

Isotope Effect in Li_xZrNCl Superconductors

Layer-structured β -ZrNCl is a band insulator and has been found by Yamanaka *et al.* [1] to become a superconductor when electrons are doped through alkali-metal intercalation. The schematic crystal structure of Li-doped ZrNCl is displayed in Fig. 1(a). Recent band calculations have predicted that the doped electrons are accommodated into double-honeycomb ZrN layers and form a rather simple, two-dimensional electronic state. The highest values of the superconducting transition temperature T_c reported thus far are 15.2 K and 25.5 K for the Zr-based material and its Hf analogue, respectively. The specific heat measurement of a $\text{Li}_{0.12}\text{ZrNCl}$ sample clearly showed [2] that the density of states at the Fermi level and the electron-phonon coupling constant are both very small for the T_c value ($=12.7$ K). Another interesting feature of this system is that the T_c value increases as the doping concentration is reduced and the band insulator is approached, takes the maximum value of 15.2 K at $x = 0.06$, and the system suddenly becomes an insulator at $x = 0.05$. On the basis of these experimental observations, it has been proposed that bosonic fluctuations other than phonon may also contribute to the pairing interaction among the electrons.

It is generally recognized that the measurement of the isotope effect on T_c (namely, the dependence of T_c on the phonon frequency) is very useful for clarifying the role played by the phonon in the pairing interaction. The purpose of the present research is to clarify the isotope effect in the Li_xZrNCl system to address the possible contribution of bosonic fluctuations other than phonon.

The N isotope effect on T_c has already been measured by Tou *et al.* [4] for the $\text{Li}_x(\text{THF})_y\text{HfNCl}$ system, which is very similar to the present Zr-based system, and was found to be very small [4]. However, the number of samples studied is not very large, and it might be the case that the difference in T_c was small by chance. Therefore, we have prepared a large number of Li_xZrNCl samples containing ^{14}N and ^{15}N isotopes, and have investigated the N isotope effect on T_c in this system [5]. Since the intercalation compounds generally have a strong tendency towards phase separation, all the samples used in this study were carefully examined by X-ray diffraction at beamline BL02B2, and were confirmed to consist of a single phase. The deduced lattice constants (a and c) are plotted in Figs. 1(b) and 1(c), respectively, as a function of Li concentration x , which was determined by ICP analysis. We also plotted the data for

previously reported ^{14}N compounds, in which undoped ZrNCl powders were prepared by a two-steps procedure as opposed to the one-step process adopted in this study. Clearly, all the ^{14}N and ^{15}N samples show very similar lattice constants, which are also in excellent accord with the previous results. This result indicates that the prepared samples are structurally almost identical to each other and should be investigated in terms of phonon frequencies and T_c in more detail. High-resolution experiments using synchrotron radiation were crucial for obtaining such systematics in the lattice parameter of Li-intercalated ZrNCl.

In Fig. 2, we show the Raman scattering spectra of $\text{Li}_{0.18}\text{Zr}^{14}\text{NCl}$ and $\text{Li}_{0.18}\text{Zr}^{15}\text{NCl}$ at room temperature. Five phonon lines (A-E) are clearly observed in this frequency range. Phonons A and B are ascribed to the normal modes, in which all the Zr, N and Cl atoms have similar vibration amplitudes according to a recent lattice dynamics calculation. Phonon C is mainly due to the motion of Zr along the c -axis, whereas higher frequency phonons D and E are basically vibration modes of N. The frequencies of phonons A, B, and C show little change whereas phonons D and E exhibit considerable softening upon ^{15}N substitution for ^{14}N . The shift of frequency is as large as 19 and 20 cm^{-1} for phonons D and E, respectively, as shown in the inset of Fig. 2. The shifts amount to 3.3% of the

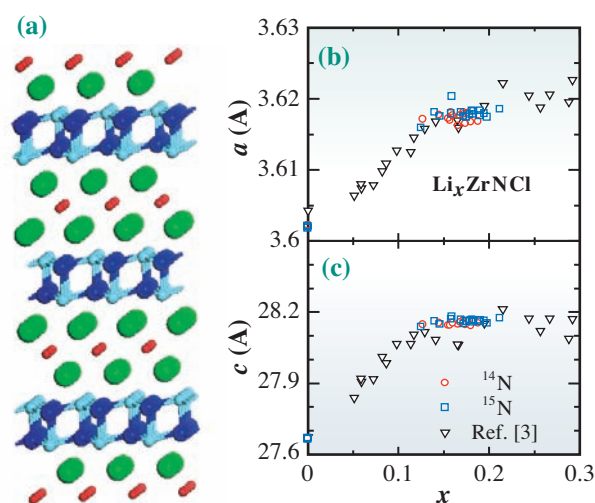


Fig.1. (a) The crystal structure of Li_xZrNCl is schematically shown. Red, light blue, blue, and green spheres represent Li, Zr, N, and Cl atoms, respectively. (b) a -axis and (c) c -axis lattice constants deduced from the diffraction measurements at BL02B2 are plotted as a function of x .

frequency, which is very close to, but certainly smaller than 3.5%, which is expected when the modes are completely due to N vibration.

