STM Observation on Layered Nitride Superconductor $K_xTiNCl$

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Abstract. Scanning tunneling microscopy (STM) measurements of an $\alpha$ (FeOCl) type layered nitride superconductor $K_xTiNCl$ (x $\sim$0.5) with $T_C$ $\sim$16 K are carried out. STM topographies show clear rectangular-shaped atomic distribution with the periods of $|\bar{a}|$=0.41 nm and $|\bar{b}|$=0.33 nm, which correspond to those observed by X-ray measurement. One-dimensional streaky structures are observed at negative biases, which is considered to be arising from N 2p - Ti 3d hybrid bands of the TiN double layers. Both negative and positive STM topographies exhibit the enhanced inhomogeneous background, which can be attributed to the intercalated potassium and/or doped carrier.

1. Introduction

Almost all the “high-$T_C$” superconductors, such as cuprates[1], layered nitrides[2], metal diborides[3] and recently discovered oxypnictides[4], commonly have two-dimensional (2D) conductive layer structures. These 2D atomic networks are considered to be responsible for the occurrence of superconductivity. Among such compounds, layered nitride superconductors $MNX$ (M=Ti, Zr, Hf, X=Cl, Br, I) are known to form the alternative types of layered structures. The $\alpha$-type one ($K_xTiNCl$, shown in Fig. 1(a)) forms conductive 2D TiN double layers with the rectangular network (Fig. 1(b)), while the $\beta$-type layered nitride superconductors, such as Hf (or Zr) NCl$_x$, forms the honeycomb network. (Fig. 1(c)). It should be very interesting to investigate whether or not the difference in the 2D networks affects the superconductivity. Moreover, these nitride superconductors are suitable to investigate possible difference in the superconductivity between the two different network systems in the same kind of materials. However, while properties of the $\beta$-type materials have been investigated by various methods[6, 7, 8], the $\alpha$-type ones have never been investigated because it is extremely reactive in air and difficult to synthesis as a stable superconductor.

Recently, the $\alpha$-type $K_xTiNCl$ superconductor was successfully synthesized with $T_C$ $\sim$ 16 K [5]. Therefore, it is now possible to clarify the superconducting properties of layered nitrides with various 2D networks. Before investigating the detailed electronic states of such 2D networks, it is important to identify such structures with atomic resolution by scanning tunneling microscopy (STM).
In this paper, we present for the first time the STM observation of atomic structures of the α-type layered nitride superconductor K$_x$TiNCl, and discuss the observed surface structures with changing the measuring conditions.

![Figure 1.](image)

**Figure 1.** (a) Schematic Lattice structure of α-K$_x$TiNCl and (b) c-plane structure. (c) c-plane structure of β-type (HfNCl$_x$).

2. **Experimental**

The polycrystalline samples of potassium intercalated superconductor K$_x$TiNCl ($x \sim 0.5, T_C \sim 16$ K) were prepared by reacting powder α-TiNCl with metal azides KN$_3$ in a vacuumed BN cells. After this procedure, the samples were annealed, then pressed into pellet. Since the samples were very reactive in air, it is mounted on the STM sample holder in a pure Ar filled grove box. The sample was then sealed in a container and carefully transferred to the ultrahigh vacuum (UHV) chamber ($P \sim 10^{-8}$ Pa), and cleaved at 77 K just prior to the STM observations. The STM equipment used in this experiment is commercially based system (Omicron LT-STM)[9, 10]. The STM observations were carried out at the temperature of 4.9 K in UHV atmosphere of $\sim 10^{-8}$Pa.

3. **Results and discussion**

Figure 2(a) shows an STM image of 4.25 nm $\times$ 4.25 nm area on the cleaved K$_x$TiNCl surface at 4.9K. The measured workfunction (local barrier height) obtained by “I-z method” [10] is about $\phi \sim 4$ eV, indicating that the interface between tip and sample was in excellent vacuum tunneling condition. From this STM image, the rectangular-shaped atomic distribution is clearly visible.

