Superconductivity in Yb_xM_yHfNCl ($M = NH_3$ and THF)

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We report the observation of superconductivity in rare-earth metal cointercalated compounds $Yb_x(M)_yHfNCl$ with $M = NH_3$ and tetrahydrofuran (THF). The superconducting transition temperature is about 23 and 24.6 K for $Yb_{0.2}(NH_3)_yHfNCl$ and $Yb_{0.3}(NH_3)_yHfNCl$, respectively. Replacing the NH_3 with a larger molecule THF, the superconducting transition temperature increases to 25.2 K in $Yb_{0.2}(THF)_yHfNCl$, which is almost the same as the highest T_c reported in the alkali-metal intercalated HfNCl superconductors. The T_c of $Yb_{0.2}(THF)_yHfNCl$ is apparently suppressed by pressure up to 0.5 GPa, while the pressure effect on T_c becomes very small above 0.5 GPa. Our results suggest that for the most part, the superconductivity in these layered intercalated superconductors does not rely on intercalated metal ions, even magnetic ions.

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High-T_c superconductivity has been observed in layered cuprates and recently discovered iron-based superconductors.[1–3] The proximity to magnetically ordered states for these systems suggests that the magnetic interactions are the crucial force for Cooper pairing in such high-T_c superconductivity, which gives rise to the unconventional nature of the superconductivity in these systems. Superconductivity in various other exotic materials, such as Na_xCoO_2, Sr_2RuO_4, and heavy-fermion systems, was also found to be closely connected to magnetism.[4–6] However, for another type of superconducting material of the layered metallonitride halides (MNX, M = Ti, Zr, Hf; X = Cl, Br, I) with the maximum T_c as high as 25.5 K,[7] their parent compounds are band insulators, and superconductivity seems to have no correlation with magnetism.[8] There exist two types of layered nitride compounds: one is the (FeOCl)-type structure (so-called α structure) with a two-dimensional (2D) metal-nitrogen (MN) layer of a rectangular lattice; the other is the (SmSI)-type structure (so-called β structure) with a 2D MN layer of a honeycomb lattice.[9] For the former, K_xTiNCl was reported to display superconductivity with T_c = 16 K.[10] For the latter, usually with M = Hf,Zr and X = Cl, a maximum of T_c = 25.5 K has been achieved in $Li_x(THF)_yHfNCl$.[7] The parent compounds of the latter, so-called β-MNCl, consist of an alternative stacking of honeycomb MN bilayers sandwiched by Cl bilayers.[11] Superconductivity is usually induced through doping charge carriers by means of alkali-metal intercalation or producing the Cl deficiency.[12,13] Unlike the large pressure effect on T_c observed in cuprates or iron-based superconductors, the T_c in this type of superconductors decreases slightly as the pressure increases.[14,15] However, for cointercalated β-ZrNCl and β-HfNCl, the interlayer spacing would strongly affect the superconducting transition temperature. An increase of the basal spacing would lead to a reduction of the negligible warping along the K_z direction, and thus to an increase in the nesting of the Fermi surface.[16] It is assumed that a modification of the Fermi surface would increase the pairing interaction among the electrons, which would enhance T_c, and the maximum T_c is found when the basal spacing increases to approximately 15 Å in this type of material.[17]

In two-dimensional superconductors, spin fluctuation may lead to unconventional pairing, and high-T_c superconductivity might emerge.[18,19] Nuclear magnetic resonance (NMR)[20] and muon spin relaxation (μSR) experiments[21,22] revealed the two-dimensional nature of superconductivity in this intercalated layered nitride MNCl. The MN bilayer honeycomb structure is thought to play a major role in superconductivity.[8] The NMR Knight shift suggested a spin-singlet pairing,[23] and tunneling spectroscopy[24,25] as well as specific heat[26] revealed a fully open s-wave-like gap. The tunneling-current measurements[27,28] and specific heat[31] revealed quite a large superconducting gap with the ratio $2\Delta/k_BT \approx 4.6$–5.6 or even larger, suggesting strong-coupling superconductivity. However, some recent results, such as the anisotropic gap in the large doping level inferred by μSR (Ref. 29) and the absence of a coherence peak in the spin-lattice-relaxation rate revealed by NMR experiment,[30] suggested unconventional pairing mechanisms. Moreover, relatively high T_c with an extremely low density of states at the Fermi level,[26,31,32] weak electron-phonon coupling,[23,31–33] and a small isotope effect[34,35] also favor the unconventional pairing mechanisms in these intercalated β-MNCl superconductors. The mystery of the superconductivity for the intercalated β-MNCl compounds has yet to be solved.

