

Superconducting characteristics in electron-doped layered hafnium nitride: ¹⁵N isotope effect studies

Hideki Tou,^{1,2,*} Yutaka Maniwa,^{2,3} and Shoji Yamanaka⁴

¹Department of Quantum Matter, AdSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

²Department of Physics, Tokyo Metropolitan University, Minami-osawa, Hachi-oji Tokyo 192-0397, Japan

³CREST, Japan Science and Technology Corporation (JST), Toshima-ku, Tokyo 171-0031, Japan

⁴Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

(Received 21 January 2003; published 31 March 2003)

We report ¹⁵N nuclear magnetic resonance (NMR) and the nitrogen-isotope effect studies on *c*-axis oriented sample of Li-doped HfNCl with superconducting transition temperature $T_c \sim 25.5$ K. ¹⁵N NMR Knight shift decreases toward zero below T_c , giving evidence that the pairing symmetry is an even-parity spin singlet, and that the nitrogen site plays an important role in the occurrence of superconductivity. A nitrogen isotope shift is found to be quite small, $\Delta T_c \sim 0.1$ K ($\alpha_N = 0.07 \pm 0.02$), which cannot reproduce such a high T_c within the traditional BCS framework.

DOI: 10.1103/PhysRevB.67.100509

PACS number(s): 74.70.-b, 74.25.Ha, 76.60.Cq

The molecular based compounds have attracted a great deal of attention because of their structural flexibility and intriguing physical properties. For instance, in fullerene systems the insulating compounds after intercalation with alkali-metal ions become metallic conductors accompanied with the expansion of the lattice constant and show superconductivity at remarkably high T_c up to 33 K (Ref. 1) for noncuprate materials.

β -HfNCl is a layered molecular semiconductor, where the Cl-[HfN]-[NHf]-Cl slabs stack along *c* axis with a band gap of ~ 4 eV.²⁻⁴ Li atoms are cointercalated with THF (tetrahydrofuran; C₄H₈O) molecules into the weak van der Waals gap between the Cl layers and the bulk superconductivity of Li_{*x*}(THF)_{*y*}HfNCl appears in the doping contents of $0.13 < x < 0.98$ and $y \sim 0.3$. The basal plane spacing *d* increases from 9.23 Å of β -HfNCl to 18.7 Å of Li_{0.48}(THF)_{0.3}HfNCl (Li-HfNCl).² T_c is almost constant (~ 25.5 K) up to $x \sim 0.5$ but gradually decreases to ~ 24.4 K toward $x \sim 1$.³ A simple estimate from the valency implies a low-carrier density system, i.e., $\sim 10^{21}$ cm⁻³. An issue whether the superconductor having a low-carrier density in the vicinity of insulating phase is conventional or not comes into question because the electronic properties might be quite different from that in usual metals.

The electronic structure of HfNCl is dominated by a quasi-two-dimensional band derived from strong hybridization of planer hafnium $5d_{xy}$, $5d_{x^2-y^2}$ with nitrogen $2p_x$, $2p_y$ orbitals.⁶⁻⁸ Band structure calculations suggested that this system is a weakly correlated electron system.⁶⁻⁸ Such two dimensionality of the electronic states was actually confirmed by experimental studies.^{9,10}

In order to explain the high $T_c \sim 25.5$ K, the exchange of optical phonons, due to light nitrogen ions with the characteristic frequency of $\omega \sim 600$ cm⁻¹, between carriers might be a possible mechanism of the high T_c superconductivity in Li-HfNCl. Such an optical phonon mechanism is believed to be realized in A₃C₃₀ (A is an alkali metal)¹ and recently discovered MgB₂.¹¹⁻¹³ In these materials, a substantial carbon^{14,15} or boron¹⁶ isotope effect was observed, strongly

supporting the phonon mechanism. As for hafnium nitrides, on the other hand, the theoretical calculation by Weht *et al*, predicted that the electron-phonon coupling strength of HfNCl is too small to gain $T_c \sim 25.5$ K within the phonon mechanism including the optical phonon mechanism.⁸ Meanwhile, electronic mechanisms such that the pairing interaction is mediated by the exchange of plasmons between carriers have been studied from a viewpoint of layered structure, in which the screening of the Coulomb interaction is very different from that of three dimensional materials.^{17,18} Bill and co-workers have provided an explanation that the high T_c in hafnium nitrides is possible to be realized by the aid of the acoustic plasmon exchange between carriers in addition to the optical-phonon exchange. Anyway, further experimental and theoretical examinations are required.

