristine powder sample is in good agreement with the data obtained by the single-crystal study performed by Chen et al.:[6] the crystallographic

Table 1. Lattice Parameters and Atomic Coordinates of β-ZrNCl and K-Intercalated Compounds

	β-ZrNCl[a]	β-ZrNCl	$K_{0.26}ZrNCl$	$K_{0.08}(THF)_yZrNCl$	$K_{0.26}(PC)_yZrNCl$
space group	$R\bar{3}m$ (No. 166)	$R\bar{3}m$ (No. 166)	$P\bar{3}m$ (No. 164)	$P\bar{3}m$ (No. 164)	$P\bar{3}m$ (No. 164)
Z	6	6	2	2	2
lattice parameters					
a (Å)	3.6046(4)	3.6057(1)	3. 6295(3)	3.6143(2)	3.625(3)
c (Å)	27.672(4)	27.6748(4)	10. 9650(11)	13.1449(12)	21.830(5)
V (Å^3)	311.38(7)	311.60(1)	125.10(2)	148.71(2)	28.43(7)
atomic coordinates (x, y, z)					
Zr	0, 0, 0.11924(1)	0, 0, 0.11950(1)	$^2/_3$, $^1/_3$, 0.6095(3)		
N	0, 0, 0.38780(3)	0, 0, 0.38737(3)	$^2/_3$, $^1/_3$, 0.4072(13)		
Cl	0, 0, 0.19771(8)	0, 0, 0.20241(11)	0, 0, 0.2065(13)		
K[b]			$^2/_3$, $^1/_3$, 0		
R_{wp}, R_{exp} (%)		5.10, 1.81	6.32, 2.07		

[a] Single-crystal data taken from ref 6. [b] The occupancy of K in $K_{0.26}ZrNCl$ is 0.52.

parameters are given in Table 1, and the Rietveld refinement is given in Figure S1a of the Supporting Information. The XRD pattern of the co-intercalation phase $K_{0.08}(THF)_yZrNCl$ was also refined via the Rietveld method (see Figure S1b of the Supporting Information), ignoring the presence of organic solvent molecules. The organic molecules have a weak contribution to the total XRD pattern. The pattern can also be indexed using the same space group, $P\bar{3}m$, and the lattice parameters could be refined as shown in Table 1. In the pristine β-ZrNCl, two adjacent layers are stacked, to form octahedral coordination interstices between the Cl layers. Upon potassium intercalation, two layers are mutually shifted to form trigonal prism coordination interstices, which are partially occupied by K atoms, as schematically shown in Figure 3. The composition $K_{0.5}ZrNCl$ corresponds to a full occupancy of the trigonal prism sites.

For the co-intercalation compound $K_{0.08}(THF)_yZrNCl$, the d-spacing of the pristine sample was increased to 13.14 Å from 9.22 Å. The expansion, $\Delta d = 13.14 - 9.22$ Å $= 3.92$ Å, suggests that the molecular plane of THF is oriented parallel to the ZrNCl layer. THF molecules in the co-intercalated phase were removed from the interlayer space via a simple evacuation at 200 °C for 4 h, and a new phase with a basal spacing of 10.22 Å was obtained (see Figure 1c). The ICP analysis revealed that the K/Zr atomic ratio was maintained at 0.08 after the evacuation. The basal spacing (10.22 Å) of the evacuated phase is smaller than that of the K-atom-alone intercalated phase $K_{0.26}ZrNCl$ with a spacing of 10.96 Å. Although the potassium content in the 10.22 Å phase is much lower than that of the 10.96 Å phase, the K atoms in the interlayer space should keep the layers apart by size in a similar way in the 10.96 Å phase (the first-stage phase), giving a similar basal spacing value. The spacing should not be dependent on the potassium content in the compounds without co-intercalation. Spacing smaller than that of the first-stage phase can be explained in terms of the formation of an intermediate phase between the first-stage and the nonintercalated phases. When the first-stage phase with a spacing 10.96 Å and the nonintercalated phase with a spacing 9.22 Å are regularly stacked upon each other, the second-stage compound having an identity period of $d = 9.22 + 10.96$ Å $= 20.18$ Å would be formed. On the other hand, when the two types of layers with different basal spacings are randomly stacked, an intermediate stage compound is obtained; we will have an average spacing of $d = (9.22 + 10.96)/2$ Å $= 10.09$ Å. Unlike the regular second-stage compound, the intermediate stage compound does not have an integral series of reflections for the basal reflections; only the d_{001} reflection shows a steep diffraction peak for the average spacing, and other peaks are rather broad, as shown in Figure 1c. Very similar results were reported on the intermediate-stage compound of Na-intercalated $Na_{0.125}HfNCl$,[33] which does not form any co-intercalation compound with THF. Intermediate-stage compounds are often observed in mixed-layer clay systems or interstratified clay minerals.[37]

