Evidence for quasi-two-dimensional superconductivity in electron-doped Li$_{0.48}$(THF)$_2$HfNCl

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Dc-magnetization and NMR measurements were carried out on a layered superconductor Li$_{0.48}$(THF)$_2$HfNCl having $T_c\sim26$ K. For the magnetic field applied perpendicular to the basal plane ($ab$ plane) above 10 kOe, we found a pronounced broadening of the superconducting transition in temperature dependence of magnetization and the substantial diamagnetic signals were observed as high as 2$T_c$, indicating the existence of superconducting fluctuations. Analysis based on the anisotropic Ginzburg-Landau model reveals that the present system is a highly anisotropic superconductor. 1Li-NMR signals were observed around zero Knight shift, indicating that the local Fermi-level density of states, $N(E_F)$, at Li site is practically nothing and the superconductivity is derived from the HfNCl layer. We have shown the unambiguous evidence for the quasi-two-dimensional superconducting character in this system.

The recent discovery of the layered nitride superconductors, alkali (Li, Na) intercalated ZrNCl ($T_c\sim15$ K) and HfNCl ($T_c\sim26$ K),2 have attracted a great deal of attention because of the variety of physical properties. The mother compound, $\beta$-MNCI ($M$=Zr, Hf), is a semiconductor having a band gap of $\sim3-4$ eV. The crystal structure is isostructural with SmSi type layered structure having a double-honeycomb (MN)$_2$ conducting layer sandwiched between Cl$_2$ block layer. Since the Cl layers are coupled by a weak van der Waals force, alkali atoms can be cointercalated with organic molecules, such as tetrahydrofuran (THF)$\cdot$C$_4$H$_8$O) or propylene carbonate (PC)$\cdot$C$_4$H$_6$O$_3$), between the Cl layers. On intercalation, electrons are doped into the (MN)$_2$ layer and the system shows superconductivity.

Band calculations indicate that the conduction band is primarily in $M$ (Zr, Hf) d bands hybridized with N 2p states.3–8 The electronic structure, however, is rather controversial. Hase and Nishizawa, Felser and Seshadri, and Weht et al. have independently predicted that this system has a two-dimensional (2D) electronic structure originating in planer $d_{3z^2}$ and $d_{x^2-y^2}$ characters,5,6,8 whereas Istomin et al. have claimed that it has a three-dimensional (3D) electronic structure originating in $d_{z^2}$ character.7

The bulk superconductivity of Li-doped hafnium nitride, Li$_x$(THF)$_2$HfNCl, appears in the doping contents of 0.13 $<x<0.98$, where $T_c$ is almost constant ($\sim26$ K) up to $x$ $\sim0.5$ but gradually decreases to $T_c\sim15$ K with increasing doping.2 The interplane distance $d$ increases from $\sim9.23$ Å for $\beta$-HfNCl to $\sim18.7$ Å for Li$_{0.48}$(THF)$_2$HfNCl, as schematically shown in Fig. 1. Owing to the layered crystal structure with the large interplane distance, the electronic properties both above and below $T_c$ are expected to be highly anisotropic. Actually, Uemura et al. carried out $\mu$SR measurements on Li-HfNCl and suggested that this material is a quasi-2D superconductor.9

As yet, however, no clear experimental evidence for the 2D electronic state has been presented, and the nature of the superconducting (SC) state also remains unsettled. In this paper, we present characteristic SC parameters of oriented Li$_{0.48}$(THF)$_2$HfNCl.

The sample was prepared at Hiroshima University as described in Ref. 2. The THF content was determined to be $y = 0.3 \pm 0.05$ by thermogravimetric analysis. The powder sample was pressed into pellet form to orient the HfN planes ($ab$ plane). The sample, which is unstable in air, was sealed in a quartz tube with a thin wall at the center, in helium at 350 torr. The magnetization was measured using a commercial superconducting quantum interference device magnetometer (Quantum Design Ltd., MPMS). The ferromagnetic background corresponding to $\sim0.5$ %/spin per formula unit independent of field directions, which should be due to impurity domains, was subtracted from the raw data to obtain the magnetization. The NMR experiments were carried out

FIG. 1. Schematic structural model of Li$_{0.48}$(THF)$_2$HfNCl.
using a conventional pulse NMR spectrometer with a magnetic field of 39.4 and 94 kOe.

