# Electronic structure of quasi-one-dimensional conductors $Nb_3X_4$ (X=S,Se,Te) studied by angle-resolved photoemission spectroscopy

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High-resolution angle-resolved photoemission spectroscopy (ARPES) has been performed on quasi-onedimensional (1D) compounds Nb<sub>3</sub>X<sub>4</sub> (X=S, Se, Te). We have experimentally determined the band structure of these compounds and compared with several different band calculations. We found a fairly straight 1D Fermi surface in Nb<sub>3</sub>Te<sub>4</sub> (charge density wave transition temperature  $T_{CDW}$ =110 K, superconducting transition temperature  $T_c$ =1.9 K), while the Fermi surface of Nb<sub>3</sub>Se<sub>4</sub> ( $T_c$ =2.4 K) and Nb<sub>3</sub>S4 ( $T_c$ =3.8 K) shows a remarkable wiggling, indicative of the more two-dimensional-like (three-dimensional-like) character. We also found a sharp quasiparticle peak near the Fermi level ( $E_F$ ) at low temperatures for Nb<sub>3</sub>S4 and Nb<sub>3</sub>Se4, while the spectral weight near  $E_F$  of Nb<sub>3</sub>Te<sub>4</sub> is considerably suppressed. These experimental results indicate that the anisotropy of the electronic structure remarkably changes with varying the chalcogen atom in the compounds.

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## I. INTRODUCTION

Low-dimensional compounds such as layered materials and quasi-one-dimensional (quasi-1D) compounds have generated considerable interest since they show a variety of interesting physical properties such as charge density wave (CDW), metal-insulator transition, and superconductivity.<sup>1</sup> In weakly correlated three-dimensional (3D) metals, the Fermiliquid theory, which describes the interaction of electrons near the Fermi energy, holds quite well, while in onedimensional (1D) or quasi-1D metals, it appears to break down due to the strong electron correlation, and the low energy excitation is well characterized by the so-called Tomonaga-Luttinger liquid. In such a low-dimensional system, the Fermi surface suffers a strong electronic instability toward the metal-insulator transition and the system often undergoes a CDW transition. On the other hand, several layered two-dimensional (2D) compounds such as transitionmetal dichalcogenides and cuprates show superconductivity with relatively high transition temperature  $(T_c)$ . These facts suggest that the dimensionality or anisotropy of a system is a key point in understanding the nature of exotic physical properties in low-dimensional compounds.

One of the suitable candidates to study the systematics and/or variation of the electronic structure as a function of dimensionality (anisotropy) is quasi-1D conductor Nb<sub>3</sub>X<sub>4</sub> (X=S,Se,Te). Nb<sub>3</sub>X<sub>4</sub> shows the superconducting transition at  $T_c$ =3.8, 2.4, and 1.9 K for sulfide, selenide, and telluride, respectively.<sup>2,3</sup> The  $T_c$  is systematically decreased when the size of the chalcogen atom is increased. In addition, Nb<sub>3</sub>Te<sub>4</sub> shows a first-order CDW transition at  $T_{CDW}$ =110 K,<sup>4-6</sup> as confirmed by the satellite reflection in the electron and x-ray diffractions,<sup>6,7</sup> accompanied by transport and magnetic anomalies at 45 K.<sup>3,4,6,8-10</sup> Nb<sub>3</sub>X<sub>4</sub> (X=S,Se,Te) belongs to the hexagonal crystal system with the space group of  $P6_3/m$ .<sup>11,12</sup> As shown in Fig. 1(a), niobium atoms are arranged in a linear zigzag chain with the metallic bonding along the c axis, while the interchain interaction is substantially reduced by intervening chalcogen atoms. For instance, in Nb<sub>3</sub>Te<sub>4</sub>, the intrachain distance ( $d_{\parallel}$ =2.973 Å) is comparable to the nearest neighbor atomic distance in Nb metal (2.859 Å), while the interchain distance  $(d_{\perp} = 3.854 \text{ Å})$  is much longer,<sup>11,12</sup> suggesting the strong 1D nature of the compound. In fact, several physical properties such as the electrical resistivity,<sup>4–6,13–15</sup> the specific heat,<sup>3,10,16,17</sup> and the magnetic susceptibility<sup>6,8,14,15,18</sup> show a strong anisotropy. By replacing the chalcogen atom from Te to S, the ratio of the inter- and the intrachain distance  $(d_{\perp}/d_{\parallel})$  is systematically reduced from 1.30 to 1.17, showing that the anisotropy becomes gradually weak from  $Nb_3Te_4$  to  $Nb_3S_4$ .

