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Superconductivity in electron-doped layered TiNCl with variable interlayer coupling

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Titanium nitride chloride (TiNCl), a band semiconductor with the α-form layered structure, becomes a superconductor with a transition temperature $T_c \approx 18.0$ K by electron doping via alkali-metal intercalation. Upon cointercalation of various kinds of organic solvent molecules with alkali atoms, the superconducting layered crystals are swelled to different extents adjusting to the size of the molecules, and the T_c decreases linearly down to 6.5 K as a function of $1/d$, where d is the interlayer separation (basal spacing) of the expanded nitride layers, implying the importance of the Coulomb interlayer coupling for superconductivity. This is in strong contrast to a previous finding that the T_c of the electron-doped ZrNCl and HfNCl with the β-form layered structure rather increases with the increase of d upon a similar cointercalation of solvent molecules.

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I. INTRODUCTION

Most recently developed high-transition-temperature (high-T_c) superconductors, such as cuprates, MgB_2, and iron pnictides, have characteristic two-dimensional layered structures.[1–3] Continuing interest has been generated in the favorable factor of two-dimensional (2D) structures in realizing high-T_c superconductivity.[4] The role of interlayer coupling for electron pairing has been discussed by various researchers.[5–7] The first systematic study on the interlayer coupling in superconductivity was made on intercalation compounds of transition-metal sulfides, 2H-TaS_2 and 2H-NbS_2, with Lewis bases by Gamble *et al*. before the discovery of cuprate high-T_c superconductors.[8] The pristine 2H-TaS_2 is a layered superconductor with $T_c = 0.8$ K. Various kinds of Lewis bases, such as pyridine, and alkyl amines can be intercalated, expanding the separation of TaS_2 superconducting layers. Lewis bases act as electron donors. Although the T_c increases upon intercalation, it is almost insensitive at about 3 K to the expansion of the basal spacing from 9 to 57 Å. The T_c of 2H-NbS_2 rather decreases from 6.2 to 2–4 K upon similar intercalation. The insensitivity of T_c to the expansion of basal spacing suggests that the interlayer coupling is not important to the stability of the superconducting state, and the attractive electron-electron interaction is confined to TaS_2 and NbS_2 metallic layers. Intercalation of organic compounds with long alkyl chains into bismuth-based high-T_c cuprates $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ ($m = 1$ and 2) was studied.[9] It was reported that even though the interlayer distance remarkably increased to tens of angstroms, the T_c was nearly the same as that of the pristine cuprates, suggesting again the superconductivity is governed by the 2D nature of the pristine compounds. Baker *et al.*[10] measured muon spin resonance (μ^+SR) of similar bismuth-based high-T_c cuprates and found that the 2D superfluid density was constant irrespective of the expanded basal spacings with long alkyl chains.

We have developed a new series of layered superconductors based on metal nitride chlorides MNCl (M = Zr, Hf) by electron doping via alkali-metal intercalation.[11] The pristine host layers have the SmSI-type structure, called the β form, containing double honeycomb nitride layers, $[MN]_2$, sandwiched by close-packed chloride layers, $Cl[MN]_2Cl$. Electrons are doped into the nitride layers, and the compounds change to superconductors with considerably high T_c's of ~15 and ~25 K for β-ZrNCl and β-HfNCl, respectively.[11,12] Organic solvent molecules are cointercalated with alkali atoms, expanding the interlayer spacing up to 28 Å, keeping the carrier concentration unchanged; T_c increases by 1.5–2 K as the spacing increases.[13,14] β-ZrNCl has a disconnected cylindrical Fermi surface characteristic of 2D crystals.[15,16] The expansion of the c lattice parameter by cointercalation is considered to make the cylindrical Fermi surface smoother to increase nesting of the Fermi surface, which would enhance the superconducting pairing interaction.[17] It has been confirmed that the electron-doped β-MNCl cannot be conventional electron-phonon BCS superconductors since the electron carrier concentration is very low,[18] and the electron-phonon coupling constant observed is too small to explain the relatively high T_c's.[19] The large gap ratios were evidenced by specific heat and tunneling spectroscopy;[17,20] the small isotope effect[21] is also unconventional. The compounds do not contain any magnetic ions; a magnetic pairing mechanism is also excluded. Charge and spin fluctuations have been proposed as the possible candidates for the pairing mechanism.[16,22]

There is another layered polymorph in MNCl with the FeOCl orthorhombic layered network, called the α form. The nitride layers in the α form are composed of an orthogonal 2D network derived from a single NaCl layer.[23] In this study, we have found that electron-doped TiNCl with the α-form layered structure becomes superconductors with $T_c \approx 18.0$ K upon alkali-metal intercalation. The compound can be cointercalated with solvent molecules, expanding the basal spacing d up to 21 Å, and the T_c decreases linearly down to 6.5 K as a function of $1/d$, implying the importance of the interlayer Coulomb coupling on the superconducting pairing.