In this paper, we report the discovery of superconductivity by cointercalating magnetic rare-earth ions of ytterbium with NH_3 or THF molecules in HfNCl. Ytterbium was cointercalated with NH_3 between HfNCl layers by the liquid ammonia method at room temperature, instead of previous methods of reacting in alkali-organic salt/organic solution,[7] electrochemical intercalation,[36] or using a solid-state reaction with K_3N.[37] Superconductivity with T_c of ∼23 or ∼24.6 K can be found in $Yb_x(NH_3)_yHfNCl$ depending on the Yb content. The THF molecule can also be cointercalated with ytterbium into HfNCl, and superconductivity with T_c as high as 25.2 K was observed from magnetic susceptibility, which is nearly the same as the reported maximum T_c in the alkali-metal intercalated HfNCl compounds. The pressure effect of this sample is negative; dT_c/dP is about −0.6 K/GPa below 0.5 GPa and it becomes −0.16 K/GPa above 0.5 GPa.

β-HfNCl was synthesized by a reaction of Hf powder and gasified NH_4Cl in an ammonia environment at 923 K for 30 min. Then the product was sealed in a quartz tube followed by a vapor transport recrystallized process from the low-temperature side to the high-temperature side at a temperature gradient of 1023–1123 K with the aid of a small amount of NH_4Cl as a transport agent. We can obtained two types of $Yb_x(NH_3)_yHfNCl$ by adjusting the Yb content: 0.1 g of recrystallized HfNCl together with 0.053 or 0.068 g of ytterbium. Then the mixture was loaded in a 50 mL autoclave which was cooled with liquid nitrogen; the autoclave was slowly filled with 15 mL liquid ammonia and sealed. The sealed autoclave was kept at room temperature for one to three days before it was opened and dried in a glove box. The products were rinsed using liquid ammonia to eliminate soluble impurities, thus we could obtain the final product. The actual Yb concentration (x) of these two samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the actual x values are 0.2 and 0.3, respectively. $Yb_{0.2}(THF)_yHfNCl$ can be synthesized by immersing the $Yb_{0.2}(NH_3)_yHfNCl$ powder into a THF solution for one to two days; however, we cannot obtain $Yb_{0.3}(THF)_yHfNCl$ using the same method. All the experiments were performed in an Ar atmosphere to prevent air and water contamination. X-ray diffraction (XRD) was performed on a Smartlab-9 diffractometer (Rikagu) using Cu $K\alpha$ radiation. XRD was carried out with samples sealed in capillaries that were made of special glass No. 10 and purchased from Hilgenberg GmbH. The magnetization measurement was performed using SQUID MPMS-5T (Quantum Design). The magnetization under pressure was measured by incorporating a copper-beryllium pressure cell (EasyLab) into SQUID MPMS (Quantum Design). The sample was first placed in a teflon cell (EasyLab) with coal oil (EasyLab) as the pressure media. Then, the teflon cell was set in the copper-beryllium pressure cell for magnetization measurement.

