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Increase in T_c upon Reduction of Doping in Li$_x$ZrNCl Superconductors

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We revealed a detailed phase diagram of the very lightly doped regime in Li-intercalated superconductors, Li$_x$ZrNCl, to which previous studies have never gained access owing to the difficulty in synthesizing single-phase samples. A continuous and uniform Li intercalation without any indication of phase separation was carefully confirmed by means of synchrotron x-ray diffraction and Raman scattering experiments. Upon reducing the carrier density below $x = 0.12$, we found a rapid increase in the superconducting transition temperature (T_c) immediately followed by the superconductor-to-insulator transition (SIT). Such an increase in T_c on the verge of SIT seems to be difficult to explain by the conventional theory, but may be indicative of the charge fluctuation contribution to superconductivity in low-carrier-density systems.

The control of T_c through carrier concentration is a versatile and powerful means of elucidating the intrinsic nature of superconductivity. In recently discovered *B*-doped diamond [1], for example, it was reported [2] that T_c shows a monotonic decrease upon reducing carrier concentration. The decrease in T_c perhaps reflects a dominant role of density of states at the Fermi level [$N(0)$)] in determining T_c, indicating that the superconductivity in this system obeys the conventional Bardeen-Cooper-Schrieffer (BCS) mechanism. Here, we report that, in an electron-doped superconducting system Li$_x$ZrNCl, T_c rather increases as a band insulator is approached by reducing the carrier concentration.

Pristine β-ZrNCl and its Hf analogue are band insulators, and become superconductors with $T_c = 13$ and 25 K, respectively, by alkali-metal intercalation [3,4]. These materials have layered structures in which Zr-N or Hf-N double honeycomb layers are sandwiched by Cl bilayers, and Li atoms are intercalated into the van der Waals gap of the Cl bilayers [5,6], as schematically shown in Fig. 1(a). According to band calculations [7–11], electrons are accommodated in the conduction band consisting mainly of Zr 4d or Hf 5d orbitals. One of the unique characteristics is that $N(0)$ is very small for their T_c, as clearly evidenced by a magnetic susceptibility measurement [12] of Li$_{0.48}$(THF)$_y$HfNCl as well as a specific heat measurement [13] of Li$_{0.12}$ZrNCl. Since this system has a two-dimensional electronic structure [7–11], $N(0)$ is expected to be weakly dependent on band filling. Then, T_c would also be almost independent of the alkali-metal concentration x if the superconductivity in this system is within the simple BCS scheme. Indeed, an almost doping-independent T_c has been reported [14] for the A_xZrNCl (A = alkali metal) system with $x > 0.16$. However, it should be noted that a very careful sample characterization by multiple techniques would be necessary for meaningful discussion about the doping dependence of T_c because of a possible phase separation [4,15] which is often encoun-

tered in intercalation compounds. A more important question is how T_c varies as the band insulator is approached from the superconducting side while reducing x below 0.16, which is the lowest value reported in Ref. [14] because of the difficulty in synthesizing single-phase samples with very low Li concentrations. To address these issues and gain some insight into the mechanism of superconductivity in this system, we attempted to investigate the very lightly doped regime of the Li$_x$ZrNCl system, and succeeded in synthesizing single-phase Li$_x$ZrNCl samples from $x = 0.05$ to 0.31. This enabled us to observe the critical region of SIT as a function of x for the first time. Furthermore, we observed an increase in T_c at the verge of SIT with decreasing x, which is anomalous in the light of general tendency towards decrease in T_c upon reducing carrier concentration, but possibly indicative of charge fluctuation contribution [16–19] to the superconductivity in low-carrier-density systems.
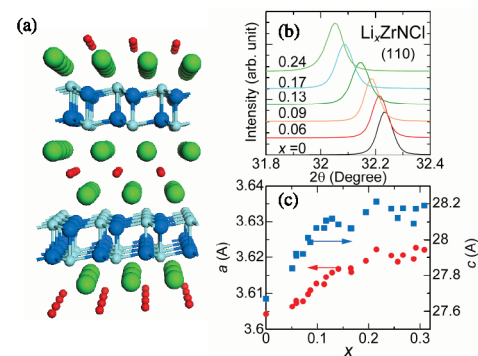

FIG. 1 (color). (a) A crystal structure of Li$_x$ZrNCl is schematically shown. Red, light blue, blue, and green spheres represent Li, Zr, N, and Cl atoms, respectively. (b) (110) reflection peak of synchrotron x-ray diffraction pattern for selected Li$_x$ZrNCl samples. (c) a- and c-axis lattice constants are plotted against x in red circles and blue squares, respectively. The estimated errors are smaller than the symbols.

