Superconductivity in Yb$_2$(Me)$_3$HfNCl ($Me = NH_3$ and THF)

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The intercalated layered nitride $\beta$-HfNCl has attracted much attention due to the high superconducting transition temperature up to 25.5 K. Electrons can be introduced into the layered mettallonitride halides ($MN\_X$, $M = Ti, Zr, Hf$; $X = Cl, Br, I$) 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$^6$. However, for another type of superconducting material of the layered metalonitride 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$^6$. There exist two types of the layered nitride compounds: one is the (FeOCl)-type structure (so called $\alpha$ structure) with the 2D metal-nitrogen ($MN$) layer of rectangular lattice; the other is the (SmSi)-type one (so called $\beta$ structure) with the 2D MN layer of honeycomb lattice$^2$. For the former, $K_c$TiNCl was reported to display superconductivity with $T_c = 16$ K$^10$ For the latter, usually with $M = Hf, Zr$ and $X = Cl$, maximum of $T_c = 25.5$ K has been achieved in Li$_4$(THF)$_2$HfNCl$^2$. The parent compounds of the latter, so-called $\beta$-MNCI, consist of alternative stacking of honeycomb MN bilayer sandwiched by Cl bilayer$^1$. 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 $\beta$-ZrNCl and $\beta$-HfNCl, the interlayer spacing will strongly affect the superconducting transition temperature. Increase of the basal spacing would lead to the reduction of the tiny warping along the $K_c$ direction, thus to increase the nesting of the Fermi surface$^{16}$. It is assumed that the 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 is increased to $15$ Å in this type of materials$^{17}$.

In two dimensional superconductors, the 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 ($\mu$SR) experiments$^{21,22}$ revealed the two-dimensional nature of superconductivity in this intercalated layered nitride MNCI. The MN bilayer honeycomb structure is thought to play a main role for the happening of superconductivity. 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$^{29}$ gave a quite large superconducting gap with the ratio $2\Delta/k_B T \approx 4.6-5.2$ or even larger, suggesting the strong coupling superconductivity. However, some recent results, such as the anisotropic gap in large doping level inferred by $\mu$SR$^{29}$ and the absence of coherence peak in spin-lattice-relaxation rate revealed by NMR experiment$^{30}$, suggested the unconventional pairing mechanisms. Moreover, relatively high $T_c$ with extremely low density of states at Fermi level$^{30,31,32}$.
The mystery of the superconductivity for the intercalated ytterbium with NH$_3$ salt/organic solution, instead of previous methods by reacting in alkali-organic solvent molecules in intercalated HfNCl compounds. The pressure effect of this sample is negative, d$T_c$/dP is about -0.6 GPa/K below 0.5 GPa and it becomes -0.16 GPa/K above 0.5 GPa.

Figure 1 shows the X-ray diffraction (XRD) patterns of $\beta$-HINCl, $\beta$-$\text{Yb}_0.2$(NH$_3$)$_y$HINCl, $\beta$-$\text{Yb}_0.3$(NH$_3$)$_y$HINCl and $\beta$-$\text{Yb}_0.2$(THF)$_y$HINCl using Cu $K_\alpha$ radiations. The XRD pattern of pristine $\beta$-HINCl can be well indexed based on the space group $R\overline{3}m$, and the lattice parameters are determined to be $a=$3.58 Å and $c=27.71$ Å, being consistent with the previous report. In comparison with that of the pristine $\beta$-HINCl, the XRD patterns of $\beta$-$\text{Yb}_0.2$(NH$_3$)$_y$HINCl, $\beta$-$\text{Yb}_0.3$(NH$_3$)$_y$HINCl and $\beta$-$\text{Yb}_0.2$(THF)$_y$HINCl can be indexed based on the space group $P\overline{3}m$. The lattice parameters are determined to be $a=$3.59 Å and $c=13.20$ Å for $\beta$-$\text{Yb}_0.3$(NH$_3$)$_y$HINCl, respectively. The lattice parameters of $\beta$-$\text{Yb}_0.3$(NH$_3$)$_y$HINCl and $\beta$-$\text{Yb}_0.2$(THF)$_y$HINCl are pro-