Figure 1 shows the XRD patterns of β-HfNCl, $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.3}(NH_3)_yHfNCl$, and $Yb_{0.2}(THF)_yHfNCl$ using Cu $K\alpha$ radiation. The XRD pattern of pristine β-HfNCl can be well indexed based on the space group $R\bar{3}m$, and the lattice parameters are determined to be $a = 3.58$ Å and $c = 27.71$ Å, which is consistent with the previous report.[7] In comparison with pristine β-HfNCl, the XRD patterns of $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.3}(NH_3)_yHfNCl$, and $Yb_{0.2}(THF)_yHfNCl$ can be indexed based on the space group $P\bar{3}m$. The lattice parameters are determined to be $a = 3.59$ Å and $c = 11.95$ Å for $Yb_{0.2}(NH_3)_yHfNCl$, and $a = 3.59$ Å and $c = 13.20$ Å for $Yb_{0.3}(NH_3)_yHfNCl$, respectively. The lattice parameters become $a = 3.59$Å and $c = 15.05$ Å for $Yb_{0.2}(THF)_yHfNCl$. The lattice parameters in the ab plane are almost unchanged for all the intercalated samples, but the stacking pattern of the layers is changed so much, leading to the change in the space group from $R\bar{3}m$ to $P\bar{3}m$. The d spacing between HfNCl layers increases from 9.24 Å for pristine β-HfNCl to 11.95 and 13.20 Å for superconducting $Yb_{0.2}(NH_3)_yHfNCl$ and $Yb_{0.3}(NH_3)_yHfNCl$, and to 15.05 Å for superconducting $Yb_{0.2}(THF)_yHfNCl$, respectively. The interlayer spacing d between MNCl (M = Zr or Hf) layers is strongly dependent on the amounts and types of metal ions and the cointercalated solvent molecules in intercalated MNCl superconductors. The c-axis lattice parameter of $c = 11.95$ Å for $Yb_{0.2}(NH_3)_yHfNCl$ is nearly the same as $c = 12.1$ Å of $Li_{0.37}(NH_3)_yHfNCl$.[16] This indicates that the stacking structure for NH_3 cointercalated HfNCl with Yb should be similar to that of $Li_{0.37}(NH_3)_yHfNCl$, while for $Yb_{0.3}(NH_3)_yHfNCl$, the d spacing increases to 13.20 Å, which may be due to the different Yb amount and orientation of NH_3. The spacing between MNCl (M = Zr or Hf) layers increases to 14.9 or 18.5 Å for $Li_x(THF)_yZrNCl$,[38] while it increases to 13.6 or 18.7 Å (Ref. 16) for $Li_x(THF)_yHfNCl$. The different spacing between MNCl layers depends strongly on the amounts of lithium and the orientation of THF. The c-axis parameter increases to 15.05 Å for $Yb_{0.2}(THF)_yHfNCl$, which is very close to 14.9 Å for $Li_x(THF)_yZrNCl$. This suggests that the stacking structure of $Yb_{0.2}(THF)_yHfNCl$ is the same as that of $Li_x(THF)_yZrNCl$. The schematic structural models for pristine HfNCl, $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.3}(NH_3)_yHfNCl$, and $Yb_{0.2}(THF)_yHfNCl$ are proposed as shown in Fig. 2, respectively.

The temperature dependence of zero-field-cooling (ZFC) and field-cooling (FC) magnetic susceptibilities for the

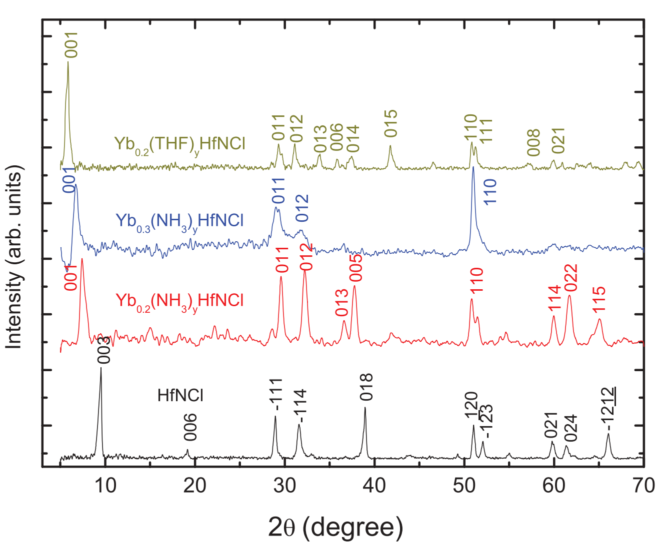

FIG. 1. (Color online) The x-ray diffraction patterns of pristine β-HfNCl and the superconducting samples of $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.3}(NH_3)_yHfNCl$, and $Yb_{0.2}(THF)_yHfNCl$, respectviely.

