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Changes of electronic structure across the insulator-to-metal transition of quasi-two-dimensional Na-intercalated β-HfNCl studied by photoemission and x-ray absorption

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We use photoemission (PE) and x-ray absorption (XA) spectroscopy to study intercalation-induced changes in the electronic structure of β-HfNCl and $Na_{0.22}HfNCl$. PE shows appearance of new states in $Na_{0.22}HfNCl$ within the gap of β-HfNCl, with negligible changes in the energy positions of valence-band features of the parent, suggesting a non-rigid-band behavior. N $1s$ XA results show that the tail of the conduction band, with a quasi-two-dimensional character, extends to lower energy in $Na_{0.22}HfNCl$ than in β-HfNCl. The study provides information on the electronic structure and its change across the insulator-to-metal transition of the new class of superconductors.

INTRODUCTION

Recently, Yamanaka *et al.* reported that Li-intercalated HfNCl shows superconductivity below 25.5 K.[1] This new superconductor with a relatively higher transition temperature (T_c) has characteristic features both in the crystal and electronic structures. It possesses double Hf-N layers.[2] The mother compound (β-HfNCl) has a rather wide optical band gap of about 4 eV (Ref. 3) and, upon intercalation, the system becomes metallic and superconductive due to carriers introduced into the Hf-N layers.[1] Similar characteristics have been observed in β-ZrNCl.[4] The low-dimensionality and changes in electronic properties on carrier doping are reminiscent to those of high-temperature superconductors (HTSC's), although the nature of the insulating phases are, of course, different: an antiferromagnetic insulator due to strong electron correlation between Cu $3d$ electrons in HTSC's (Ref. 5) and a band insulator in hafnium (zirconium) nitride chloride.[6]

Due to these distinctive features, hafnium (zirconium) nitride chloride can be classified as a new type of superconductors.[6,7] In order to understand the mechanism of the superconductivity and relatively high T_c, we need to know how the electronic structure changes with intercalation and what is the character of the states at the Fermi level (E_F) that are responsible for the superconductivity. To our knowledge, studies of the electronic structure of this new superconductor using electron spectroscopic techniques have not been reported so far.

In this paper, we report results of photoemission (PE) and x-ray-absorption (XA) spectroscopy from the c axis oriented $Na_x HfNCl$, with special care taken to ensure negligible degradation of samples during preparation (see experimental procedures). PE spectra from the intercalated compound show appearance of new states at E_F that are not observed in the pristine compound, with negligible changes in the energy positions of valence-band structures of the mother compound, suggesting a non-rigid-band behavior. Simultaneously, N $1s$-$2p$ XA spectra show that the bottom of the conduction band, with substantial two-dimensional character, extends to lower energy in $Na_{0.22}HfNCl$ compared to β-HfNCl. These results represent the change of electronic structures across the insulator-to-metal transition of Na-intercalated hafnium nitride chloride. We discuss possible origins for the intercalation-induced changes.

EXPERIMENT

β-HfNCl was prepared by the reaction of Hf (99.9%, 325 mesh) with NH$_4$Cl (99.5%) at 730 °C for 30 min under the flow of NH$_3$ gas (99.9%, 20–50 cm^3/min). Obtained samples were purified by a chemical-vapor-transport method as described in the literature.[1,4] Na intercalation in β-HfNCl was performed by dispersing the samples in Na naphthalene solution of tetrahydrofuran in an Ar-filled glove box for 4 days. Pressed pellets were found to have strong preformed orientation, i.e., the pellet plane normal to the c axis.[9] Since the samples are very sensitive to air, the PE and XA measurements were carried out on samples that were transferred in an Ar-gas atmosphere to a glove bag connected to the quick entry chamber of the spectrometer. Samples were mounted onto substrates inside the glove bag using double-side con-
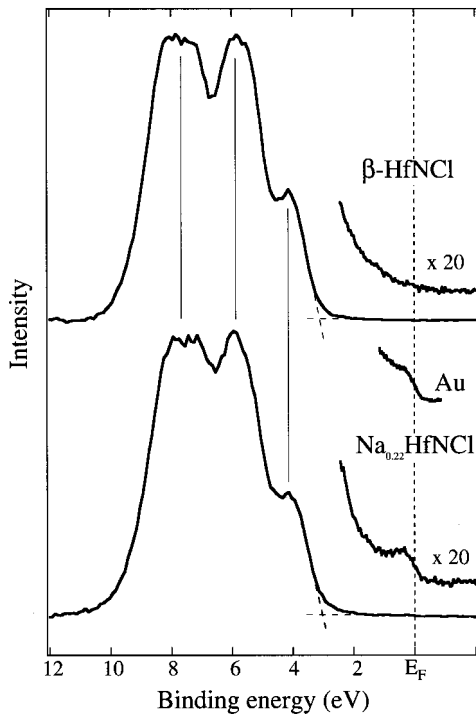
RESULTS AND DISCUSSION