In Fig. 3, we show a magnified view of the temperature variation of the magnetization near T_c for three representative samples of ^{14}N and ^{15}N . Although the difference between ^{14}N and ^{15}N samples is very small, it is clear that ^{15}N samples have a lower T_c than ^{14}N samples in accord with expectations. For a more quantitative discussion on the isotope effect on T_c , we obtained the T_c values of all the samples indicated in Fig. 3, and plotted them as a function of x in the inset of Fig. 3. The arrow in the inset indicates the expected change in T_c if the relative change in T_c were equal to the relative change in the phonon frequency of the N vibration mode. Clearly, the experimentally observed change is much smaller than the expected change. The solid line and dashed line correspond to two different fits to the data, and the relative change in T_c is estimated to be $-(0.5 \pm 0.3)\%$. If we calculate the isotope shift coefficient α ($T_c \propto M^{-\alpha}$) for N, we have $\alpha = 0.07 \pm 0.04$ as an upper limit. This value is in excellent accord with the value reported for the Hf system by Tou *et al.* [4].

Our experimental observation that the shift of T_c is much smaller than that of the phonon frequency strongly indicates that T_c in this system is not dominated by the phonon alone, but that bosonic fluctuations other than phonon also contribute to the pairing interaction in this class of layered superconductors.

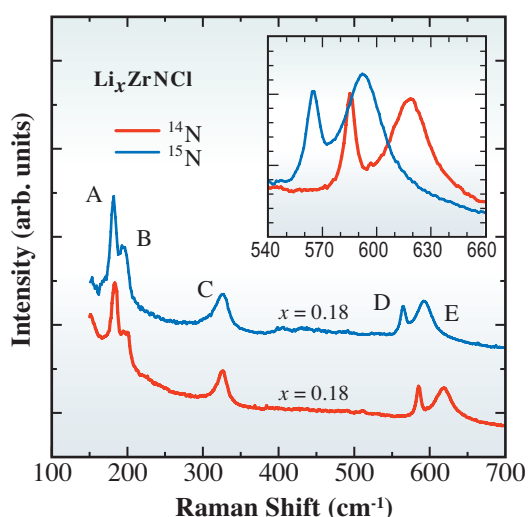


Fig. 2. Raman scattering spectra of $\text{Li}_{0.18}\text{Zr}^{14}\text{NCl}$ and $\text{Li}_{0.18}\text{Zr}^{15}\text{NCl}$ compounds at room temperature. The inset shows a magnified view of the N vibration modes.

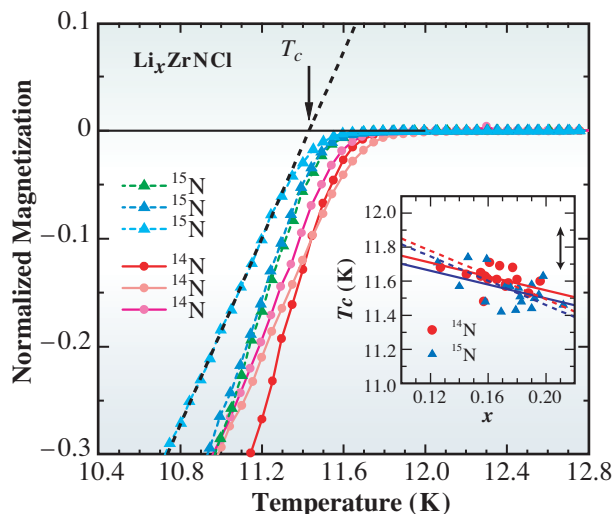


Fig. 3. Temperature dependence of normalized magnetization near T_c for representative ^{14}N and ^{15}N samples. The inset shows the doping dependence of T_c for both isotope samples. The solid line and dashed line represent linear fits to the data based on two different analyses. The solid arrow corresponds to the expected change in T_c if the relative change in T_c were equal to that in the frequency of the N vibration mode.

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