![Image](336x561 to 548x719)

**FIG. 1:** The x-ray diffraction patterns of pristine $\beta$-HINCl and the superconducting samples of $\beta$-$\text{Yb}_0.2$(NH$_3$)$_y$HINCl, $\beta$-$\text{Yb}_0.3$(NH$_3$)$_y$HINCl and $\beta$-$\text{Yb}_0.2$(THF)$_y$HINCl, respectively.

![Image](317x344 to 341x372)

**FIG. 2:** The schematic structural models for (a): the pristine HINCl; (b): $\beta$-$\text{Yb}_0.2$(NH$_3$)$_y$HINCl; (c): $\beta$-$\text{Yb}_0.3$(NH$_3$)$_y$HINCl and (d): $\beta$-$\text{Yb}_0.2$(THF)$_y$HINCl, respectively.

weak electron-phonon coupling and small isotope effect also favor the unconventional pairing mechanisms in these intercalated $\beta$-MCl superconductors.
TABLE I: Lattice parameters and $T_c$ of Yb$_2$(Mc)$_y$HfNCl ($Mc = \text{NH}_3$ and THF).

|                  | $\beta$-HfNCl | Yb$_{0.2}$(NH$_3$)$_y$HfNCl | Yb$_{0.3}$(NH$_3$)$_y$HfNCl | Yb$_{0.2}$(THF)$_y$HfNCl |
|------------------|---------------|-----------------------------|-----------------------------|---------------------------|
| Space group      | R3m           | P3m                        | P3m                        | P3m                       |
| 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                       |                           |

**FIG. 3**: (a): The ZFC and FC susceptibility taken at 10 Oe for Yb$_{0.2}$(NH$_3$)$_y$HfNCl, Yb$_{0.3}$(NH$_3$)$_y$HfNCl and Yb$_{0.2}$(THF)$_y$HfNCl. 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$_3$)$_y$HfNCl taken at 5K.

**FIG. 4**: Temperature dependence of susceptibility for the superconducting samples of (a): Yb$_{0.2}$(NH$_3$)$_y$HfNCl and (b): Yb$_{0.2}$(THF)$_y$HfNCl in the ZFC measurements under different magnetic fields. (c): The $H_{c2}$ versus $T_c$ for the samples of Yb$_{0.2}$(NH$_3$)$_y$HfNCl and Yb$_{0.2}$(THF)$_y$HfNCl.
around under various pressures. The inset is the enlarged area

\[ H_{c2}(0) = 0.693\left\{ -(dH_{c2}/dT) \right\}_T T_c. \]

Using the data of \( H_{c2}(T) \) derived from the susceptibility measurement, one obtains \( -(dH_{c2}/dT) \) to be about 0.25 T/K and 0.38 T/K for \( \text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl} \) and \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \), respectively. Thus, the \( H_{c2}(0) \) can be estimated to be 4 T and 6.6 T for \( \text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl} \) and \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \), respectively.

Figure 5(a) shows the temperature dependence of the susceptibility in ZFC measurements for \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \) under various pressures. The inset of Fig. 5(a) shows the enlarged area around \( T_c \). The \( T_c \) 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 with increasing the pressure. \( T_c \) decreases at a relative quick speed with \( dT_c/dP = -0.6 \) GPa/K below 0.5 GPa. While the pressure effect becomes very small above 0.5 GPa with \( dT_c/dP = -0.16 \) GPa/K. Such behavior is similar to the observation in the alkali-metals intercalated HfNCl and ZrNCl.\(^{14,15}\)

