PHYSICAL REVIEW B, VOLUME 63, 020508(R)

Evidence for quasi-two-dimensional superconductivity in electron-doped $Li_{0.48}(THF)_yHfNCl$

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(Received 2 October 2000; published 20 December 2000)

Dc-magnetization and NMR measurements were carried out on a layered superconductor $Li_{0.48}(THF)_yHfNCl$ having $T_c \sim 26$ 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 $2T_c$, indicating the existence of superconducting fluctuations. Analysis based on the anisotropic Ginzburg-Landau model reveals that the present system is a highly anisotropic superconductor. ^{7}Li-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.

DOI: 10.1103/PhysRevB.63.020508 PACS number(s): 74.70.−b, 74.25.Ha, 76.60.Cq

The recent discovery of the layered nitride superconductors, alkali (Li, Na) intercalated ZrNCl ($T_c \sim 15$ K)[1] and HfNCl ($T_c \sim 26$ K),[2] have attracted a great deal of attention because of the variety of physical properties. The mother compound, β-MNCl (M=Zr, Hf), is a semiconductor having a band gap of ~ 3–4. 3 eV. The crystal structure is isostractural with SmSI type layered structure having a double-honeycomb $(MN)_2$ conducting layer sandwiched between Cl_2 block layer.[3,4] 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:C_4H_8O) or propylene carbonate (PC:$C_4H_6O_3$), 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.[5–8] 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_{xy} 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, $Li_x(THF)_yHfNCl$, appears in the doping contents of $0.13 < x < 0.98$, where T_c is almost constant (~ 26 K) up to $x \sim 0.5$ but gradually decreases to $T_c \sim 15$ K with increasing doping.[2] The interplane distance d increases from ~ 9.23 Å for β-HfNCl to ~ 18.7 Å for $Li_{0.48}(THF)_yHfNCl$, 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 μSR 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 $Li_{0.48}(THF)_yHfNCl$.

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 ~ 0.5 %/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

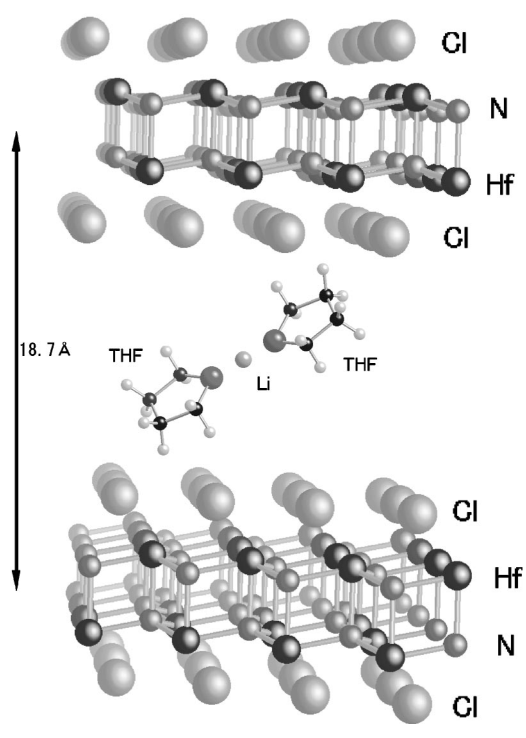

FIG. 1. Schematic structural model of $Li_{0.48}(THF)_yHfNCl$.

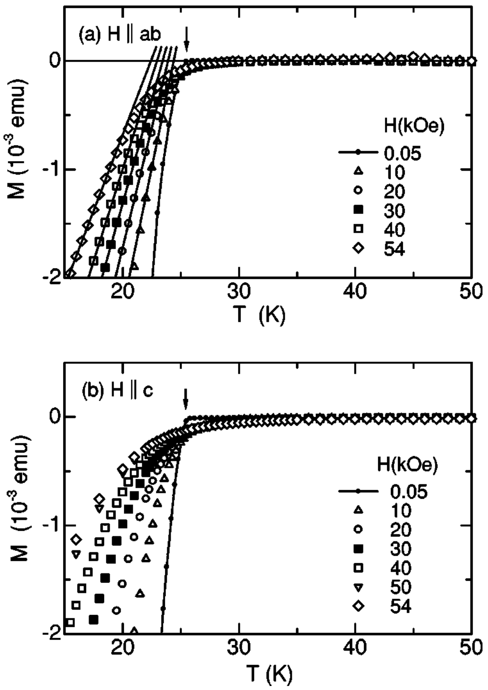

FIG. 2. Temperature (T) dependence of magnetization curves for (a) $H\|ab$ and (b) $H\|c$. Arrow shows T_c at $H=50$ Oe. The data were corrected for a T-independent background.