To understand the mechanism of CDW and superconducting transitions in  $Nb_3X_4$ , Oshiyama has performed the firstprinciples self-consistent nonrelativistic band calculation on Nb<sub>3</sub> $X_4$  (X=S,Se,Te)<sup>19,20</sup> and reported that there exist three conduction bands which cross the Fermi level  $(E_F)$  owing to the presence of three Nb chains in the unit cell. These three Fermi surfaces consist of warped or undulating planelike sheets, consistent with the strong anisotropy observed in the transport and magnetic measurements.<sup>6,8,14,15,18</sup> Temperature dependence of the resistivity, as well as the angular dependence of the upper critical field, has been explained well using this band calculation. Recently, angle-resolved photoemission spectroscopy (ARPES) has been performed on Nb<sub>3</sub>Te<sub>4</sub> by Fujisawa *et al.*<sup>21</sup> and the overall electronic band structure has been elucidated. However, since there are no ARPES reports so far on Nb<sub>3</sub>S<sub>4</sub> and Nb<sub>3</sub>Se<sub>4</sub>, the systematic variation of the electronic structure as a function of chalcogen atom has not been elucidated yet.



FIG. 1. (a) Projected view of Nb<sub>3</sub> $X_4$  crystal along the *c* axis, together with the view of zigzag Nb chain along the *c* axis (right) (Ref. 13). The unit cell contains six Nb atoms and eight chalcogens. Each Nb chain is linked to adjacent chains via chalcogen atoms to form hexagonal channels parallel to the *c* axis. (b) Half the Brillouin zone of Nb<sub>3</sub> $X_4$  (X=S,Se,Te). Cleavage plane ( $\Gamma AML$  plane) is indicated by the shaded area. (c) Schematic view of the sample orientation for the ARPES measurements along the  $\Gamma A$  and  $\Gamma M$  cuts.

In this paper, we report a systematic high-resolution ARPES study on Nb<sub>3</sub> $X_4$  (X=S,Se,Te). We found a strong anisotropy in the band dispersion near  $E_F$ , as well as in the Fermi surface for all compounds. We also found a dimensional crossover of the Fermi surface as a function of X, which suggests that the interchain interaction is important in understanding the mechanism of the superconductivity and CDW in Nb<sub>3</sub> $X_4$ .

### **II. EXPERIMENTS**

Single crystals of Nb<sub>3</sub> $X_4$  were grown by the iodine-vapor transport method. Details of the sample preparation have been described elsewhere.<sup>5,12,22,23</sup> The physical properties such as  $T_c$  and/or  $T_{CDW}$  of crystals used in the present ARPES measurement were confirmed to be identical to those in the previous reports.<sup>5,22,23</sup> ARPES measurements were performed using Gammadata-Scienta SES-200 and SES-2002 spectrometers with a high-flux discharge lamp and a toroidal grating monochromator at Tohoku University. We used the He I $\alpha$  ( $h\nu$ =21.218 eV) resonance line to excite photoelectrons. The energy and angular (momentum) resolutions were set at 10–20 meV and 0.2° (0.007 Å<sup>-1</sup>), respectively. The sample orientation was determined by the Laue diffraction measurement. Crystals were cleaved *in situ* in an ultra-



FIG. 2. ARPES spectra near  $E_F$  of (a) Nb<sub>3</sub>S<sub>4</sub>, (b) Nb<sub>3</sub>Se<sub>4</sub>, and (c) Nb<sub>3</sub>Te<sub>4</sub> measured at 30 K with the He I $\alpha$  line along the  $\Gamma A$  direction. Spectra at the  $\Gamma$  and A points are indicated by thick lines.

high vacuum of  $2 \times 10^{-11}$  Torr to obtain a clean surface for the measurement. The natural cleavage plane of the sample is the  $\Gamma AML$  plane in the k space, as indicated by the shaded area in Fig. 1(b). The typical size of the crystals is  $5 \times 0.2$  $\times 0.2$  mm<sup>3</sup>, and the cleaved surfaces show a single shiny mirrorlike surface with a sharp reflection spot of laser. ARPES spectra were measured by rotating the sample while keeping the analyzer fixed, so that the polarization vector of incident light with respect to the sample varies during the measurement. Figure 1(c) shows the actual sample orientation for the ARPES measurements along the  $\Gamma A$  and  $\Gamma M$ directions. As for the measurement along the  $\Gamma A$  cut, we obtained ARPES spectra along the cut perpendicular to the chains ( $\Gamma M$  direction) by the simultaneous collection of photoelectrons with the finite angular range ( $\sim 13^{\circ}$ ). By changing the tilting angle  $\theta$  which corresponds to the angle between the sample normal and the sample-to-analyzer direction, we measured the ARPES spectra in a 2D Brillouin zone including the  $\Gamma A$  cut. As for the measurement along the  $\Gamma M$  cut, we rotated the sample azimuth by 90°. All spectra in Figs. 2-7 were measured at 30 K while those in Fig. 9(a)were at 10 K. The Fermi level of the sample was referred to that of a gold film evaporated onto the sample substrate.



