Tunneling spectroscopy of the electron-doped layered superconductor $Li_{0.48}(THF)_{0.3}HfNCl$

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Abstract

Tunneling measurements on the electron-doped layered superconductor $Li_{0.48}(THF)_{0.3}HfNCl(THF;C_4H_8O)$ with $T_c = 25.5$ K have been carried out. Since the surface of this compound is very reactive, we have employed *in situ* break junction to obtain unaffected interface. The result shows the gap value of $2\Delta = 9$ - 12 meV, which leads to the strong-coupling gap ratio $2\Delta/k_BT_c \simeq 5$. This is the largest value among non-cuprate superconductors.

Key words: Tunneling spectroscopy ;Superconducting gap ;Break junction ;$Li_{0.48}(THF)_{0.3}HfNCl$

The layered nitride $Li_{0.48}(THF)_{0.3}HfNCl$ is known to exhibit superconductivity with $T_c = 25.5$K [1]. This T_c is higher than that of the intermetallic compounds except for MgB_2 [2]. The superconductivity of this compound appears when the N layers of the semiconducting β-HfNCl (SmSI type) are electron doped by the intercalation of Li ions and THF molecules between the Cl layers [1]. Such a semiconductor-metal transition and the layered crystal structure, as well as the low-carrier characteristic and suggested secondary role of the electron-phonon interaction are in a sense similar to those of the copper oxide superconductors [3, 4]. Therefore, it should be interesting to investigate the nature of the energy gap, which is the most fundamental property of the superconductivity. In this paper, we report on the electron-tunneling measurements of $Li_x(THF)_yHfNCl$ for the first time. The electron-tunneling spectroscopy provides the most direct technique to observe the energy gap. The sample used here was the c-axis oriented polycrystalline pellet. Since this compound is very reactive against the ambient atmosphere, its handling was done in an Ar-filled glove box before mounting it to the tunneling apparatus. We have employed *in situ* break-junction method, in which the superconductor-insulater-superconductor (SIS) junction can be obtained at 4.2 K. In this junction geometry, the peak-to-peak bias separation of the superconducting gap in the conductance corresponds to 4Δ/e. The tunneling-current direction is designated within the *ab* plane.

Figure 1 shows the tunneling conductance from two different break junctions. The high-bias junction resistance was ranging from 1 k to 10 k ohms, which are usual magnitudes for the superconducting gap measurements. For the conductance labeled *a*, the calculated SIS-junction conductance with the similar gap value is also presented using the broadened BCS density of states. In this comparison, the largely suppressed gap-edge feature is recognized in the experimental conductance. In spite of this broadened feature, the well-defined conductance peaks can be seen at ± 9 mV, which correspond to ± 2Δ/e. The shoulders at ± 4 - 5 mV correspond to half the gap value ± 2Δ/e (= ± 9 mV), which are probably due to either the 2-particle tunneling or a local formation of SIN (N = normal metal) junction. The origin of the broad hump around zero bias can be connected with a

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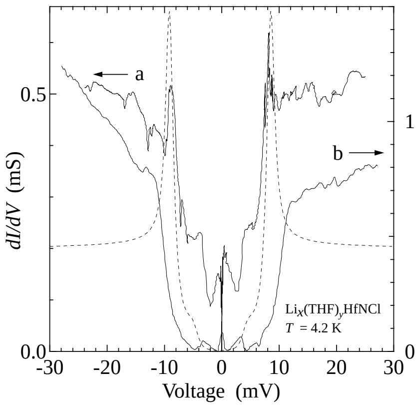

Fig. 1. Tunneling conductance for two different $Li_{0.48}(THF)_{0.3}HfNCl$ break junctions. The broken curve represents the calculated BCS density of states with the small broadening parameter (= 0.1 Δ).

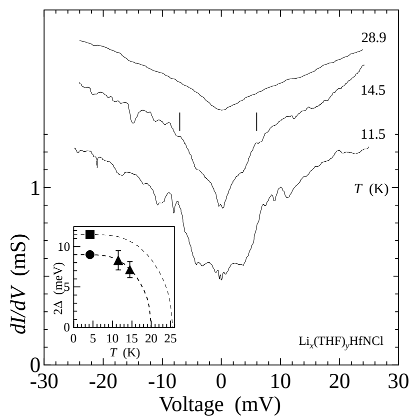

Fig. 2. Temperature variations of the tunneling conductance of $Li_{0.48}(THF)_{0.3}HfNCl$. Inset shows the temperature dependence of the energy gap. The broken curves represent the BCS prediction.

weak link or a metallic contact in the junction. For the conductance b, the weakened gap edge peaks at $\pm$ 11 - 12 mV, which correspond to $\pm\, 2\Delta$/e, occur with very low leakage current. Such a feature in fact deviates from that of the BCS density of states. The broadness of the spectra in Fig. 1 can be connected with the fact that the quality of this compound is severely degraded in consequence of the room-temperature handling. The gap anisotropy expected from the layered structure also might cause such a broadened gap. More information about the gap could be obtained by normalizing the superconducting conductance by the interpolated normal-state one from the high biases. However, we do not measure such a high-bias conductance because of increasing instability of the junction with increasing the bias. Such obscured gap features have been also observed in the tunneling measurements on high-T_c superconductors using polycrystals [5]. Despite the substantial difference in the conductance features between a and b, the gap values 2Δ = 9 - 12 meV are almost reproducible.

Figure 2 shows the tunneling conductance at various temperatures. The junction is different from that in Fig. 1. With increasing the temperature, the gap feature becomes further broadened. At the temperature above $T_c = 25.5$ K, the structures in the conductance disappear, indicating that the features seen at low temperatures arise from the superconducting gap. The 14.5 K spectrum is largely obscured, but we can recognize the features at $\pm \simeq 7$ mV as the gap edge. In the inset, the temperature dependence of the gap is shown. The gap value of 9 meV at 4.2 K taken from Fig. 1 a is smoothly connected to the gaps of Fig. 2 using the BCS temperature dependence of the gap. This can be extrapolated to $T_c \simeq 20$ K, which is lower than the bulk $T_c = 25.5$ K of $Li_{0.48}(THF)_{0.3}HfNCl$. Such a T_c reduction can be primarily due to local inhomogeneity of the intercalating ions. From the extrapolated gap value $2\Delta(0\text{ K}) = 9$ meV and $T_c \simeq 20$ K, the gap ratio $2\Delta(0\text{ K})/k_BT_c \simeq 5.2$ is obtained. For the gap of $2\Delta = 11$ - 12 meV shown in Fig. 1 b, the gap-closing temperature is deduced to be $\simeq$ 25-27 K assuming the same ratio 5.2, which is very close to $T_c = 25.5$ K of this compound.

From above systematic results, the gap ratio $2\Delta(0\text{ K})/k_BT_c \simeq 5$ is confirmed, which indicates very strong-coupling superconductivity in $Li_{0.48}(THF)_{0.3}HfNCl$. This is the largest value among the superconductors except for copper oxides, and noted to be comparable to that of MgB_2 [6].

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