The aim of the present paper is to (1) clarify the symmetry of the Cooper pairs from ¹⁵N-NMR and (2) elucidate the nature of its superconductivity from ¹⁵N isotope effect experiments. Here, NMR Knight-shift studies for superconductors provide directly the orbital symmetry of the Cooper pairs associated with the pairing interaction. Isotope effect studies give us an important clue to judge whether it is conventional superconductivity or not.

For conventional phonon mediated superconductors, we have the versatile prescription for T_c given by McMillan,¹⁹ and Allen and Dynes:²⁰

$$T_c = \frac{\langle \omega_{ph} \rangle}{1.2} \exp \frac{-1.04(1 + \lambda_{ep})}{\lambda_{ep} - \mu^*(1 + 0.62\lambda_{ep})}, \quad (1)$$

where $\langle \omega_{ph} \rangle$, λ_{ep} , and μ^* are the typical phonon energy, electron-phonon coupling constant, and the Coulomb pseudopotential, respectively. A relation of Eq. (1) and mass independent λ_{ep} yields¹⁹

$$T_c \sim M^{-\alpha}, \quad (2)$$

where M is the mass of the element and α the isotope shift

coefficient. For the weak electron-phonon coupling theory, α is equal to 0.5. More detailed theories extended by Garland and McMillan predict slight deviations from $\alpha=0.5$ owing to the Coulomb repulsion μ^* , as follows:^{19,21}

$$\alpha = \frac{1}{2} \left\{ 1 - \frac{1.04(1 + \lambda_{ep})(1 + 0.62\lambda_{ep})\mu^{*2}}{[\lambda_{ep} - \mu^*(1 + 0.62\lambda_{ep})]^2} \right\}. \quad (3)$$

If the superconductivity of Li-HfNCl is mediated by the phonon mechanism, the isotope exchange from ^{14}N to ^{15}N is expected to bring about sizable change in T_c , such as C_{60} superconductors^{14,15} and MgB_2 .¹⁶ In general, however, it is necessary to check whether or not the N site is intrinsic in the pairing. One aspect of this judgement is ^{15}N -NMR Knight-shift (K) study, where the isotropic part of the Knight shift (K_{iso}) provides information on the local Fermi-level density of states at an interesting atomic site through the Fermi contact hyperfine interaction.²² NMR Knight-shift studies therefore bring about not only the important information on the pairing symmetry, but also local electronic state at nitrogen site.

The ^{15}N -enriched β -HfNCl was prepared by the method using a sealed glass tube;³ 99% ^{15}N -enriched ammonium chloride (Isotech Inc., Ohio) was vacuum sealed with hafnium metal powder with a molar ratio of 1.05:1 in silica glass tubes, which were first heated at 450°C for one day. Then as-prepared 99% ^{15}N -enriched β -HfNCl was purified for five days by a chemical transport technique using a furnace with a temperature gradient of 750–850°C.³ The preparation of Li and THF intercalated samples of β -HfNCl was described elsewhere.^{2,3} Obtained samples were compressed into a pellet under a pressure of 1.5 kbar in argon atmosphere.^{3,9} The THF content was determined to be $y = 0.3 \pm 0.05$ by thermogravimetric analysis. We prepared four oriented pellets, No.1 (^{14}N), No.2 (^{14}N), No.3 (^{15}N), and No.4 (^{15}N) for the present studies. The samples No.1 and No.2 are from the same batches as in the previous papers.^{5,9} The static magnetic susceptibility was measured using a commercial superconducting quantum interference device magnetometer (MPMS, quantum design). The NMR experiments were carried out at Tokyo Metropolitan University using a conventional pulse NMR spectrometer with a magnetic field of ~ 94 kOe (JMTC-400/89 with field homogeneity of 10^{-2} ppm/h).