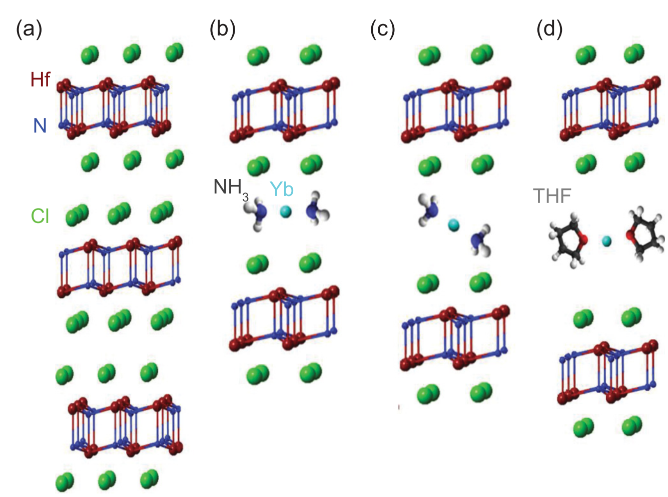

FIG. 2. (Color online) The schematic structural models for (a) pristine HfNCl; (b) $Yb_{0.2}(NH_3)_yHfNCl$; (c) $Yb_{0.3}(NH_3)_yHfNCl$, and (d) $Yb_{0.2}(THF)_yHfNCl$, respectively.

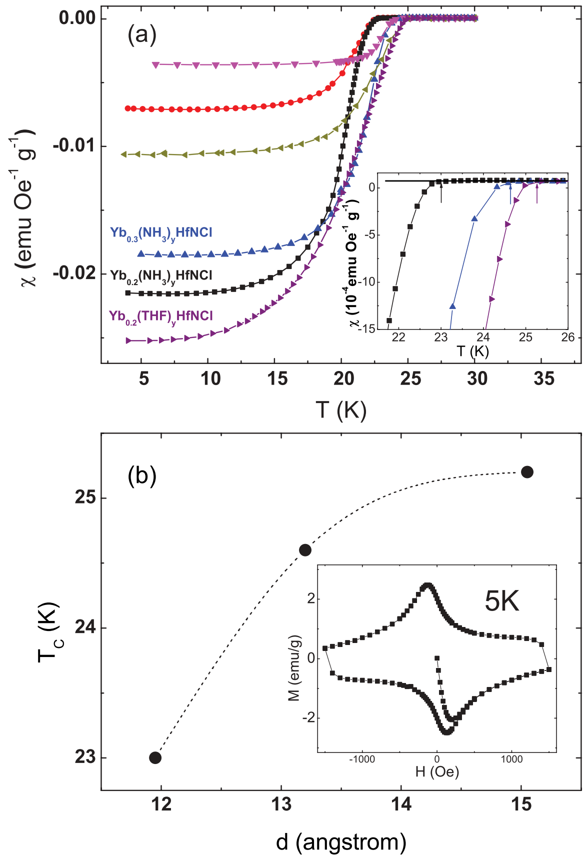

FIG. 3. (Color online) (a) The ZFC and FC susceptibility taken at 10 Oe for $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.3}(NH_3)_yHfNCl$, and $Yb_{0.2}(THF)_yHfNCl$. The inset shows the enlarged area around T_c. (b) Interlayer spacing d dependence of T_c for all the superconducting samples. The inset shows the isothermal magnetization hysteresis of $Yb_{0.2}(NH_3)_yHfNCl$ taken at 5 K.

superconducting $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.3}(NH_3)_yHfNCl$, and $Yb_{0.2}(THF)_yHfNCl$ is shown in Fig. 3(a). The ZFC susceptibilities shown in the inset of Fig. 3(a) indicate a clear superconducting transition at about 23 K for $Yb_{0.2}(NH_3)_yHfNCl$, at 24.6 K for $Yb_{0.3}(NH_3)_yHfNCl$, and at 25.2 K for $Yb_{0.2}(THF)_yHfNCl$, respectively. The shielding fractions estimated from the ZFC data were about 170%, 145%, and 160% for $Yb_{0.2}(NH_3)_yHfNCl$, $Yb_{0.3}(NH_3)_yHfNCl$, and $Yb_{0.2}(THF)_yHfNCl$, respectively. Such large values might be due to the demagnetizing effect of the tiny single crystals contained in our samples. An interlayer spacing d dependence of T_c for all the superconducting samples is shown in Fig. 3(b). T_c increases slightly from 23 to 25.2 K as interlayer spacing d increases from 11.95 to 15.05 Å. A similar behavior has been observed in Li_xM_yHfNCl ($M = NH_3$ and THF).[16] The inset of Fig. 3(b) shows the isothermal magnetization hysteresis for $Yb_{0.2}(NH_3)_yHfNCl$ at 5 K. Similar behavior in the M-H is observed for the samples of $Yb_{0.3}(NH_3)_yHfNCl$ and $Yb_{0.2}(THF)_yHfNCl$. The lower critical field (H_{c1}) for all the superconducting samples is around 80 Oe, which is the same as that of alkali-metal cointercalated HfNCl.[38] Lattice parameters and T_c of $Yb_x(M)_yHfNCl$ ($M = NH_3$ and THF) are summarized in Table I.

