Fermi Surface Reconstruction in the CDW State of CeTe₃ Observed by Photoemission

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CeTe₃ is a layered compound where an incommensurate charge density wave (CDW) opens a large gap ($\simeq$400 meV) in optimally nested regions of the Fermi surface (FS), whereas other sections with poorer nesting remain ungapped. Through angle-resolved photoemission, we identify bands backfolded according to the CDW periodicity. They define FS pockets formed by the intersection of the original FS and its CDW replica. Such pockets illustrate very directly the role of nesting in the CDW formation but they could not be detected so far in a CDW system. We address the reasons for the weak intensity of the folded bands, by comparing different foldings coexisting in CeTe₃.

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Many different kinds of electronic instabilities, such as charge and spin density waves, introduce a new periodicity in a solid, thereby breaking the lattice periodicity which defines the band structure. For a commensurate instability, it is well known that bands of the original ("extended") zone must be folded back into a smaller ("reduced") zone according to the new periodicity in order to establish the equivalency among all reduced zones. Whether this reasoning still applies to an *incommensurate* periodicity raises more complex questions because the structure is not truly periodic anymore [1]. Angle-resolved photoemission spectroscopy (ARPES) is the most direct technique to visualize the dispersion of occupied bands and should then be an ideal witness for such behaviors. Surprisingly, the new periodicity in the charge density wave (CDW) state is often difficult to detect[2]. This is mainly because the intensity of the bands folded according to the CDW periodicity, called *shadow bands*, is proportional to the CDW coupling and often too weak to be detected. In a few cases, shadow bands have been observed *but only in the gapped regions*, as in the quasi-1D systems $(TaSe_4)_2I$ [1] or $NbSe_3$ [3].

The fate of the shadow bands in the metallic regions, when some remain, is of fundamental interest to understand the impact of the CDW and its periodicity on the metallic properties. Many spin density wave and/or CDW systems indeed exhibit residual metallicity (as Cr [4], $NbSe_3$ [5], or CeTe₃ [6]) because deviation from perfect nesting leaves pockets of itinerant carriers. The reduction of the size of the Fermi surface (FS) at the transition has been studied extensively [4], especially through quantum oscillations in transport or magnetic properties that are sensitive to the *area* of certain sections of the FS pockets (see for example [7] for a discussion of the situation in organic conductors). However, the location of these FS pockets, as well as their shape, could never be mapped out directly by ARPES.

We present here an ARPES study of CeTe₃, whose goal is precisely to reconstruct the FS of the CDW state. CeTe₃ is made out of square Te planes alternating with weakly coupled Ce/Te slabs (see ref. [8] or sketch in Fig. 2). Magnetic susceptibility measurements indicate that the Ce is trivalent [6]. The donated electrons completely fill the Te p orbitals in the Ce/Te slab and partially those in the planes [9,10]. The metallic Te planes host an incommensurate CDW that was first detected by transmission electron microscopy (TEM) [10] and that is already present at room temperature. It is characterized by a very large gap (about 400 meV), an order of magnitude larger than in transition-metal dichalgogenides. This allowed Gweon *et al.* to measure accurately with ARPES the gap anisotropy in SmTe₃, and they found that it corresponds well to the nesting properties of the FS [11]. In this Letter, we focus our attention on the modifications of a model FS of one single Te plane, induced by two couplings that tend to set new periodicities. (i) *The transverse coupling between the planes and the slabs*: The 3D unit cell has a base in the (a,b) plane rotated by 45° and larger by $\sqrt{2}$ compared to the square unit of a Te plane [Fig. 2(a)]. We will study to what extent this unit cell is relevant for describing the electronic properties of one plane. (ii) *The CDW instability:* The electron-phonon coupling stabilizes an incommensurate lattice modulation at wave vector $q_{CDW} \approx 5/7 \times 2\pi/a$, where $a = 4.4$ Å [10,11].

We clearly detect folded bands associated with both couplings and investigate further the topology of the CDW FS. Indeed, CeTe₃, like other RTe₃ compounds [12], remains a fairly good metal despite the large amplitude CDW; the in-plane resistivity is 50 $\mu\Omega$ cm at 300 K [6]. We show that, besides the region where the FS is destroyed by the opening of the large CDW gap, "pockets" are formed between original and folded bands.