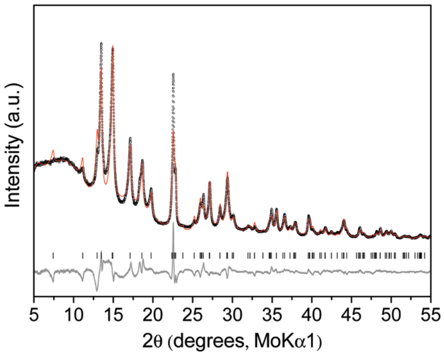
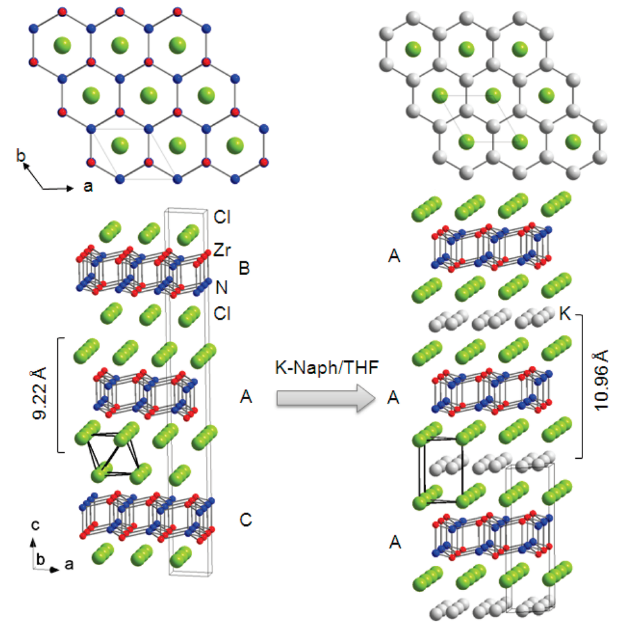


Figure 2. Rietveld analysis of the X-ray diffraction (XRD) pattern of $K_{0.26}ZrNCl$, measured using a Guinier camera with Mo Kα_1 radiation. Open circles show the observed data points, and the solid line (in red) represents the calculated diffraction pattern.

The intermediate-stage phase with a spacing of 10.22 Å reversibly reverted to the initial co-intercalated phase with a basal spacing of 13.14 Å upon immersion into THF (Figure 1d). A possible reaction mechanism of the reversible change is schematically shown in Figures 4c and 4d. The co-intercalation compound $K_{0.08}(THF)_yZrNCl$ is the first-stage compound with a stacking of the same type of the intercalated layer [I_c]. The first-stage compound is changed to the intermediate-stage compound with a random stacking of the two types of layers, [I] and [P], intercalated and nonintercalated layers, respectively shown in Figures 4a and 4b. The occupancy by K atoms in $K_{0.08}(THF)_yZrNCl$ may be too low for the first-stage phase without the presence of co-intercalated THF, and, upon removal of THF, K atoms migrate to form domains with a higher potassium concentration within the same layers, leaving nonintercalated regions as shown in Figure 4d (i.e., a phase separation occurs within the same interlayer space). The phase separation results in the random stacking of the two types of layers in the



β-ZrNCl ($R\bar{3}m$) K$_{0.26}$ZrNCl ($P\bar{3}m$)

Figure 3. Polytype change from pristine β-ZrNCl ($R\bar{3}m$) to the first-stage K$_{0.26}$ZrNCl ($P\bar{3}m$). Structures A, B, and C show the stacking sequence of [Cl−Zr−N−N−Zr−Cl] slabs; the Zr, N, Cl, and K atoms are colored red, blue, green, and gray, respectively. K atoms are located at the trigonal prism sites between the Cl layers.