FIG. 3. Band structures along the  $\Gamma A$  direction determined by ARPES for (a) Nb<sub>3</sub>S<sub>4</sub>, (b) Nb<sub>3</sub>Se<sub>4</sub>, and (c) Nb<sub>3</sub>Te<sub>4</sub>. Bright areas correspond to the bands.



FIG. 4. Comparison of the band structure along the  $\Gamma A(KH)$  direction between the ARPES experiment and the band calculations. [(a)–(c)] Experimental band structure of Nb<sub>3</sub>S<sub>4</sub> compared with the first-principles self-consistent nonrelativistic band calculation using the linear combination of atomic orbital (LCAO) method (Ref. 20), the self-consistent band calculation using the linear muffin tin orbital (LMTO) method (Ref. 26) and the tight-binding (TB) calculation (Ref. 24), respectively. (d) and (e) are for Nb<sub>3</sub>Te<sub>4</sub> with the LCAO and the LMTO calculations (Refs. 20 and 25).

## **III. RESULTS AND DISCUSSION**

## A. Band structure parallel to chain direction

Figure 2 shows ARPES spectra near  $E_F$  of Nb<sub>3</sub>X<sub>4</sub> (X=S,Se,Te) measured at 30 K along the  $\Gamma A$  direction in

the Brillouin zone, which corresponds to the chain direction in the crystal, as shown in Fig. 1. In Nb<sub>3</sub>S<sub>4</sub> [Fig. 2(a)], we observe several peaks which disperse toward the higher binding energy on approaching the A point from the  $\Gamma$  point. These bands all have the bottom of dispersion at the A point. We also find an electronlike band with the bottom of dispersion at 0.3 eV around the  $\Gamma$  point. All these bands are attributed to the Nb 4d bands according to the band calculations.<sup>20,24-26</sup> Although the gross feature of band dispersion looks similar among the three compounds, several quantitative differences are clearly noticed. For example, the number of distinguishable peaks at the A point is four to five in Nb<sub>3</sub>Se<sub>4</sub> and Nb<sub>3</sub>Te<sub>4</sub>, while that of Nb<sub>3</sub>S<sub>4</sub> is two to three. The width of the peak in the spectra is apparently broad in  $Nb_3S_4$  in contrast to the relatively sharp feature in  $Nb_3Se_4$ and Nb<sub>3</sub>Te<sub>4</sub>. Further, several additional small peaks are clearly observed near  $E_F$  around the  $\Gamma$  point in Nb<sub>3</sub>Se<sub>4</sub>.

To see more clearly the dispersive feature of bands in the ARPES spectra, we have mapped out the band structure and show the result in Fig. 3. The experimental band structure has been obtained by plotting the spectral intensity by gradual shading as a function of the wave vector and the binding energy. Bright areas correspond to the experimental bands. As seen in Fig. 3, we observe several dispersive bands in all the compounds. As described above, bands which have the bottom of dispersion at the A point are ascribed to the Nb 4d band. The width of band dispersion, namely, the energy separation between the top and the bottom of the band, becomes gradually smaller on going from Nb<sub>3</sub>S<sub>4</sub> to Nb<sub>3</sub>Te<sub>4</sub> (1.1, 0.9, and 0.8 eV for  $Nb_3S_4$ ,  $Nb_3Se_4$ , and  $Nb_3Te_4$ , respectively). This systematic change in the band width is explained well in terms of the decrease in the overlap of the wave function of the Nb 4d orbital in the zigzag chain in the crystal, since the distance between Nb atoms in the chain  $(d_{\parallel})$ systematically increases from the sulfide to the telluride  $(d_{\parallel})$ =2.881, 2.885, and 2.973 Å for X=S, Se, and Te, respectively<sup>11,12</sup>). As seen in Figs. 2(c) and 3(c), there is a holelike steep band with the top of dispersion at 1.6 eV at the  $\Gamma$  point in Nb<sub>3</sub>Te<sub>4</sub>, which is assigned to the Te 5*p* band from the band calculations.<sup>20,24,25</sup>