The detailed temperature ($T$) dependence of magnetization $M(T)$ around $T_c$ is shown in Fig. 2. Here, the data were corrected for a $T$-independent normal-state background. The mean-field transition temperature, $T_c(H)$, under the applied field is tentatively determined by linear extrapolations of the $T$ linear region in $M(T)$ curves. For $H > 10$ kOe, we notice that the substantial diamagnetic signals become apparent as the magnetic field increases, and that the signals are observed as high as $2T_c$. Since the $T$ linear regions in $M(T)$ were hardly observed for $H > 30$ kOe, we cannot determine $T_c(H)$ by the linear extrapolation method.

Theoretically, these features are explained by the concept that, with increasing $H$, fluctuations in the amplitude of the SC order parameter occur in the vicinity of $T_c$ because of the confinement of the quasiparticles to low Landau orbits under the field and lead to the pronounced broadening of the SC transition. In order to determine $T_c(H)$ for $H || c$, we applied the lowest-Landau-level (LLL) scaling analyses to the present system. According to Ullah and Dorsey, $M(T)$ is scaled as $M(T) / (TH)^n = F[A(T - T_c(H)) / (TH)^n]$, where $F$ is a scaling function, $A$ is a coefficient that is independent of both $T$ and $H$, and $n = 2/3$ for an anisotropic 3D system and $n = 1/2$ for a 2D system. In Fig. 3, we show the magnetization data for $H || c > 10$ kOe scaled by the LLL model. The scaling with $n = 2/3$ is satisfactory as shown in Fig. 3(a), although the 2D LLL scaling with $n = 1/2$ [Fig. 3(b)] is also fitted well. The $T_c(H)$’s determined for $n = 2/3$ and $1/2$ are not meaningfully different from each other. Thus it is strongly suggested that this material is located at the threshold from a highly anisotropic 3D to a 2D superconductor.

The $T$ dependence of the upper critical magnetic field $H_{c2}(T)$ for $H || ab$ plane and $H || c$ axis is illustrated in Fig. 4. $T_c(H)$ was determined by three methods: 3D LLL scaling (●), the linear extrapolation method [○, see Fig. 2(a)], and NMR measurement (□, with $T_c(H)$ tentatively defined as the point where both NMR shift and linewidth begin to

![FIG. 2. Temperature ($T$) dependence of magnetization curves for (a) $H || ab$ and (b) $H || c$. Arrow shows $T_c$ at $H = 50$ Oe. The data were corrected for a $T$-independent background.](image1)

![FIG. 3. Lowest Landau Level (LLL) scaling of high-field magnetization curves for $H || c$: (a) 3D LLL scaling and (b) 2D LLL scaling behaviors.](image2)

![FIG. 4. Temperature ($T$) dependence of the upper critical field $H_{c2}$ for $H || ab$ and $H || c$. The mean-field transition temperature $T_c(H)$ was determined by three methods: 3D LLL scaling (●), linear extrapolation (○), and NMR measurement (□). The dashed lines are theoretical curves for the clean limit. Inset shows $T$ dependence of the $^7$Li-NMR linewidth at 39.4 kOe for $H || c$.](image3)
TABLE I. Characteristic SC parameters of Li-HfNCl (upper critical field \(H_{c2}\), Clogston limit \(H_{pl}\), lower critical field \(H_{c1}\), thermodynamic critical field \(H_c\), GL coherence length \(\xi_{GL}\), GL penetration depth \(\lambda_{GL}\), GL parameter \(\kappa\), and anisotropy parameter \(\Gamma\)) estimated using theoretical relations (see text).