FIG. 1. Total valence-band PE spectra of β-HfNCl (upper panel) and $Na_{0.22}$HfNCl (lower panel) obtained at 20 K using 174 eV photon energy (thick lines) together with enlarged ($\times 20$) spectra near E_F region. The Fermi-edge spectrum of gold near E_F is also shown. Thin lines indicate no shift in binding energy of valence-band features upon intercalation. Thin broken lines are guide to the eyes representing the gap in the occupied DOS, reflecting the large gap seen in optical measurements.

ductive adhesive tapes and transferred into the spectrometer chamber without ever exposing the samples to air.

PE and XA measurements were performed at BL19B in Photon Factory, KEK with linearly polarized light. The base pressure of our measurement chamber was better than 5×10^{-10} Torr. XA measurements in the fluorescence detection mode were performed using an x-ray ultraviolet (XUV) silicon photodiode with an energy resolution of ~ 0.2 eV at the N $1s$-$2p$ absorption threshold. XA measurements were carried out at room temperature without scraping the surface since the fluorescence detection mode is rather bulk sensitive. For PE, a CLAM4 spectrometer was used. To get better signal-to-noise ratio for the measurements of the states near E_F within a limited machine time, we used 174 eV photon energy, since the grating we used has an intensity maximum around this photon energy. The total energy resolution was set to 0.4 eV. The samples were scraped to get fresh surfaces at 20 K and kept at the same temperature during measurements in order to prevent surface degradation. Normally, a scraping procedure removes all angle- or k-resolved information, and thus the obtained PE spectra reflect the integrated density of states (DOS). All PES results reported here have been obtained within 2 h of scraping and no spectral changes were observed during the measurements, indicating that spectra shown here represent intrinsic electronic structures of the compounds.

The upper and lower panels of Fig. 1 show total valence-band spectra of β-HfNCl and $Na_{0.22}$HfNCl, respectively, obtained at 20 K using 174 eV photon energy. Normalization of the spectra was performed with the area under the curve from 11 to -2 eV binding energy after subtraction of an integral background. The spectra near E_F are also shown on an enlarged intensity scale. The spectrum of β-HfNCl has three prominent structures at 4, 6, and 7.5 eV, which are ascribed to Cl $3p$ and N $2p$ mixed states by comparing these to band-calculation results.[7,10] The spectral intensity is highly suppressed below ~ 3 eV binding energy and shows a monotonic decrease through E_F with no Fermi-edge structure, indicating that the width of the band gap in the occupied density of states is ~ 3 eV. On the other hand, optical spectroscopic studies reported that the direct band gap of β-HfNCl is about 4 eV.[3] Band-structure calculations of β-HfNCl predict that the top of the valence band is located at the Γ point but the smallest direct band gap opens along Σ axis in the Brillouin zone.[11] These results indicate that E_F of β-HfNCl is expected to lie just below the bottom of the conduction band. This is most likely because of pinning due to hydrogen impurity states and is consistent with transport measurements of β-HfNCl reporting an activation energy of ~ 180 meV.[3] The possibility of pinning due to hydrogen impurity states is discussed for β-ZrNCl, which is classified as an n-type semiconductor with an activation energy of 60 meV from transport measurements.[12]