We show in Fig. 4 the comparison of the experimental band structures along the  $\Gamma A$  direction with three different band calculations available at present. Figures 4(a)-4(c)show comparison of the band structure of Nb<sub>3</sub>S<sub>4</sub> with the first-principles self-consistent nonrelativistic band calculation using the linear combination of atomic orbital (LCAO) method,<sup>20</sup> the self-consistent band calculation using the linear muffin tin orbital (LMTO) method,<sup>25,26</sup> and the tightbinding calculation,<sup>24</sup> respectively. Figures 4(d) and 4(e)compare the band structure of Nb<sub>3</sub>Te<sub>4</sub> with the LCAO and the LMTO calculations.<sup>20,25</sup> We find in Fig. 4 that the three band calculations look very similar to each other and show good qualitative agreement with the experimental result. However, there are several quantitative disagreements even among the calculations themselves, as well as with the experiment. For example, in Nb<sub>3</sub>S<sub>4</sub>, the observed energy position of the bottom of the Nb 4d bands at the A(H) point (1.6 eV) is reproduced well by the LCAO calculation [Fig. 4(a), while the LMTO and the tight-binding calculations [Figs. 4(b) and 4(c)] predict it at 1.7-1.8 eV. The character-



FIG. 5. [(a)–(c)] ARPES spectra and [(d)–(f)] the experimental band structure in the close vicinity of  $E_F$  along the  $\Gamma A$  direction measured with the He I $\alpha$  line for Nb<sub>3</sub>S<sub>4</sub>, Nb<sub>3</sub>Se<sub>4</sub>, and Nb<sub>3</sub>Te<sub>4</sub>, respectively.

istic W-shaped band dispersion near  $E_F$  around the  $\Gamma(K)$  point observed in the experiment is also seen in the LCAO and the LMTO calculations [Figs. 4(a) and 4(b)] but not in the tight-binding calculation [Fig. 4(c)]. The substantially strong intensity within 0.1 eV from  $E_F$  at the  $\Gamma(K)$  point suggestive of a small electron pocket centered at the  $\Gamma(K)$  point is reproduced only by the LMTO calculation [Fig. 4(b)]. The LCAO and the LMTO calculations reproduce well the narrowing of the Nb 4*d* bands, as well as the small elec-



FIG. 6. ARPES spectra near  $E_F$  of (a) Nb<sub>3</sub>S<sub>4</sub>, (b) Nb<sub>3</sub>Se<sub>4</sub>, and (c) Nb<sub>3</sub>Te<sub>4</sub> measured at 30 K with the He I $\alpha$  line along the  $\Gamma M$  direction.



FIG. 7. ARPES spectra in the close vicinity of  $E_F$  at 30 K of (a) Nb<sub>3</sub>S<sub>4</sub>, (b) Nb<sub>3</sub>Se<sub>4</sub>, and (c) Nb<sub>3</sub>Te<sub>4</sub>, measured along the  $\Gamma M$  direction with higher energy resolution (12 meV) and smaller energy interval (4 meV).

tronlike dispersive band near  $E_F$  in Nb<sub>3</sub>Te<sub>4</sub> [Figs. 4(d) and 4(e)]. These comparisons indicate that the band calculation serves as a good starting point to describe the gross band structure of Nb<sub>3</sub>X<sub>4</sub>, although there are several non-negligible quantitative disagreements between the experiment and the calculation.

To clarify the band structure in the close vicinity of  $E_F$ , we show in Fig. 5 ARPES spectra measured in the energy region within 0.6 eV from  $E_F$  together with the intensity plot as a function of the wave vector and the binding energy. We find in Fig. 5 that several bands cross  $E_F$  in all the compounds. In Nb<sub>3</sub>S<sub>4</sub> [Fig. 5(d)], we observe a relatively strong intensity very close to  $E_F$  at the  $\Gamma(K)$  point, which suggests a small electron pocket at the  $\Gamma(K)$  point. Another band, which shows the characteristic W-shaped dispersion around the  $\Gamma(K)$  point, crosses  $E_F$  midway between the  $\Gamma(K)$  and A(H)points, producing a large electron pocket centered at the  $\Gamma(K)$  point. In Nb<sub>3</sub>Se<sub>4</sub>, we clearly find a small electron pocket centered at the  $\Gamma(K)$  point, which looks slightly larger than in Nb<sub>3</sub>S<sub>4</sub>, since the Fermi vector  $(k_F)$  appears slightly away from the  $\Gamma(K)$  point compared to that of Nb<sub>3</sub>S<sub>4</sub>. In Nb<sub>3</sub>Te<sub>4</sub>, the bottom of the electron band at the  $\Gamma(K)$  point is located at about 0.3 eV and the band is very steep around the  $k_F$  point. The relatively high density of states (DOS) at  $E_F$ observed for all emission angles in Nb<sub>3</sub>Te<sub>4</sub> may be due to "ill-defined" conservation of  $k_{\parallel}$  caused by the indirect transition during the photoexcitation process. Imperfection of crystal surface might account for the high DOS at  $E_F$ . However, this may not be the case because the cleaved surface shows a shinny mirrorlike plane with a sharp single reflection spot of laser and the observed band dispersions show that the periodicity matches well with the bulk Brillouin zone, indicating the high quality of the cleaved surface. These experimental results in Fig. 5 suggest the substantial difference in the topology of the Fermi surface among the three different  $Nb_3X_4$  compounds. This point will be discussed later in detail.