TABLE I. Lattice parameters and T_c of $Yb_x(M)_yHfNCl$ ($M = NH_3$ and THF).

	β -HfNCl	$Yb_{0.2}(NH_3)_y$ HfNCl	$Yb_{0.3}(NH_3)_y$ HfNCl	$Yb_{0.2}(THF)_y$ HfNCl
Space group	$R\bar{3}m$	$P\bar{3}m$	$P\bar{3}m$	$P\bar{3}m$
a (Å)	3.58	3.59	3.59	3.59
c (Å)	27.71	11.95	13.20	15.05
d spacing (Å)	9.24	11.95	13.20	15.05
T_c (K)		23	24.6	25.2

Figures 4(a) and 4(b) show the temperature dependence of the susceptibility in ZFC measurements under various magnetic fields for $Yb_{0.2}(NH_3)_yHfNCl$ and $Yb_{0.2}(THF)_yHfNCl$, respectively. T_c and the diamagnetic signal are gradually suppressed, and the superconducting transition becomes significantly broad with the application of magnetic fields. Within the

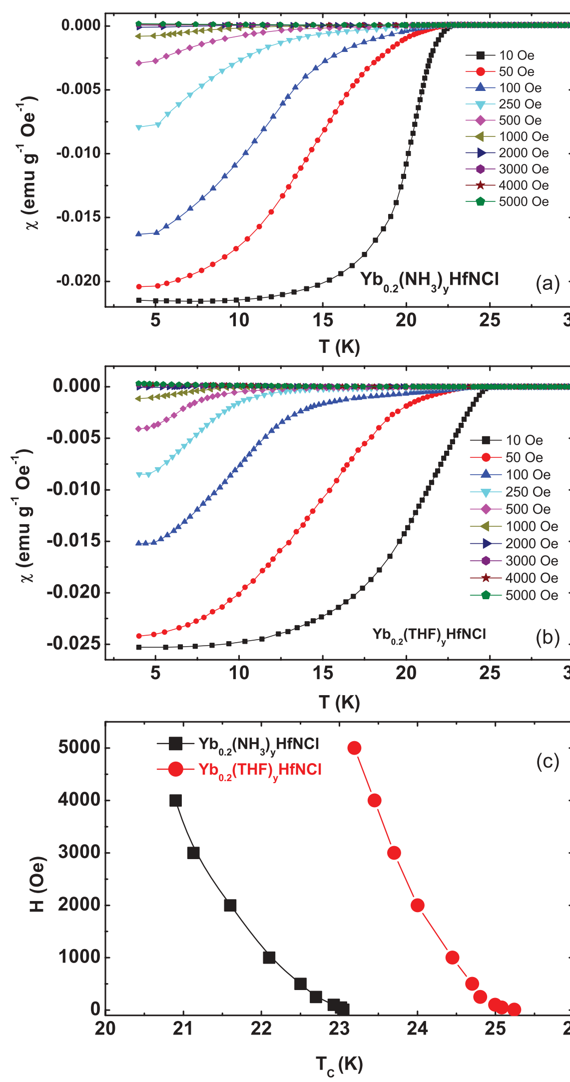

FIG. 4. (Color online) Temperature dependence of susceptibility for the superconducting samples of (a) $Yb_{0.2}(NH_3)_yHfNCl$ and (b) $Yb_{0.2}(THF)_yHfNCl$ in the ZFC measurements under different magnetic fields. (c) H_{c2} vs T_c for the samples of $Yb_{0.2}(NH_3)_yHfNCl$ and $Yb_{0.2}(THF)_yHfNCl$.