As for $Na_{0.22}$HfNCl (lower panel), the overall valence-band spectral shape is similar to that of β-HfNCl at a first glance. Please note that the energy positions of the three structures in $Na_{0.22}$HfNCl are nearly the same as those in β-HfNCl. The enlarged spectrum of $Na_{0.22}$HfNCl, however, shows a qualitative difference compared to that of β-HfNCl. In contrast to the spectrum of β-HfNCl, that of $Na_{0.22}$HfNCl shows new states with a clear Fermi-edge cutoff. These observations are consistent with the insulator-to-metal transition due to electron doping[1] and represent intercalation-induced changes in the electronic structure. The exceedingly small intensity at E_F compared to that of the valence band may suggest a dominant Hf $5d$ character for the states at E_F, since the ionization cross section at 174 eV for Hf $5d$ is very small compared to those for Cl $3p$ and N $2p$ (Hf $5d$:Cl $2p$:N $2p = 1.1$:35:11).[13] We also find that the spectra of β-HfNCl and $Na_{0.22}$HfNCl do not exhibit a clear "incoherent band" reported for titanate compounds, which is believed to be due to electron-correlation effects[14] and/or impuritylike states.[15,16] This confirms the band-insulating nature of β-HfNCl.

It is widely accepted that changes in electronic structure due to intercalation can be described well by the rigid-band model,[17] where the crystal and electronic structure are considered to remain the same and only the number of electrons is changed. According to recent neutron-diffraction studies, hafnium nitride chloride changes its crystal structure from SmSI type ($R\bar{3}m$) for β-HfNCl (Ref. 8) to YOF type ($R\bar{3}m$) for $Na_{0.22}$HfNCl (Ref. 2). This would induce changes in the electronic structure. However, an important consequence from band calculations is that the electronic
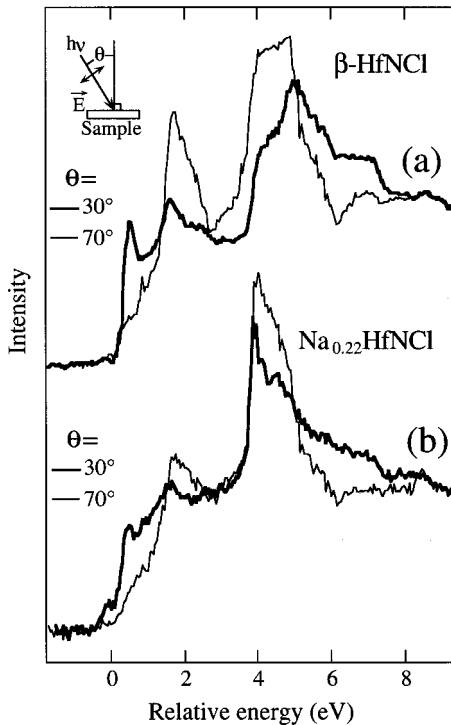
FIG. 2. N $1s$ XA spectra of β-HfNCl (a) and Na$_{0.22}$HfNCl (b) measured at $\theta = 30°$ (thick lines) and 70° (thin lines) in the total fluorescence yield mode, where θ is the polar angle of the direction of incident light with respect to the surface normal.

structures of β-HfNCl and intercalated HfNCl are nearly the same, including the size of the band gap.[10,11] If the empty conduction band is filled with electrons from intercalated Na atoms, the energy positions of the valence bands are supposed to shift to higher binding energies. According to the calculations, the Na content 0.22 locates the position of E_F at $\sim$0.4 eV from the bottom of the conduction band, indicating a $\sim$0.4-eV shift of observed valence-band features, since the actual position of E_F in the mother compound is expected to be located just below the conduction band, as discussed above. From an experimental point of view, the shift of the valence-band positions may be nearly 1 eV, because the tail of the new PE states extends to $\sim$1 eV (see the lower panel of Fig. 1).[18] But these are not the cases from the present experimental results, implying that unusual changes are occurring in unoccupied states.