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β-ZrNCl was prepared following the procedures described in Ref. [20]. Obtained β-ZrNCl powder was dispersed into n-BuLi/hexane solutions (ca. 5 mL) of appropriate molarity for the intended doping level x ($0 \le x \le 0.3$) for 1 d in an Ar-filled glove box. In the cases of $x > 0.16$, the solutions were kept at 70 °C for 2 h after the 1 d of soaking at ambient temperature to promote Li intercalation. The powder was collected by filtration and samples with $x < 0.10$ were subjected to annealing in sealed quartz tubes at 600 °C for 30 min. Powder x-ray diffraction patterns were taken at BL02B2, SPring-8. The x-ray wavelength is 1.00132(7) Å. Li concentration (x) in the products was determined within an accuracy of ± 0.01 by inductively coupled plasma (ICP) spectroscopy. Thus determined x values are used throughout the Letter. Raman spectra of the powder samples sealed in capillaries were recorded at ambient temperature, using a micro-Raman spectrometer with an excitation wavelength of 532 nm. For resistivity measurement, we prepared c-axis oriented, compressed pellets and adopted the conventional four-probe method with current flowing parallel to the conduction plane. Magnetization measurements were performed using a SQUID magnetometer.

An inspection of synchrotron x-ray powder diffraction profiles revealed that all the doped samples were of single phase, and the stacking sequence along the c axis changed from that of the SmSI type to that of the YOF type upon Li doping in accord with previous results [5,6]. In Fig. 1(b), we show (110) x-ray diffraction peaks of selected Li$_x$ZrNCl samples. As x is increased, the peak clearly shifts to a lower angle, indicating the expansion of the in-plane lattice constant. This indicates that the Li atoms are really intercalated into the bulk sample, accompanied by electron transfer from the Li site to Zr-N conduction planes. In Fig. 1(c), the lattice constants deduced from the x-ray diffraction data are plotted against x. Although there seems to be a discontinuity between $x = 0$ and 0.05, probably because of the aforementioned change of the stacking sequence along the c axis, both a and c gradually and continuously increase as x is increased above 0.05. Therefore, it can safely be said that this material forms a

solid solution system. This is very rare from the viewpoint of the materials chemistry of intercalation compounds.

To clarify the effect of doped electrons on lattice dynamics, we have performed Raman scattering experiments. Figure 2(a) shows Raman scattering spectra at ambient temperature for selected Li$_x$ZrNCl samples. In this frequency region, five phonon lines (labeled A–E) are clearly observed in agreement with previous results [21,22]. All the peaks become slightly broader and shift to lower frequencies as x is increased, but the changes are much smaller than those observed in MgB$_2$ [23], implying a much weaker interaction between electrons and phonons at least at the Γ point of the Brillouin zone in the present material. All the phonon lines are symmetric with no indication of Fano resonance, further ensuring that electron-phonon interaction is weak in the present system. Normalized phonon frequency is plotted in Fig. 2(b) as a function of x. The peaks A, C, and D show rather strong doping dependences, and the phonon frequencies of B and E are weakly dependent on x. According to lattice dynamics calculation [22], phonons B, C, and D are ascribed to vibration modes along the c axis whereas phonons A and E to vibration modes parallel to the conduction plane. Continuous shifts in phonon frequencies are another evidence for a steady incorporation of Li into the bulk crystal and the subsequent electron transfer from Li to the conduction plane in accord with the results of x-ray diffraction. Phonon A shows the largest change in frequency (ca. 7%) among these modes in this doping region of $0 \le x \le 0.31$. The x variation of phonon frequency and linewidth are strongly dependent on the particular phonon mode, and systematic analysis is now in progress.

In Fig. 3(a), resistivity data are plotted against temperature for pristine and lightly doped samples below 200 K. The pristine sample exhibits an insulating temperature dependence throughout the region. The low-temperature resistivity below about 70 K of pristine ZrNCl well obeys the activation-type dependence with an activation energy of 21 meV, which corresponds to a transport gap energy of 42 meV and is much smaller than the optical gap energy. As
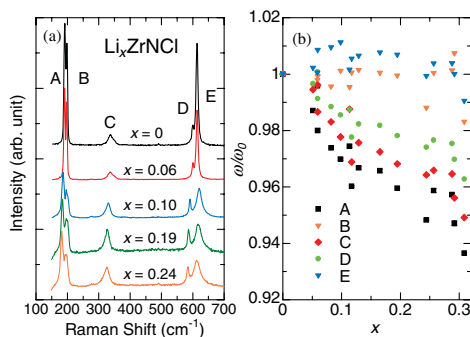