Large, high-quality single crystals of CeTe₃, with residual resistance ratios in excess of 100, were grown

by slow cooling a binary melt [6]. The crystals cleave easily between two Te planes, providing a good surface quality for ARPES. All the data were collected at the BL 10.0.1 of the Advanced Light Source with a Scienta SES-2002 analyzer. Figure 1 displays a map of the ARPES spectral weight in CeTe$_3$ integrated between E_F and $E_F - 200$ meV. The main features of this map are very close to those observed in SmTe$_3$ [11], confirming the minor role of the rare earth in this electronic structure. The solid black lines are guides for the eye adjusted to the two main pieces in the map: a "square" centered at (0,0) and a larger "outer FS" at (0,2) and (2,0). The lower intensity in the vicinity of the $k_y = 0$ axis denotes the presence of the large CDW gap in this region [11], which breaks the near equivalency between k_x and k_y. This implies that the long-range ordering of the CDW yields domains at least larger than the beam spot (~ 100 μm), as was also the case in previous ARPES and TEM experiments [10,11].

A very simple electronic structure is expected for a Te plane, with perpendicular chains of in-plane p_x and p_y orbitals playing the only significant role, since band calculations show that p_z is completely filled [9,13]. An elementary 2D tight-binding calculation including only these two orbitals gives the following dispersion for p_x (p_y is identical but perpendicular):

$$E_{p_x}(\mathbf{k}) = t_{\parallel} \cos\left[(k_x - k_y)\frac{a}{2}\right] + t_{\perp} \cos\left[(k_x + k_y)\frac{a}{2}\right], \quad (1)$$

where the overlap integrals $t_{\parallel} = -4$ eV and $t_{\perp} = 0.75$ eV are taken from the calculation of Kikuchi in
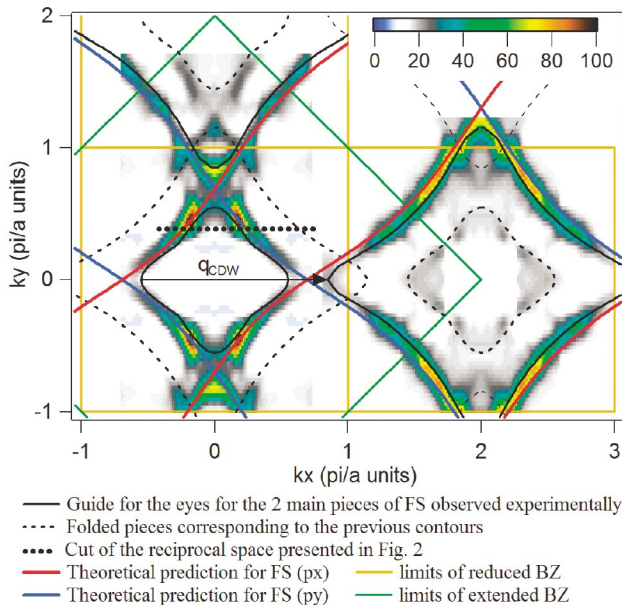

FIG. 1 (color). Map of the spectral weight in CeTe$_3$ obtained at 25 K, with photon energy $h\nu = 55$ eV and polarization nearly perpendicular to sample surface. Data were symmetrized with respect to $k_x = 0$, $k_x = 2$, and, for $k_x = 1$ to 2, $k_y = 0$.

—— Guide for the eyes for the 2 main pieces of FS observed experimentally
---- Folded pieces corresponding to the previous contours
•••• Cut of the reciprocal space presented in Fig. 2
—— Theoretical prediction for FS (px)   —— limits of reduced BZ
—— Theoretical prediction for FS (py)   —— limits of extended BZ

LaTe$_2$ [9], which contains isostructural Te planes. With E_F fixed according to the filling of the orbitals expected from stoichiometry, we obtain a contour for the FS shown as red and blue lines in Fig. 1, for p_x and p_y respectively. They describe extremely well the location of the high-intensity regions in the map, except, of course, at the crossing between p_x and p_y, where their mutual inter-action, totally neglected in our calculation, separates the square from the outer FS. This good agreement leads us to use Eq. (1) below as a guide for backfolding the bands.