#### B. Band structure perpendicular to chain direction

Figure 6 shows ARPES spectra near  $E_F$  of Nb<sub>3</sub>X<sub>4</sub> (X=S, Se, Te) measured at 30 K along the  $\Gamma M$  direction, which

corresponds to the direction perpendicular to the chain, as shown in Fig. 1. In sharp contrast to the  $\Gamma A$  direction (Fig. 2), peaks in the ARPES spectra are less dispersive or almost dispersionless, reflecting the substantial 1D nature of the electronic structure of  $Nb_3X_4$ , as evident from the strong anisotropy in the electrical conductivity.<sup>4–6,14,15</sup> In Nb<sub>3</sub>Te<sub>4</sub> [Fig. 6(c), most of the peaks are dispersionless while the intensity shows a slight variation as a function of wave vector. We do not find  $E_F$  crossing of band in Nb<sub>3</sub>Te<sub>4</sub>, indicative of the strong 1D nature of the Fermi surface. In contrast, there are several bands with a small but finite energy dispersion near  $E_F$  in Nb<sub>3</sub>S<sub>4</sub> and Nb<sub>3</sub>Se<sub>4</sub> [Figs. 6(a) and 6(b)]. Particularly in Nb<sub>3</sub>S<sub>4</sub>, a sharp peak just below  $E_F$  at the  $\Gamma$  point appears to lose its spectral weight on approaching the M point, suggesting that this band actually crosses  $E_F$  midway between the  $\Gamma$ and M points.

In order to see these dispersive features in more detail, we measured the ARPES spectra very close to  $E_F$  with a higher energy resolution and a smaller energy interval and show the result in Fig. 7. As clearly seen in Fig. 7(a), a sharp peak located at 50 meV at the  $\Gamma$  point in Nb<sub>3</sub>S<sub>4</sub> disperses toward  $E_F$  on approaching the M point and suddenly loses its intensity near the M point, indicating that the small electronlike Fermi surface centered at the  $\Gamma(K)$  point is closed in the  $\Gamma M$ direction in Nb<sub>3</sub>S<sub>4</sub>. Such band crossing is not seen in Nb<sub>3</sub>Se<sub>4</sub> although a band close to  $E_F$  shows a large energy dispersion of about 150 meV. In contrast to the highly dispersive nature of bands near  $E_F$  in Nb<sub>3</sub>S<sub>4</sub> and Nb<sub>3</sub>Se<sub>4</sub>, all bands near  $E_F$  in  $Nb_3Te_4$  are almost dispersionless, as seen in Fig. 7(c), exhibiting the strong 1D character of the electronic structure near  $E_F$ . This systematic change in the band dispersion perpendicular to the chain clearly demonstrates that the anisotropy and/or dimensionality of the electronic structure is certainly different among the three compounds. It is noted here that we observe a finite spectral intensity at  $E_F$  in Nb<sub>3</sub>Te<sub>4</sub>. This may originate from the angle-integrated-type background caused by indirect transitions, as described above. To elucidate the origin of this high spectral DOS at  $E_F$  in more detail, it is desirable to measure the photon-energy dependence in the normal emission with synchrotron radiation.

#### C. Fermi-surface topology

Figure 8 shows the ARPES-intensity plot at  $E_F$  of Nb<sub>3</sub>X<sub>4</sub> (X=S, Se, Te) as a function of the two-dimensional wave vector. To map out the Fermi surface, we obtained  $\sim 700$ ARPES spectra at one-quarter of the first Brillouin zone with approximately 20  $\times$  35 momentum mesh ( $k_x$  and  $k_y$ ) and interpolated them. Next, we have symmetrized the original image by taking account of the tetragonal symmetry of the crystal. The intensity is obtained by integrating the spectral weight within 20 meV with respect to  $E_F$ . Also presented in Fig. 8 are the momentum distribution curves (MDCs) at  $E_F$ along the  $\Gamma A$  cut, together with the result of fitting. To estimate the position of the Fermi surface, we fit MDC at  $E_F$  by Lorentzians and determined the location of the peak maximum in the k space which is defined as the  $k_F$  point. Next, we smoothly traced the set of  $k_F$  points and obtained experimental Fermi surfaces (gray curves in Fig. 8). As seen in Fig.