In Fig. 1, we show the ^{15}N ($I=1/2$) NMR spectra of (a) pure HfNCl and (b) Li-HfNCl obtained by the Fourier-transform technique of free-induction decay signals, together with (c) the expected powder line shapes (for details, see figure caption). Here, we assume that the principal axes of chemical shift $\tilde{\sigma}$ and Knight shift \tilde{K} are the same and the total shift tensor $\tilde{\sigma} + \tilde{K}$ is given by $(\sigma_1 + K_1, \sigma_1 + K_1, \sigma_3 + K_3)$, where $2\sigma_1 + \sigma_3 = 0$ and $2K_1 + K_3 = 0$. Since the honeycomb lattice has threefold rotational symmetry, we can apply the axial-symmetric model to the present materials. Here we should note that the linewidth for Li-HfNCl is very narrow in comparison with that for pure HfNCl. This means that the traceless anisotropic part of the chemical and Knight shift have opposite sign from each other.

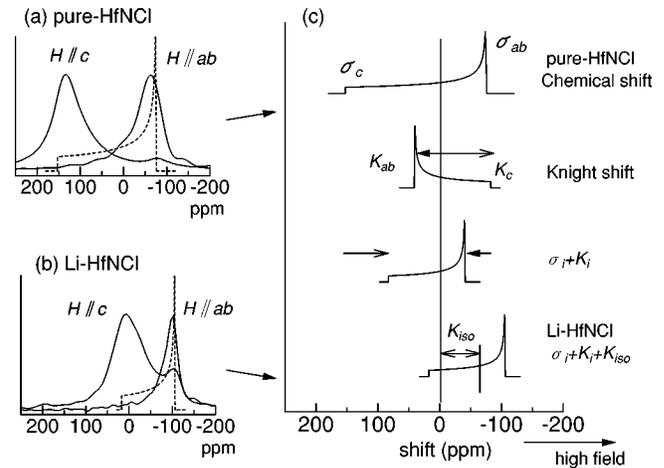


FIG. 1. ^{15}N NMR spectra in (a) pure Hf^{15}NCl and (b) $\text{Li-Hf}^{15}\text{NCl}$ (No.3) measured at 40.540 MHz and $T=25$ K. (c) Expected powder line shapes: (I) in the case of axial-symmetric chemical shift tensor with $(\sigma_1, \sigma_2, \sigma_3) = (-76, -76, 152)$ ppm, (II) in the case of the axial-symmetric Knight shift tensor of $(K_1, K_2, K_3) = (35, 35, -70)$ ppm, (III) in the case of coexistence of axial-symmetric chemical shift and Knight shift tensors of $(\sigma_1 + K_1, \sigma_1 + K_1, \sigma_3 + K_3) = (-41, -41, 82)$ ppm, (IV) observed shift tensor $\delta_i = \sigma_i + K_i + K_{iso}$, with $K_{iso} = -65$ ppm.

The spectra for Li-HfNCl show the negative isotropic shift of $K_{iso} = -65$ ppm with respect to the isotropic shift of the pure HfNCl indicating that the Knight shift at ^{15}N site is dominated by a core polarization-type contact hyperfine interaction where spins on the outer $2p$ shell polarize the inner s shells. Knight-shift tensors are extracted to be $(K_1, K_2, K_3) = (35, 35, -70)$ ppm (see caption of Fig. 1). Also, the Knight-shift anisotropy indicates that a finite conduction-electron density exists at nitrogen p_x and p_y states. Actually, this is confirmed by the fact that the calculated $K_1^{cal} \sim 33$ ppm is consistent with the value, $K_1 = 35$ ppm, extracted experimentally. Here in calculation, we use the relation of

