Enhancement of Pairing Interaction and Magnetic Fluctuations toward a Band Insulator in an Electron-Doped Li_xZrNCl Superconductor

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(Received 30 April 2009; published 14 August 2009)

The doping dependence of specific heat and magnetic susceptibility has been investigated for Li_xZrNCl superconductors derived from a band insulator. As the carrier concentration is decreased, the anisotropy of superconducting gap changes from highly anisotropic to almost isotropic. It was also found that, upon reducing carrier density, the superconducting coupling strength and the magnetic susceptibility are concomitantly enhanced in parallel with T_c, while the density of states at the Fermi level is kept almost constant. Theoretical calculations taking into account the on-site Coulomb interaction reproduced the experimental results, suggesting a possible pairing mediated by magnetic fluctuations, even in the doped band insulators.

DOI: 10.1103/PhysRevLett.103.077004 PACS numbers: 74.70.−b, 74.20.Mn, 74.25.Bt

High-T_c superconductivity has often been observed in layered materials such as cuprates [1] and recently discovered Fe-based pnictides [2]. In these systems, undoped materials commonly exhibit antiferromagnetic ordering due to the correlation effects although conducting properties are quite different. Doping charge carriers suppresses the antiferromagnetic phase, thereby inducing the superconducting phase with high T_c. The proximity of the magnetic phase to the superconducting phase implies Cooper pairing with exotic symmetry, mediated by the magnetic fluctuations [3,4]. β-TNCl (T = Zr and Hf) is another example of layered materials in which superconductivity with moderately high T_c (~15 K for Zr and ~25 K for Hf systems, respectively) is induced by doping charge carriers by means of alkali metal intercalation [5–8]. The unique feature of this system as compared with cuprates or pnictides is that the pristine materials are band insulators without magnetic ordering.

Crystal structure of pristine ZrNCl is composed of alternate stacking of Zr-N double honeycomb layers sandwiched by Cl layers along the hexagonal c axis. Alkali metals can be intercalated into the van der Waals gaps between the Cl layers, affording electron-type charge carriers into the Zr-N layers. According to band structure calculations [9–13], the conduction band is mainly of $4d$ character, and the Fermi surface consists of two disconnected, quasi-two-dimensional cylinderlike sheets centered at the corner of hexagonal Brillouin zone, K and K' points. Because of this Fermi surface topology, interband pairing is more favorable than intraband pairing so as to minimize the total momentum of Copper pairs. Interestingly, the disconnectivity of the Fermi surface is also observed in pnictides [14]. Thus far, several experiments [7,15,16] and theories [11,13] have suggested unusual features, such as a small density of states (DOS) at the Fermi level, weak electron-phonon interaction for their T_c values, and an anomalous enhancement of T_c on the verge of superconductor-insulator (SI) transition at $x \sim 0.05$. This enhancement of T_c was tentatively interpreted as being due to the enhanced charge fluctuation in the low-carrier-density regime [7,17,18]. Nevertheless, the origin of the evolution of T_c, as well as the pairing symmetry, has remained unclear. In this Letter, we present detailed and systematic thermodynamic measurements for a series of Li_xZrNCl with controlled x. We have found that the strength of the superconducting pairing and magnetic fluctuations are concomitantly enhanced in parallel with T_c as the SI transition is approached with reducing carrier density, while the DOS shows little dependence on the doping. This result may indicate the possible pairing mediated by the magnetic fluctuations rather than charge fluctuations even in the superconductors derived from a band insulator without magnetic ordering.

Li_xZrNCl powders were prepared in the same manner as already reported in Ref. [7]. We used pellets with a high degree of c-axis orientation by compressing the powder which is composed of fine particles with highly anisotropic platelike shape. The distribution of the c-axis orientation was revealed to be within $\pm 5°$ by the rocking curve experiment, in accord with previous reports [16,19,20]. We applied the magnetic field along the c axis in all the measurements. We performed specific heat and magnetic susceptibility measurements using a Physical Property Measurement System and a SQUID magnetometer (Quantum Design), respectively. We also used ^{3}He refrigerator for some of the samples for specific heat measure-

ments. The magnetic susceptibility was deduced by taking the difference of the magnetization at 3 and 5 T to eliminate the tiny amount of ferromagnetic contribution [21]. We performed theoretical calculations for the Hubbard model on a lattice similar to the lattice structure of the Zr-N layer [21]. The wave-number-dependent spin susceptibility was calculated by applying the fluctuation exchange approximation [22].