FIG. 8. ARPES spectral intensity plots as a function of 2D wave vectors of (a) Nb<sub>3</sub>S<sub>4</sub>, (b) Nb<sub>3</sub>Se<sub>4</sub>, and (c) Nb<sub>3</sub>Te<sub>4</sub>. The gray lines trace the local maxima of intensity, corresponding to the experimentally determined Fermi surface. The momentum distribution curve at  $E_F$  along the  $\Gamma A$  cut (thick solid curves) and the result of Lorentzian fitting (thin solid curves) are also shown for each compound.

8(c), the Fermi surface of Nb<sub>3</sub>Te<sub>4</sub> is open and almost flat along the  $\Gamma M$  direction, fulfilling a good nesting condition. In fact, a clear CDW transition in Nb<sub>3</sub>Te<sub>4</sub> has been reported by the electron diffraction experiment.<sup>7</sup> Since both  $\Gamma$  and M points are in the occupied side, as found in the band dispersion in the  $\Gamma M$  direction [Fig. 7], the Fermi surface of  $Nb_3Te_4$  [Fig. 8(c)] is found to be electronlike, consistent with the observed negative thermopower.<sup>4,9</sup> In Nb<sub>3</sub>Se<sub>4</sub>, we observe two distinct Fermi surfaces, both of which show a finite wiggling along the  $\Gamma A$  direction, indicative of a slight reduction of the one dimensionality in Nb<sub>3</sub>Se<sub>4</sub>. In Nb<sub>3</sub>S<sub>4</sub>, the separation of the inner and outer Fermi surfaces becomes more apparent, and more importantly, the inner Fermi surface is *closed* in the  $\Gamma M$  direction, forming an ellipsoidal shape. Furthermore, the outer Fermi surface undulates more drastically than that in Nb<sub>3</sub>Se<sub>4</sub>. These experimental results indicate that the replacement of chalcogen atom in  $Nb_3X_4$ significantly affects the dimensionality of the electronic structure, leading to the different topology of the Fermi surface. This systematic change of the Fermi-surface topology with X is explained in terms of the difference in the strength of the interchain interaction. The shortest Nb-Nb distance between neighboring chains in the crystal  $(d_{\perp})$  is 3.369, 3.567, and 3.854 Å for X=S, Se, and Te, respectively,<sup>11,12</sup> indicating that the interchain interaction becomes monotonically stronger from Nb<sub>3</sub>Te<sub>4</sub> to Nb<sub>3</sub>S<sub>4</sub>, as expected from the present ARPES result (Fig. 8). It is noted that the ratio of the effective electron mass perpendicular and parallel to the caxis  $(m_{\perp}/m_{\parallel})$  at low temperatures estimated from the angular dependence of the critical field is approximately 110 in  $Nb_3Te_4$  (Ref. 4) and 20 in  $Nb_3S_4$ ,<sup>17</sup> indicating the stronger anisotropy in Nb<sub>3</sub>Te<sub>4</sub>, consistent with the present ARPES experiment. Since there are three Nb-Nb chains (six Nb atoms) in a unit cell in the crystal, it is expected that three bands cross  $E_F$  if the bands do not degenerate. In the present ARPES experiment, we observe two different Fermi surfaces in Nb<sub>3</sub>S<sub>4</sub> and Nb<sub>3</sub>Se<sub>4</sub>, which suggests that the inner or the outer Fermi surface may nearly degenerate. Since the separation in the momentum space between the inner and outer

Fermi surfaces would be a measure of the interaction between the neighboring chains in the crystal, the systematic decrease in the separation between the inner and outer Fermi surfaces from Nb<sub>3</sub>S<sub>4</sub> to Nb<sub>3</sub>Te<sub>4</sub> as seen in Fig. 8 (the separation along the  $\Gamma A$  cut is 0.21, 0.11, and 0.03 Å<sup>-1</sup> for Nb<sub>3</sub>S<sub>4</sub>, Nb<sub>3</sub>Se<sub>4</sub>, and Nb<sub>3</sub>Te<sub>4</sub>, respectively) is understood in terms of the gradual reduction of the interchain interaction from Nb<sub>3</sub>S<sub>4</sub> to Nb<sub>3</sub>Te<sub>4</sub>. We infer that there are at least two different Fermi surfaces also in Nb<sub>3</sub>Te<sub>4</sub> in analogy to Nb<sub>3</sub>S<sub>4</sub> and Nb<sub>3</sub>Se<sub>4</sub>, although the observed Fermi surface looks to be composed of a straight single line, as seen in Fig. 8(c). We have fitted the MDC at  $E_F$  parallel to the  $\Gamma A$  direction and found that the MDC of Nb<sub>3</sub>Te<sub>4</sub> cannot be fitted satisfactorily with a single Lorentzian but fairly well with two Lorentzians. This suggests that there are also two different Fermi surfaces in Nb<sub>3</sub>Te<sub>4</sub> which are very close to each other in the momentum space. The nesting vector in Nb<sub>3</sub>Te<sub>4</sub> observed by the electron diffraction<sup>7</sup> is  $[(1/3)a^* + (1/3)b^*] + (3/7)c^*$ . The z component  $[(3/7)c^*]$  is closer to the momentum separation of the outer Fermi surface  $(0.40 \pm 0.05c^*)$  than to that  $(0.33 \pm 0.05c^*)$  of the inner Fermi surface.

