NMR studies of the electron-doped hafnium nitride superconductor

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Abstract

We report on Nuclear Magnetic Resonance measurements on an oriented polycrystalline sample of the layered superconductor $Li_{0.48}(THF)_{0.3}HfNCl$ having T_c ~26 K. ^{35}Cl-NMR signals were observed around zero Knight shift, suggesting that the partial Fermi-level density of states, $N^{Cl}(E_F)$, at Cl site is practically nothing, and the superconductivity is derived from the [HfN] double-honeycomb network. These results reconfirm that $Li_{0.48}(THF)_{0.3}HfNCl$ is a quasi-two-dimensional superconductor.

Key words: Layered superconductor ;HfNCl ;Nuclear Magnetic Resonance ; Low carrier system

In 1998, Yamanaka and his coworkers discovered a new type of superconductor, Li-doped β-HfNCl [1]. This material has attracted a great deal of attention because of the variety of its physical property. The relatively high transition temperature of T_c =25.5 K is realized by a small amount of Li-intercalation to the layered insulator HfNCl with a band gap of ∼ 4 eV. On intercalation, the interlayer distance d increases from 9.23 Å of β-HfNCl to 18.7 Å of $Li_{0.48}(THF)_yHfNCl$, as schematically shown in Fig.1, and electrons are believed to be doped into the double HfN layer.

The bulk superconductivity suddenly appears at T_c ∼ 25.5 K for the doping contents of x ∼ 0.13. T_c is almost constant (∼ 25.5 K) up to x ∼ 0.5 but gradually decreases to ∼ 24.4 K toward x ∼ 1 [1]. A question why such a high T_c is realized in the vicinity of insulating phase naturally arises.

Uemura *et. al.* pointed out the exotic nature of superconducting properties near the Bose-Einstein condensation limit from muon spin relaxation (μSR) measurements [6]. Recently, we reported the quasi-two-dimensional superconducting character in this system from dc-magnetization and H-, Li-NMR measurements and clarified that the superconductivity is derived from the HfNCl layer [7,8]. Furthermore, we reported that the small Fermi level density of states (∼ 0.25 states/eV) fail to explain the origin of the high T_c in terms of the conventional BCS model[9]. Anyway, whether or not the Cl block layers are related to the occurrence of superconductivity remain to be

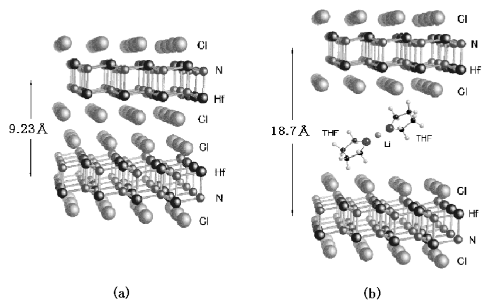

Fig. 1. Schematic structural model of (a) pristine HfNCl and (b) $Li_{0.48}(THF)_{0.3}HfNCl$.

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clarified. In this report, we present Cl-NMR results in the oriented $Li_{0.48}(THF)_{0.3}HfNCl$.

Detailed sample preparation and experimental procedure were reported previously [1,8,9]. Magnetization mesurements were performed up to $H = 15T$ to check the superconducting transition temperature.

Figure 2 shows the T dependence of ^{35}Cl-NMR spectra of $Li_{0.48}(THF)_{0.3}HfNCl$ measured in the magnetic field $H \sim 9.4$T. Note that the ^{35}Cl-NMR spectra were observed around zero Knight shift. Here, the origin of the Knight shift is referred to the center-of-mass position of the spectrum of the pristine HfNCl, which is the isotropic chemical shift, ∼120 ppm, with respect to spectrum of standard 1M-LiCl. The linewidth of ∼600 ppm is comparable to the chemical shift range, 0 ∼ 1000 ppm, in insulating covalent compounds such as CCl_4. Thus, it is reasonable to consider that the ^{35}Cl NMR shift is due to the chemical shift

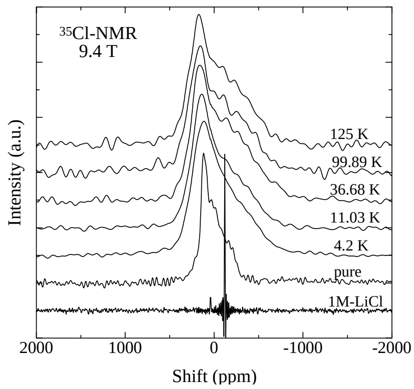

Fig. 2. Temperature dependence of ^{37}Cl-NMR spectra.

Figure 3 shows the T dependence of ^{37}Cl NMR shift. Below $T_c = 20.5$ K, the decrease of ^{35}Cl NMR shift below T_c, ~ -8 ppm (∼0.6 Oe), is explained by the superconducting diamagnetic contribution in the vortex lattice, as discussed previously [7,8]; superconducting diamagnetic shift H_{dia} is estimated to be ∼ 0.4 Oe at H =94 kOe by using the relation $H_{dia} = H_{c1} ln(0.381e^{-0.5}d/\xi)/ln\kappa$ [10] for $\kappa = \sqrt{\kappa_{\|ab}\kappa_{\|c}} \sim 151$, $\xi = \sqrt{\xi_{ab}\xi_c} \sim 307$, $H_{c1}^{\|ab} = 9$ Oe, $d = 160$ Å which is the nearest neighbor vortex lattice spacing at 94 kOe. These results indecate that the partial Fermi level density of states, $N^{Cl}(E_F)$, at Cl site is considerably small. Together with the previous reports [8], $[HfN]_2$-honeycomb network plays a major role in occurrence of the superconductivity in this system. These results are consistent with the results from band calculations; the conduction band has a two-dimensional (2D) character originating in planer hafnium d_{xy} and $d_{x^2-y^2}$ hybridized with nitrogen p_x, p_y [3–5].

In summary, we measured ^{35}Cl-NMR in the T range of 4∼ 150K across T_c for $Li_{0.48}(THF)_{0.3}HfNCl$.

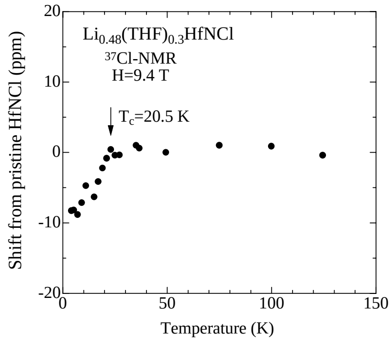

Fig. 3. Temperature dependence of ^{37}Cl-NMR shift.

Present studies demonstrate that the superconductivity in this system is derived from the two-dimensional $[HfN]_2$ honeycomb-network and consistent with the previous results [7,8]. In order to clarify the question why such a high T_c is realized in the vicinity of insulating phase, ^{15}N-NMR measurements are now in progress and details will be reported elsewhere.

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