Figures 1(a) and 1(b) show the temperature (T) dependence of the electronic part of the specific heat (C) divided by T, $\Delta C/T$, for Li_xZrNCl with $x = 0.10$ and 0.28, respectively. We estimated the electronic part of specific heat as $\Delta C(H, T) \equiv [C(H, T) - C(H > H_{c2}, T)]$, where H_{c2} is the upper critical field [15]. In zero magnetic field, the jump of the specific heat is clearly discernible at T_c. Taking entropy balance into account, we obtain $T_c = 14.0$ and 11.6 K for $x = 0.10$ and 0.28, respectively. In this plot, the normal-state Sommerfeld constant γ_n can be estimated as $\gamma_n \equiv -\Delta C/T(T \to 0, H = 0)$. At 2 K, $\Delta C/T$ at 0 T is almost the same value for both compounds. However, $\Delta C/T$ shows saturation below 2.5 K for $x = 0.10$, in contrast with the $x = 0.28$ sample which still shows continuous decrease even at 2 K. These results indicate a slight

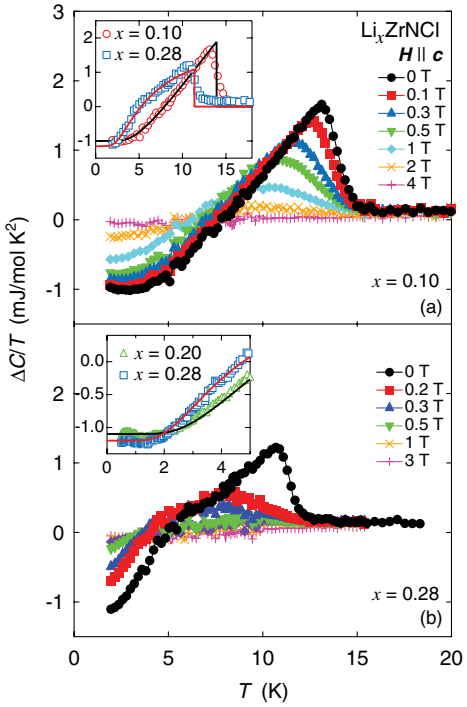

FIG. 1 (color). Electronic contribution of the specific heat $\Delta C/T$ as a function of temperature T down to 2 K in several magnetic fields applied along c axis for (a) $x = 0.10$ and (b) 0.28. T dependence of $\Delta C/T$ in zero field (open symbols) with the theoretical curves assuming the BCS relation (solid lines) is shown for $x = 0.10$ and 0.28 samples in the inset of (a) and for $x = 0.20$ and 0.28 samples in the inset of (b), which shows a magnified view of $\Delta C/T$ below 5 K measured using ^{3}He cryostat. Here, Shottky-like upturn at very low temperatures is subtracted.

enhancement of γ_n with increasing x. Both materials exhibit a very small γ_n ($\sim$1 mJ/mol K^2) for their T_c values, only amounting to approximately 1/20 of $LiTi_2O_4$ [23] and κ-(BEDT-TTF)$_2$Cu[N(CS)$_2$]Br [24] with similar T_c values. A difference is also found between two samples in the magnetic field effect. $\Delta C/T$ for $x = 0.28$ almost fully recovers to the normal-state value $\Delta C/T \to 0$ at $H = 0.5$ T, a much smaller field than that for $x = 0.10$. This behavior cannot be explained by the difference in H_{c2} alone, providing important information about the pairing symmetry, as discussed later.

