Tunneling STM/STS and break-junction spectroscopy of the layered nitro-chloride superconductors \( MNCl \) (\( M = Ti, Hf, Zr \))

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Abstract. The layered superconductors \( \beta\)-\( MNCl \) with the critical temperatures \( T_c = 14 \, \text{K} \) (\( M = Zr \)) - 25 K (\( M = Hf \)) were investigated by means of scanning-tunneling microscopy/spectroscopy and break-junction tunneling spectroscopy. The STM/STS was used to investigate the surface electronic structures in nanometer length scale, while the BJTS was employed to precisely determine the gap characteristics. Both techniques consistently clarified the unusually large size of the superconducting gap. Wide gap distributions with large-scale maximum gap values were also revealed in \( \alpha\)-\( K\)\( TiNCl \) with a different crystal structure.

1. Introduction

The layered compounds \( \beta\)-\( MNCl \) are well known to exhibit superconductivity with high critical temperatures \( T_c = 14 \, \text{K} \) (\( Zr \)) - 25 K (\( Hf \)) [1,2]. Superconductivity emerges after electron doping of the pristine semiconducting \( \beta\)-\( MNCl \) [1,2]. Similar doping effect has been reported in another polymorph \( \alpha\)-\( MNCl(M = Ti) \) with \( T_c = 16 \, \text{K} \) [3]. The \( MN \) bilayers inserted between Cl layers constitute the main frame of the crystal structure, in which nitrogen \( p \) and metal \( d \) states dominate the valence and conduction bands, respectively [4]. Because of the relatively high \( T_c \), a question arose about the relevant superconductivity mechanism. Among experimental methods of investigating such mechanisms, electron-tunneling spectroscopy is an essential technique since it directly probes the energy gap \( 2\Delta \). It seems that the huge gap previously found by us to be far above the weak-coupling BCS cannot be explained by the conventional approach [5-7]. In particular, the strong-coupling Migdal-Eliashberg theory fails to explain superconductivity of \( MNCl \) [4]. In this paper, the superconducting gaps of \( \alpha\)- and \( \beta\)-types of \( MNCl \) having different crystal structures are examined at the nanometer length scale by scanning-tunneling spectroscopy (STS) and are compared with their counterparts found from the break-junction tunneling spectroscopy (BJTS) measurements [5-7].
2. Experimental procedures

Polycrystals of \( MNCl \) were synthesized by a method reported elsewhere [1-3]. Since the samples were very sensitive to air humidity, they were treated in Ar-filled glove box. The STM (scanning-tunneling microscopy)/STS measurements were done with a modified Omicron low-temperature ultra-high vacuum (UHV) STM apparatus. The sample contained in a UHV sealed box was brought into an UHV chamber with the residual pressure of \( \sim 10^{-8} \text{ Pa} \) just before the measurements to avoid contamination of the crystal surface. Then, the sample was cleaved along the layers at \( 3 - 77 \text{ K} \). The \( c \)-axis-oriented single-crystal domain facet of \( \sim 100 \, \mu \text{m}^2 \) was used to probe the surface. Before the scanning measurements, a Pt/Ir tip was cleaned by a high-voltage field emission process with the Au single-crystal target, resulting in the local work function of \( \sim 2 - 4 \text{ eV} \). The BJTS was employed to obtain surface-contamination-free spectra appropriate to fresh and clean superconductor – insulator – superconductor (SIS) junction interfaces at 4.2 K. This is in contrast to SIN (I symbolizes the vacuum and N a normal metal) junctions inherent to STS. The BJTS is a very sensitive probe to detect the gap structure.