#### **D.** Spectral line shape

To study the spectral line shape in the vicinity of  $E_F$  and its relation to the physical properties, we have performed ARPES measurement at very low temperature (10 K) with higher energy resolution (10 meV) and smaller angular interval  $(0.15^{\circ})$ . The result is shown in Fig. 9. The spectra have been measured at the  $E_F$ -crossing point  $(k_F)$  along the  $\Gamma A$ direction of the inner Fermi surface for each compound. We clearly find a striking difference of the spectral line shapes between Nb<sub>3</sub>Te<sub>4</sub> and the other two compounds. Nb<sub>3</sub>S<sub>4</sub> and  $Nb_3Se_4$  show a sharp quasiparticle peak at  $E_F$  while it is substantially suppressed in Nb3Te4. To elucidate the CDWgap induced spectral change in Nb<sub>3</sub>Te<sub>4</sub>, we plot in Fig. 9(c)the temperature dependence of the ARPES spectra measured at the  $k_F$  point of the outer Fermi surface along the  $\Gamma A$  direction. The inset shows the ARPES spectra symmetrized with respect to  $E_F$  to remove the effect of the Fermi-Dirac distribution function. As seen from the figure, we find small but finite suppression of the spectral weight (pseudogap) within  $\sim 20$  meV with respect to  $E_F$ . This pseudogap may be related to the CDW-gap opening since it is not clearly seen above  $T_c$  (150 K). The appearance of a clear Fermi edge at 20 K also suggests that the CDW gap is not a full gap but a partial gap, and 2D or 3D character may remain in Nb<sub>3</sub>Te<sub>4</sub> due to the finite interchain interaction.<sup>21</sup> In fact, the partially nested nature of the Fermi surface is suggested by the electrical resistivity measurements,<sup>6,15</sup> which show the persistence of the metallic behavior even below  $T_{CDW}$ .

Now, we discuss the origin of the absence of a sharp quasipasticle peak and the suppression of spectral weight in Nb<sub>3</sub>Te<sub>4</sub>, as seen in Fig. 9(a). The first possibility is the Tomonaga-Luttinger-like quasi-1D character of the electronic structure.<sup>27,28</sup> However, the residual Fermi edge, suggestive of the deviation from the ideal 1D character, is inconsistent with this interpretation. The second possibility is the effect of CDW.<sup>4–10</sup> However, the absence of a sharp peak



FIG. 9. (a) ARPES spectra measured at 10 K at the  $E_F$ -crossing  $(k_F)$  point along the  $\Gamma A$  direction for each Nb<sub>3</sub> $X_4$  (X=S,Se,Te). (b) Schematic diagram of each Fermi surface and  $k_F$  point along the  $\Gamma A$  direction. (c) Temperature dependence of the ARPES spectra on Nb<sub>3</sub>Te<sub>4</sub> measured at the  $k_F$  point of the outer Fermi surface along the  $\Gamma A$  direction. (d) ARPES spectral intensity plot of Nb<sub>3</sub>Te<sub>4</sub> as a function of wave vector and binding energy, measured at 30 K along the  $\Gamma A$  direction near the  $k_F$  points. The black area corresponds to the higher intensity. Lines of constant intensity are indicated by solid curves. (e) MDC at  $E_F$  (circles) for Nb<sub>3</sub>Te<sub>4</sub> as a function of wave vector relative to the  $k_F$  point of the inner Fermi surface, together with the result of fitting (solid line) by two Lorentzians (dashed lines). The length of the arrows denotes the full width at half maximum of the peak.