To perform quantitative analysis of the x dependence of C, we focus on the $\Delta C/T$ data at zero field [inset of Fig. 1(a)]. The T dependence below T_c is clearly different between two distinct dopings. We fitted these data [21] to the empirical theory [25] with an assumption of isotopically gapped state, and the results reproduce the experimental data quite well, including the data at low T down to 0.5 K [inset of Fig. 1(b)]. The qualitative difference in the shape of $\Delta C/T$ is attributed to the difference in the $2\Delta_0/k_BT_c$ value, 4.14 for $x = 0.10$, which well exceeds the BCS weak coupling limit ($2\Delta_0/k_BT_c = 3.54$), and 2.9 for $x = 0.28$. Interpretation of the shoulderlike structure observed around 5 K in $x = 0.28$ in terms of the two-gap scenario can be ruled out since the second band is not yet occupied for $x = 0.28$ in view of the absence of the expected sudden jump of γ_n [Fig. 4(b)] as a function of x. The strong coupling in the low doping region is consistent with previous reports [15]. Thus, $2\Delta_0/k_BT_c$ is considerably enhanced upon reducing the carrier density, similarly to T_c.

Next, we discuss the field dependence of the electronic specific heat coefficient $\gamma(H)$. In superconductors with nodes (other than s-wave symmetry) or substantial anisotropy (including anisotropic s-wave symmetry) in the gap, $\gamma(H)$ exhibits a steeper increase than H-linear behavior in superconductors with isotropic gap [26]. Figure 2 shows $\gamma(H) \equiv [\Delta C(H) - \Delta C(0)]/T$ normalized by γ_n as a function of magnetic field normalized by x-dependent H_{c2}, which were taken from the results of resistivity measurements for the samples with a wide range of doping level [19]. Clearly, the field dependence is distinct between the lowest doping ($x = 0.07$) and the other doping region, nearly H-linear behavior up to H_{c2} for $x = 0.07$, while there is a much steeper increase at the low field region $x > 0.10$.

To examine doping evolution, we defined the characteristic magnetic field H^*/H_{c2} as exemplified for the case of $x = 0.12$ (Fig. 2). As shown in the inset of Fig. 2, H^*/H_{c2} is nearly unity at the lowest doping, but it steeply decreases with increasing x and then almost saturates. Although steep increase of $\gamma(H)$ at low H has also been observed in a multiband superconductor with distinct gaps (such as MgB_2 [27]), the possibility of multiple gaps can be ruled out on the basis of the absence of the jump in x dependence of γ_n, as already mentioned. Therefore, this result should be interpreted as indicating that the gap is almost isotropic in the very lightly doped region and becomes anisotropic

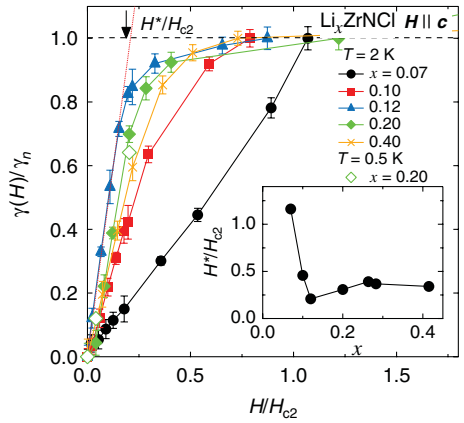

FIG. 2 (color). Main panel: Normalized electronic specific heat coefficient $\gamma(H)/\gamma_n$ at 2 K as a function of magnetic field normalized by x-dependent H_{c2}. For $x = 0.20$, $\gamma(H)/\gamma_n$ at 0.5 K is also shown (open symbols). The dotted line is the linear extrapolation of initial slope for $x = 0.12$, and the H^* is defined as the intersect of the dotted line and $\gamma(H)/\gamma_n = 1$ (dashed line). Inset: Determined H^*/H_{c2} is plotted against carrier density.

with increasing doping, implying possible pairing state with exotic symmetry other than s wave.

