Fermi Surface Reconstruction in CeTe$_2$ Induced by Charge Density Wave: ARPES Study

J.-S. Kang$^1$, D. H. Kim$^1$, H. J. Lee$^1$, J. H. Hwang$^1$, Han-Koo Lee$^2$, H.-D. Kim$^2$, B. H. Min$^3$, K. E. Lee$^3$, Y. S. Kwon$^3$, J. W. Kim$^4$, Kyoo Kim$^4$, B. H. Kim$^4$, and B. I. Min$^4$

$^1$Department of Physics, The Catholic University of Korea, Bucheon 420-743, Korea
$^2$Pohang Accelerator Laboratory, POSTECH, Pohang 790-784, Korea
$^3$Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea and
$^4$Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea

(Dated: September 5, 2011)

Electronic structures of a charge-density-wave (CDW) system CeTe$_2$ have been investigated by employing angle-resolved photoemission spectroscopy (ARPES). The observed Fermi surface (FS) agrees very well with the calculated FS for the undistorted CeTe$_2$ both in shapes and sizes. The metallic states crossing the Fermi level (E_F) are observed in ARPES. The carriers near E_F have mainly the Te(1) 5p character, with the negligible contribution from Ce 4f states to the CDW formation. The supercell (shadow) bands and the corresponding very weak FS’s are found to arise from band-folding due to the interaction with Ce-Te(2) layers. This work shows that the origin of the CDW formation in CeTe$_2$ is the FS nesting and that the CDW modulation vector is along Γ-X (Q_{CDW}≈X).

PACS numbers: 79.60.-i, 71.45.Lr, 71.18.+y, 71.20.-b

The charge-density-wave (CDW) formation is one of the most interesting phenomena in solid state physics.\[3\] CeTe$_2$ is known as a CDW system having a high CDW transition temperature of T_{CDW}∼1000 K, and the CDW state in CeTe$_2$ coexists with magnetism and also with superconductivity (T_c=2.7 K) under pressure.\[4\] CeTe$_2$ crystallizes in the quasi-two dimensional layered Cu$_2$Sb-type tetragonal structure with two types of Te sites: Te(1) and Te(2). Te(1) atoms form planar square sheets, which are sandwiched along the c axis by the corrugated double layers of Ce and Te(2) atoms (Fig. 1a). The square configuration of CeTe$_2$ is considered to be Ce$^{3+}$Te(2)$^2$Te(1)$^{1-}$, so that hole carriers are produced in Te(1) sheets.\[5\] Then the square net of Te(1) would be easily distorted by the Peierls-like mechanism\[6\] due to the partial filling. Underneath this picture is the assumption of trivalent Ce\[3+\] states.\[7\] Band-structure calculations indicate that the CDW instability occurs due to the nesting between the Fermi surfaces in Te(1) square sheets in the ab plane,\[8\] 10 which was supported experimentally.\[11\]

Due to the difficulty in growing high-quality single crystals for the angle-resolved photoemission spectroscopy (ARPES) study, there have been only a few ARPES studies of CeTe$_2$. A couple of works reported the Fermi surface (FS) topology in the non-CDW phase of CeTe$_2$, as well as that in a similar CDW system LaTe$_2$, by using ARPES.\[12\] 14 Shin et al.\[12\] reported that the FS topology of CeTe$_2$ in the k$_x$-k$_y$ plane is different from that of LaTe$_2$.\[13\] The small square FS centered around Γ, predicted by band calculations, was not observed in ARPES. So they conjectured that the CDW gap $E_g$ is larger than $\geq$ 600 meV, and that the magnitude of $E_g$ varies around the FS. This minimum value of $E_g$ ≈ 600 meV is much larger than $E_g$ ≈ 100 meV, found in another ARPES study.\[3\] The CDW distortion probed by TEM\[12\] was somewhat different from that in the literature\[11\] which was attributed to the variation of the Te deficiency produced by different sample growth techniques. Ito et al.\[14\] examined the FS along the k$_z$ axis, and observed a systematic intensity modulation in the spectral weight at FS.