even above  $T_{CDW}$  (150 K), as seen in Fig. 9(c), is hardly explained by the CDW-gap opening. CDW fluctuation which causes the pseudogaplike feature above  $T_{CDW}$ , as seen in the ARPES spectra of other quasi-1D compounds,<sup>29</sup> is also insufficient to explain our result since the energy scale of the spectral-weight suppression is about 100 meV [Fig. 9(a)] while the size of the CDW gap is much smaller  $(\sim 20 \text{ meV})$ . The third possibility is the cross-section and matrix-element effects which reduce the weight of the quasiparticle peak only in Nb<sub>3</sub>Te<sub>4</sub>. By taking account of the facts that electronic states at  $E_F$  are of mainly the Nb 4d character and the gross band structure is similar among the three compounds, it would be unlikely to ascribe the absence of the peak to the cross-section and matrix-element effects. The fourth possibility is the presence of highly renormalized quasiparticles due to the strong interaction. $^{30,31}$  The interaction reduces the weight of the coherent quasiparticle peak in the vicinity of  $E_F$  and also increases the weight of the incoherent part located at higher binding energies, producing an almost featureless broad spectral line shape. One candidate to account for the origin of interaction is a strong electron correlation. However, as seen from Figs. 4(d) and 4(e), the overall experimental band structure of Nb<sub>3</sub>Te<sub>4</sub> shows reasonable agreement with the band calculations, especially in the bandwidth, indicating the little importance of the electron correlation. Alternatively, the electrons coupled to the lattice, namely, polaronic quasiparticles, more naturally explain the absence of a well-defined peak, as in the case of other quasi-1D systems.<sup>30-32</sup> As seen in Fig. 9(d), ARPES intensity near  $E_F$  along the  $\Gamma A$  direction does not increase with approaching  $E_F$ , unlike the simple expectation from the behavior of the coherent quasiparticle band where the peak becomes sharper and more intense with approaching  $E_F$ . This behavior is rather similar to the previous ARPES reports on quasi-1D compounds such as 1T-TaSe<sub>2</sub>,<sup>30</sup> K<sub>0.3</sub>MoO<sub>3</sub>,<sup>31</sup> and  $(TaSe_4)_2I_{,32}^{,32}$  where formation of small polarons was suggested from the broad and incoherent nature of the ARPES spectra in the vicinity of  $E_F$ . As shown in Fig. 9(e), we have fitted MDC at  $E_F$  and obtained the momentum widths of peaks ( $\Delta k$ ) to be 0.075 and 0.055 Å<sup>-1</sup>, for inner and outer Fermi surfaces, respectively, which correspond to the coherence length of 13–18 Å when the experimental momentum resolution is taken into account. This value is considerably shorter than that of ordinal metals (100-1000 Å) but is rather similar to the value of quasi-1D compounds K<sub>0.3</sub>MoO<sub>3</sub> and  $(TaSe_4)_2 I$  (~10 Å),<sup>31,32</sup> implying the presence of strong scattering in Nb<sub>3</sub>Te<sub>4</sub>, possibly due to interaction of electrons with the lattice (formation of small polarons). The broad spectral feature in Nb<sub>3</sub>Te<sub>4</sub> may be due to the reduction (increase) of the weight of the coherent (incoherent) part caused by the multiple polaron and/or phonon excitations. While it is difficult to fit energy distribution curves by the model spectral function<sup>31,32</sup> because the spectrum at  $k_F$  point is fairly broad and the peak position is ill defined, the appearance of a Fermi edge suggests the finite contribution from the coherent part which may be created by the relatively weaker electron-phonon coupling in Nb<sub>3</sub>Te<sub>4</sub> than that in other strong-coupling quasi-1D compounds.<sup>30–32</sup>

### **IV. CONCLUSION**

We have performed high-resolution ARPES on  $Nb_3X_4$ (X=S, Se, Te) to study the electronic band structure and the Fermi surface. We determined the band structure parallel and perpendicular to the Nb zigzag chain in the crystal and compared the result with three different band calculations. We found that the band calculation serves as a good starting point to describe the gross band structure of  $Nb_3X_4$ , although there are several quantitative disagreements between the experiment and the calculation. We observed a fairly straight 1D Fermi surface in Nb<sub>3</sub>Te<sub>4</sub>, while the Fermi surfaces of Nb<sub>3</sub>Se<sub>4</sub> and Nb<sub>3</sub>S<sub>4</sub> show a remarkable wiggling along the direction parallel to the chain. This systematic change of the Fermi-surface topology with X is explained in terms of the difference in the strength of the interchain interactions. We observed a sharp quasiparticle peak in Nb<sub>3</sub>S<sub>4</sub> and Nb<sub>3</sub>Se<sub>4</sub>, while the spectral intensity near  $E_F$  in Nb<sub>3</sub>Te<sub>4</sub> is remarkably suppressed, possibly due to the formation of polaronic quasiparticles.

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