II. EXPERIMENT

The host compound TiNCl was prepared by a method described elsewhere.[23] Alkali metal A (A = Li, Na, K, Rb) intercalation was carried out using 0.1 M alkali-metal naphthalene solutions in tetrahydrofuran (A-Naph/THF).[24] The reactants were mixed in such a ratio that the resulting compositions have a molar ratio A/TiNCl ≈ 0.25. Alkali-metal contents of the resulting compounds were determined to be $Li_{0.13}$-, $Na_{0.16}$-, $K_{0.17}$-, and $Rb_{0.24}$-TiNCl by inductively coupled plasma (ICP) analysis. The as-prepared compounds with A = Li and Na were THF-cointercalated phases, which were changed into uncointercalated compounds A_xTiNCl by evacuation. Propylene carbonate (PC) and butylene carbonate (BC) cointercalated compounds with Na were derived from the as-prepared $Na_{0.16}(THF)_y$TiNCl by immersion in the respective solvents (Solv). Powder x-ray diffraction (XRD) patterns were measured using an imaging plate (IP) Guinier camera (Huber 670G) with $CuK_{\alpha 1}$(λ = 1.540596 Å) and $MoK_{\alpha 1}$ radiation (λ = 0.709260 Å), where the air-sensitive samples were sealed in a thin Pyrex glass capillary and rotated on the goniometer to avoid preferred orientation. Magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design SQUID VSM) in zero-field-cooled (ZFC) and field-cooled (FC) modes. The anisotropic effect of magnetization was measured on uniaxially oriented pellet samples; x-ray rocking curve measurement revealed that the *ab* plane of the crystals was oriented in ±4°. Electrical resistivity was measured by a Lake Shore ac resistance bridge (Model 370AC) using a cell with an indium gasket.[23] The manipulation of samples was performed in an Ar-filled glove box (MBRAUN).

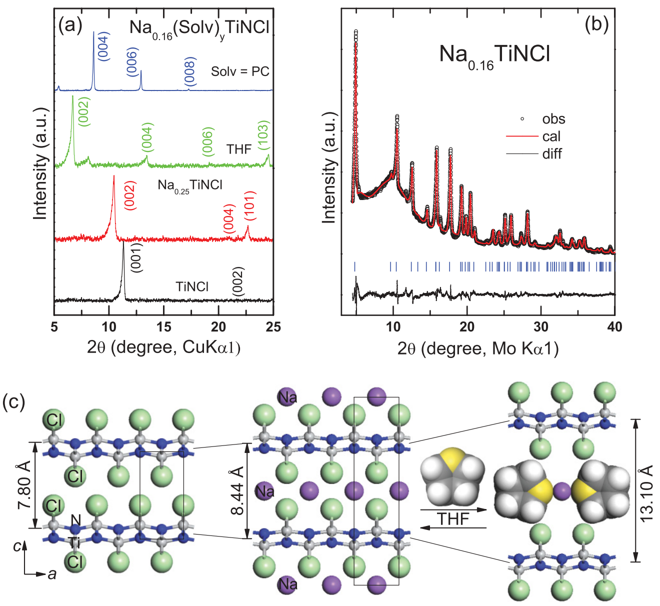

FIG. 1. (Color) (a) XRD patterns of TiNCl and the intercalation compounds $Na_{0.16}(Solv)_y$TiNCl(Solv = THF, PC) with expanded *d* spacing in a low-angle reflection range. (b) The Rietveld analysis of the XRD pattern of $Na_{0.16}$TiNCl with space group *Bmmb*. (c) Schematic illustration showing the expansion of the basal spacing of TiNCl upon Na and THF cointercalation.