FIG. 2 (color). (a) Raman scattering spectra of selected Li$_x$ZrNCl samples. (b) Normalized phonon frequency is plotted against x for five phonon lines (A–E).
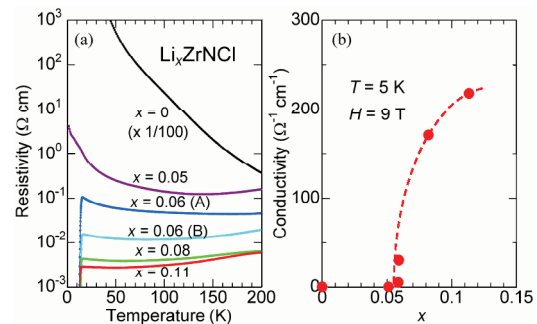

FIG. 3 (color). (a) Temperature variation of resistivity for lightly doped Li$_x$ZrNCl. The data of pristine ZrNCl is multiplied by 1/100. (b) Normal state conductivity at 5 K is plotted against x. Superconductivity is suppressed by applying a magnetic field of 9 T. The dashed curve is a guide to the eyes.

Li atoms are intercalated, resistivity becomes progressively and systematically smaller. A sample with $x = 0.05$ shows an upturn at approximately 140 K although the temperature dependence above 140 K is metallic and the absolute value of resistivity is largely reduced compared with that of the pristine sample. With a further increase in doping level, resistivity becomes smaller and smaller, but even the sample with $x = 0.11$ shows an upturn at about 50 K. Such upturns that are observed robustly at low temperatures are ascribed to the Anderson localization effect due to the disorder, which is probably reinforced by the nature of the present specimen, namely, a compressed pellet. The Anderson localization is signaled by the conductivity of $x = 0.05$ material that almost obeys the $T^{0.5}$ dependence at low temperatures, reaching zero at a finite temperature [24]. The samples with x larger than 0.05 show superconducting transition at low temperatures. The critical resistivity that divides the insulating and superconducting phases is roughly estimated to be 10^{-1} Ω cm, which corresponds to a sheet resistance of 10^6 Ω. This value is approximately 2 orders of magnitude larger than the quantum resistance $h/4e^2$, where disorder-driven SIT has been reported to occur [25]. However, the absolute value of the resistivity in the present experiment should not be taken as it is because of the nature of the compressed pellet.

To discuss the critical region in more detail, we show in Fig. 3(b) the evolution of conductivity in the normal state [26] as a function of x. The conductivity for $x < 0.05$ is essentially zero, but it becomes finite, and increases gradually and continuously as x is increased above 0.05. Therefore, the doping-induced insulator-to-metal transition takes place at approximately $x = 0.06$ in this system. This is the first experimental observation of the critical region of insulator-to-metal transition in this class of layered nitride superconductors as a function of doping level.

To clarify the x dependence of T_c, we measured the magnetization of Li$_x$ZrNCl. Figure 4(a) shows the temperature variation of magnetization in zero-field cooled runs for selected Li$_x$ZrNCl samples. In all the samples, the onset of the superconducting transition is slightly obscured because of a strong two-dimensional superconducting fluctuation and/or slight inhomogeneity of the samples. Nevertheless, it is clear that T_c gradually and systematically increases as x is reduced. To show that these diamagnetic responses represent bulk property, we plot in Fig. 4(b) the superconducting volume fraction [27] as a function of x. The imperfect correction of the demagnetizing field is the reason why the estimated volume fraction exceeds 100%, but the important point is that this result clearly shows that the superconducting signal originates from the entire bulk sample. For three samples with $x < 0.07$, the volume fractions seem to be small compared with those of the rest of the samples; however, they are still sufficiently high to ensure that the superconductivity is bulk property of these samples.

Having confirmed that the samples are of high quality in terms of superconducting volume fraction, we discuss the
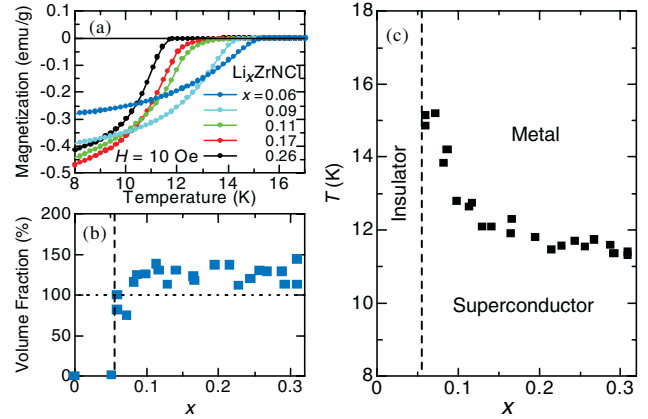

FIG. 4 (color).   (a) Magnetization at a field of 10 Oe (without correction for demagnetizing field) is plotted against temperature for selected samples. (b) x dependence of the superconducting volume fraction determined by MH measurements at 2 K (or 5 K). Imperfect correction of the demagnetizing field is the reason the estimated volume fraction exceeds 100%. (c) x dependence of T_c, exemplifying rapid increase in T_c below $x = 0.12$.

x dependence of T_c [28], which is shown in Fig. 4(c). For the doping region of $0.12 \leq x \leq 0.31$, T_c slightly increases as x is reduced in accordance with the previous result [14]. However, when x is further reduced below 0.12, the trend changes and T_c rapidly increases to reach 15.2 K at $x = 0.06$, then suddenly disappears [29] at $x = 0.05$.