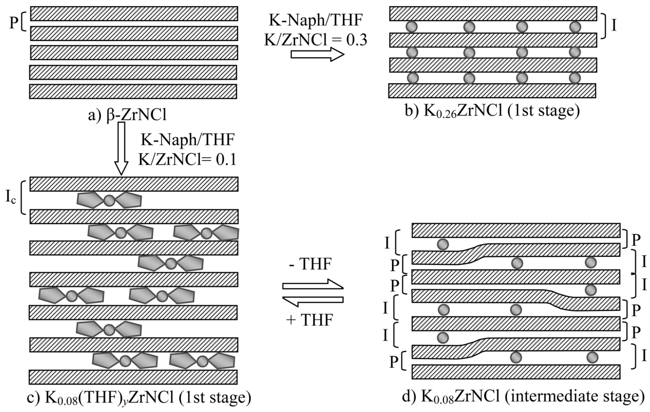


Figure 4. Schematic illustration of the two types of first-stage K-intercalated compounds (b) K$_{0.26}$ZrNCl and (c) K$_{0.08}$(THF)$_y$ZrNCl obtained by the reaction of (a) β-ZrNCl with K-Naph/THF in different molar ratios. The first-stage compound K$_{0.08}$(THF)$_y$ZrNCl (panel c) is changed into the intermediate-stage compound K$_{0.08}$ZrNCl (panel d) upon removal of THF, which reverts to the first-stage compound reversibly upon immersion into THF. Solid circles and pentagons denote K atoms and THF molecules, respectively. P, I, and I$_c$ represent the spacings of the pristine β-ZrNCl, K-intercalated, and K/THF-co-intercalated phases, respectively.

intermediate-stage phase. Upon immersion into THF, K atoms are redistributed uniformly with co-intercalation of THF, and the compound returns to the first-stage structure. The K$_{0.26}$ZrNCl phase does not co-intercalate THF with a dipole moment of 1.75 D (D = 3.3356×10^{-30} C m), but via immersion into PC with a much larger dipole moment of 4.94 D, a new co-intercalated compound K$_{0.26}$(PC)$_y$ZrNCl with an expanded spacing as large as 21.83 Å is obtained. A similar co-intercalation was reported in the preparation of Na$_{0.28}$(PC)$_y$HfNCl with a spacing of 22.2 Å by Hotehama et al.[19] The first-order reflection for the expanded spacing is not measured in Figure 1f, because of the out-of-range 2θ values covered by the Guinier camera with Cu Kα_1 radiation. The pattern can also be indexed on space group $P\bar{3}m$; the lattice parameters including the basal spacing (the c parameter) are given in Table 1.

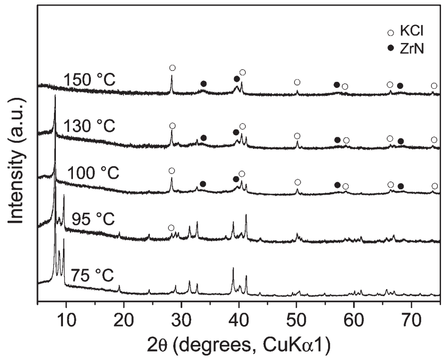


Figure 5. XRD patterns of the samples obtained by the direct reaction β-ZrNCl with potassium metal at temperatures ranging from 75 °C to 150 °C.