$$K_1^{cal} = 0.4 \left\langle \frac{1}{r^3} \right\rangle_{E_F} \chi_s \sim 0.4 \frac{N^N(E_F)}{N(E_F)} \left\langle \frac{1}{r^3} \right\rangle \chi_s, \quad (4)$$

where $N^N(E_F) \sim 0.035$ states/(eV spin f.u.),^{6,8,7} $N(E_F) \sim 0.25$ (states/eV spin f.u.),⁵ $\langle 1/r^3 \rangle \sim 3.1/a_B^3$, and $\chi_s = 1.7 \times 10^{-5}$ emu/mol⁵ are the partial Fermi-level density of states at nitrogen site, total Fermi-level density of states, nitrogen $2p$ expectation value of $1/r^3$, and the Pauli susceptibility, respectively. The present result agrees well with the predictions from band-structure calculations that the conduction band has mixed Hf $5d_{xy}$, $5d_{x^2-y^2}$, and $\text{N } 2p_x$, $2p_y$ character. Thus, the nitrogen site should be relevant to the superconductivity.

In Fig. 2, we show the temperature dependence of ^{15}N NMR shift, $^{15}\delta_1$, for $H \parallel ab$ plane. The $\delta_1 \sim -106$ ppm above T_c increases toward ~ -88 ppm in the superconducting state. This can be explained by the combined effect of the decrease of the spin susceptibility in the superconducting state and the superconducting diamagnetic contributions.

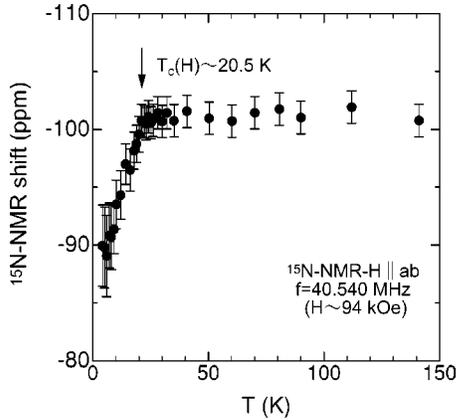


FIG. 2. Temperature dependence of ^{15}N NMR shift for $H\parallel ab$ plane measured at 40.540 MHz.

That is, the observed shift in the normal state given by $\delta_1 = \sigma_1 + K_1 + K_{iso} \sim (-76) + (+35) + (-65) = -106$ ppm should become $\delta_1 = \sigma_1 + K_1 + K_{iso} + \delta_{dia} \sim (-76) + (0) + (0) + (-10) = -86$ ppm at 4.2 K in the superconducting state for the spin-singlet state.²⁴ Here, we take into account the superconducting diamagnetic shift $\delta_{dia} \sim -10$ ppm extracted from the Cl-NMR for $H \sim 94$ kOe.²³ A good agreement between the calculation (-86 ppm) and observed value (~ -88 ppm) provides direct evidence that the pairing symmetry is a even-parity spin singlet and that the nitrogen site is actually relevant to pair formation.

Figure 3 shows the dc magnetic-susceptibility data mea-

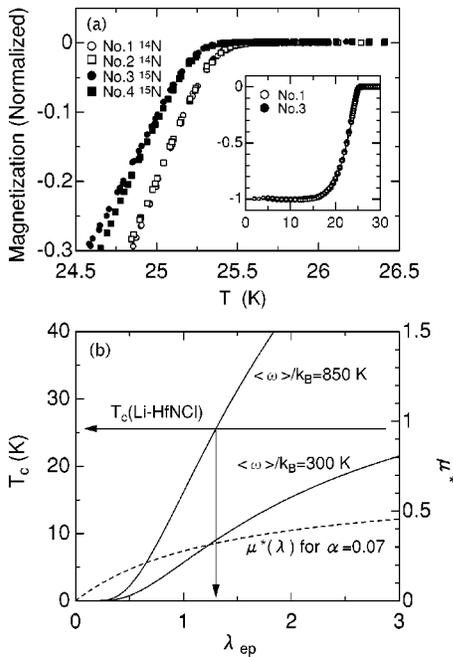


FIG. 3. (a) Sections near T_c of the Meissner curves of several samples of Li-HfNCl at the field of 5 G for $H\parallel c$ axis. Inset shows normalized Meissner curves of samples No.1 and No.3 for field cooling, where the change of T_c due to isotope exchange cannot be distinguished. (b) T_c , μ^* vs λ_{ep} calculated using Eqs. (1) and (3) for $\alpha = 0.07$.