In the simplest version of the BCS theory, T_c scales as $T_c \propto \omega \exp(-1/N(0)V)$, where ω and V are the relevant phonon frequency and effective attractive interaction between electrons, respectively. It is well known that $N(0)$ is constant as a function of carrier density in a free electron model in two dimension. In fact, band calculations [7–11] for this material suggest that $N(0)$ remains almost constant, or rather decreases, as Fermi level is reduced, and hence doping independent, or rather decreasing T_c with reducing x would naively be expected on the basis of the conventional BCS theory. In addition, as noted earlier, the insulator that locates just next to the superconducting phase is an Anderson insulator. In the typical case [25] of the transition to an Anderson insulator, T_c decreases as the transition point is approached from the superconducting side. Therefore, the increase in T_c below $x = 0.12$ is really a surprising result. Even if we take the change in phonon frequency into account, we cannot fully explain the magnitude of the increase: From the Raman data, the increase in phonon frequency is at most 7% as x is reduced from 0.31 to 0 while the increase in T_c is about 25%, indicating that the shift in phonon frequency alone cannot explain the observed increase in T_c. If V is enhanced when x is reduced, then the increase in T_c may be accounted for, but there is no obvious reason for the increase in V.

Alternatively, there may be another explanation for the increase in T_c upon reducing x. As pointed out by Takada [18], when the carrier density is small as in the case of the present system, the effective electron-electron interaction

can become attractive, making a positive contribution to superconductivity in sharp contrast with the detrimental contribution usually encountered in superconductors with high carrier densities. As x is reduced, the dynamical part of the screened Coulomb interaction becomes progressively important; consequently, T_c may be enhanced rapidly below $x = 0.12$. In the present system, the widely used r_s parameter (defined as being in a two-dimensional system), which corresponds to the mean electron distance, increases from 7.3 to 10.3 as the doping level is reduced from $x = 0.12$ to 0.06. According to Takada [18], T_c of s-wave superconductivity due to a purely electronic mechanism is negligible for small r_s values, but begins to increase rapidly at approximately $r_s = 8$ which is close to the r_s value for the $x = 0.12$ compound although a three-dimensional case is considered in his study. The importance of charge fluctuation is also stressed for low-carrier-density superconductors by Kohno *et al.* [19], and for the present superconductor by Bill *et al.* [16,17] in the context of layered structures.

In conclusion, we synthesized a series of single-phase Li$_x$ZrNCl compounds with $0 \leq x \leq 0.31$. Characterization by means of synchrotron x-ray powder diffraction and Raman scattering clearly indicated that Li atoms are continuously and uniformly intercalated into the bulk sample throughout the entire concentration range without phase separation. A SIT was found to occur at approximately $x = 0.06$. As the critical carrier concentration is approached from the superconducting side, T_c very gradually increases, but shows a rapid increase below $x = 0.12$, reaching a maximum of 15.2 K at $x = 0.06$, and then suddenly disappears at $x = 0.05$. Such an increase in T_c is anomalous and may not be able to be accounted for in terms of a simple version of the BCS theory. The increase may be a subtle signature of the charge fluctuation contribution to superconductivity in low-carrier-density systems.

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[26] For the superconducting samples, we have applied a magnetic field of 9 T and suppressed superconductivity. For these materials, H_{c2} in the $H \parallel c$ direction is approximately 5 T.

[27] The superconducting volume fraction was estimated from the zero-field cooled MH measurement (-20 Oe $\leq H \leq$ 20 Oe) at 2 K (some of the samples were measured at 5 K). We performed a correction for the demagnetizing field, assuming that each powder sample consists of small plates with a completely random orientation despite the fact that there is actually some preferred orientation.

[28] We determined T_c as the temperature at which a linear extrapolation of the steepest portion of the zero-field cooled magnetization data at 10 Oe [shown in Fig. 4(a) without correction for demagnetizing field] crosses the temperature axis.

[29] For the $x = 0.05$ sample, there is a very small diamagnetic signal at low temperatures, but the estimated volume fraction is less than 2% at 2 K, indicating that superconductivity is not a bulk property but is due to the residual inhomogeneity of the sample.