The natural question is whether the FS topology and the CDW state of CeTe$_2$ are similar to those of LaTe$_2$ or not. This includes the following issues: (i) do the FS and the CDW distorted structure in CeTe$_2$ have the same symmetry as those in LaTe$_2$?, (ii) how large is the effect

![FIG. 1: (Color online) (a) Tetragonal crystal structure of CeTe$_2$ in the non-CDW phase. The unit cell of Te(1) square net is doubled in tetragonal CeTe$_2$. (b) The Brillouin Zone (BZ) of Te(1) sheets (outer square) is reduced to half (inner square) because of the larger cell size of Ce-Te(2) layers. (c) Fermi surface of CeTe$_2$ in the tetragonal BZ of the non-CDW phase, corresponding to the inner square in (b).\[12\] Γ, X, and M represent k=(0, 0, 0), $\frac{2\pi}{a}(1/2, 0, 0)$, and $\frac{2\pi}{a}(1/2, 1/2, 0)$, respectively.

\[\text{Diagram Image}\]
of the band folding, due to the interaction between Te(1) and Ce-Te(2) layers, on the FS of Te(1) sheets, and (iii) what is the CDW modulation vector, \( \mathbf{Q}_{\text{CDW}} \)? As shown in Fig. 1(b), the Brillouin Zone (BZ) of Te(1) sheets is reduced to half, and thereby, the bands are folded into the reduced BZ to yield the supercell (shadow) bands. The FS’s, denoted with dotted lines in Fig. 1(b), come from those shadow bands. We have resolved these questions by performing careful ARPES measurements for high-quality stoichiometric single crystals of CeTe\(_{2-x}\)Sb\(_x\) \((x = 0, 0.05)\). We also report the detailed study of the FS topology, the energy-dependent behavior of the constant energy (CE) map, and the clearly dispersive feature of the states near the Fermi level (\( E_F \)) in CeTe\(_2\).

High-quality CeTe\(_{2-x}\)Sb\(_x\) single crystals having very low residual resistivity were grown by using the self-fluxed Bridgeman method. The quality and the orientation of the single crystal were checked by Laue patterns.

ARPES experiments were carried out at the 3A1 beamline of the Pohang Light Source (PLS) with the beam size of < 50 \( \mu \text{m} \) and using a Scienta SES-2002 electron energy analyzer. Single crystals were cleaved \textit{in situ} at \( T \sim 30 \text{ K} \) under the pressure better than \( 5 \times 10^{-11} \) Torr, which exposed the (001) surfaces. The Fermi level and the overall instrumental resolution of the system were determined from the Fermi edge of an evaporated Cu metal. The energy resolution (\( \Delta E \)) and the momentum resolution (\( \Delta k \)) were set to be \( \Delta E \sim 80 \text{ meV} \) and \( \Delta k \approx 0.01 \text{Å}^{-1} \), respectively, at \( h\nu \sim 110 \text{ eV} \).

Figure 2 shows the first derivatives of the CE maps of CeTe\(_2\) (Left) and CeTe\(_{1.95}\)Sb\(_{0.05}\) (Right) vs. the initial-state energy \( E_i \) of \(-1.4 \text{ eV} \leq E_i \leq -0.02 \text{ eV} \). These data were obtained at \( T \sim 30 \text{ K} \) with \( h\nu \approx 115 \text{ eV} \). In plotting each CE map, the spectral intensity of \( E_i \pm 100 \text{ meV} \) was integrated. This figure shows that the CE maps of \( x=0 \) and \( x=0.05 \) are essentially the same in their shapes, sizes, and energy-dependent behavior. But the CE maps of \( x=0.05 \) are sharper than those of \( x=0 \). Thus the energy-dependent evolution of the CE map is manifested more clearly in \( x=0.05 \) than in \( x=0 \).[15]