sured at applied field of 5 G parallel to the oriented c axis for the field cooling of Li-Hf ^{14}N Cl and Li-Hf ^{15}N Cl. The data show clearly the occurrence of the Meissner shielding at the onset temperature of ~ 25.5 K and ~ 25.4 K for Li-Hf ^{14}N Cl and Li-Hf ^{15}N Cl, respectively. The plotted magnetization data are all normalized to unity at 4 K for easier comparison (see inset). The nitrogen isotope coefficient α_N was calculated to be $\alpha_N = 0.07 \pm 0.02$, using a relation $\alpha_N = -(\Delta \ln T_c(N)/\Delta \ln M_N)$. Here, T_c 's were determined at the 5% level of the total Meissner effect in order to eliminate ambiguity arising from the shearing correction of demagnetizing field. For the calculation of α_N , no adjustment for the isotope exchange is necessary because the exchange is close to 100%. Other adjustments, e.g., hafnium, chlorine, lithium, proton, carbon, and oxygen atoms would be neglected, i.e., $\alpha \sim \alpha_N = 0.07$ because of following reasons: (1) Hf isotope exchange would bring about negligible isotope shift because of heavy mass itself. (2) As for other atoms, their partial Fermi-level density of states are almost nothing both from previous NMR studies^{9,23,25} and band-structure calculations,⁶⁻⁸ and it is difficult to imagine that any phonon branches by atoms outside the two-dimensional $[\text{HN}]_2$ superconducting layer cause such a high T_c in the conventional phonon mechanism.

The obtained value of $\alpha \sim 0.07$ is quite small and excludes the weak coupling case of $\lambda_{ep} < 0.3$ within the phonon mechanism²¹ because α becomes 0.5 using $\mu^* \sim 0$ in order to gain $T_c = 25.5$ K. That is, the small isotope exponent of 0.07 implies a relatively large Coulomb repulsion; high T_c involves this large Coulomb repulsion and then implies a large λ_{ep} .¹⁹ To check this, in Fig. 3(b) we show T_c , μ^* vs λ_{ep} curves using Eqs. (1) and (3) for $\alpha \sim 0.07$. We found, however, that the observed T_c cannot be reproduced for $\langle \omega_{ph} \rangle / k_B = 300$ K, which is the upper limit among the conventional superconductors, except A_3C_{60} and MgB_2 .¹⁹ Although the McMillan relation gives us underestimates of T_c (40% of the exact solution from the strong coupling Eliashberg theory) in the extremely strong-coupling case, $\lambda_{ep} \gg 1$,¹⁹ we cannot explain such a high T_c in the case of usual phonon frequency less than 300 K even if we take into account this correction.

Instead, we found that $T_c \sim 25.5$ K can be reproduced by using the optical phonon of $\langle \omega_{ph} \rangle / k_B = 850$ K ($\sim 600 \text{ cm}^{-1}$) for the strong-coupling case, same as MgB_2 or A_3C_{60} . However, the obtained parameters of $\mu^* \sim 0.35$ and $\lambda_{ep} \sim 1.35$ seem to be quite extraordinary to realize the conventional phonon mediated superconductivity nevertheless.^{5,8} At present, the origin of the small isotope shift is still unclear and remains an open question. Actually, the recent tunneling spectroscopy experiments by Ekino *et al.* provided the Bardeen-Cooper-Schrieffer (BCS) ratio of $2\Delta/k_B T_c \sim 5$,²⁶ which is inconsistent with the theoretical prediction that the BCS ratio should be close to ~ 3.5 in the case of optical-phonon mechanism even for the strong electron-phonon coupling case.²⁷

Such discrepancies may be reconciled in such a context that the electronic structure of Li-HfNCl is rather two

dimensional^{9,10,18} than those of A_3C_{60} or MgB_2 . Anyway, further experimental and theoretical examinations are desirable.