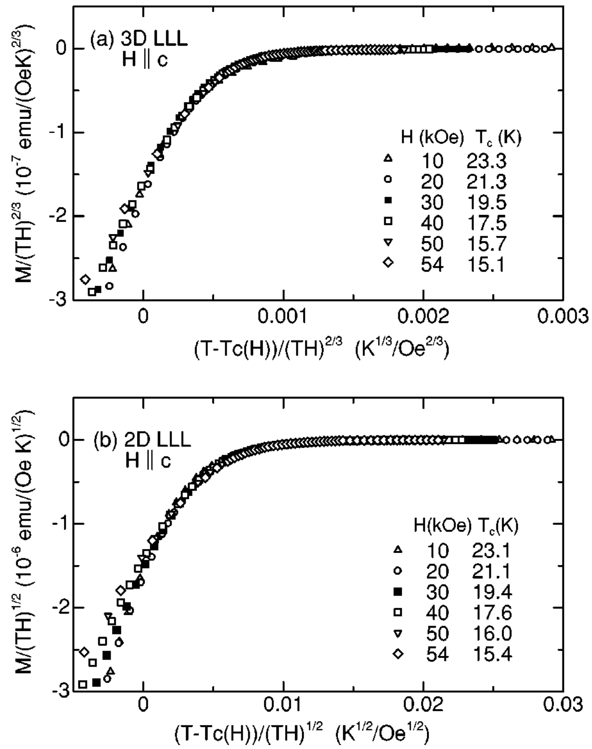

FIG. 3. Lowest Landau Level (LLL) scaling of high-field magnetization curves for $H\|c$: (a) 3D LLL scaling and (b) 2D LLL scaling behaviors.

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 $H\|c>10$ 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 $H\|c>30$ 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.[10,11] Thus, the present finding strongly suggests the existence of 2D SC fluctuations.[11,12] 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,[11,12] $M(T)$ 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

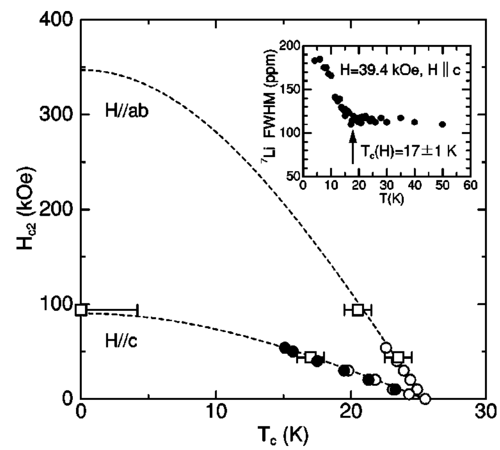

FIG. 4. Temperature (T) dependence of the upper critical field H_{c2} for $H\|ab$ and $H\|c$. The mean-field transition temperature $T_c(H)$ was determined by three methods; 3D LLL scaling (●), linear extrapolation (○), and NMR measurement (□). The dashed lines are theoretical curves for the clean limit.[13] Inset shows T dependence of the ^{7}Li-NMR linewidth at 39.4 kOe for $H\|c$.

TABLE I. Characteristic SC parameters of Li-HfNCl (upper critical field H_{c2}, Clogston limit H_{p0}, lower critical field H_{c1}, thermodynamic critical field H_c, GL coherence length ξ_{GL}, GL penetration depth λ_{GL}, GL parameter κ, and anisotropy parameter Γ) estimated using theoretical relations (see text).

	H_{c2} (kOe)	H_{p0} (kOe)	H_{c1} (Oe)	H_c (Oe)	ξ_{GL} (Å)	λ_{GL} (Å)	κ	Γ
		469		845				14
$\|ab$ plane	348		8.9		59.6	4630	291	
$\|c$ axis	93		33.5		15.9	17300	78	

change). The initial slope of the H_{c2} vs T curve is $(-dH_{c2}/dT)_{T_c}=18.8$ 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, $H_{c2}(0)=0.727[(-dH_{c2}/dT)_{T_c}]T_c$,[13] under the clean limit yield $H_{c2}^{\|ab}(0)\sim 348$ kOe and $H_{c2}^{\|c}(0)\sim 93$ kOe.[14] The paramagnetic limiting field, $H_{p0}=18.4\ T_c$ (kOe),[15] is calculated to be $H_{p0}=469$ kOe. The relation $H_{p0}>H_{c2}(0)$ implies that the paramagnetic limitation does not play a role in this system.