The four-fold symmetry is observed in the FS\(_{05}\) and CE maps for both \( x=0 \) and 0.05. The feature of the four-fold symmetry is shown more clearly in the CE map for \( E_i = -1.0 \text{ eV} \) (Fig. 2(c)), which was obtained from a different cleave. Two diamond-shaped contours are observed in the FS map, which is similar to the case of LaTe\(_2\).[13] This finding implies that Ce 4f electrons hardly contribute to the states near \( E_F \). Note that the inner-diamond FS is clearly seen in both \( x=0 \) and 0.05, in contrast to the case of Ref.[12]. With increasing \( E_i \), the size of the inner diamond increases, while that of the outer diamond remains nearly the same. Such an energy-dependent behavior is consistent with that of the calculated FS’s, shown in Fig. 2(d).

Figure 2(e) shows the FS of CeTe\(_{1.95}\)Sb\(_{0.05}\), drawn in the periodic zone scheme. This FS map was generated by the reflections of the map data that were obtained for a smaller region of the BZ. (d) The calculated FS map of CeTe\(_2\) as a function of \( E_i \). (e) The experimental FS map of CeTe\(_{1.95}\)Sb\(_{0.05}\). (f) Comparison of the experimental FS map (blue dotted lines) and calculated FS map (red solid lines).

FIG. 2: (Color online) (a) First derivatives of the constant-energy (CE) map of CeTe\(_2\) with the increasing binding energy (BE) between BE=0.02 eV and BE \sim 1.4 eV. (b) Similarly for CeTe\(_{1.95}\)Sb\(_{0.05}\). Here BE=\( |E_i| \), where \( E_i \) denotes the initial-state energy. Dotted lines denote the BZ. (c) The experimental CE map of CeTe\(_2\) for BE=1.0 eV, drawn in the periodic zone scheme. This map was generated by the reflections of the map data that were obtained for a smaller region of the BZ. (d) The calculated CE map of CeTe\(_2\) as a function of \( E_i \). (e) The experimental FS map of CeTe\(_{1.95}\)Sb\(_{0.05}\). (f) Comparison of the experimental FS map (blue dotted lines) and calculated FS map (red solid lines).
nesting vectors, one parallel to Γ-X (Q_1≈X), and the other parallel to Γ-M (Q_2≈M/2) for both LaTe_2 and CeTe_2. In general, Q_{CDW} is determined by the FS nesting vector. In real systems, however, the CDW transition occurs only when there exists a soft phonon mode at a specific Q_{CDW}. In order to check the existence of a soft phonon mode in CeTe_2, we have calculated the phonon frequency. Phonon softening occurs at Q_{LaTe} = Q_1.The phonon frequency. Phonon softening occurs at Q_{LaTe} = Q_1.

FIG. 3: (Color online) Phonon dispersion ω(q) of undistorted LaTe_2. Negative ω(q) here represents the imaginary part of the phonon frequency. Phonon softening occurs at Q_1≈X (ω^2(Q_1) < 0).

RESULTS

In Fig. 4, we have compared the ARPES intensity plots of CeTe_2 with the band structures, calculated for the non-CDW lattice.[1] Left sides of Fig. 4(a) and (b) show the ARPES data of CeTe_2 along Γ-M in two different paths, along A and along D, respectively, as shown in Fig. 4(c). ARPES intensity plots were made by taking second derivatives of the ARPES data, obtained with hv ≈ 104 eV. The experimental band structures of CeTe_{1.95Sb_{0.05}} (not shown here) are found to be essentially the same as those of CeTe_2 without a noticeable energy shift within the instrumental resolution.[1] Many dispersive bands, observed clearly in ARPES, indicate the good quality of the samples employed in this study. The overall band structures of Fig. 4(a) and (b) are similar to each other.