Electron-doping of \( \beta \)-HfNCl is usually realized by the intercalation of alkali metals or cointercalation of alkali metals with molecules. Here, we report the superconductivity in electron-doped HfNCl by cointercalation of rare-earth magnetic ion with molecules. It is striking that the maximum \( T_c \) of 25.2 K observed in \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \) is almost the same as the highest \( T_c \) in the alkali metals intercalation with THF. It indicates that superconductivity in the intercalated HfNCl does not rely on the different intercalated ions, even magnetic ion. It is intriguing that the intercalation of magnetic ion of rare-earth metal Yb does not affect the superconductivity relative to the intercalation of alkali-metal ion. It indicates that magnetism does not suppress the superconductivity, being an evidence for unconventional superconductivity. The \( T_c \) increases from 23 K to 25.2 K with increasing the interlayer spacing from 11.95 Å to 15.05 Å. A similar behavior has been observed in \( \text{Li}_q\text{Me}_n\text{HfNCl} (n=\text{NH}_3 \text{ and THF})^{16} \). The inset of Fig. 3(b) shows the isothermal magnetization hysteresis for \( \text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl} \) at 5 K. Similar behavior in the M-H is observed for the samples of \( \text{Yb}_{0.3}(\text{NH}_3)_y\text{HfNCl} \) and \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \). The lower critical field \( (H_{c1}) \) for all the superconducting samples are around 80 Oe, which are the same as that of alkali-metal cointercalated HfNCl.\(^{16} \) Lattice parameters and \( T_c \) of \( \text{Yb}_{0.2}(\text{Me})_y\text{HfNCl} (\text{Me} = \text{NH}_3 \text{ and THF}) \) are summarized in Table 1.

Figure 4(a) and (b) show the temperature dependence of the susceptibility in ZFC measurements under various magnetic fields for \( \text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl} \) and \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \), 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 weak-coupling BCS theory, the upper critical field \( H_{c2} \) at \( T = 0 \) K can be determined by the Werthamer-Helfand-Hohenberg (WHH) equation

\[ H_{c2}(0) = 0.693\left\{ -(dH_{c2}/dT) \right\}_T T_c. \]

Using the data of \( H_{c2}(T) \) derived from the susceptibility measurement, one obtains \( -(dH_{c2}/dT) \) to be about 0.25 T/K and 0.38 T/K for \( \text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl} \) and \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \), respectively. Thus, the \( H_{c2}(0) \) can be estimated to be 4 T and 6.6 T for \( \text{Yb}_{0.2}(\text{NH}_3)_y\text{HfNCl} \) and \( \text{Yb}_{0.2}(\text{THF})_y\text{HfNCl} \), respectively.

Materials and Methods \( \beta \)-HfNCl was synthesized by reacting of Hf powder and gasified \( \text{NH}_3\text{Cl} \) in the environment of ammonia at 923 K for 30 minutes, then the product was sealed in a quartz tube followed by a vapor transport recrystallized process from low tem-
temperature side to high temperature side at the temperature gradient of 1023 K to 1123 K with the aid of a small amount of NH$_4$Cl as transport agent. We can obtain two types of Yb$_2$(NH$_3$)$_y$HfNCl by adjusting the Yb content. 0.1 gram of recrystallized HfNCl together with 0.053 or 0.068 gram of ytterbium, then the mixture were loaded in a 50 ml autoclave which was cooled by liquid nitrogen, the autoclave was slowly filled with 15 ml liquid ammonia and sealed. The sealed autoclave was kept at room temperature for 1-3 days before it was opened and dried in the glove box. The products were rinsed by using liquid ammonia to eliminate soluble impurities, thus we can obtain the final product. The actual Yb concentrations (x) of these two samples were 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)$_y$HfNCl can be synthesized by immersing the Yb$_{0.2}$(NH$_3$)$_y$HfNCl powder into THF solution for 1-2 days, while we can not obtain Yb$_{0.3}$(THF)$_y$HfNCl by the same method. All the experiments were performed under Ar atmosphere to prevent it from air and water contamination. The x-ray diffraction (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 by 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 firstly 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.

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