Because the system is strongly 2D, it seems natural to obtain a good description of the electronic structure with a calculation based on one Te plane. However, the stacking of the planes is such that the Brillouin zone (BZ) in the plane for the 3D unit cell (the orange squares in Fig. 1) is different from the 2D BZ of one plane (larger green square), leading to the obvious problem that the 1st and 2nd BZ of the true 3D structure are not equivalent for the calculated FS. This equivalency should be obtained by folding back the bands along the reduced zone boundaries [or equivalently translating them by $2\pi/a$; see the sketch of Fig. 2(d)], which gives the dashed contours in Fig. 1. With data collected over many BZs (in contrast with [11]), it is clear that the intensity along this "folded FS" is drastically reduced, except near $k_y = \pm 1$ or, to a lesser extent, for the square of the second BZs. This raises questions about the meaning of the reduced or extended zone scheme for an experimental technique like ARPES. Voit et al. [1] recently clarified this problem by stressing that *the intensity of a folded FS in ARPES is proportional to the coupling responsible of the folding.* CeTe$_3$ clearly illustrates this principle: the lower intensity of the folded FS is a direct consequence of the weak coupling between Te planes and the magnetic slab, in other words, of the 2D character of the system [14].

The band structure along the thick dotted line of Fig. 1 is presented in Fig. 2 to detail the interactions between the main and the folded bands. The two bands dispersing towards the Fermi level in Figs. 2(b) and 2(c) correspond to p_x and p_y and form the small square around Γ point; the bands below E_F at $k_x = 0$ probably correspond to the filled p_z orbital and will not be further discussed. Figure 2(d) indicates the dispersion expected for all bands after Eq. (1). Although the folded bands are hardly visible in Figs. 2(b) and 2(c), a break in the dispersion of the main bands is clearly observed at $E = -0.8$ eV, when they cross the folded bands. Such a break typically results from the interaction between two bands in a perturbation model. The transverse coupling $V_{3D}(q = 2\pi/a)$ adds a small admixture of $|k + q\rangle$ into $|k\rangle$ with a weight depending on the coupling strength and decreasing very fast away from the crossing. This gives rise to a new dispersion sketched by black lines in Fig. 2(c) with a thickness proportional to this weight, as is also the ARPES intensity [1]. This scheme also predicts that the intensity of the folded FS will be stronger near the zone boundary at
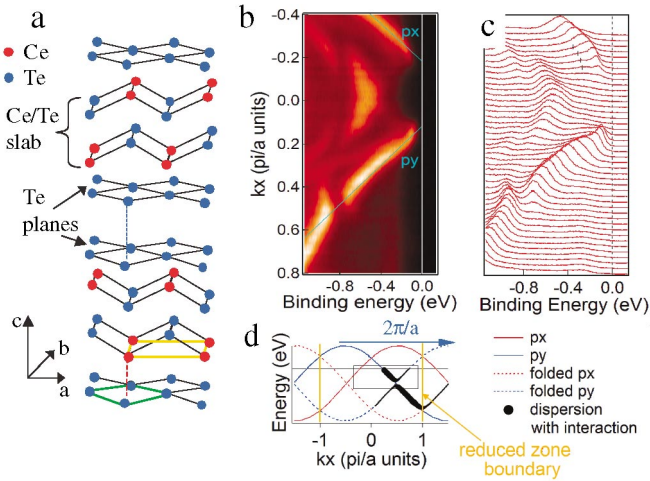
FIG. 2 (color). (a) Sketch of the CeTe$_3$ structure, indicating the unit cells corresponding to the orange and green BZ represented in Fig. 1. (b) Color-scale image and (c) Energy-distribution curve stacks of the band structure for $k_y = 0.45\pi/a$. In (b), the light blue lines are guide for the eyes. (d) Sketch of the dispersion for p_x and p_y (solid lines) and the folded bands (dotted lines), illustrating the situation for data in (b) (black rectangle). The thick black lines represent the dispersion after letting the main and folded bands interact. The thickness is proportional to the ARPES spectral weight.