But there are also some differences between two, which seem to arise from (i) the band-folding effect due to the increased unit cell (see Fig. 1(b)), and (ii) differences in the topography of the cleaved surfaces.[22] The band-folding effect is clearly seen in the calculated band structures, shown on the right sides of Fig. 4(a) and (b). For the calculated band structure and FS, the band unfolding scheme[23] is adopted to separate out the shadow bands and the corresponding FS in the larger BZ from the non-shadow (main) bands and the corresponding FS. In this scheme, the intensity of the Te(1) supercell band is proportional to the interaction between the Te(1) layer and the underlying Ce-Te(2) layer. If the interaction is weak, it results in the weakening of weights of supercell-folded bands and the corresponding FS. In Fig. 4(a), the wide in-plane Te(1) 5p band (see Fig. 1(b)) starting from M at ~ −6.2 eV to near Γ (~0.2M) at EF is prominent, while in Fig. 4(b), the in-plane Te(1) 5p band starting from Γ’ at ~ −4.5 eV to near M (~0.7M) at EF is prominent. In fact, the latter is seen as a dim shadow band in Fig. 4(a), and vice versa in Fig. 4(b). The main and shadow bands in Fig. 4(a) produce the bright inner FS and the dim outer FS in the first BZ, respectively, shown in the top BZ of Fig. 4(c).

FIG. 4: (Color online) (a) ARPES along A (Γ-M), with the calculated band structures along M-Γ on the right, which is attached as a mirror image. (b) Similarly for along D (Γ-M). (c) Unfolded FS in the extended BZ, where two different Γ-M paths, i.e. along A and D, are indicated. Note that the shadow bands and the corresponding FS are barely seen. The expected E_F-crossing positions in ARPES agree very well with those in the calculated bands for the non-CDW phase of CeTe_2 (see Fig. 3, which have mainly Te(1) 5p character.[10] As shown in Fig. 4(c), two bands near Γ (~0.2M) and M (~0.7M) in Fig. 4(b) would produce...
FIG. 5: (Color online) (a) Near-E_F ARPES intensity plots of CeTe_{0.95}Sb_{0.05} along E (see Fig. [2]c)). (b) Near-E_F ARPES of CeTe along Γ′-M in the first BZ. (c) Near-E_F ARPES of CeTe_{0.95} along D (Γ′-M) in the second BZ. (d) Stack of MDC’s, corresponding to (e). The top and bottom MDC curves correspond to E_g = 0 (E_F) and E_i = −0.4 eV, respectively. (e) Calculated FS maps for the non-CDW state of CeTe_{0.95}. Dotted lines represent the folded FS’s. (f) Experimental FS map of CeTe_{0.95}Sb_{0.05}. (g) Similarly for CeTe_{2}. In (f) and (g), Γ and Γ′ denote the Γ points in the first BZ and the second BZ, respectively.

The inner (bright) FS and outer (dim) FS’s along Γ-M in the first BZ, respectively. Similarly, the band near M (~0.7 M) in Fig. [2]c would produce the larger FS along Γ-M in the second BZ. The much weaker spectral weight of the band near M in Fig. [2]b, as compared to that near Γ, is attributed to its nature of the shadow band, which originates from the band-folding.

The vanishing spectral intensity near E_F in Fig. 5 is considered to be related to the opening of the CDW gaps in some part of the FS’s. This feature is revealed more clearly in Fig. 5f) and 5g), which show the experimental FS maps of the first BZ and the second BZ, respectively, obtained by integrating E_F ± 100 meV. These are not the derivative data, but raw data. The inner FS near Γ is certainly observed in Fig. 5f), while the outer diamond FS is very weak. In contrast, the inner diamond FS near Γ′ is hardly seen in Fig. 5g) but the outer diamond FS is apparent. In view of the calculated FS’s in Fig. 5c) and Fig. 5e), such differences can be interpreted as the fact that the FS’s in Fig. 5f) correspond to those in the first BZ, whereas the FS in Fig. 5g) corresponds to that in the second BZ.

The feature of the vanishing spectral weight is also observed in some part of the FS’s: for example, in Fig. 5f), the spectral weight near M is almost vanishing, and the outer diamond FS shows an intermittent feature. The polarization effect is not likely the origin of an intermittent feature of the outer FS since this feature is common for all four sides of the outer diamond. Instead, this region would correspond to the k-points where CDW gaps open. Therefore the diminishing feature in Fig. 5b) and (c) reflects the opening of the CDW gap. One can estimate the size of the CDW energy gap as being E_g ≃ 50 meV near M, in agreement with our previous finding in a different ARPES study.