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

$$\sqrt{\Gamma}=\sqrt{\frac{m_c}{m_{ab}}}=\frac{H_{c2}^{\|ab}}{H_{c2}^{\|c}}=\frac{\xi_{ab}}{\xi_c}=\frac{\lambda_c}{\lambda_{ab}}=\frac{\kappa_{\|ab}}{\kappa_{\|c}}\sim\frac{H_{c1}^{\|c}}{H_{c1}^{\|ab}}, \qquad (1)$$

where ξ_i, and λ_i are the GL coherence length, and GL field penetration depth along the i direction ($i=ab$ plane, c axis), respectively. $H_{c2}^{\|i}$, and $H_{c1}^{\|i}$, $\kappa_{\|i}$ 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 $H_{c2}^{\|c}=\phi_0/(2\pi\xi_{ab}^2)$, where ϕ_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 $H_{c1}\ll H\ll H_{c2}$, the field penetration depth λ_{ab} can be estimated to be ~ 4630 Å using the relation $\sqrt{(\Delta H)^2}\sim 6.088\times 10^{-2}\phi_0/\lambda_{ab}^2$ for the triangular vortex lattice,[16] where $(\Delta H)^2\sim(5.9)^2$ Oe^2 is the second moment of the NMR spectrum. Then λ_c is evaluated to be 17 300 Å using Eq. (1). The anisotropic GL parameters, $\kappa_{\|ab}=\sqrt{\lambda_{ab}\lambda_c/(\xi_{ab}\xi_c)}$ and $\kappa_{\|c}=\lambda_{ab}/\xi_{ab}$, are evaluated to be 291 and 78, respectively. We also evaluate the lower critical fields, $H_{c1}^{\|c}=33.5$ Oe and $H_{c1}^{\|ab}=8.9$ Oe using $H_{c1}^{\|c}=\phi_0\ln\kappa_{\|c}/(4\pi\lambda_{ab}^2)$ and Eq. (1). The thermodynamic critical field is calculated to be $H_c(0)=H_{c2}^{\|ab}/(\sqrt{2}\kappa_{\|ab})\sim 845$ 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 ξ_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, $K_s=(8\pi/3)\langle|\Psi(0)|^2\rangle\chi_s$, where χ_s is the spin susceptibility and $\langle|\Psi(0)|^2\rangle$ the electron probability density.[19]

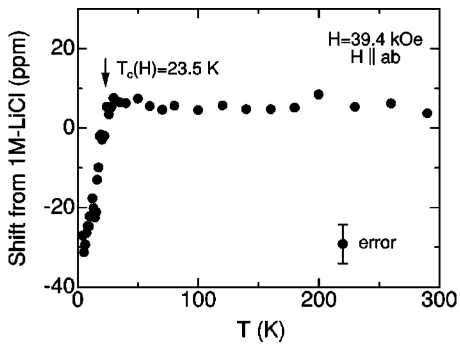

FIG. 5. Temperature dependence of ^{7}Li-NMR shift at 39.4 kOe for $H\|ab$.

Figure 5 shows the T dependence of ^{7}Li NMR shift of $Li_{0.48}(THF)_{0.3}HfNCl$ for $H\|ab$. Above T_c, ^{7}Li NMR signals were observed around 4∼8 ppm, which can be explained by the chemical shift, ∼5–6 ppm, within the experimental error of ±5 ppm,[20] i.e., $K_s\sim 0$ ppm. The observed shift is about two order of magnitude smaller than the Knight shift of Li metal ($K_s\sim 260$ ppm).[19] Even if we assume $K_s\sim 5$ ppm, the electron probability density at Li site of Li-HfNCl is roughly estimated to be less than ∼2% of the Li metal. Anyhow, ^{7}Li-NMR result indicates that the Fermi-level density of states, $N(E_F)$, at Li site is practically nothing within the experimental accuracy. This is consistent with the predictions from the band calculations that the conduction band is primarily in Hf d bands hybridized with N $2p$ states.[5,6,8]

The decrease of ^{7}Li NMR shift below T_c, $\Delta K\sim 35$ ppm (∼1.3 Oe), is comparable with the SC diamagnetic contribution $H_{dia}\sim 1.0$ Oe at $H=39.4$ kOe. For an estimate of H_{dia}, we use the relation $H_{dia}=(1-N)H_{c1}ln(0.381e^{-0.5}d/\xi)/ln\kappa$ (Ref. 21) for $\kappa=\sqrt{\kappa_{\|ab}\kappa_{\|c}}\sim 151$, $\xi=\sqrt{\xi_{ab}\xi_c}\sim 30.7$ 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 consistent with the predictions from the band calculations.[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.

