

Isotope effect in Li_xZrNCl superconductors

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The N-isotope effect has been investigated for a series of layered superconductors Li_xZrNCl with small carrier density. The N-vibration phonon mode around 615 cm^{-1} interacting most strongly with electronic system has shown softening by about 20 cm^{-1} ($\approx 3.3\%$) upon ^{15}N substitution. On the other hand, the decrease in the superconducting critical temperature (T_c) upon ^{15}N substitution has been found to be only $0.06 \pm 0.03\text{ K}$ ($\approx 0.5 \pm 0.3\%$). This small change in T_c corresponds to an isotope shift coefficient $\alpha = 0.07 \pm 0.04$, which is much smaller than the conventional value of 0.5, implying the relevance of other fluctuations than the phonon to the pairing interaction.

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Superconductivity is one of the most fascinating phenomena that solid state materials exhibit. Although the electron is most prominent in the phenomenon, the phonon also plays a very important role as the glue that binds the electrons in conventional superconductors. Historically, the importance of the phonon was first noticed by researchers when the isotope effect on superconducting critical temperature (T_c), namely, the dependence of T_c on the phonon frequency, was revealed. In the standard BCS theory, T_c is proportional to the relevant phonon frequency, and hence, the well-known value of $\alpha = 0.5$ is obtained for a simple metal. Here, isotope shift coefficient α is defined as $T_c \propto M^{-\alpha}$, in which M represents the atomic mass.

Recently, alkali-metal intercalated ZrNCl and HfNCl superconductors have attracted much interest because of their higher T_c (≈ 15 and 25 K , respectively) than are expected from the several physical parameters that usually determine T_c values in conventional phonon-mediated superconductors, such as electron-phonon coupling constant and/or electronic density of states at the Fermi level. Undoped ZrNCl and HfNCl are band insulators with the layered structure in which a double-honeycomb ZrN or HfN layer is sandwiched by Cl layers. These materials have been found to become superconductors upon electron doping by Yamanaka *et al.*^{1,2} The electron doping is achieved by means of alkali-metal intercalation in between van der Waals bonded Cl layers. According to band calculations,³⁻⁷ electrons are accommodated into a highly two-dimensional band consisting of $\text{Zr } 4d$ ($\text{Hf } 5d$) orbitals with strong hybridization with $\text{N } 2p$ states. The two-dimensional nature of the electronic state has been confirmed by magnetic and x-ray absorption measurements.^{8,9} As a result of the two-dimensionality of the electronic states, the density of states at the Fermi level is almost independent of the carrier concentration. Recently, it has been demonstrated by a magnetic susceptibility measurement¹⁰ on a Hf compound and a specific heat measurement¹¹ on a Zr compound that the constant values of the density of states are remarkably small for their T_c . In the specific heat measurement of $\text{Li}_{0.12}\text{ZrNCl}$, the electron-phonon coupling constant λ has been determined to be less than 0.22 from the comparison of measured electronic spe-

cific coefficient γ and calculated density of states at the Fermi level. Such a small value of λ is consistent with rather weak broadening of the phonon lines upon electron doping as revealed by Raman scattering,^{12,13} making a marked contrast with the cases of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (Ref. 14) and MgB_2 (Ref. 15) in which substantially strong electron-phonon interaction is considered to be the origin of their high- T_c values. For the present system, it has also been predicted theoretically^{3,7} that the electron-phonon coupling is so weak that the experimentally observed value of T_c cannot be reproduced by the conventional formula using the Hopfield parameter or the Eliashberg function. In contrast to these observations that indicate weak electron-phonon coupling, large values of superconducting gap ratio exceeding 4.5 have been inferred from tunneling spectroscopy¹⁶ and the low-temperature behavior of electronic specific heat.¹¹ This strong coupling nature has also been indicated by μSR measurements.^{17,18} In order to understand these apparently contradicting observations in a consistent manner, charge fluctuation has been proposed^{19,20} to contribute to the pairing interaction in addition to the phonon. The importance of the charge fluctuation was emphasized particularly for small-carrier-density systems,^{21,22} and the recent experimental observation of increased T_c upon decreasing x has been interpreted in terms of enhanced charge fluctuation contribution in the reduced carrier-density regime.¹² Although there seems to be much supporting evidence that the T_c in this system cannot be accounted for by the phonon contribution alone, it would still be very important to collect further information on the roles played by the phonon. For that purpose, we have investigated the N isotope effect on T_c and the phonon frequency for the Li_xZrNCl system. The N isotope effect has already been investigated for $\text{Li}_x(\text{THF})_y\text{HfNCl}$ by Tou *et al.*,²³ and a very small value of α (≈ 0.07) has been reported. In this paper, we investigated the N-isotope effect on T_c in the Li_xZrNCl system by synthesizing many samples to ensure that the result does not depend on particular sample quality, such as randomness and disorder. In addition, we measured Raman scattering spectra to examine the change of phonon frequencies upon isotope substitution and clarified the direct correlation between the phonon frequency and T_c .