In summary, ^{15}N NMR measurements and the N-isotope effect studies were carried out on Li-doped $HfNCl$ with $T_c \sim 25.5$ K. The NMR measurements demonstrated that the pairing symmetry is an even-parity spin singlet, and that the nitrogen site plays an important role in the occurrence of

superconductivity. The isotope effect studies revealed a quite small nitrogen isotope shift which is too small to explain the high $T_c \sim 25.5$ K within the conventional BCS framework.

The authors gratefully acknowledge H. Kohno, K. Miyake, T. Ekino, I. Hase, and S. Shamoto for their informative discussions. This work was supported by grants and the COE Grant No. 13CE2002 from the Ministry of Education, Sport, Science and Culture in Japan.

*Email address: tou@hiroshima-u.ac.jp

¹K. Tanigaki *et al.*, *Nature (London)* **352**, 222 (1991).

²S. Yamanaka, K. Hotehama, and H. Kawaji, *Nature (London)* **392**, 580 (1998).

³S. Yamanaka, *Annu. Rev. Mater. Sci.* **30**, 53 (2000).

⁴S. Shamoto *et al.*, *J. Phys. Chem. Solids* **60**, 1431 (1999).

⁵H. Tou, Y. Maniwa, T. Koiwasaki, and S. Yamanaka, *Phys. Rev. Lett.* **86**, 5775 (2001).

⁶I. Hase and Y. Nishihara, *Phys. Rev. B* **60**, 1573 (1999); *Physica B* **281–282**, 788 (2000).

⁷C. Felser and R. Seshadri, *J. Mater. Chem.* **9**, 459 (1999).

⁸R. Weht, A. Filippetti, and W.E. Pickett, *Europhys. Lett.* **48**, 320 (1999).

⁹H. Tou, Y. Maniwa, T. Koiwasaki, and S. Yamanaka, *Phys. Rev. B* **63**, 020508(R) (2001).

¹⁰T. Yokoya *et al.*, *Phys. Rev. B* **64**, 153107 (2001).

¹¹J. Nagamatsu *et al.*, *Nature (London)* **410**, 63 (2001).

¹²J. Kortus *et al.*, *Phys. Rev. Lett.* **86**, 4656 (2001).

¹³H.J. Choi *et al.*, *Nature (London)* **418**, 758 (2002).

¹⁴A.P. Ramirez *et al.*, *Phys. Rev. Lett.* **68**, 1058 (1992).

¹⁵C.C. Chen and C.M. Lieber, *Science* **259**, 655 (1993).

¹⁶S.L. Bud'ko *et al.*, *Phys. Rev. Lett.* **86**, 1877 (2001).

¹⁷H. Kohno, K. Miyake, and H. Harima, *Physica B* **312–313**, 148 (2002).

¹⁸A. Bill, H. Morawitz, and V.Z. Kresin, *Phys. Rev. B* **66**, 100501 (2002).

¹⁹W.L. McMillan, *Phys. Rev.* **167**, 331 (1968).

²⁰P.B. Allen and R.C. Dynes, *Phys. Rev. B* **12**, 905 (1975).

²¹J.W. Garland, *Phys. Rev. Lett.* **11**, 114 (1963).

²²C. P. Slichter, *Principles of Magnetic Resonance*, Springer Series in Solid-State Science Vol. 1 (Springer-Verlag, New York, 1996).

²³H. Tou, Y. Maniwa, S. Yamanaka, and M. Sera, *Physica B* (to be published).

²⁴K. Yosida, *Phys. Rev.* **110**, 769 (1958).

²⁵H. Tou *et al.*, *Physica C* **341–348**, 2139 (2000).

²⁶T. Ekino, T. Takasaki, H. Fujii, and S. Yamanaka, *Physica B* (to be published).

²⁷F. Marsiglio and J.P. Carbotte, *Phys. Rev. B* **33**, 6141 (1986).