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Valence-band photoemission study of β-ZrNCl and the quasi-two-dimensional superconductor Na_xZrNCl

T. Yokoya,[1,*] T. Takeuchi,[2] S. Tsuda,[1] T. Kiss,[1] T. Higuchi,[2] S. Shin,[1,3] K. Iizawa,[4] S. Shamoto,[4] T. Kajitani,[4] and T. Takahashi[5]

[1]*Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan*
[2]*Department of Applied Physics, Science University of Tokyo, Tokyo 162-0825, Japan*
[3]*The Institute of Physical and Chemical Research(RIKEN), Sayo-gun, Hyogo 679-5143, Japan*
[4]*Department of Applied Physics, Faculty of Engineering, Tohoku University, Sendai 980-8579, Japan*
[5]*Department of Physics, Tohoku University, Sendai 980-8578, Japan*

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We have performed photoemission (PE) spectroscopy of β-ZrNCl and Na_xZrNCl to study intercalation-induced change in the electronic structure. The valence band PE spectrum of β-ZrNCl shows a small intensity region within ~2.5 eV of E_F with a very small hump at E_F that can be ascribed to hydrogen impurity states. These provide spectroscopic evidence that β-ZrNCl is an *n*-type semiconductor. Upon Na intercalation, new states possibly involving hybridized Zr4*d* and N2*p* systematically evolve at E_F, with a negligible shift in the valence band structures. Similar results in β-HfNCl and Na_xHfNCl indicate that these results represent common electronic features of the layered nitride chloride superconductors.

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INTRODUCTION

Alkali metal intercalated zirconium nitride chloride is a new layered superconductor with a transition temperature (T_c) of 15 K.[1,2] The crystal structure of the mother compound β-ZrNCl consists of double Zr-N layers sandwiched between Cl layers, and Cl-Zr-N-N-Zr-Cl slabs are stacked along the *c* axis, bonded by the van der Waals force, as shown in Fig. 1.[3] Intercalated alkali-metal ions enter between Cl layers with a slight modification in the crystal structure.[3] For β-ZrNCl, while optical studies have reported a band gap of 3.4 eV,[4] resistivity measurements together with the sign of the thermoelectric power have indicated that β-ZrNCl is an *n*-type semiconductor with an activation energy of 50–60 meV.[4,5] Upon intercalation, the system becomes metallic and superconducting below 15 K most likely due to carriers introduced into the Zr-N layers.[1,2]

After the discovery of Li-intercalated HfNCl with T_c's as high as 25.5 K,[6] the layered nitride chlorides have attracted more attention.[7] Band structure calculations have reported that these new compounds can be classified into a new family of superconductors, due to distinctive features both in the crystal (the low dimensionality) and electronic structure (the wide band gap in the mother compound and the carrier-doping induced semiconductor-to-metal transition).[8,9] While several theoretical models including unconventional mechanisms to explain the relatively high T_c have been proposed,[10] experimental studies have reported interesting observations. Nuclear magnetic resonance studies have shown that the superconductivity of intercalated HfNCl cannot be well described within the simple BCS theory.[11] μSR and tunneling studies have reported strong-coupling superconductivity.[12,13] In addition, recent photoemission (PE) and x-ray absorption studies have shown the novel electronic evolution near the Fermi level (E_F) that cannot be described with a simple rigid band behavior alone.[14] However, electronic structures of the new superconductors have not been extensively studied possibly because of unstableness of intercalated samples. Therefore, it is essential to investigate the electronic structures for each sample to understand the physical properties and/or superconductivity.

In this paper, we report PE spectroscopy of Na_xZrNCl with special care taken to ensure negligible degradation of samples during preparation. The results include spectroscopic evidence that β-ZrNCl is an *n*-type semiconductor and the appearance of intercalation-induced states at E_F corresponding to the semiconductor-to-metal transition. We compare the present results with the PE results of β-HfNCl and Na_xHfNCl to investigate common electronic states of the layered nitride chloride superconductors. Possible origins of the intercalation induced states are also discussed.

EXPERIMENT

β-ZrNCl was prepared by the reaction of Zr (99.9%, 325 mesh) with NH_4Cl (99.5%) at 650 °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.[2,6] Na intercalation in β-ZrNCl was performed by dispersing the samples in Na naphthalene solution of tetrahydrofuran (THF) in an Ar-filled glove box for 4 days. Pressed pellets were found to have strong preferred orientation, i.e., the pellet plane being normal to the *c* axis.[15] Since the samples are very sensitive to air, the PE measurements were carried out on samples which 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-sided conductive adhesive tapes and transferred into the spectrometer chamber without ever exposing the samples to air.