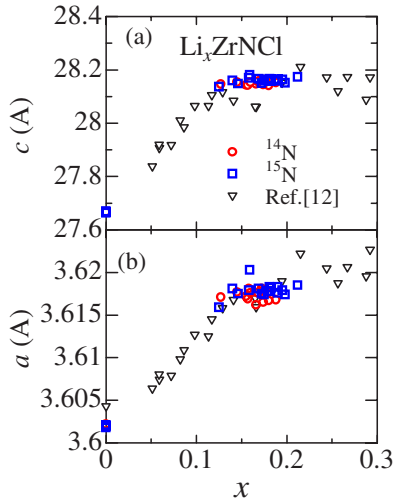


FIG. 1. (Color online) (a) c -axis and (b) a -axis lattice constants are plotted against Li concentration x . Lattice constants of the samples reported in Ref. 12 are also plotted.

It turned out that the change of T_c is substantially smaller than the shift of the frequency of the important N-vibration mode that has the strongest interaction with the electronic system. This fact also indicates that the T_c in this system is not determined by the phonon alone, and the other interaction should be needed for the understanding of the present superconductor.

Undoped β -Zr¹⁴NCl and β -Zr¹⁵NCl were synthesized by using a chemical vapor transport technique. As-purchased ¹⁴NH₄Cl and ¹⁵NH₄Cl were mixed with ZrH₂, and sealed in evacuated quartz tubes, which were placed in a two-zone furnace with a temperature gradient of 750 and 850 °C for 36 h. Li intercalation was performed by using *n*-BuLi/hexane solutions in an Ar-filled glove box to avoid the sample degradation due to the oxygen and/or moisture. The obtained powder was sealed in a capillary for x-ray diffraction and Raman measurements, and in a glass tube together with He exchange gas for the magnetization measurement. All the samples used in the present measurements were confirmed to be of single phase by synchrotron x-ray diffraction experiment performed at BL02B2, SPring-8,²⁴ and the lattice constants were deduced from the diffraction patterns. The Li contents (x) in the intercalated samples were determined within an accuracy of ± 0.01 by inductively coupled plasma spectroscopy technique at analytical research core for advanced materials, IMR, Tohoku University, and thus determined values of x are used throughout the paper. Raman spectra of the samples were recorded at ambient temperature, using a micro-Raman spectrometer with an excitation wavelength of 532 nm. Magnetization measurements were performed by using a commercial superconducting quantum interference device magnetometer.

In Figs. 1(a) and 1(b), a and c axis lattice constants are plotted against the Li concentration x , together with the previous results for Li _{x} Zr¹⁴NCl samples, in which pristine Zr¹⁴NCl were synthesized through two-step procedures.¹² Although the intercalation was carried out under the same condition for all the samples used in this study, there is a

slight distribution in the intercalated Li concentration. Nevertheless, the lattice constants of all the ¹⁴N and ¹⁵N samples are almost the same and also in accord with the previous result. Therefore, it is safely claimed that the synthesized materials are almost identical in terms of the structure, and that the only difference among the samples is the intercalated Li content.