$k_y = \pm 1$, because the bands cross there nearer to E_F, as is observed.

Let us note that, although there are two Te planes per unit cell, shifted by $a/2$ with respect to each other, this stacking does not define a new unit cell, and therefore does not induce any folding. On the other hand, it could split p_x and p_y into two bands, similar to the bilayer splitting well known from ARPES studies of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [15]. This could be the origin of the shoulder of p_y indicated by the black bars in Fig. 2(b). The intensity of this shoulder strongly depends on photon energy; it is nearly as intense as the main band at 35 eV.

We have discussed this folding in some detail, because the formation of the CDW can be described in identical terms; only the origin of the coupling is different and the periodicity is incommensurate. A spontaneous distortion of the lattice at wave vector **q** will be stabilized if this allows enough pairs of states $|\mathbf{k}\rangle$ and $|\mathbf{k}+q\rangle$ to lower their energies through the opening of a gap at E_F. This is the case here for $\mathbf{q}_{CDW}$, which nests the square into the outer FS part (see Fig. 1). For clarity, we refer in the following to the bands induced by the 3D structure as "folded" and to those of the CDW as "shadow." We can anticipate observing weak shadow bands at positions translated by $\mathbf{q}_{CDW}$ from the main bands that either (i) interact with the main band to create the CDW gap, if they cross near E_F (more precisely, if the distance between the crossing and E_F is smaller than the gap), or (ii) draw a FS replica that closes the FS pockets, when the bands cross away from E_F, i.e., for poorer nesting.

Figure 2(c) gives an example of the first case. p_x and p_y clearly *bend away* from E_F, leaving a gap $\Delta \simeq 120$ meV (at this position, the gap has significantly reduced), which is obtained by connection with the CDW shadow band.

The second case, yielding the FS pockets, is detailed in the images of Fig. 3. In the bottom image of Fig. 3(a1), the holelike square has become ungapped and is nearly closing. For higher k_y values, the electronlike outer FS piece of FS develops itself around $k_x = 0$. This evolution follows very well the theoretical dispersion of Eq. (1), shown as thick blue and red lines. In this region, the folded outer FS is also quite clear, giving rise to a second parabola, which becomes increasingly visible from Figs. 3(a1) to 3(a5) (dashed lines). However, two other weak lines are visible, most clearly in image Fig. 3(a3). They cannot be attributed to a substructure of another line, such as the bilayer splitting previously discussed, because their slope is opposite to that of the next dashed or thick lines [13]. *They are the CDW shadow bands*; their position exactly matches the one of p_x or p_y translated by $\mathbf{q}_{CDW}$ (thin blue or red line) and so does their evolution as a function of k_y. The location of the different cuts are indicated in Fig. 3(b) and the Fermi level crossings on the shadow
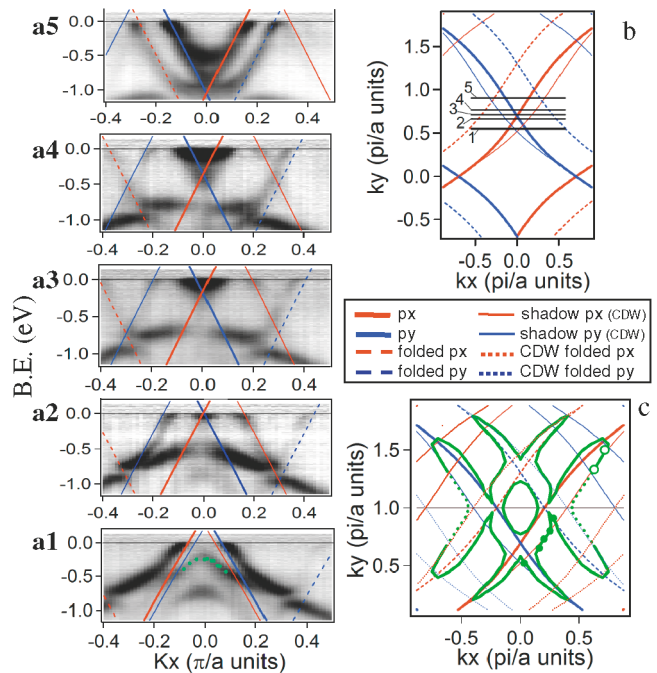

