Mechanism of Gap Opening in a Triple-Band Peierls System: In Atomic Wires on Si

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One dimensional (1D) metals are unstable at low temperature undergoing a metal-insulator transition coupled with a periodic lattice distortion, a Peierls transition. Angle-resolved photoemission study for the 1D metallic chains of In on Si(111), featuring a metal-insulator transition and triple metallic bands, clarifies in detail how the multiple band gaps are formed at low temperature. In addition to the gap opening for a half-filled ideal 1D band with a proper Fermi surface nesting, two other quasi-1D metallic bands are found to merge into a single band, opening a unique but k-dependent energy gap through an interband charge transfer. This result introduces a novel gap-opening mechanism for a multiband Peierls system where the interband interaction is important.

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Low-dimensional metals are extremely susceptible to external or internal perturbations and are thus unstable at low temperature (LT). The ground states of low-dimensional metals, such as the charge density wave (CDW) or the spin density wave and superconductors [1,2], result from the breakdown of a translational or gauge symmetry as mediated by a specific phonon. These states have typically been discussed within the scheme of a single metallic band [1,2]. That is, the theory for conventional superconductors assumes an isotropic energy gap which is formed by a momentum-independent electron-phonon interaction [2]. The original density wave theories postulate a single 1D metallic band, which leads to a unique band gap [1]. However, most real materials have the complexities due to multiple and/or anisotropic band structures, which were recently recognized as the sources of a few interesting phenomena. Some of the recent examples are the unusual superconductivity in MgB_2 with the double band gaps [3], the triple band gaps of superconducting $2H$-$NbSe_2$ [4], and the 1D CDW's of $NbSe_3$ with the multiple bands and the dual phase transitions [5]. The intriguing physical issues of the above systems are closely related to the momentum dependence of the electron-phonon and/or interband interaction.

Recently, as a new type of low-dimensional metallic systems, the self-organized In atomic wires on Si(111) [the Si(111)(4 × 1)-In surface] were found to possess the triple 1D metallic bands and to undergo a metal-insulator transition with a periodic lattice distortion (PLD) at about 125 K [6]. Mainly from the presence of the half-filled metallic band with a nearly flat Fermi surface (FS), this transition was interpreted to originate from the Peierls instability and the 1D CDW formation [6]. The flat (so called "nested") FS ensures a maximized electron-phonon interaction at a unique k vector [1]. However, while recent angle-resolved photoemission (ARP) studies agreed at least on the existence of the band gap itself, the first-principles calculation for the LT phase could not reproduce a sizable gap opening [7]. Furthermore, even the ARP studies showed the apparent discrepancies in the LT band dispersions and in the size/nature of the band gaps [8,9]. These results, which we believe are related to the complexity of the triple metallic bands, cast doubts on the origin of the phase transition and on the nature of the LT broken-symmetry state. The complexity of the multiple metallic bands is also important for understanding the ground states of the similar self-organized atomic wires formed on stepped Si surfaces with Au adsorbates [10,11].

In this Letter, we investigate the LT band structure and its temperature dependence extensively over the whole Brillouin zone (BZ) using high-resolution ARP. The result details the interesting band structure of the broken-symmetry phase. A solid band gap was observed for the half-filled 1D band at the proper nesting k vector (q_{CDW}). What is more interesting is that the other two quasi-1D bands interact strongly with each other through a charge transfer between them to form a single band with its band gap located very close to the original nesting vector of the phase transition. This unprecedented observation of the band restructuring introduces another gap-opening mechanism in a multiband system through a strong interband interaction.