To obtain information on the change of phonon frequencies upon isotope substitution, we have measured Raman scattering spectra for both ¹⁴N and ¹⁵N samples. In Fig. 2(a), we show the Raman scattering spectra of Zr¹⁴NCl and Zr¹⁵NCl with and without Li intercalation. In this frequency region, we observed five phonon lines, which are referred to as A–E hereafter. According to a lattice dynamics calculation,²⁵ phonons B, C, and D are vibrations along the c axis, and phonons A and E are vibrations within the ab plane. Phonons A and B are the normal modes in which all the Zr, N, and Cl have the similar amplitude of vibration. On the other hand, phonon C is ascribed mainly to the vibration of Zr ion whereas higher-lying phonons D and E are primarily those of N ion. It is readily noticed that the phonons D and E exhibit large shift in frequency upon isotope substitution for both doped and undoped materials whereas the phonons A, B, and C show little variation. This observation is in accord with the above-mentioned mode assignments, and also a clear indication of the successful N-isotope substitution in the prepared samples.

In Figs. 2(b)–2(d), the peak positions of scattering intensity for all the phonon lines are plotted against doping rate x for both ¹⁴N and ¹⁵N series. Solid and dashed lines are the fits to the data of ¹⁴N and ¹⁵N compounds, respectively, and the slope of these lines are assumed to be the same. It is clearly seen that the frequencies of phonons A, B, and C are essentially the same for both isotope compounds whereas phonons D and E show softening in frequency as large as 19 and 20 cm^{−1}, respectively, upon ¹⁵N substitution for ¹⁴N. If we calculate the normalized frequency shifts $[-(\omega_{15} - \omega_{14})/\omega_{14}]$ for phonon D and E at $x=0.17$, they are both 3.3%. These values are very close to, but certainly smaller than 3.5%, which is the expected value when these normal modes are completely of N vibration. These results of sample characterization by means of x-ray diffraction and Raman scattering ensure that the series of Li _{x} ZrNCl samples synthesized with and without ¹⁵N substitution are suitable for discussing the isotope effect on T_c .

In Fig. 3(a), we show a magnified view of the temperature variation near T_c of the magnetization of four samples with $0.170 \leq x \leq 0.185$ for both ¹⁴N and ¹⁵N isotopes. The difference of T_c is very small, but there is clear tendency that ¹⁵N samples have lower T_c than those of ¹⁴N counterparts. To discuss the isotope effect on T_c quantitatively, we defined the transition point of each sample to be the crossing point of the two lines of $M=0$ and the steepest portion of the magnetization (represented as a dashed line), as exemplified for one of the ¹⁵N materials in Fig. 3(a). Thus determined T_c values are plotted against the doping rate x in Fig. 3(b). The T_c values are scattered most probably due to the sample-dependent disorder or randomness. Despite the relatively large scattering of the data, it is barely discernible that the T_c for ¹⁵N mate-