In conclusion, the FS measured by ARPES agrees very well with the calculated FS for the undistorted CeTe_{2} both in shapes and sizes, and the EQ-crossing metallic states are clearly observed in ARPES. We have found the following answers to the questions addressed in the beginning: (i) The measured FS is similar to that of LaTe_{2}, implying that Ce 4f states have a minor contribution to the CDW formation in CeTe_{2}. (ii) The band-folding originating from the interaction with Ce-Te(2) layers produces the shadow bands and the corresponding FS’s, which have very weak spectral weight. (iii) The CDW modulation vector is estimated to be Q_{CDW} = Q_1 ≈ X.

This work was supported by the NRF under Contract No. 2009-0064246 and No. 2009-0079947. YSK acknowledges the NRF grant under Contract No. 2006-2002165 and 2009-0078025. PLS is supported by POSTECH and MEST in Korea.

[1] J. Voit, et al., Science 290, 501 (2000).
[2] T. Kasuya, M. H. Jung, and T. Takabatake, J. Magn. Magn. Mater. 220, 235 (2000).
[3] T. Yokoya, et al., Science 294, 2518 (2001).
[4] M. H. Jung, et al., Phys. Rev. B 67, 212504 (2003).
[5] J.-S. Kang, et al., Phys. Rev. B 74, 085115 (2006).
[6] J. K. Burdett and S. Lee, J. Amer. Chem. Soc. 105, 1079 (1983).
[7] J.-S. Kang, et al., J. Phys.: Condens. Matter 16, 9163 (2004).
[8] A. Kikuchi, J. Phys. Soc. Jpn. 67, 1308 (1998).
[9] E. DiMasi, et al., Phys. Rev. B 54, 13587 (1996).
[10] J. H. Shim, J.-S. Kang, and B. I. Min, Phys. Rev. Lett. 93, 156406 (2004).
[11] K. Stöwe, J. Alloy Compd. 307, 101 (2000).
[12] K. Y. Shin, et al., Phys. Rev. B 72, 085132 (2005).
[13] D. R. Garcia, et al., Phys. Rev. Lett. 98, 166403 (2007).
[14] T. Itô, et al., J. Magn. Magn. Mater. 310, 431 (2007).
[15] We have employed the FLAPW band method in the LSDA+U+SO scheme. H. J. F. Jansen, A. J. Freeman, Phys. Rev. B 30, 561 (1984); P. Blaha et al., WIEN2k (ISBN 3-950131-1-1), Karlheinz Schwarz, Techn. Universität Wien, Austria (2001).
[16] B. H. Min, H. Y. Choi, and Y. S. Kwon, Physica B 312-313, 203 (2002); ibid 312-313, 205 (2002).
[17] The ground state and the electronic structures of CeTe remain almost the same in CeTe_{0.95}Sb_{0.05} in this energy scale since the Sb-concentration in CeTe_{0.95}Sb_{0.05} is very low (2.5%).
[18] The map with E_g = −0.2 eV can be regarded as the FS because E_F ≡ 0 is included in this map.
[19] M. Lavagnini, et al., Phys. Rev. B 75, 205133 (2007).
[20] K. E. Lee, et al., Phys. Rev. B 78, 134408 (2008).
[21] QUANTUM ESPRESSO code, Giannozzi, et al., J. Phys. Condens. Matter 21, 395502 (2009).
[22] All the cleaved surfaces were mirror-shiny, but had many stepped planes. Due to a finite acceptance angle of the electron analyzer and a different topography of a cleaved surface, each cleaved surface is expected to have a different yield.

[23] W. Ku, T. Berlijn, C.-C. Lee, Phys. Rev. Lett. 104, 216401 (2010).
[24] In the energy distribution curves (EDC’s), the photoemission peaks that cross $E_F$ were not observed clearly. Nevertheless, the $E_F$-crossing of these bands is supported by the slope of these bands.