PE measurements were performed at BL19B in Photon Factory, KEK, with a CLAM4 spectrometer. The base pres-

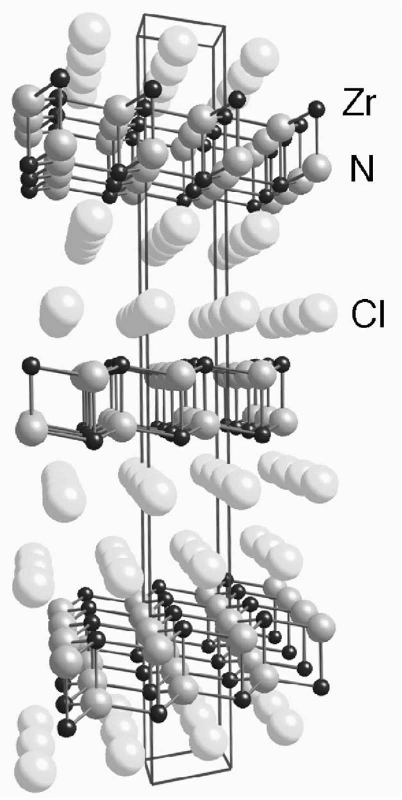

FIG. 1. Crystal structure of β-ZrNCl.

sure of the measurement chamber was better than 5×10^{-10} Torr. In order to obtain high signal to noise ratio for the measurements of the states near E_F, we mostly used 174 eV photon energy, since the grating we used has an intensity maximum around this photon energy. We also used 90 eV photon energy to study the photon energy dependence of states near E_F. 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 momentum-resolved information, and thus obtained PE spectra reflect the integrated density of states (DOS). All PE results reported here have been obtained within 2 h of scraping and no spectral changes were observed during the measurements, indicating that the spectra shown here represent intrinsic electronic structures of the compounds.

RESULTS AND DISCUSSION

Figure 2 shows the valence band PE spectra of β-ZrNCl, which corresponds to $x=0.0$, and $Na_{0.42}ZrNCl$ obtained using 174 eV photon (open circles) and 90 eV photon (a broken line). The 174 eV spectra were normalized to area under the curve from −3 to 13 eV binding energy after subtracting an integral background. The valence band spectrum for β-ZrNCl has three prominent structures around 3.5, 5.5, and 7.5 eV, respectively. Within ~2.5 eV of E_F, the intensity is very small compared to the prominent structures, indicating the size of the band gap in the occupied part of ~2.5 eV. By comparing with calculations,[8] the structures around 3.5 and 5.5 eV are nonbonding states with dominant N 2p and Cl 3p characters, respectively. The 7.5 eV structure is bonding states of both N 2p and Cl 3p characters. As x is increased to 0.42, the overall spectrum becomes broader. More importantly, we see a very small feature near E_F as indicated by an arrow.

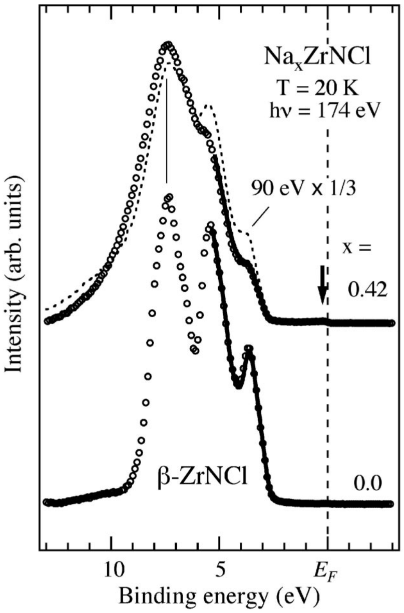

FIG. 2. Valence band PE spectra of β-ZrNCl($x=0.0$) and $Na_{0.42}ZrNCl$ obtained at 20 K using 174 eV (open circles) and 90 eV (a broken line) photon energies. Note that 90 eV spectrum is scaled down by three times. Thick lines above 5 eV binding energy are the same spectra of β-ZrNCl and $Na_{0.42}ZrNCl$ shown in Fig. 3.