III. RESULTS AND DISCUSSION

Lattice parameters of TiNCl and Na-intercalated samples are compared in Table I. The parameters in the *ab* plane are essentially unchanged upon intercalation, while the *c* parameter increases depending on the sizes of alkali-metal atoms and cointercalated molecules as evidenced by the XRD patterns in Fig. 1(a). The Rietveld analysis of $Na_{0.16}$TiNCl is shown in Fig. 1(b). It was found that upon Na intercalation, the space group (SG) of the pristine TiNCl is changed from *Pmmn* to *Bmmb* having a centered cell with a mutual shift of TiNCl layers by $\mathbf{a}/2$ along the *ab* plane. The *d* spacing of the centered cell corresponds to half of the *c* parameter. The interlayer spacing of $Na_{0.16}$TiNCl expands to 13.1 Å upon cointercalation of THF as shown in Fig. 1(c). The spacing further increased up to 21 Å with cointercalation of larger solvent molecules PC and BC (Table I). A_xTiNCl (A = K and Rb) have SG *Immm*, suggesting that TiNCl layers are mutually shifted in the *ab* plane by $\mathbf{a}/2 + \mathbf{b}/2$, with the alkali atoms being coordinated by eight chlorine atoms between the chlorine layers. All of the cointercalated compounds were found to have SG *Immm*. The lattice parameters and SG of $Li_{0.13}$TiNCl were unchanged from those of the pristine TiNCl.

The temperature dependence of the magnetic susceptibility of the Na-intercalated compounds $Na_{0.16}(Solv)_y$TiNCl (Solv = THF, PC) is shown in Fig. 2(a). The uncointercalated compound $Na_{0.16}$TiNCl shows a clear superconducting transition at T_c = 18.1 K with a high shielding superconducting volume fraction (VF). In a previous study we prepared similar alkali-metal-intercalated TiNCl by using reactions with alkali-metal azides AN_3 (A = Li, Na, K, Rb) at elevated temperatures of 280–350 °C in vacuum.[11] The reaction was not mild, and partial deintercalation of chlorine atoms took place simultaneously, forming $A_x TiNCl_{1-y}$ (y = 0.1–0.25). Although the

TABLE I. Crystallographic and superconducting characteristic parameters of the intercalation compounds $Na_{0.16}(Solv)_y$TiNCl.

		Intercalation compounds		
	TiNCl	$Na_{0.16}$	$Na_{0.16}(THF)_y$	$Na_{0.16}(PC)_y$
Space group	*Pmmn*	*Bmmb*	*Immm*	*Immm*
a (Å)	3.9370(2)	4.0187(3)	3.9687(6)	3.982(1)
b (Å)	3.2548(1)	3.2738(2)	3.2694(5)	3.273(1)
c (Å)	7.7979(4)	16.884(1)	26.210(4)	41.07(1)
d (Å)	7.7979(4)	8.442(1)	13.105(2)	20.53(1)
T_c (K)		18.0	10.2	7.4
Volume fraction (%)		∼100	60	38
γ		1.2	1.5	
ξ_{ab}, ξ_c (Å)		33, 28	55, 35	84, $\cdots$

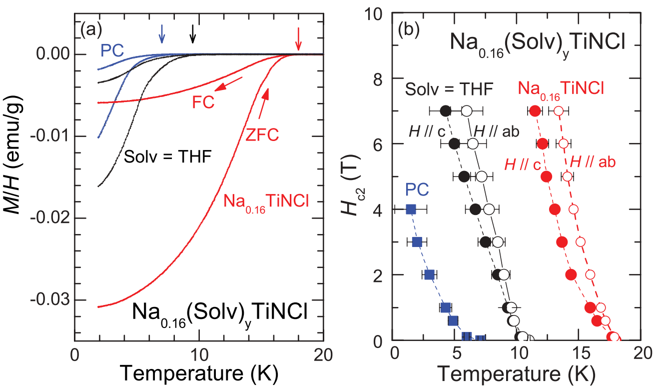

FIG. 2. (Color) (a) The temperature dependence of the magnetic susceptibility of the Na-intercalated compounds with and without cointercalation under a magnetic field strength of 10 Oe. (b) H_{c2}-T phase diagram of Na-intercalated compounds with and without cointercalation.

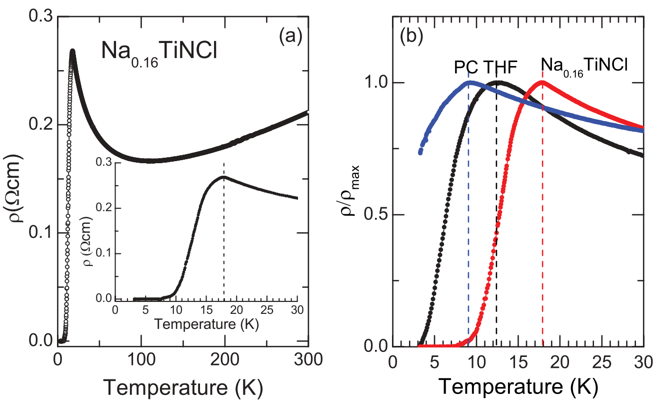

FIG. 4. (Color) (a) The temperature dependence of the electrical resistivity of $Na_{0.16}TiNCl$; the inset shows an expanded-scale plot around T_c. (b) Normalized resistivity ρ/ρ_{max} for $Na_{0.16}TiNCl$ and cointercalation compounds at low temperatures.

reaction products had similar lattice parameters and showed superconductivity, the T_c's were ~16.3 K for all kinds of alkali-metal intercalation compounds. The superconducting volume fractions were as low as 0.1%–30%. It is likely that the samples prepared in the previous study using thermal decomposition suffered from serious structural damage.