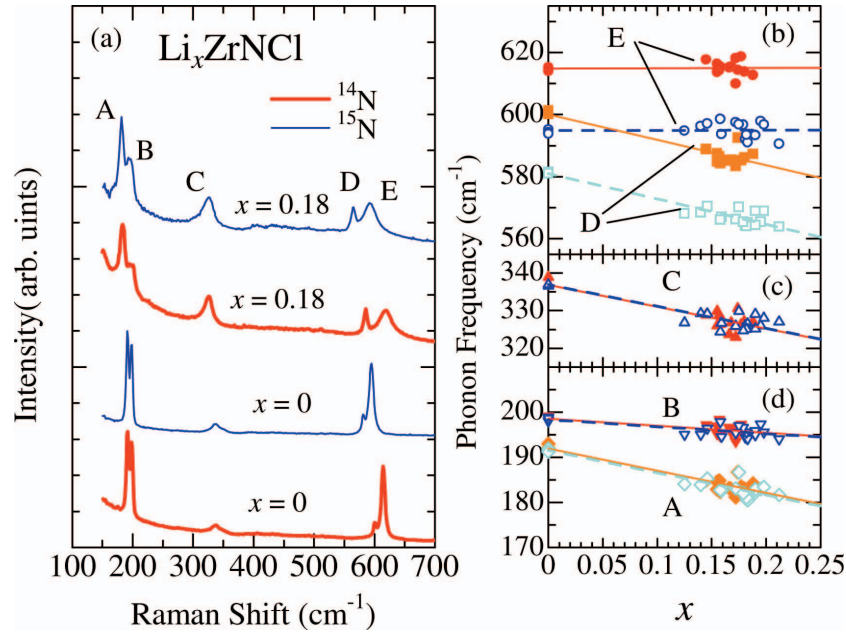


FIG. 2. (Color online) (a) Raman scattering spectra of pristine ZrNCl and $x=0.18$ samples with ^{14}N and ^{15}N isotope. The phonon frequencies of (b) D and E, (c) C, and (d) A and B are plotted against Li concentration x for both isotope. Solid and dashed lines are the fits to the data of ^{14}N and ^{15}N samples, respectively.

rials are lower than those for ^{14}N samples although the difference is very small. For the analysis, we assumed a linear relation between T_c and x in this doping range with an equal value of the slope for both isotope series, namely, $T_c^{14}(x) = T_{c0}^{14} - ax$ and $T_c^{15}(x) = T_{c0}^{15} - ax$. In the fitting procedure, we attempted two kinds of alternatives. (A) All of the a , T_{c0}^{14} , and T_{c0}^{15} are regarded as fitting parameters. (B) Only T_{c0}^{14} and T_{c0}^{15}

are varied, and a is fixed at the value ($=3.572$ K) which is obtained from a fit to the previously reported data¹² with wider Li-concentration range than the present study as displayed in the inset of Fig. 3(b). The fitting results are shown as solid lines (A) and dashed lines (B), respectively. From these fittings, we obtained²⁶ $\Delta T_c \equiv T_{c0}^{15} - T_{c0}^{14} = 0.06 \pm 0.03$ for analysis (A) and $\Delta T_c = 0.05 \pm 0.03$ for