In order to see the changes in the unoccupied states, we have performed XA spectroscopy across the N $1s$-$2p$ threshold. In Figs. 2(a) and 2(b), we show N $1s$ XA spectra of β-HfNCl and Na$_{0.22}$HfNCl measured at $\theta = 30°$ (thick lines) and 70° (thin lines), respectively. Here, θ is the polar angle of the direction of incidence light with respect to the surface normal as described in the figure. This means that the spectra will increasingly reflect contribution from in-plane electronic structures with decreasing θ. The horizontal axis is shown on a relative energy scale with respect to the energy position of the intensity threshold for β-HfNCl compound.[19] Normalization of the spectral intensity for different θ as well as for different samples is made at an energy of 9 eV. From the dipole selection rule, obtained N $1s$ XA spectra reflect N $2p$

partial DOS hybridized with Hf $5d$ states. The spectra of β-HfNCl have several structures, whose intensities change as θ is changed, indicative of highly anisotropic electronic structures. The intensities of the structures around the bottom of the conduction band and around 6 eV increase as θ is decreased, while those of structures around 2 and 4 eV show opposite behavior. Similar results are observed in Na$_{0.22}$HfNCl and thus it is clear that the bottom of the conduction band of β-HfNCl and Na$_{0.22}$HfNCl is highly two-dimensional, consistent with the result from the band calculation,[7] which ascribes it to mixed states of Hf d_{xy}, $d_{x^2-y^2}$, and N p_x,p_y. In addition, the spectrum of β-HfNCl at $\theta = 30°$ has a sharp pileup of spectral weight at the threshold, indicating a strong excitonic effect at the bottom of the conduction band. The intensity of the corresponding structure at 0 eV in the $\theta = 30°$ spectrum of Na$_{0.22}$HfNCl is strongly reduced and, importantly, the edge of the bottom of the conduction band in Na$_{0.22}$HfNCl becomes broader than in β-HfNCl and extends to lower energy.

The present PE and XA study shows that, upon intercalation, new states appear near E_F in the occupied states without a substantial shift of the main valence-band features, while, in the unoccupied states, the bottom of the conduction band with a substantial two-dimensional character extends to lower energy. The appearance of new states with the Fermi-edge structure in Na$_{0.22}$HfNCl relates to the insulator-to-metal transition. One possible origin for the non-rigid-band behavior observed in PES may be discussed in terms of the surface and bulk contributions.[20] A part of the doped electrons, may be in the near-surface region, forms localized states within the band gap, but close to the bottom of the conduction band. This might be the feature around E_F in the PE spectrum of Na$_{0.22}$HfNCl. On the other hand, a relatively small number of doped electrons, possibly deeper in the bulk, populate the bottom of the conduction band in a primary rigid-band fashion. Since the number of electrons in the conduction band are presumably small, they cause only a small shift of E_F. There may be another possibility that the underlying electronic structure itself changes, since the appearance of the new states at E_F in the PE spectrum in Na$_{0.22}$HfNCl seems to have a closer connection to the modification of the bottom of the conduction band. In order to further study the origin of the non-rigid-band-like modifications across the insulator-to-metal transition in detail, both angle-resolved-PE and inverse-PE spectroscopy are necessary and worth trying.

CONCLUSION

We have performed PE and XA spectroscopy of Na-intercalated β-HfNCl superconductor to study intercalation-induced changes in the electronic structure. PE spectrum from β-HfNCl indicates a band gap of 3 eV in the occupied DOS, and comparison with the optical band gap ($\sim$4 eV) taking the predicted band structure into consideration confirms that β-HfNCl is an n-type semiconductor. PE spectrum from Na$_{0.22}$HfNCl shows new states at E_F with negligible changes in the energy positions of the valence band of the parent, suggesting a non-rigid-band behavior. XA spec-

troscopy across the N $1s$-$2p$ threshold shows that the tail of the conduction band having substantial two-dimensional character extends to lower energy upon intercalation. These results provide information on the electronic structure and the changes across the insulator-to-metal transition of the new class of superconductors.

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[18] One might think that the valence-band features do not show a substantial shift if most portion of the width ($\sim$1 eV) is due to resolution broadening ($\sim$0.4 eV), but the actual movement of E_F into the conduction band can be much smaller than the width. However, if we assume a 0.1-eV shift of E_F, which is difficult to be detected from the present study, we should find an observed peak with its peak position nearly at E_F owing to the Fermi function and the resolution. This is not consistent with the present PE spectrum, where the position of E_F is nearly located at the mid point of the Fermi edge. This fact rules out the possibility related to the resolution broadening.

[19] Note that the relative energy being zero in Figs. 2(a) and 2(b) does not mean the position of E_F. But it does correspond to the same photon energy for XA spectra of two compounds within an error of ±0.2 eV.

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