In order to study the change of DOS within the band gap, which is directly related to the semiconductor-to-metal transition, in more detail, we measured samples of β-ZrNCl($x=0.0$) and Na_xZrNCl ($x=0.24$ and 0.42) with a smaller step size as shown in Fig. 3. Here, we normalized with the intensity above E_F, which is considered to be nearly proportional to the photon flux. Actually, the spectra for β-ZrNCl and $Na_{0.42}ZrNCl$ scaled by the same factors can be superimposed on the valence band spectra (thick lines up to 5 eV binding energy in Fig. 2), guaranteeing that intensity variation near E_F is not an artifact caused by the way of the normalization. In the spectrum of β-ZrNCl, we see a small hump near E_F. In β-ZrNCl, it has been reported that hydrogen atoms are taken up during the preparation process and bonded to N atoms covalently[16,17] to form shallow impurity states around 50–60 meV below the bottom of the conduction band.[4,5] Thus we can assign the small hump near E_F to hydrogen impurity states. The impurity states pin the position of E_F just below the bottom of the conduction band which is predicted to be located around the middle of the $\Gamma(Z)$-$F(L)$ line of the Brillouin zone.[8] Since the momentum position of the top of the valence band is located at the Γ point, different than that of the bottom of the conduction band, the observed band gap of ~2.5 eV (see Fig. 2) gives a rough estimate for an indirect band gap value, which is larger than the direct band gap value of 3.4 eV (Ref. 4). Thus, the

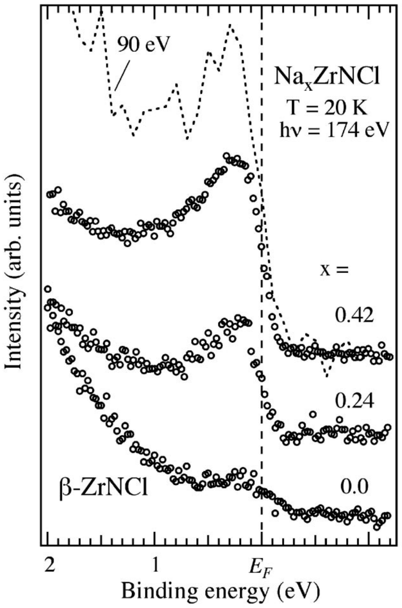

FIG. 3. Near-E_F PE spectra of of β-ZrNCl($x=0.0$) and Na_xZrNCl ($x=0.24$ and 0.42) obtained at 20 K using 174 eV (open circles) and 90 eV (a broken line). We see an intensity evolution of states at E_F as a function of x concentration.

PE observations provide evidence that β-ZrNCl is an n-type semiconductor, supporting the assignment of the transport measurements.[4,5] In the $x=0.24$ spectrum, intensity at E_F increases and a clear Fermi-edge structure appears, indicating the origin of metallic conductivity. As x is increased to $x=0.42$, the intensity at E_F further increases accompanied with the broadening of the new states. Here it should be noted that the positions of the valence band structures do not shift much compared to the width of the states at E_F.

To understand the evolution of the states at E_F, it is essential to characterize their nature. Thus we measured the photon-energy dependence of the states for $x=0.42$ samples using a 90 eV photon, where the ionization cross section of Zr 4d is close to its local minimum (Cooper minimum) while those for N 2p and Cl 3p are enhanced [Zr $4d$:N $2p$:Cl $3p=0.1:0.11:0.35$ for 174 eV and Zr $4d$:N $2p$:Cl $3p=0.05:0.7:0.84$ for 90 eV (Ref. 16)], as shown in Figs. 2 and 3 by broken lines. The normalization of the 90 eV spectrum to the 174 eV one was performed using the intensity of a Cl 3s shallow core level at 17.5 eV binding energy taking an ionization cross section (0.30 for 90 eV and 0.12 for 174 eV) into account,[18] as the intensity variation of the valence band reflects change in ionization cross sections. We observed that, by reducing the photon energy to 90 eV, while the intensity of the total valence band increases nearly three times, the intensity at E_F only increases 1.5 times. Here, we can rule out the possibility that the observed increase in intensity is due to an increase of hydrogen atoms, since the ionization cross section of hydrogen 1s increases 10 times for lower photon energy. Assuming that the valence band dominantly consists of nearly the same volume of N 2p states and Cl 3p states, the three-times increase of the valence band intensity seems consistent with the difference and change of the cross sections $[(0.7+0.84)/(0.11+0.35)=3.3]$. For explaining the 1.5 times increase of the states at E_F, a Zr 4d contribution is necessary. On the other hand, intercalation-induced modification of N 2p partial DOS at the bottom of a conduction band has been observed in Na_xHfNCl.[14] Therefore we know that observed change near E_F is due to appearance of new states possibly involving Zr 4d and N 2p hybridization. This implies that the doped carriers are introduced into the Zr-N layers. The evolution of new states with a clear Femi edge structure is consistent with the semiconductor-to-metal transition and reflects change in the bulk DOS upon intercalation.