<table>
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<th>(H_{c2})</th>
<th>(H_{pl})</th>
<th>(H_{c1})</th>
<th>(H_c)</th>
<th>(\xi_{GL})</th>
<th>(\lambda_{GL})</th>
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change). The initial slope of the \(H_{c2}\) vs \(T\) curve is \((-dH_{c2}/dT)\)\(_r\) = 18.8 and 5.1 kOe/K for \(H_{||ab}\) and \(H_{||c}\), respectively. As indicated by the dashed lines in the figure, calculations using the Werthamer-Helfand-Hohenberg (WHH) relation, \(H_{c2}(0) = 0.727((-dH_{c2}/dT)_r)T_c\), under the clean limit yield \(H_{c2}^{ab}(0)\) = 348 kOe and \(H_{c2}^{c}(0)\) = −93 kOe. The paramagnetic limiting field, \(H_{pl}^{ab} = 18.4 T_c\) (kOe),\(^15\) is calculated to be \(H_{pl}^{ab} = 469\) kOe. The relation \(H_{pl}^{ab} > H_{c2}^{ab}(0)\) implies that the paramagnetic limitation does not play a role in this system.

The anisotropy parameter \(\Gamma\) was found to be ~14, using the anisotropic Ginzburg-Landau (GL) relation

\[
\sqrt{\Gamma} = \sqrt{\frac{m_c}{m_{ab}}} = \frac{H_{c2}^{ab}}{H_{c2}^{c}} = \frac{\xi_{ab}}{\xi_{c}} = \frac{\lambda_{ab}}{\lambda_{c}} = \frac{\kappa_{ab}}{\kappa_{c}} \sim \frac{H_{c2}^{c}}{H_{c2}^{ab}},
\]

where \(\xi_i\) and \(\lambda_i\) are the GL coherence length and GL field penetration depth along the \(i\) direction (\(i = ab\) plane, \(c\) axis), respectively. \(H_{c2}^{ab}\) and \(H_{c2}^{c}\), \(\kappa_i\), are the upper critical field, lower critical field, and GL parameter for \(H_{||i}\), respectively.

Using the anisotropic GL formulas for the upper critical fields, \(H_{c2}^{ab} = \phi_0/(2\pi \xi_{ab} \xi_{c})\) and \(H_{c2}^{c} = \phi_0/(2\pi \xi_{c}^2)\), where \(\phi_0\) is the flux quantum, we estimate the coherence lengths as \(\xi_{ab} = 59.6\) Å and \(\xi_{c} = 15.9\) Å. The field penetration depth is estimated from the \(^7\)Li NMR linewidth at 39.4 kOe for \(H_{||c}\), as shown in the inset in Fig. 4. At the lowest \(T\) in the field range \(H_{c1} < H < H_{c2}\), the field penetration depth \(\lambda_{ab}\) can be estimated to be ~4630 Å using the relation \((\Delta H)^2 \approx 6.088 \times 10^{-2} \phi_0 / \lambda_{ab}^2\) for the triangular vortex lattice,\(^16\) where \((\Delta H)^2 \approx (5.9)^2\) Oe is the second moment of the NMR spectrum. Then \(\kappa_{ab}\) is evaluated to be 17 300 Å.\(^17\) The thermodynamic critical field is calculated to be \(H_c(0) = H_{c2}^{ab}/(\sqrt{2} \kappa_{ab}) \approx 845\) Oe.