There are two types of polytypes for β-MNX (M = Zr, Hf; X = Cl, Br, I): the SmSI and YOF types with the same space group $R\bar{3}m$. The stacking sequence of [X−M−N−N−M−X] slabs are the ZrCl and the ZrBr types, respectively.[15,16] β-MNX with halogen atoms with large ionic sizes, such as ZrNI, HfNI, and HfNBr, adopt the YOF type, and the other compounds adopt the SmSI type. Upon Li intercalation in β-ZrNCl, the polytype changes from the SmSI to the YOF type, and the Li atoms are expected to have the octahedral interstices between the Cl layers.[38] In Na-intercalated β-HfNCl, it has been reported that the polytype also changed from the SmSI type to the YOF type.[2] Upon K intercalation in β-ZrNCl in this study, the polytype has changed to the new one with the space group $P\bar{3}m$, and the K atoms are located in the trigonal prism sites. The polytype change associated with the K intercalation in β-ZrNCl is schematically shown in Figure 3. Note that the stacking of the [Cl−Zr−N−N−Zr−Cl] slabs is changed from C−A−B to A−A−A in the K-intercalated compound, forming the trigonal prism coordination by Cl atoms to have K atoms in the interstices.

Potassium Intercalation by the Direct Reaction with Metal and XRD Study. Figure 5 shows the XRD patterns of the products obtained from the direct reaction of potassium metal with β-ZrNCl (K/Zr molar ratio of 0.5) at temperatures in the range of 75−150 °C for 6 h, which is higher than the melting point of potassium (63 °C). At 75 °C, the product was a mixture of three phases with basal spacings of 10.96, 10.22, and 9.22 Å. These spacings respectively correspond to the first-stage, intermediate-stage, and unreacted pristine phases found in the preparation using K-Naph/THF solutions. The content of the first-stage phase increases as the reaction temperature was increased up to 95 °C with the unreacted pristine phase remaining; the formation of small amount of KCl was observed. At the reaction temperature of 100 °C, the pristine ZrNCl and the intermediate phase disappeared, and broad diffraction peaks due to the formation of ZrN appeared. At 150 °C, the product consisted of only ZrN and KCl. The reaction was too rigorous to control the reaction products. We could not obtain the intermediate- and first-stage phases separately as single phases.

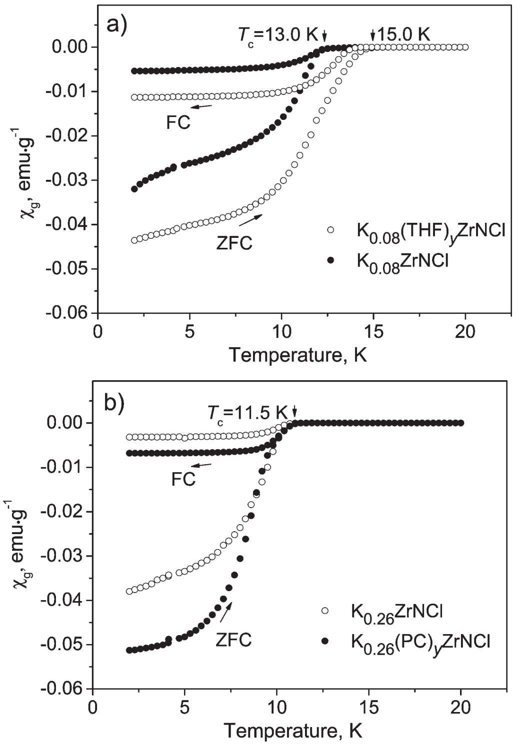


Figure 6. Magnetic susceptibilities of K-intercalated β-ZrNCl compounds: (a) $K_{0.08}(THF)_yZrNCl$ and $K_{0.08}ZrNCl$; (b) $K_{0.26}ZrNCl$ and $K_{0.26}(PC)_yZrNCl$.