3. Results and discussion

Figure 1 shows STM images of the cleaved \( ab \)-plane at 4.9 K for (a) \( \beta \)-HfNCl\(_{0.7} \), (b) \( \beta \)-ZrNCl\(_{0.7} \), and (c) \( \alpha \)-K\(_{0.5}\)TiNCl. In the figure, the triangular lattices of bright spots are easily visible against the weakly inhomogeneous background with the vertical deviation of \( \sim 0.2 \text{ nm} \) (a) and \( \sim 0.07 \text{ nm} \) (b) [6,7]. On the other hand, the rectangular lattice spots are seen in Fig. 1 (c). Therefore, we can readily distinguish between the lattice networks. This means that the cleaved surface is clean and stable in contrast to that exposed to the ambient atmosphere where the chemical decomposition easily occurs.

The nearest-neighbour spot intervals of \( \sim 0.36 \text{ nm} \) for (a) and (b), and the nearest and the next nearest spot intervals of \( \sim 0.33 \text{ nm} \) and \( \sim 0.41 \text{ nm} \), respectively, for (c) are determined from the two-dimensional fast Fourier-transform analysis. They are consistent with the X-ray diffraction measurements [1-3]. Since the observed interval between the bright spots is consistent with the unit cell size, these spots can be attributed to metallic ions in the conducting \( MN \) network on the \( ab \)-plane. This feature is the same for all studied compounds except for the degree of atomic corrugations.

Figure 2 shows the local STS conductance (\( dI/dV = G(V) \)). The line profiles of \( G(V) \) are shown for the line cuts with the intervals of (a) 10 nm and (b) and (c) 5 nm. The spatial distributions of the gap values (the gap maps) are also presented for (a) \( \beta \)-HfNCl\(_{0.7} \) and (c) \( \alpha \)-K\(_{0.5}\)TiNCl. The \( G(V) \) exhibits variations within the \textit{nanometer} length scale, and the majority of \( G(V) \) dependences are asymmetric. The curves \( G(V) \) for \( \beta \)-HfNCl\(_{0.7} \) exhibit broadened gap structures but are rather homogeneous over the sampling area of \( \sim 100 \, \text{nm}^2 \), while the inhomogeneity occurs on the shorter length scale for \( \beta \)-ZrNCl\(_{0.7} \).
One sees that the conductance $G(V)$ for $\alpha$-K$_{0.5}$TiNCl also exhibits substantial nanometer-scale gap distribution. The spatial range of this distribution for (b) and (c) seems to be comparable or shorter than the superconducting coherence length [3]. The origin of the inhomogeneous distribution due to the cleaved layered crystal structure is unlikely because a fairly homogeneous mapping pattern is obtained in $\beta$-HfNCl$_{0.7}$. The asymmetric $G(V)$ may be provoked by modified surface electronic states with the obscured electron spectrum due to the dispersion of incident electrons.

**Figure 2.** Line profiles of the conductance and gap maps for (a) $\beta$-HfNCl$_{0.7}$ (10 nm), (b) $\beta$-ZrNCl$_{0.7}$ (5 nm, without the gap map), and (c) $\alpha$-K$_{0.5}$TiNCl (5 nm).

The STS gap distribution inferred from the conductance $G(V)$ was measured at 4.9 K. The gap maps are presented in figure 2 (a) and (c). In figure 3, we show the gap histograms obtained from the STS gap maps displayed in figure 2. The wide spread of the gap values in $\alpha$-K$_{0.5}$TiNCl is obviously seen as compared with $\beta$-HfNCl$_{0.7}$, which is in accordance with the spatial mapping features in figure 2. For $\beta$-HfNCl$_{0.7}$, the spatially averaged gap value defined by the peak-to-peak interval of $G(V)$ is $2\Delta_{\text{avg}} \sim 24$ meV over the area of $\sim 100$ nm$^2$. The gap distribution spreads up to $2\Delta \sim 40$ meV with a sharp cut-off at $2\Delta \sim 10 - 12$ meV. The gap-to-$T_c$ ratio estimated from these data is an order of magnitude larger than the Bardeen-Cooper-Schrieffer (BCS) value 3.53 appropriate to $s$-wave superconductivity. This conclusion remains valid even if we somewhat overestimated the peak-to-peak value of the gap [6].

