Specific heat study of electron-doped ZrNCl superconductors

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Abstract. We report on the results of specific heat studies in the layered nitride superconductor LiₓZrNCl with different values of electron doping. With increasing x from 0.12 to 0.26, electronic specific heat coefficient γₙ slightly increases from 1.0 to 1.2 mJ/mol K², whereas the magnitude of the gap ratio 2∆₀/k_BTₐ decreases from strong- to weak-coupling regime. These results indicate that the strength of electron-Boson interaction plays a dominant role in the enhancement of Tₐ observed on the verge of superconductor-insulator transition in this compound.

1. Introduction
Layered nitride β-(Zr,Hf)NCl is a band insulator in which double honeycomb (Zr,Hf)₂N₂ and Cl₂ layers stack alternately along the c axis. As alkali metals are intercalated in between the Cl₂ layers, electrons are transferred from Li sites into (Zr,Hf)₂N₂ layers. Upon Li intercalation, superconductivity appears with the transition temperature Tₐ ≈ 25 K and 15 K for Liₓ(THF)ₙHfNCl (THF=tetrahydrofuran) and LiₓZrNCl, respectively [1, 2]. According to band calculations [3, 4, 5, 6, 7], the conduction band has a highly two-dimensional anisotropy, and consists of Zr(Hf) 4d(5d) orbitals strongly hybridized with N 2p states whereas the valence band is mainly of N 2p states. As a result, the Fermi surface of doped material is comprised of two sheets that are centered at K and K’ in the hexagonal Brillouin zone, and almost cylindrical shape. It was also found to be possible that polar organic molecules, such as THF and propylene carbonate, are simultaneously cointercalated with Li [1]. Recently, systematic synthesis of both Zr- and Hf-system was carried out and it was revealed that the interlayer distance and carrier concentration are independently controlled in these systems [8, 9].

Experimental and theoretical studies have revealed the unique physical properties of the Zr- and Hf-based systems. Relatively high Tₐ values are realized despite the small value of the density of states (DOS), as evidenced by magnetic susceptibility and specific heat measurements [10, 11]. These observations imply that electron-boson interaction must be rather strong. Actually, strong coupling nature has been indicated by tunneling spectroscopy and µSR measurements [12, 13, 14]. On the other hand, however, the estimated electron-phonon coupling constant in Zr system was found to be too small to reproduce the observed value of Tₐ [11]. Weak electron-phonon interaction has also been predicted by theoretical calculations [3, 7]. Moreover,
an anomalous feature was found in the $T_c$ versus $x$ phase diagram of Li$_x$ZrNCl, which is shown in Fig. 1[8]. $T_c$ increases rapidly with decreasing doping $x$ on the verge of superconductor-insulator (S-I) transition, making marked contrast with the little doping dependence found above $x \sim 0.20$. This behaviour is unusual for a superconductor-insulator transition if the insulating phase is of Anderson type due to randomness. Therefore, additional bosonic fluctuations, for instance charge fluctuation, have been proposed to contribute to the pairing process besides the conventional electron-phonon channel [8, 10, 15, 16]. In this paper, to shed light on the anomalous behaviour of $T_c$ on the verge of S-I transition, we performed specific heat measurements on Li$_x$ZrNCl with different values of $x$.

2. Experimental

Pristine β-ZrNCl powders have been prepared in a sealed quartz tubes by using a chemical vapor transport technique. We used an n-butyl-lithium solution in hexane to intercalate Li into the pristine β-ZrNCl. The intercalation process was performed in a glove box with high-purity Ar gas to avoid the degradation of the sample due to moisture and/or oxygen. Using the inductively coupled plasma spectroscopy technique, we determined the intercalated Li concentration $x$ within an accuracy of 0.01. The $x$ values of the samples used here are found to be 0.12 and 0.26. For both samples, a sharp superconducting transition and nearly full Meissner signal were confirmed by the magnetization measurements using a SQUID magnetometer. We also confirmed that the samples were of single phase by performing the synchrotron powder X-ray diffraction experiments at BL02B2, SPring-8. We prepared pellets with a high degree of $c$-axis orientation by compressing the powder sample. Heat capacity measurements were done by using a physical property measurement system (Quantum Design). All measurements were performed with the configuration that the magnetic field $H$ is applied parallel to the $c$ axis ($H \parallel c$).

