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STM/STS measurements of the layered superconductor β-$HfNCl_{1-x}$

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ABSTRACT

Scanning tunneling microcopy/spectroscopy (STM/STS) measurements have been carried out on SmSI (β) type $HfNCl_{1-x}$ ($x \approx 0.3$) samples with $T_c = 24$ K. The STM image on the cleaved surface of *ab* plane at 5 K clearly reveals a triangular arrangement of bright spots. The separation of the nearest-neighbor spots, 0.369 nm, is in agreement with the *a* lattice parameter. The STS measurements at 5 K reveal almost constant gap values $2\Delta = 20$ meV within the area of at least 10×10 nm^2, thus demonstrating a huge ratio $2\Delta/k_BT_c = 10$. This ratio is very similar to that found in high-T_c oxide and organic superconductors.

1. Introduction

High-T_c superconductivity of the compound β-$HfNCl_{1-x}$ with layered metal–nitrogen structure was discovered by Yamanaka et al. [1] Superconductivity with $T_c = 24$ K is induced in this compound by electron doping to HfN double honeycomb layers through the de-intercalation of Cl atoms. Band calculations showed that strongly hybridized Hf 5*d* and N 2*p* orbitals form the conduction band [2]. Our previous tunneling break-junction studies clarified very large gap ratio $2\Delta/k_BT_c > 6$ [3], which unambiguously exceeds the BCS weak-coupling ratio 3.52, where 2Δ is the superconducting energy gap. Such a huge gap ratio is very rare for conventional superconductors [4], while it is routinely observed in high-T_c cuprate or organic superconductors [5,6]. Other features, for example, low carrier density, the semiconductor–metal transition on carrier doping, the quasi-two-dimensional layered crystal structure, etc. are also similar to those of the copper-based oxides [7].

In this paper, we widened the scope of measurements. In particular, scanning tunneling microcopy/spectroscopy (STM/STS) measurements have been carried out to elucidate the interrelationship between local superconducting energy gap magnitudes and atomic lattice structures. Since we have already measured FeOCl(α) type K_yTiNCl by STM/STS [8], it seems instructive to investigate the difference and/or similarity of the superconducting electronic properties between β-$HfNCl_{1-x}$ with the double honeycomb network and the α-K_yTiNCl with the rectangular one.

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2. Results and discussion

The STM/STS measurements were done with the modified Omicron LT (low temperature) UHV (ultrahigh vacuum) STM system. Just before the measurements, the sample was cleaved at pressure $\sim 10^{-8}$ Pa in the LT–UHV preparation chamber, and then it was carefully *in situ* transferred to the LT–UHV–STM stage. Scanning measurements were done with a PtIr tip.

Fig. 1 shows the STM image taken at 5 K on the cleaved *ab* surface of the β-$HfNCl_{1-x}$ sample ($x \approx 0.3$). The sample bias was V = 0.2 V and the tunnel current was I = 0.4 nA. A triangular arrangement of bright spots is clearly visible against the weakly inhomogeneous background. These bright spots correspond to a higher altitude of the scanning tip. The total difference in altitude was 0.2 nm. We can always obtain such quality of the surface, which means that the cleaved surface of β-$HfNCl_{1-x}$ is clean and stable under the UHV condition in strong contrast to the cleavage in the ambient atmosphere. From the two-dimensional fast Fourier-transform analysis, the separation of the nearest-neighbor spots was found to be 0.369 nm, which corresponds to the *a* lattice parameter deduced from X-ray diffraction measurements. By considering the atomic arrangement in the conducting double honeycomb metal–nitrogen network on the *ab*-plane of β-$HfNCl_{1-x}$, we attributed the bright spots to metallic Hf atoms.

To investigate the local superconducting-gap-related features on the nanometer scale, we carried out STS measurements at 5 K simultaneously with the STM measurements. The conductance, $G(V) = dI/dV$, map within the area of at least 10 nm $\times$ 10 nm in the *ab* plane reveals fairly uniform magnitudes exhibiting almost constant gap-edge peak positions. Fig. 2 shows such a profile of the STS conductance along the distance of 10 nm.

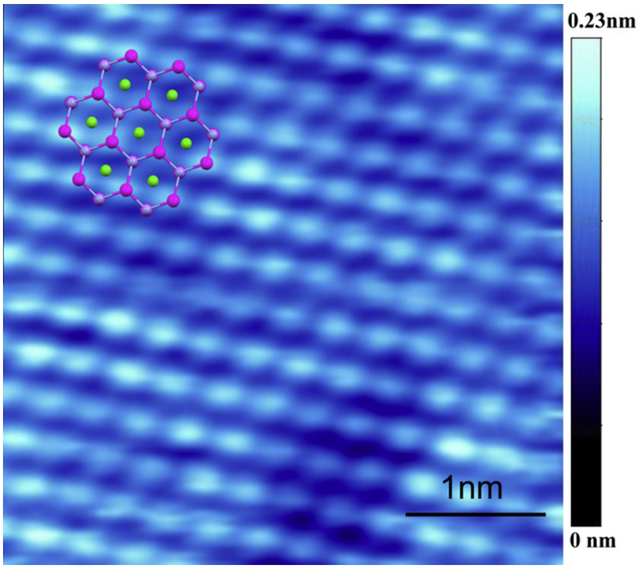

Fig. 1. STM image of β-HfNCl$_{1-x}$ ($V = 0.2$ V, $I = 0.4$ nA, $T = 5$ K).