In the recent work of Na_xHfNCl,[14] we reported that the valence band of the mother compound β-HfNCl have three structures with a small intensity region within ~3 eV of E_F. The difference in the band gap size (~2.5 eV for β-ZrNCl and ~3.0 eV for β-HfNCl) in the occupied part from PE measurements seems related to the difference in the optical band gap size (3.4 eV for β-ZrNCl and >4.3 eV for β-HfNCl) (Ref. 7). We also reported an appearance of intercalation-induced new states at E_F with a negligible shift in the position of the valence band structures. The observations in Na_xHfNCl are similar to the present observations of Na_xZrNCl. Therefore it is reasonable to think that the relatively wide gaps in the pristine compounds and the appearance of the intercalation-induced new states at E_F with a negligible shift in the valence band are common and characteristic electronic structural features in the layered nitride chlorides.

Lastly, we would like to speculate on possible origins of the new states. Recent neutron diffraction studies have revealed structural change from *SmSI*-type ($R\bar{3}$-m) for β-ZrNCl and β-HfNCl to β-YOF-type ($R\bar{3}$-m) for $Li_{0.16}$ZrNCl and $Na_{0.29}$HfNCl (Refs. 3,19), with a disappearance of a stretching in Zr-N layers only in $Li_{0.16}$ZrNCl.[3] The disappearance of the Zr-N stretching in intercalated ZrNCl gives rise to a shortening of Zr-Zr distance. This leads to a larger hybridization of Zr 4d bands and consequently makes the dispersion of the band forming the bottom of conduction band larger, inducing a drastic reduction of the band gap size.[8] Such a modification seems to explain the observation of the appearance of new states without an obvious shift of the valence band. However, a comparison with Na_xHfNCl might deserve further considerations because, for Na-intercalated HfNCl, such a modification of the crystal structure has not been observed, and consequently the size of the calculated band gap remains nearly the same. So, the PE results for $Na_{0.22}$HfNCl cannot be simply explained by the band structure calculations. It might be more natural to consider that the common experimental observation stems from a common origin other than the expected modification of the band dispersion. One possibility is that we just observe surface electronic structures, where localized states might exist, as in the case for perovskite vanadium oxides.[20] However, our recent soft x-ray emission studies have shown new states with N 2p character in Na_xHfNCl within the band gap of β-HfNCl, clarifying that the new states in the PE spectrum correspond to a bulk DOS.[21] Another possibility might be that the alkali-metal intercalation would modify the bottom of the conduction band, similar to the formation of an "intercalant layers band" as reported in $LiTiS_2$,[22] or would cause a formation of "in-gap states" within the gap, as in the cuprates.[23,24] This is an open question and requires further experimental work. We hope that the present study motivates further experimental and theoretical studies to understand the physical properties and superconductivity of the layered nitride chloride superconductors.

CONCLUSION

We report on the PE spectroscopy of Na_xZrNCl. The valence-band spectrum of β-ZrNCl shows three prominent structures with a very small intensity region within ~2.5 eV of the Fermi level (E_F), and the detailed study near E_F reveals a very small hump just below E_F that can be ascribed to hydrogen impurity states. These provide spectroscopic evidence for β-ZrNCl being an n-type semiconductor. Upon intercalation, new states, possibly with hybridized Zr4d/N2p character, evolve at E_F. The relatively wide gap in the pristine compound and the appearance of the intercalation-induced new states at E_F with a negligible shift in the valence band in Na_xZrNCl are similar to those observed in hafnium nitride chlorides, indicating that these observations reflect common and characteristic electronic structures of the layered nitride chloride superconductors.

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*Present address: JASRI/Spring8, Hyogo 679-5198, Japan.

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