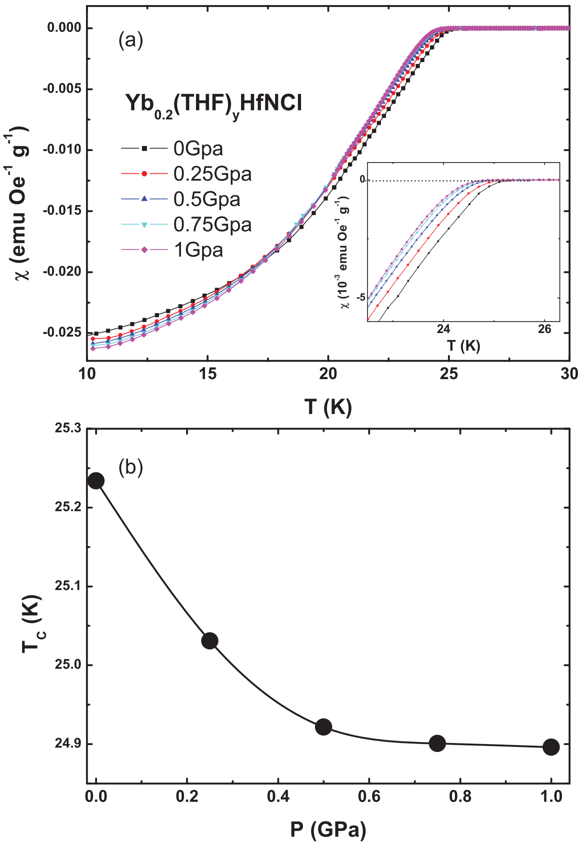

FIG. 5. (Color online) (a) Temperature dependence of susceptibility for the sample $Yb_{0.2}(THF)_yHfNCl$ in the ZFC measurements under various pressures. The inset is the enlarged area around T_c. (b) Pressure dependence of T_c for the sample $Yb_{0.2}(THF)_yHfNCl$.

weak-coupling BCS theory, the upper critical field H_{c2} at $T = 0$ K can be determined by the Werthamer-Helfand-Hohenberg (WHH) equation[39] $H_{c2}(0) = 0.693[-(dH_{c2}/dT)]_{T_c}T_c$. Using the data of H_{c2} (T) derived from the susceptibility measurement, one obtains $[-(dH_{c2}/dT)]_{T_c}$ to be about 0.25 and 0.38 T/K for $Yb_{0.2}(NH_3)_yHfNCl$ and $Yb_{0.2}(THF)_yHfNCl$, respectively. Thus, $H_{c2}(0)$ can be estimated to be 4 and 6.6 T for $Yb_{0.2}(NH_3)_yHfNCl$ and $Yb_{0.2}(THF)_yHfNCl$, respectively.

Figure 5(a) shows the temperature dependence of the susceptibility in ZFC measurements for $Yb_{0.2}(THF)_yHfNCl$ under various pressures. The inset of Fig. 5(a) shows the enlarged area around T_c. T_c is defined as the temperature at which the susceptibility starts to decrease. The pressure dependence of T_c was shown in Fig. 5(b). T_c decreases upon increasing the pressure. T_c deceases at a relatively quick speed with $dT_c/dP = -0.6$ K/GPa below 0.5 GPa, while the pressure effect becomes very small above 0.5 GPa with $dT_c/dP = -0.16$ K/GPa. Such behavior is similar to the observation in the alkali-metal intercalated HfNCl and ZrNCl.[14,15]

Electron-doping of β-HfNCl is usually realized by the intercalation of alkali metals or the cointercalation of alkali metals with molecules. Here, we report superconductivity in electron-doped HfNCl by cointercalation of rare-earth magnetic ions with molecules. It is striking that the maximum T_c of 25.2 K observed in $Yb_{0.2}(THF)_yHfNCl$ is almost the same as the highest T_c in the alkali metals cointercalation with THF. This indicates that superconductivity in the intercalated HfNCl does not rely on the different intercalated ions, even magnetic ions. It is intriguing that the intercalation of magnetic ions of rare-earth metal Yb does not affect the superconductivity relative to the intercalation of alkali-metal ions. This indicates that magnetism does not suppress superconductivity, which is evidence of unconventional superconductivity. T_c increases from 23 to 25.2 K upon increasing the interlayer spacing from 11.95 Å for $Yb_{0.2}(NH_3)_yHfNCl$ to 15.05 Å for $Yb_{0.2}(THF)_yHfNCl$. Such a slight enhancement of T_c induced by a large increase of the interlayer spacing indicates a good two-dimensional electronic system for the intercalated HfNCl superconductors, which could be the reason why superconductivity in intercalated HfNCl does not rely on intercalated ions. An interesting question is whether T_c could be raised to above 25.5 K in the intercalated HfNCl system or not.

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