The T_c's and the superconducting VF of the Na-intercalated compounds obtained in this study are listed in Table I. Figure 3 shows the T_c's determined by magnetic susceptibility measurements as a function of $1/d$ for alkali metals and solvent cointercalated compounds prepared in this study. T_c decreases with the increase of the basal spacing. The data fit on a linear line passing through the origin, suggesting the importance of the Coulomb interlayer coupling in the pairing mechanism in this system. It should also be noted that the T_c of uncointercalated compounds A_xTiNCl (A = Na, K, Rb) also fit on this line except $Li_{0.13}TiNCl$. The as-prepared sample $Li_{0.13}(THF)_yTiNCl$ has a basal spacing of 13.0 Å similar to that of $Na_{0.16}(THF)_yTiNCl$ and a $T_c = 10.0$ K. The uncointercalated compound $Li_{0.13}TiNCl$ was obtained by evacuation at 150 °C, which has the smallest basal spacing of 7.8 Å, the same as that of the pristine TiNCl. However, T_c was found to be ~6.0 K, much lower than the value expected for the small basal spacing of Fig. 3. Li ions are small enough in size to penetrate into chlorine layers, forming double LiCl layers between TiN layers, $[TiN]_2(Li_{0.13}Cl)(ClLi_{0.13})[TiN]_2$, in which Li ions are located close to TiN superconducting layers in parallel with Cl atoms. On the other hand, in the THF cointercalated compound, Li ions are coordinated with THF molecules between chlorine layers $[ClTi_2N_2Cl]Li_{0.26}(THF)_y[ClTi_2N_2Cl]$. The low T_c of $Li_{0.13}TiNCl$ with the small d spacing suggests that the location of positive centers may also influence the Coulomb interlayer coupling for superconductivity. The linear relation shown in Fig. 3 appears to be applied to the structure where the positive centers are located between the chlorine layers as shown in Fig. 1(c) for the Na-THF cointercalated compound. In the preparation of Na-intercalated compounds, we obtained samples with varying Na contents, Na_xTiNCl and $Na_x(THF)_yTiNCl$ ($0.06 \leqslant x \leqslant 0.23$). The T_c's were constant at 18.0 and 10.2 K, respectively, in this range.

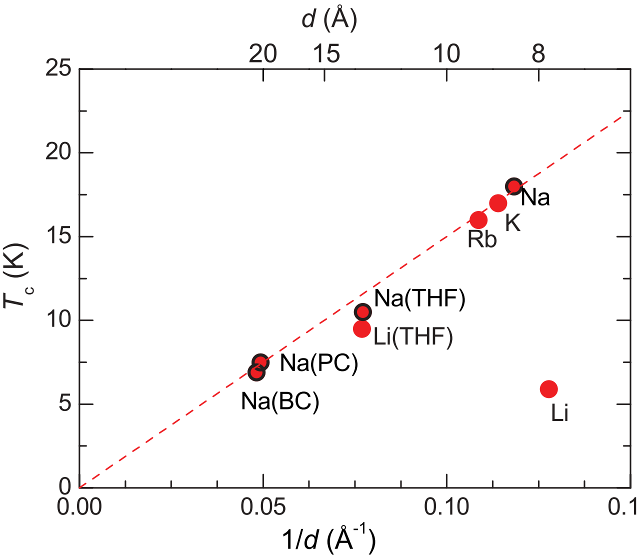

FIG. 3. (Color) T_c vs $1/d$ for A_xTiNCl (A = Li, Na, K, Rb) superconductors with and without cointercalation prepared in this study.