3. Results and Discussions

Figure 2 shows the electronic part of the heat capacity $C_{el}$ as a function of the temperature $T$ for $x = 0.12$ and 0.26 in $H = 0$ T. The $H$-independent lattice contribution is eliminated via the following procedure: $\Delta \gamma = [C(0 T, T) - C(5 T, T)]/T$ is plotted against $T$, then the saturation value of $\Delta \gamma$ at low temperatures corresponds to $-\gamma_n$ ($\gamma_n$ is the normal-state electronic specific heat coefficient). Using thus determined $\gamma_n$, $C_{el}$ is calculated as $C_{el} = (\Delta \gamma + \gamma_n)T$. Here, $H = 5$ T is larger than the upper critical field along the $c$ axis [17], and high enough to suppress the superconductivity. In Fig. 2, the jump of $C_{el}$ is clearly observed at the transition for both Li concentrations. Taking the entropy balance into account, we obtained $T_c = 12.7$ K and 11.6 K for $x = 0.12$ and 0.26, respectively. As the temperature decreases, $C_{el}$ continuously decreases and finally saturates below about 3.5 K for $x = 0.12$. This behavior is in accord with the s-wave symmetry of the superconducting gap. Indeed, data below 5 K are fitted to a formula $C_{el} = AT^{-3/2} \exp\left(-\frac{\Delta_n^2}{k_B T}\right)$. We have measured several samples from the same batch, and have found that scattering of $\Delta_0/k_B$ and $\gamma_n$ is small. We obtained the gap value $2\Delta_0/k_B T_c \approx 5.2$ for $x = 0.12$, which belongs to the strong coupling regime and is consistent with previous reports [12, 13, 14]. Contrastingly, for $x = 0.26$, we found $2\Delta_0/k_B T_c \approx 3.2$, which is close to, or even smaller than, the BCS value of 3.5, indicating weak coupling superconductivity in this doping range. Compared to the large increase in $2\Delta_0/k_B T_c$ with decreasing $x$ from 0.26 to 0.12, the change in $\gamma_n$ is tiny: $\gamma_n$ slightly decreases from 1.2 to 1.0 mJ/mol K$^2$. The magnitude of $\gamma_n$ seems to be very small for superconductors with relatively high $T_c$ above 10 K. For example, an oxide superconductor LiTi$_2$O$_4$ with $T_c = 11.4$ K shows $\gamma_n = 19.2$ mJ/mol K$^2$ [18], which is almost 20 times as large as those of the present materials. The observed change of $\gamma_n$ is opposite to the variation of $T_c$. Therefore, our results lead us to infer that doping variation of the pairing interaction strength gives rise to the enhancement of $T_c$ with decreasing electron
Figure 1. $T_c$ versus Li concentration $x$ phase diagram of $\text{Li}_x\text{ZrNCl}$. Superconductor-insulator (S-I) transition occurs at $x \sim 0.05$, towards which $T_c$ rapidly increases as $x$ is reduced.

concentration, and that the change of DOS plays a minor role. In view of the weakened electron-phonon interaction in the reduced doping regime as probed by Raman scattering [19], other bosonic fluctuation than phonon such as magnetic or charge fluctuations may contribute to, and reinforce, the pairing interaction in the lightly doped region of $\text{Li}_x\text{ZrNCl}$ superconductors.

4. Conclusion
In summary, we performed heat capacity measurement on layered nitride superconductor $\text{Li}_x\text{ZrNCl}$ with $x = 0.12$ and 0.26. Whereas the electronic specific heat coefficient is nearly independent of $x$ with relatively small values of $\gamma_n \simeq 1 \text{ mJ/mol K}^2$, the magnitude of the gap ratio changes from weak- to strong-coupling regime with decreasing $x$ as the superconductor-insulator transition is approached and as the $T_c$ is rapidly enhanced. These results demonstrate that the strength of the pairing interaction among electrons, as opposed to the density of states at the Fermi level, dominates the enhancement of $T_c$ in the lightly doped regime.

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Figure 2. Electronic part of the heat capacity ($C_{el}$) is plotted as a function of $T$ for $x = 0.12$ (solid circles) and $x = 0.26$ (open squares).

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