All the parameters thus evaluated are summarized in Table I.\(^17\)

Magnetization measurements thus demonstrated the highly anisotropic character for the present superconductor. Actually, the fact that \(\xi_c\) is shorter than the interplane distance \(d = 18.7\) Å implies that superconductivity is presumably coupled by Josephson tunneling between the adjacent layers.\(^18\) In order to check the anisotropic character from microscopic viewpoints, we carried out \(^7\)Li-NMR shift measurements. Here, Li atoms occupy the interstitial site with THF molecules between Cl layers, as schematically shown in Fig. 1. The NMR Knight shift \(K_s\) provides information on the local Fermi-level density of states at Li site through the Fermi contact hyperfine interaction, \(K_s = (8\pi/3)(|\langle \Psi(0) \rangle|^2)\chi_s\), where \(\chi_s\) is the spin susceptibility and \(|\langle \Psi(0) \rangle|^2\) the electron probability density.\(^19\)

Figure 5 shows the \(T\) dependence of \(^7\)Li-NMR shift at 39.4 kOe for \(H_{||ab}\).

The decrease of \(^7\)Li NMR shift below \(T_c\), \(\Delta K \approx 35\) ppm (−1.3 Oe), is comparable with the SC diamagnetic contribution \(H_{dia} \approx 1.0\) Oe at \(H = 39.4\) kOe. For an estimate of \(H_{dia}\), we use the relation \(H_{dia} = (1 - N)H_c \ln(0.381 e^{-0.5 d/\xi})/N\kappa\) (Ref. 21) for \(\kappa = \sqrt{\kappa_{ab} \kappa_c} \approx 151\), \(\xi = \sqrt{\xi_{ab} \xi_c} \approx 30.7\) Å, \(H_{c1}^{ab} = 8.9\) Oe, \(d = 246\) Å which is the nearest-neighbor vortex lattice spacing at 39.4 kOe and the demagnetization factor, \(N = 0.1\). These NMR results indicate that the superconductivity of Li-HfNCl is derived from the HfNCl layer. Namely, this material is characterized as a quasi-2D superconductor.

In summary, dc magnetization and NMR measurements were carried out on the layered superconductor, Li_{0.48}(THF)_{0.3}HfNCl. Dc-magnetization measurements demonstrated the highly anisotropic character for Li-HfNCl. We also presented anisotropic SC parameters of this material. Li-NMR measurements revealed that \(N(E_F)\) at Li site is negligibly small, and the HfNCl-layer plays an important role in occurrence of the superconductivity. Present results are con-
sistent with the predictions from the band calculations.\textsuperscript{5,6,8} The present study established that this system is a different class of the quasi-2D superconductor. The issue of why such a high $T_c \sim 26$ K is realized, however, remains an open question. The two-dimensionality in the electronic properties may have an important role in the mechanism of the high-$T_c$ superconductivity in Li-HfNCl.

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\textsuperscript{14} The slope $(-dH_c^2/dT)_f = 5.1$ kOe/K is consistent with the clean limit value of $\sim 5.6$ kOe/K in the WHH theory (Ref. 13). If our assumption of the clean limit is not valid, either $H_c^2(0)$ should be less than 3 T for the weak electron-phonon coupling case (Ref. 13) or an upward curvature of $H_c^2(T)$ should be observed for the strong coupling case [M. Affronte \textit{et al.}, Phys. Rev. B \textbf{49}, 3502 (1994)]. Thus, we treat this material as a clean limit superconductor.
\textsuperscript{16} W. Barford and J. M. F. Gunn, Physica C \textbf{156}, 515 (1988); For square lattice, $k_{GL}^{ab}$ can be estimated to be $\sim 3980$ Å using the relation of $\sqrt{\Delta H} = \phi/(k_{GL} \sqrt{1/4})$ [P. Pincus \textit{et al.}, Phys. Lett. \textbf{13}, 21 (1964)]. This value agrees well with $\sim 3800$ Å obtained by $\mu$SR measurement (Ref. 9). Their estimate is based on the square lattice. For the triangular lattice, their value is replaced by $\lambda = 4410$ Å.
\textsuperscript{17} For the square lattice, some parameters are modified as $\kappa_{ab} = 3980$ Å, $\kappa_c = 14900$ Å, $\kappa_{ab} = 250$, $\kappa_c = 67$, $H_c^{ab} = 11.7$ Oe, $H_c^c = 43.7$ Oe, and $H_c = 983$ Oe.