To investigate the atomic periodicity, 2D fast Fourier transform (FFT) image (Fig. 2(b) inset) and its profile curves (Fig. 2(b)) were obtained from the STM image. The open circles in Fig. 2(b) inset indicate the Bragg peaks from the basic lattice structures of the STM image. From Fig. 2(b), the main peaks of the blue (A) and red (B) profiles show 0.41 nm and 0.33 nm, respectively, which correspond to a and b lattice parameters observed by X-ray measurement ($|\vec{a}| = 0.406$ nm, $|\vec{b}| = 0.329$ nm) [5]. These results indicate that the observed surface within the scanning area is c-plane of K$_x$TiNCl, and thus the crystal is c-axis oriented sample. Furthermore, since the lattice interval corresponds to the unit cell, a specific kind of atom is visible as the bright spots in the STM image. It is considered that other kinds of atoms are invisible and/or
observed as dark spots. As shown in the schematic \( \alpha \)-type crystal structure of \( c \)-plane (Fig. 1(b)), all kinds of atoms (K, Ti, N, Cl) have same interval distance at topmost surface or second top surface. Taking into account the total amount of intercalated potassium (50\% per unit cell), the bright atomic spots do not correspond to the occupied potassium atoms. Generally, in the case of layered nitride superconductors, since the conducting layer consists of the metal-nitride double layer, it is reasonable to attribute that the observed structure is the network of the TiN layer. However, it is difficult to identify the kind of atoms from this unipolar STM image.

To further investigate the visible atoms and surface properties, we have measured the bias voltage dependence of STM images. Figure 3 shows the STM images with various bias voltages ((a) and (b) are in the positive sample bias (0.1V, 0.3V), (c) and (d) are in the negative sample bias (-0.1V, -0.2V)). By comparing the STM images, we can find several characteristic features as follows.

Firstly, the common feature is that all of the STM images exhibit the inhomogeneous enhanced bright areas as surrounded by the dashed lines in Fig. 3(a). The enhanced areas are similar among (a) - (d), although there are some discrepancies among them. The enhanced bright areas occupy about 55\% of whole the STM observed area of 4.25 nm \( \times \) 4.25 nm. This rate is comparable to the nominal ratio of potassium intercalation (\( x \sim 0.5 \)). Therefore, it is considered that these enhanced areas are related to the intercalated potassium atoms and/or other doped carriers.

Secondly, the different feature is that the positive bias STM images show clearer lattice structures than the negative bias one. The negative bias images show one-dimensional (1D) streak like pattern in contrast to the spot like pattern for the positive biases. According to the band calculations of HfNCl or TiNCl, the filled state (negative bias side) consists of N 2\( p \) band and the empty state (positive bias side) dominantly Ti 3d or Hf 4d band[11, 12, 13]. Since N 2\( p \) - Ti 3d hybrid bands might be dominated in the negative bias, STM can detect the convolution of atomic lattice structures and these hybrid bands. Within this condition, the STM images at negative bias cannot resolve atoms in the \( b \)-axis direction, because the \( b \)-axis length is shorter than the \( a \)-axis one, then, they show the 1D streaky pattern along \( b \)-axis.
Figure 3. Bias dependence of STM image. (I_t =0.1nA) (a) V_{sample} = 0.1 V. (b) V_{sample} = 0.3 V, (c) V_{sample} = −0.1 V, (d) V_{sample} = −0.2 V.

4. Summary
The STM measurements were carried out on the layered nitride superconductor K_xTiNCl. The observed STM images show clear rectangular-shaped atomic distributions with the periods of |\( \vec{a} \)|=0.41 nm and |\( \vec{b} \)|=0.33 nm, respectively, thereby indicating that the observed sample surface is c-axis oriented one. The STM images at various bias voltages are commonly distributed with the enhanced inhomogeneous background. These enhanced background areas are considered to be related to the intercalated potassium and/or injected carrier density. The STM images at negative biases show 1D streaky structures along b-axis, which can be attributed to the N 2p - Ti 3d hybrid bands observed on the TiN double layer.

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