Figure 3 shows the T dependence of spin susceptibility $\chi_s(T)$ in $\boldsymbol{H}$ along the c axis. The samples with $x = 0.0$ and 0.03 are insulators and the others are superconductors. The magnitude of χ_s is very small and comparable to diamagnetic contributions. We estimated χ_s by subtracting the possible diamagnetic contributions [21]. For the pristine material, χ_s is dominated by a Curie term, which is perhaps due to a tiny amount of localized electrons arising from the Cl vacancies. Clear anomaly of χ_s has not been observed for the doped, but nonsuperconducting, sample of $x = 0.03$. As Li is further intercalated, Curie-like upturn is suppressed (although discernible at low temperatures below 30 K), and χ_s becomes nearly T independent in a wide range of temperatures down to ~60 K. With increasing x, $\chi_s(T)$ clearly decreases and tends to show gradual decrease with decreasing T for x above 0.20.

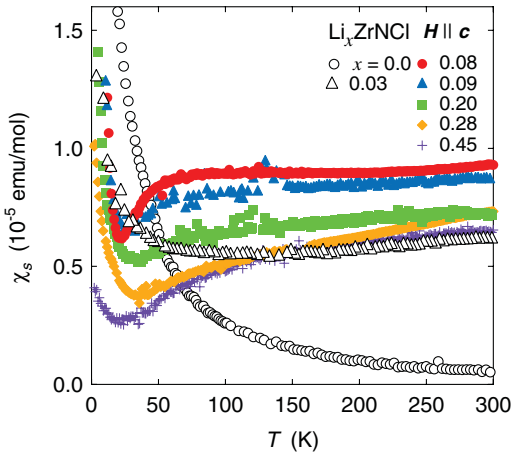

FIG. 3 (color). Spin susceptibility χ_s measured in the magnetic field $\boldsymbol{H}$ along c axis is plotted as a function of temperature.

Based on the above experimental observations, we summarized the doping variation of various properties of Li_xZrNCl in Figs. 4(a)–4(d). Whereas T_c is nearly x independent for $x \gtrsim 0.20$, T_c exhibits unusual enhancement on the verge of SI transition at $x \sim 0.05$ [Fig. 4(a)] [7]. γ_n shows weak doping dependence, reflecting the two-dimensional nature of the electronic state. Nevertheless, γ_n rather decreases slightly as x is reduced [Fig. 4(b)]. By contrast, $2\Delta_0/k_BT_c$ significantly increases as the carrier density is reduced [Fig. 4(c)]. Although the change in the anisotropy of the gap is indicated, Δ_0 should be interpreted as the average of the gap amplitude, since detailed wave vector dependence of the gap function is not known. Therefore, these results strongly indicate that the unusual enhancement of T_c on the verge of SI transition originates from the reinforcement of the pairing interaction, rather than that of DOS. (Doping dependence of T_c and γ_n alone implies the enhancement of pairing interaction, in accord with the above conclusion deduced from the doping dependence of $2\Delta_0/k_BT_c$.) Here, it is important to note that several experiments have suggested that conventional electron-phonon interaction cannot explain the enhancement of T_c. Raman scattering experiment revealed that the coupling between electron and Raman-active N-vibration

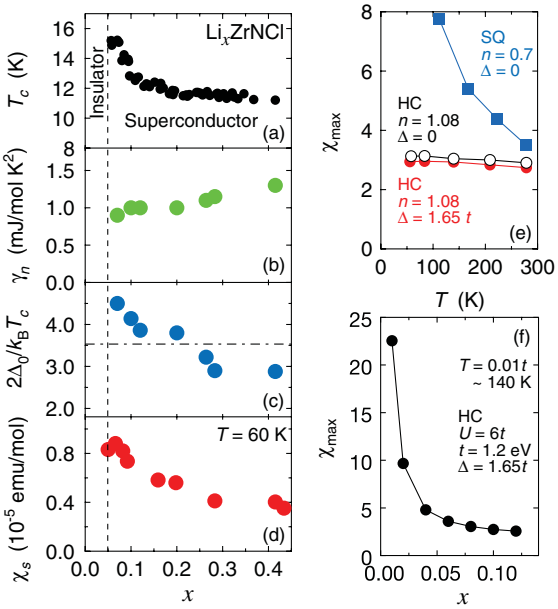

FIG. 4 (color). x dependence of (a) T_c, (b) Sommerfeld constant γ_n, (c) superconducting gap ratio $2\Delta_0/k_BT_c$ obtained from the fitting analysis, and (d) spin susceptibility χ_s along the c axis at 60 K. The dash-dotted line in (c) represents $2\Delta_0/k_BT_c = 3.54$. (e) Temperature and (f) x dependence of maximum value of the wave-number-dependent spin susceptibility (at a finite wave vector), calculated for the Hubbard model on a honeycomb (HC) lattice with a level offset $\Delta = 1.65t$. In (e), we also show the results for the honeycomb lattice with $\Delta = 0$ and for the square (SQ) lattice with $\Delta = 0$ and $n = 0.7$.