Magnetic Susceptibility Study. Magnetic susceptibility was measured on the K-intercalated compounds obtained in the reaction of β-ZrNCl with K-Naph/THF, and the results are shown in Figure 6. All of the K-intercalated compounds show a strong diamagnetic transition that is due to superconductivity (the Meissner effect). The first-stage co-intercalated compound $K_{0.08}(THF)_yZrNCl$ showed the highest T_c value at 15.0 K. Upon the removal of THF, the resulting intermediate-phase $K_{0.08}ZrNCl$ has a lower T_c value of 13.0 K, which reverts to 15.0 K upon reswelling by immersion into THF (see Figure S2 in the Supporting Information). The ICP analysis of the evacuated sample showed that the K/Zr atomic ratio was maintained at 0.08 by evacuation, implying that the decrease of the spacing is responsible for the decrease in the T_c value. The first-stage compound $K_{0.26}ZrNCl$ exhibited the lowest T_c value (11.5 K). The T_c value was not changed at 11.5 K upon co-intercalation of PC. As mentioned in the Introduction, it has been reported that the T_c value of electron-doped β-ZrNCl decreases as the doping amount increases,[8,17] and the increase in the spacing by co-intercalation increases the T_c value by ~2 K.[18] Because of these unusual superconducting behaviors, the electron-doped β-ZrNCl is considered to be an unconventional superconductor.[8,18] The T_c value of 11.5 K for $K_{0.26}ZrNCl$ is less than that of $K_{0.08}ZrNCl$ (13.0 K), and the co-intercalated phase $K_{0.08}(THF)_yZrNCl$ exhibited the highest T_c value in this study (15.0 K). These T_c values are comparable to the results reported by Taguchi et al.[8] for Li_xZrNCl ($0.06 \leq x \leq 0.3$) and by Kasahara et al.[39] for the co-intercalated compounds $Li_{0.05}M_yZrNCl$ (M = THF, PC). Our present results also support the unconventional superconductivity of the electron-doped β-ZrNCl.

The mechanism of the unconventional superconducting behavior of the electron-doped and co-intercalated β-ZrNCl is not clear. According to a theoretical physicist, the two-dimensionality of the electronic state may play an essential role in increasing the T_c value.[29,39] The enhancement of T_c upon co-intercalation was discussed in terms of the nesting properties of the Fermi surface. Upon the increase of the interlayer separation by co-intercalation, the 2D nature of the electronic structure becomes stronger, which reduces the skew of the cylindrical Fermi surface along the k_z-direction and improves the nesting properties of the Fermi surface. The nesting of the Fermi surface enhances the charge susceptibility and/or spin susceptibility.[18] In the conventional BCS phonon mechanism, the nesting of the Fermi surface is not related to the enhancement of the T_c value. The effect of the formation of the intermediate-stage compound is not clear. The decrease of the doping concentration in the intermediate phase may have an effect of increasing the T_c value; however, inhomogeneous distribution of the charge, as shown in Figure 4d, may be not favorable for superconductivity. The THF-co-intercalated phase $K_{0.08}(THF)_yZrNCl$ is the first-stage compound with the expanded spacing and has the highest T_c value in this study. The PC-co-intercalated phase $K_{0.26}(PC)_yZrNCl$ also has an expanded spacing as large as 21.83 Å, but it did not show the increase in T_c. Although the reason is not yet clear, it is likely that the electron-doping level in $K_{0.26}ZrNCl$ is so high that the expansion of the spacing hardly influenced the T_c value.

■ CONCLUSIONS

New stage and polytypic compounds were prepared in the K-intercalated β-ZrNCl system with the aid of co-intercalation of THF molecules. The reversible change of the structures between the $K_{0.08}ZrNCl$ (intermediate-stage) and $K_{0.08}(THF)_yZrNCl$ (first-stage) phases suggests a structural model for the intermediate-stage compound, where the K atoms are distributed in domains. Upon K intercalation, the stacking sequence of the β-ZrNCl slabs are changed from $R\bar{3}m$ to $P\bar{3}m$, with regard to the space group, and the K atoms occupy the trigonal prism sites between the Cl layers. The increase of the T_c value of the new intercalated compounds as a function of the decrease of the doping concentration and the increase of the basal spacing implies unconventional superconductivity of the electron-doped β-ZrNCl.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Rietveld analysis of the XRD diffraction patterns of β-ZrNCl and $K_{0.08}(THF)_yZrNCl$; magnetic susceptibility of $K_{0.08}(THF)_yZrNCl$ obtained by immersion of the evacuated sample $K_{0.08}ZrNCl$ into THF. (PDF) This information is available free of charge via the Internet at http://pubs.acs.org.

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