Figure 4 shows the temperature dependence of the resistivity of Na-intercalated compounds with and without cointercalation. Although the transition was broad, zero resistivity was obtained on the Na and Na-THF cointercalated samples. The transition temperatures correspond to the temperatures found by the magnetic susceptibility measurements in Fig. 2. The gradual increase in the resistivity prior to the superconducting transition would not be intrinsic, but rather extrinsic due to grain boundaries. A similar negative slope of resistivity near T_c was also observed on electron-doped β-structured ZrNCl and HfNCl.[12,25]

The temperature dependence of the upper critical magnetic fields H_{c2} was measured on preferred-orientation pellet samples $Na_{0.16}TiNCl$ and $Na_{0.16}(Solv)_yTiNCl$ (Solv = THF, PC) with the magnetic field parallel ($H\|c$) and perpendicular ($H\perp c$) to the c axis, as shown in Fig. 2(b). The T_c's were determined on the temperature sweep curves at variously fixed magnetic fields. The cointercalated samples showed broad transitions at high magnetic fields due to a reversible temperature range[14] and correspondingly had large error bars in Fig. 2(b). The H_{c2}/T curves show an upturn from a low magnetic field due to the low-dimensional nature of the samples. The anisotropic γ of the anisotropic Ginzburg-Landau (GL) model was estimated from the equation, $\gamma = (dH_{c2}^{\perp c}/dT)/(dH_{c2}^{\parallel c}/dT)$ under a magnetic field stronger than 1 T. The GL coherence lengths (ξ_{ab} and ξ_c) were determined using the relations $-(dH_{c2}^{\parallel c}/dT)_{T_c} \approx \Phi_0/(2\pi\xi_{ab}^2 T_c)$ and $-(dH_{c2}^{\perp c}/dT)_{T_c} \approx \Phi_0/(2\pi\xi_{ab}\xi_c T_c)$, together with $\gamma = \xi_{ab}/\xi_c$.[26] The results are listed in Table I. Note that although the anisotropic parameter of the THF cointercalated compound is larger than that of the uncointercalated compound, the β-structured superconductor $\mathrm{Li}_{0.48}(\mathrm{THF})_y\mathrm{HfNCl}$ was reported to have a much larger value of 3.7, and the coherence lengths $\xi_{ab}/\xi_c = 59.6$ Å/15.9 Å.[22]

As mentioned in the previous paragraph, the T_c dependence to the d spacing of the TiNCl intercalation compounds is quite different from that of β-MNCl (M = Zr, Hf). The β-form compounds have a disconnected cylindrical Fermi surface favorable for nesting,[15,16] while the electron-doped α-structured TiNCl has a single oval Fermi surface centered at the Γ point,[27] suggesting that the possible nesting of Fermi surfaces discussed for the β-form compounds should be excluded in the TiNCl compounds. The anisotropic properties on H_{c2} are quite different between the α- and β-structured compounds. The anisotropy GL parameter for β-$\mathrm{Li}_{0.48}(\mathrm{THF})_y\mathrm{HfNCl}$ is much larger than that of $\mathrm{Na}_{0.16}(\mathrm{THF})_y\mathrm{TiNCl}$, and the coherence length ξ_c was estimated to be 15.9 Å, comparable to the basal spacing of 17.8 Å, suggesting that the layers are weakly Josephson coupled. In $\mathrm{Na}_{0.16}(\mathrm{THF})_y\mathrm{TiNCl}$, the coherence length $\xi_c = 35$ Å is much larger than the basal spacing of 13 Å, implying the importance of interlayer coupling.

This is the first intercalated system with T_c sensitive to interlayer coupling over a wide range of variable spacings. Harshman *et al.*[6] have discussed the importance of the Coulomb interlayer coupling and 2D carrier concentration in layered high-T_c superconductors. Yin *et al.*[27] also proposed a possible pairing assisted by charge fluctuations in nonmagnetic TiNCl superconductors. Bill *et al.*[7] proposed the importance of electronic collective modes to explain the relatively high T_c of β-HfNCl intercalation compounds and showed that even if the structure has strong anisotropy, it cannot be reduced to a purely 2D model, and interlayer Coulomb interaction should be taken into account for superconductivity. Kusakabe[28] has discussed theoretically the pair-hopping mechanism in the superconductivity of K-doped TiNCl. In layered $\mathrm{K}_{0.25}\mathrm{TiNCl}$, single-particle interlayer hopping may be prohibited. The Cooper pairs formed in the superconductor layer can be scattered from a layer to the neighboring layer through quantum density-density fluctuation, and the three-dimensional (3D) superconducting state may appear in the layered compound. More detailed theoretical investigation of the interlayer interaction is one of the keys to understanding the superconductivity of layered material.

IV. SUMMARY

In summary, we have measured the superconductivity of the electron-doped TiNCl with variable interlayer distances and found that the superconducting layers are Coulomb coupled. Although the compound has the anisotropic 2D structure like β-structured MNCl, the coherence length along the c direction is much larger than the interlayer spacing, suggesting 3D superconductivity.

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