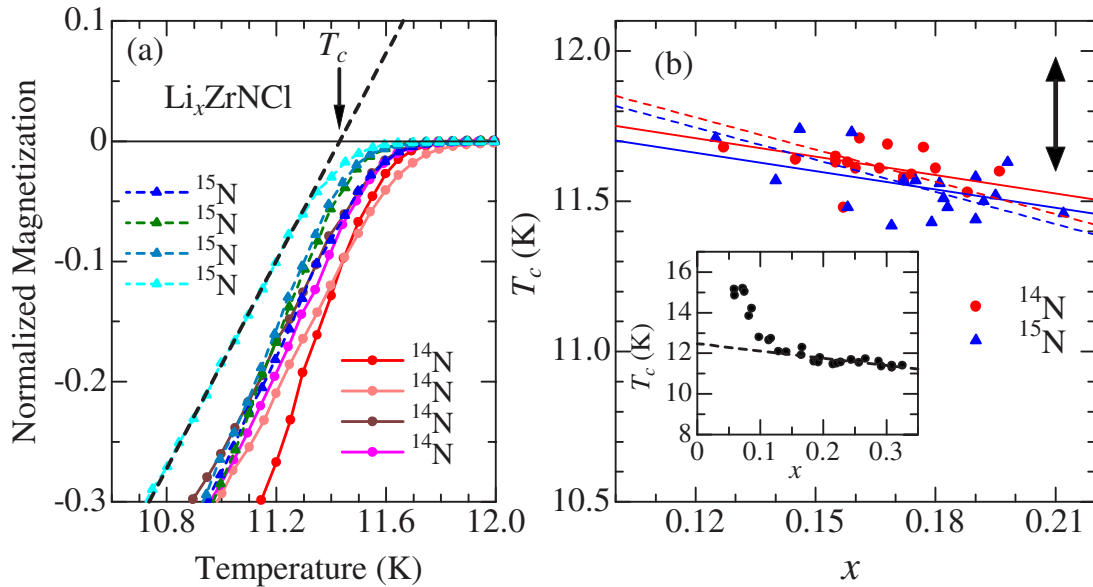


FIG. 3. (Color online) (a) Enlarged view of the temperature dependence of the magnetization around T_c for selected samples whose x value satisfies $0.170 \leq x \leq 0.185$. T_c is defined as a crossing point of $M=0$ and the steepest portion of the magnetization (represented by a dashed line). (b) T_c is plotted against Li concentration x . Solid lines and dashed lines are fit to the data by analysis (A) and (B), respectively. The arrow shows an expected change of T_c if a relation of $\Delta T_c/T_c = \Delta\omega/\omega$ were valid. The inset shows the x dependence of T_c (reported in Ref. 12) for a wider doping range than the present study. The dashed line is a fit to the data for $x > 0.12$, and thus determined slope is used in analysis (B).

analysis (B). If we normalize these values with T_c^{14} at $x = 0.17$, $\Delta T_c/T_c = -(0.5 \pm 0.3)\%$ and $-(0.4 \pm 0.3)\%$ are obtained for analysis (A) and (B), respectively. These results clearly indicate that the isotope effect on T_c is much smaller than the observed change in phonon frequency ($= -3.3\%$), which is indicated by an arrow in Fig. 3(b). Also, α_N values are calculated to be 0.07 ± 0.04 and 0.06 ± 0.04 , respectively. Taking larger values in these analysis, we have $\Delta T_c/T_c = -(0.5 \pm 0.3)\%$ and $\alpha_N = 0.07 \pm 0.04$ as an upper limit. The α_N value we obtained in this study is identical to that reported by Tou *et al.*²³ for the Hf compound.

One might consider that the important phonon that mediates the superconductivity is not the N mode but Zr mode, and this is the reason why the observed change in T_c is much smaller than that in phonon frequency of the N mode. However, this possibility can be ruled out on the basis of the following arguments. One point is that the overall electron-phonon coupling is very weak in this system, as manifested itself as little enhancement of the observed Sommerfeld constant γ over the calculated one¹¹ and the absence of Fano asymmetry in the phonon line shape.¹³ Therefore, the important phonons should have high frequency and should be N mode. Second, an analysis of the temperature and doping evolution of the phonon linewidth has revealed¹³ that the Zr mode around 330 cm^{-1} has negligibly weak interaction with the electronic system, and that the only phonon that has appreciable interaction with electronic system is the N mode around 615 cm^{-1} , in excellent accord with the theoretical prediction.⁷ From these arguments, we can ensure that the important phonon for the superconductivity should be the N

mode around 615 cm^{-1} . Therefore, the small value of isotope shift should have essential implication about the mechanism of the superconductivity in this system. As discussed in much of the literatures,^{10–12,19,20,23} the T_c in this system is possibly enhanced by charge fluctuation contribution in addition to the conventional phonon contribution. In this case, the T_c value is not determined by the phonon-related properties alone, and the isotope effect on T_c would be weaker than in the case of conventional superconductors. Therefore, the small value of isotope shift would be another evidence for the relevance of other fluctuation than phonon in this system.

In summary, we synthesized a series of Li_xZrNCl samples for ^{14}N and ^{15}N isotope, which were confirmed to be structurally identical to each other by synchrotron x-ray diffraction. Raman scattering measurements revealed significant change ($= 3.3\%$) in frequency upon isotope substitution only for two N-vibration modes around 600 and 615 cm^{-1} . Despite the softening of the N-vibration modes over 3% , the decrease in T_c was found to be only $0.5 \pm 0.3\%$, giving the small value of isotope shift coefficient $\alpha_N = 0.07 \pm 0.04$. The present observation would also imply that the superconductivity in this system is mediated not only by the phonon but also by other bosonic excitation.

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