**Figure 3.** Histogram of the superconducting gaps for $\alpha$-K$_{0.5}$TiNCl and $\beta$-HfNCl$_{0.7}$.

Similar and widely spread gap values were also found for $\beta$-ZrNCl$_{0.7}$ whatever the bulk $T_c$ values. The gap distribution for $\alpha$-K$_{0.5}$TiNCl is even much broader. It starts at a few meV and ends above $\sim 40$ meV with $2\Delta_{\text{avg}} \sim 28$ meV. We emphasize that $T_c$ of $\alpha$-K$_{0.5}$TiNCl is $\sim 10$ K lower than that of $\beta$-HfNCl$_{0.7}$. Since we observed such a scatter notwithstanding the regular atomic arrangements on the crystal surface, it is most probably due to the electronic inhomogeneity.
inhomogeneity in the $\alpha$-type crystals is much stronger than in the $\beta$-type ones could be due to the difference in the lattice symmetry in the $ab$ plane.

In Table 1, the values of $T_c$, the average gap, and the gap spread are listed for three nitro-chloride superconductors. One can recognize that the averaged gap values $2\Delta_{\text{avg}}$ have similar magnitudes regardless of the $T_c$ difference. At the same time, the gap spread is much wider for the lower $T_c$ compound $\alpha$-K$_{0.5}$TiNCl than that for $\beta$-HfNCl$_{0.7}$.

**Table 1.** $T_c$, the average gap $2\Delta_{\text{avg}}$, and the gap spread $\sigma$ for the nitro-chloride superconductors.

|       | $T_c$ (K) | $2\Delta_{\text{avg}}$ (meV) | $\sigma$ (meV) |
|-------|-----------|-------------------------------|----------------|
| $\alpha$-TiNCl| 16        | ~28                           | 10–20          |
| $\beta$-ZrNCl| 14        | 20–26                         | ~              |
| $\beta$-HfNCl| 25        | ~24                           | 4–10           |

The STS gap distribution at high $T$ is also unusual. The local Cooper pairing in nanometer regions is almost unchanged upon warming, while superconductivity in other surface regions is suppressed much stronger than what would have been expected from the mean-field temperature behaviour. This circumstance may be the origin of the unusual $T$-dependence of the gap values found by BJTS [5]. In figure 4, the STS conductance mapping and the averaged conductance $G(V)$ are shown at 77 K. In the $G(10\text{mV})$ mapping, the conductivity is enhanced on the cation sites and this provides a good indication of the surface cleanliness even at this high temperature. The unusually large gap observed below $T_c$ has already disappeared at 77 K leaving a quite shallow and broad dip in the $V$-shaped background. This feature is somewhat similar to that found in high-$T$ superconductors where pseudogaps are observed.

**Figure 4.** (a) Conductance $G(10\text{ mV})$ mapping (3 nm x 3 nm), and (b) the averaged $G(V)$ for $\beta$-HfNCl at 77 K.

In figure 5, we compare the conductances $G(V)$ obtained by STS and BJTS. For $\beta$-HfNCl$_{0.7}$ (a), the peak positions in the averaged $G(V)$ for STS is just twice smaller than the peak position of the single measurements of $G(V)$ by BJTS, which is consistent with the SIN and SIS geometries across the junctions, respectively. On the other hand, the STS gap-edge bends occur at the same position as the BJTS gap edge in $\beta$-ZrNCl$_{0.7}$. This is probably due to the fact that the BJTS probes the most stable bulky portion of the sample, while the STS $G(V)$ is an average over the wide spatial gap distribution.