The authors gratefully acknowledge I. Hase, S. Shamoto, Y.J. Uemura, and K. Mizuno for their valuable comments. This work was supported by the fund for Special Research Projects of Tokyo Metropolitan University and in part by grants from the Ministry of Education, Sport, Science and Culture in Japan. H. T. has been supported by Research Aid of the Sumitomo Foundation for Science.

[1] S. Yamanaka *et al.*, Adv. Mater. **9**, 771 (1996).

[2] S. Yamanaka, K. Hotehama, and H. Kawaji, Nature (London) **392**, 580 (1998); S. Yamanaka, Annu. Rev. Mater. Sci. **30**, 53 (2000).

[3] S. Shamoto *et al.*, Physica C **306**, 7 (1998); J. Phys. Chem. Solids **60**, 1431 (1999).

[4] A. Fuertes *et al.*, Chem. Mater. **11**, 203 (1999).

[5] I. Hase and Y. Nishihara, Phys. Rev. B **60**, 1573 (1999); Physica B **281&282**, 788 (2000).

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

[7] S. Y. Istomin *et al.*, Physica C **319**, 219 (1999).

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

[9] Y. J. Uemura *et al.*, Physica B **289-290**, 389 (2000).

[10] R. Ikeda and T. Tsuneto, J. Phys. Soc. Jpn. **60**, 1337 (1991).

[11] S. Ullah and A. T. Dorsey, Phys. Rev. B **44**, 262 (1991).

[12] M. Lang, F. Steglich, N. Toyota, and T. Sasaki, Phys. Rev. B **49**, 15 227 (1994).

[13] E. Helfand and N. R. Werthamer, Phys. Rev. **147**, 288 (1966); N. R. Werthamer, E. Herfand, and P. C. Hohenberg, *ibid.* **147**, 295 (1966).

[14] The slope $(-dH_{c2}^{\parallel c}/dT)_{T_c} = 5.1$ kOe/K is consistent with the clean limit value of ~ 5.6 kOe/K in the WHH theory (Ref. 13). If our assumption of the clean limit is not valid, either $H_{c2}^{\parallel c}(0)$ should be less than 3 T for the weak electron-phonon coupling case (Ref. 13) or an upward curvature of $H_{c2}^{\parallel c}(T)$ should be observed for the strong coupling case [M. Affronte *et al.*, Phys. Rev. B **49**, 3502 (1994)]. Thus, we treat this material as a clean limit superconductor.

[15] A. M. Clogston, Phys. Rev. Lett. **9**, 266 (1962).

[16] W. Barford and J. M. F. Gunn, Physica C **156**, 515 (1988); For square lattice, λ_{GL}^{ab}, can be estimated to be ~ 3980 Å using the relation of $\sqrt{(\Delta H)^2} \sim \phi/(\lambda_{GL}^2 \sqrt{16\pi^3})$ [P. Pincus *et al.*, Phys. Lett. **13**, 21 (1964)]. This value agrees well with ~ 3800 Å obtained by μSR measurement (Ref. 9). Their estimate is based on the square lattice. For the triangular lattice, their value is replaced by $\lambda = 4410$ Å.

[17] For the square lattice, some parameters are modified as $\lambda_{ab} = 3980$ Å, $\lambda_c = 14\,900$ Å, $\kappa_{\parallel ab} = 250$, $\kappa_{\parallel c} = 67$, $H_{c1}^{\parallel ab} = 11.7$ Oe, $H_{c1}^{\parallel c} = 43.7$ Oe, and $H_c = 983$ Oe.

[18] W. E. Lawrence and S. Doniach, in *Proceedings of the 12th International Conference on Low Temperature Physics*, edited by E. Kanda (Academic Press of Japan, Kyoto, 1971), p. 361.

[19] G. C. Carter, L. H. Bennet, and D. J. Kahan, *Metallic Shifts in NMR* (Pergamon Press, Oxford, 1977).

[20] R. K. Harris and B. E. Mann, *NMR and the Periodic Table* (Academic Press, London, 1978).

[21] P. G. De Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).