phonon modes becomes rather weak as the doping is reduced [28]. Moreover, very weak ^{15}N isotope effect implies the minor role of electron-phonon interaction [29,30]. Therefore, the presence of bosonic contributions other than phonon is strongly suggested, and the pairing mediated by this fluctuation seems to be enhanced toward the low doping region. Figure 4(d) shows the doping dependence of χ_s. Unexpectedly, χ_s increases with decreasing carrier density, displaying an opposite x dependence compared with γ_n, implying that the spin fluctuation is enhanced toward the band insulator.

Charge fluctuations [17,18] and impurity band formation [31] have been discussed as potential mechanisms of superconductivity in doped semiconductors. However, because χ_s and γ_n display distinct behavior, neither of these mechanisms is likely in the present case. Thus, we introduce a theoretical model [21] including the on-site Coulomb repulsion U as an alternative mechanism. The model is a half filled Hubbard model on a honeycomb lattice with an energy difference in alternating site, Δ. We take $\Delta = 1.65t$ and introduce on-site Coulomb repulsion $U = 6t$ on each site, where t is the nearest neighbor hopping integral taken as $t = 1.2$ eV so as to roughly reproduce the band structure of ZrNCl near the band gap ($\sim$2 eV) [13,32]. Figures 4(e) and 4(f) show the maximum value of the wave-number-dependent spin susceptibility plotted as a function of T and x, respectively. $n = 1.08$ [4(e)] and $T = 0.01t \simeq 140$ K [4(f)] are taken as parameter values. Here, n is the band filling, defined as the number of electrons per site, and is related to x as $x = n - 1$. The system becomes a band insulator at half filling $n = 1$, due to the introduction of Δ. In Fig. 4(e), for comparison, we also show calculation results for the honeycomb lattice with $\Delta = 0$ and for the square lattice with $\Delta = 0$ and $n = 0.7$, taking the same values for t and U. As shown in Fig. 4(e), the spin susceptibility is nearly independent of T for the honeycomb lattice, regardless of the value of Δ, in contrast to the case of the square lattice, in which the susceptibility is enhanced as the temperature is lowered. Moreover, the enhancement of the spin susceptibility towards a band insulator is qualitatively demonstrated in our model [Fig. 4(f)]. The calculated results reproduce the experimental observations surprisingly well and therefore strongly suggest that magnetic fluctuations can be enhanced on the verge of SI transition even in doped band insulators without magnetic ordering. Interestingly, this theory predicts that the presently obtained spin fluctuation induces superconductivity with a gap of $d + id'$ symmetry [32], posing further questions to be answered both experimentally and theoretically in the future.

In conclusion, our systematic thermodynamic studies of electron-doped Li_xZrNCl have revealed that the T_c enhancement with reducing x is due to the enhancement of the pairing interactions, rather than that of the density of states. Experimental observation of enhanced spin susceptibility, combined with a theoretical calculation taking into account the on-site Coulomb repulsion, provides evidence that the spin fluctuations are enhanced with approaching a band insulator, very similarly to the case of a doped Mott insulator. Concomitant enhancement of pairing interaction and spin susceptibility in parallel with T_c suggests the possibility of the pairing mediated by spin fluctuations even in a doped band insulator. The possible link between magnetic fluctuations and pairing interaction should be investigated further both experimentally and theoretically.

The authors would like to acknowledge R. Kadono and T. Oguchi for fruitful discussions. This work was supported in part by Grant-in-Aids for Scientific Research, from MEXT, Japan.

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