FIG. 3 (color). (a1)–(a5) Binding energy (B.E.) vs k_x for $k_y = 0.6, 0.69, 0.73, 0.77,$ and 0.91 (in π/a units, from bottom to top). A background was subtracted and the gray scale is logarithmic. The lines represent dispersion from Eq. (1) and backfolded bands (see legend). (b) Location of the cuts of (a) in the reciprocal space with theoretical traces of the main, folded, and shadow FS. (c) Sketch of the FS pockets reconstructed from the different FS traces (green lines, the dashed part is not observed experimentally). The green points locate the E_F crossings observed on the shadow FS [solid symbols correspond to images of (a)].

part of the FS are reported by green points on Fig. 3(c). When approaching the square, the continuity strongly suggests that the shadow FS smoothly connects to the original square and that the two bands joining each other just below E_F in image Fig. 3(a1) (green dots) actually correspond to the closed CDW replica. However, bilayer splitting effects become harder to rule out after the shadow and main bands have crossed and appear parallel.

By connecting the green points, we may start to draw the green line in Fig. 3(c) indicating the contour of the new FS. To complete this contour, we use the intersection of the main, folded, and shadow FS as a guide. This suggests two different pockets. The first one is an electronlike oval pocket centered at (0,1), formed by the interaction between the direct and folded FS. The second pocket is holelike and extends from the top of the square to the outer FS branches. We have discussed its lower part with Fig. 3(a). Along the most part of the outer FS (shown by a dashed green line in Fig. 3(c)], we do not detect shadow bands, which can be explained by the lower intensity expected theoretically because the nesting is the worst there. At the very end of the pocket, we observe shadow bands again at positions indicated by open green circles. This allows to pursue the solid green line around the closure of the pockets on the outer FS part.

The determination of this green contour was the main purpose of this Letter, as it defines the shape of the metallic pockets. However, it is only a first approximation of the FS, because we have restricted our study to the first shadow bands. For the incommensurate CDW, multiples of $\mathbf{q}_{\mathrm{CDW}}$ should create an infinity of new bands. The weight of these higher order shadow bands decreases very fast, which not only means that they will not be observable experimentally, but also that their role for many properties (e.g., transport) will become negligible. Because of this, the absence of true periodicity introduced by the incommensurate CDW does not destroy the electronic structure, a situation comparable to that of quasicrystals [16]. Similarly, the spectral weight changes along the green contour, so that the quasiclassical description of electronic orbits become nontrivial. Each quasiparticle of wave vector $\mathbf{k}$ acquires some component at vector $\mathbf{k} \pm \mathbf{q}_{\mathrm{CDW}}$ and interferences between them can occur. Recently, we have observed quantum oscillations in the magnetization of LaTe$_3$ [6], which is a promising step towards a very complete determination of the RTe$_3$ FS.

To summarize, CeTe$_3$ is particularly well suited for a detailed study of FS topology in the presence of an incommensurate periodicity. The simplicity of the electronic structure of the Te planes makes it an ideal ground to test the impact of perturbations. ARPES, for example, offers a simple image of the way the 2D electronic structure is modified by the 3D couplings. It also clearly locates the CDW gap on the best nested parts of the original FS and further reveals new bands closing the FS that can be directly traced back to the CDW periodicity. This supports intimately the description of the CDW as a nesting driven FS instability, whereas, because of the large gap, it was *a priori* not obvious that the CDW could still be viewed as a perturbation of the metallic state. Our study clarifies the original metallic properties arising from this situation, characterized by strong in-plane and out-of-plane anisotropy. As a result, the FS first appears as made of *arcs* that are not reaching the zone boundaries. This situation is reminiscent of that of complex materials exhibiting pseudogaps in some directions, as in certain phases of cuprates [15]. In CeTe$_3$, we demonstrate, for the first time in a CDW material, that these arcs can be explained to a very good approximation as in fact formed of narrow pockets resulting from the interaction between the original FS and its CDW replica.

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