**Figure 5.** Comparison of STS and BJTS conductances for (a) $\beta$-HfNCl$_{0.7}$ and (b) $\beta$-ZrNCl$_{0.7}$. The STS curves are the averaged data, while the BJTS ones are obtained from the different junctions.
We attribute the observed difference in the sharpness of the gap structures as well as in the sub-gap leakage of $G(V)$ between STS and BJTS to the difference between the junction actual interfaces, because for each compound the examined samples were taken from the same batch. Therefore, results of the BJTS measurements support STS results and both methods taken together overcome tough problems concerning the interface quality. The results also mean that there still exists much room for improvement of the STS technology to study the sample interface which is extremely sensitive to an unavoidable change of the surface during necessary STS operations.

The inhomogeneous distribution of superconducting gaps in the nitro-chloride compounds could be connected to the surface electronic instability probed by both the STS and BJTS tunneling techniques. This is because charge carrier densities in such layered compounds can be easily reduced under an external influence or an intrinsic instability (for instance, phase separation at the interface region [8]) resulting in the appearance of inhomogeneous spatial patterns. This situation inevitably leads to the spatial spread of superconducting gaps and, probably, to the suppression of superconductivity in the probed surface areas. In contrast, the deliberate charge carrier injection may enhance superconductivity. Actually, such an experiment resulted in the electric-field-induced superconductivity in the initially semiconducting $\beta$-ZrNCl$_{0.7}$ [9]. Therefore, one should bear in mind that in any conventional tunneling technique we not only probe the surface but also disturb it locally possibly changing the parent electronic states.

4. Conclusion

STM/STS and break-junction tunneling measurements of $\alpha$-K$_{0.5}$TiNCl and $\beta$-MNCI$_{0.7}$ ($M = Hf, Zr$) were carried out to clarify the nature of superconductivity. We found from STM/STS measurements that substantial nanometer-scale electronic inhomogeneity, including the broad distribution of gap values, occurs in all studied compounds showing, nevertheless, quite regular atomic lattices of the STM images which are well consistent with the X-ray diffraction data. The STS averaged superconducting gap in each compound is extremely large strongly exceeding the $s$-wave weak-coupling BCS prediction as well as conventional strong-coupling values. STS-inferred huge gaps are consistent with those revealed by the break-junction measurements, thereby giving evidence for an unusual nature of superconductivity in the doped layered nitro-chlorides.

Acknowledgement

This work was supported by a Grand-in-Aid for Scientific Research (245403770) and the FIRST Program of the Japan Society for the Promotion of Science (JSPS). The work was partially supported by the Project N 8 of the 2012-2014 Scientific Cooperation Agreement between Poland and Ukraine.

References
[1] S. Yamanaka, K. Kotehama, H. Kawaji, Nature 392 (1998) 580.
[2] S. Yamanaka, J. Mater. Chem. 20 (2010) 2922.
[3] S. Zhang, M. Tanaka, S. Yamanaka, Phys. Rev. B 86 (2012) 024516.
[4] R. Akashi, K. Nakamura, R. Arita, M. Imada, Phys. Rev. B 86 (2012) 054513.
[5] T. Takasaki, T. Ekino, A. Sugimoto, K. Shohara, S. Yamanaka, A.M. Gabovich, Eur. Phys. J. B 73 (2010) 471.
[6] A. Sugimoto, K. Shohara, T. Ekino, Z. Zheng, S. Yamanaka, Phys. Rev. B 85 (2012) 144517.
[7] T. Ekino, A. Sugimoto, A.M. Gabovich, Z. Zheng, S. Yamanaka, Physica C 494 (2013) 89.
[8] Ariando, X. Wang, G. Baskaran, Z.Q. Liu, J. Huijbens, J.B. Yi, A. Annadi, A. R. Barman, A. Rusydi, S. Dhar, Y.P. Feng, J. Ding, H. Hilgenkamp, T. Venkatesan, Nat. Commun 2 (2011) 188.
[9] J.T. Ye, S. Inoue, K. Kobayashi, Y. Kasahara, H.T. Yuan, H. Shimotani, Y. Iwasa, Nat. Mater. 9 (2011) 125.