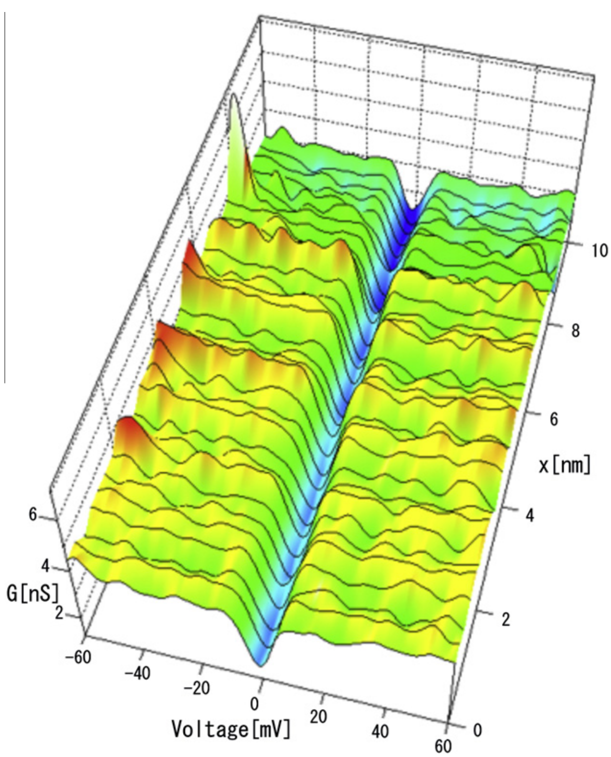

Fig. 2. Distance (x) profile of conductance $G(V)$ for β-HfNCl$_{1-x}$ at 5 K.

Relatively homogeneous gap structures are observed with slight variations in $G(V)$ magnitudes. In general, $G(V)$ are weakly asymmetric, *i.e.*, the negative-bias (corresponding to electron tunneling from the sample into the tip) backgrounds are somewhat more pronounced than their positive-bias counterparts, and the junction exhibits substantial leakage at zero bias. The gap-edge peaks at $V \approx \pm 10$ mV are discernible, although smeared. The almost homogeneous conductance profiles and gap features are in strong contrast to the case of α-K$_y$TiNCl [8], in which a wide gap distribution was observed, as in the case of bismuth high-T_c cuprates [9].

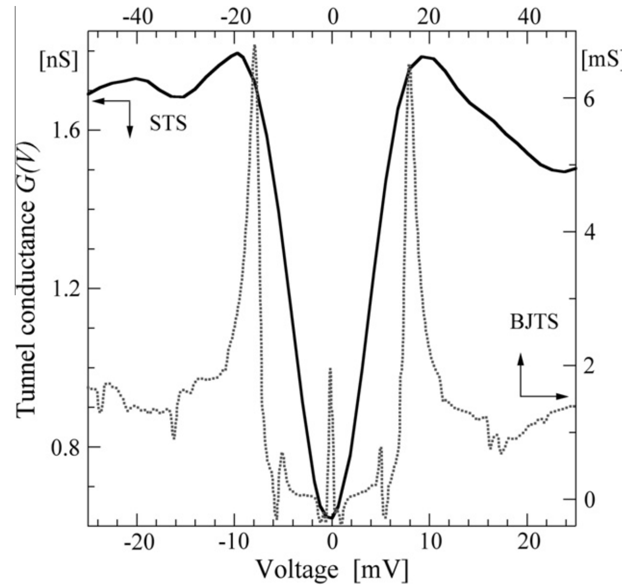

Fig. 3. Comparison of $G(V)$ from STS for β-HfNCl$_{1-x}$ (5 K) and that from break-junction tunnel spectroscopy (BJTS) for β-Li$_{0.48}$(THF)$_z$HfNCl (4.2 K).

The gap value of $2\Delta = 20$ meV in β-HfNCl$_{1-x}$ revealed by the STS measurements presented here is in accord with that obtained in our previous break-junction tunneling studies [3]. In Fig. 3, $G(V)$ for the above described SIN (superconductor–insulator–normal metal) junctions involving β-HfNCl$_{1-x}$ is compared with the break-junction SIS (superconductor–insulator–superconductor) $G(V)$ for β-Li$_{0.48}$(THF)$_z$HfNCl(THF;C_4H_8O). Since β-Li$_{0.48}$(THF)$_z$HfNCl is extremely reactive and it is more difficult to measure its tunnel spectra than those of β-HfNCl$_{1-x}$, the STM/STS measurements were done mainly on β-HfNCl$_{1-x}$. Nevertheless, it is instructive to compare data for both compounds, because the T_c's of β-Li$_{0.48}$(THF)$_z$HfNCl and β-HfNCl$_{1-x}$ are quite similar (25 K and 24 K) and other electronic properties are basically the same in spite of the chemical differences. The peak positions on both curves almost coincide after compensatory rescaling between SIN and SIS junctions as is clearly demonstrated in Fig. 3. Hence, the extremely large gap-like features found earlier in break-junction measurements are now confirmed by STS and can be unambiguously identified with superconducting gaps, inherent to the studied materials. In other words, the gap magnitudes $2\Delta = 20$ meV characterize the β-HfNCl$_{1-x}$ compound, demonstrating meanwhile a huge ratio $2\Delta/k_BT_c = 10$. This value substantially exceeds the numbers typical for conventional BCS superconductors, and is very similar to gap to T_c ratios found for high-T_c oxide and organic superconductors. We note that there is no other available gap measurements on β-HfNCl$_{1-x}$, but the specific heat of an isostructural β-ZrNCl$_{1-x}$ shows much smaller ratio [10]. The gaps observed here are so large that cannot be explained even by an extremely strong electron-intermediate boson coupling. Therefore, it is impossible to interpret our results in the framework of the conventional Cooper-pairing picture, without invoking extra so far unknown factors.

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