The Si(111)(4 × 1)-In surface was prepared by depositing In onto Si(111)(7 × 7) at room temperature (RT) with a subsequent annealing [6]. The 4 × 1 surface is composed of 1D atomic wires with a width of 1.3 nm, where each unit wire has four In atomic chains (in two zigzag rows) close packed between Si chains [Fig. 1(a)] [6,7,12]. The order of the surface and the phase transition into the LT 8 × 2 phase [the ×2 periodicity doubling

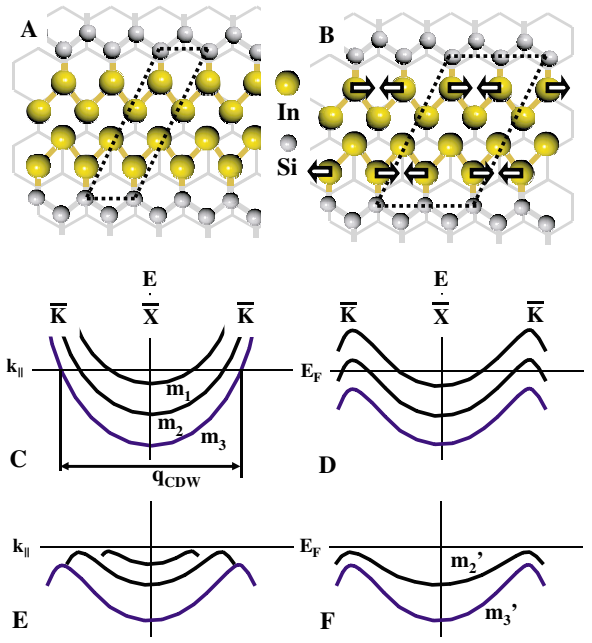

FIG. 1 (color online). Atomic structure models of the metallic 4 × 1 phase (a) and the insulating CDW 4 × 2 phase (b) [7], where unit cells are drawn by the dotted lines, and the arrows in (b) indicate the major displacements of the In atoms at LT. Schematic drawings of the triple bands in the metallic state with the nesting vector (q_{CDW}) (c) and the insulating CDW state (f) as measured in our experiment. The simple band structures expected by ×2 PLD/CDW within the simple single-gap (d) and triple-gap (e) pictures.

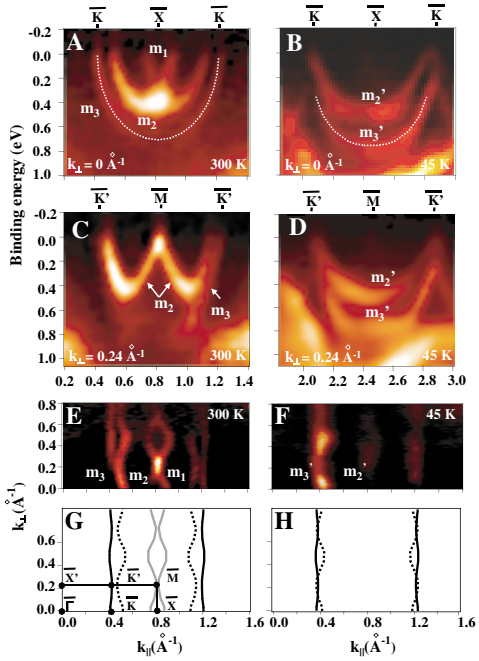

FIG. 2 (color online). Measured energy bands of In/Si(111) along the wires ($k_{\|}$) in the metallic state (RT) at two different $k_\perp$'s of 0 (a) and 0.24 Å^{-1} (c) and in the insulating state (45 K) (b),(d). Constant-energy spectral density maps at E_F showing the Fermi contours for the metallic states (e) and at a binding energy of 0.1 eV for the valence band maxima of the insulating phase (f), which are schematically depicted in (g) and (h), respectively. The first BZ of the 4 × 1 phase is drawn by the thin solid lines in (g). The wiggling Fermi contours (g) and the varying band dispersions at different $k_\perp$'s (a),(c) of m_1 and m_2 manifest the deviation from an ideal 1D nature in contrast with m_3.

along the wires [Fig. 1(b)] and the extra ×8 interwire order] were confirmed by low-energy-electron diffraction (LEED). Our quantitative LEED measurements indicate a sharp increase of the 1/2-order diffraction intensity due to the new ×2 periodicity at 120–130 K.

The ARP measurements were performed at two different locations. The higher resolution and detailed temperature-dependent measurements were done using a discharge-type uv source of $h\nu = 21.2$ eV [10] for a restricted k space. The extended band and FS mappings were carried out at a higher photon energy, $h\nu = 90$ eV, using undulator synchrotron radiation at the Advanced Light Source [6]. The nominal energy and angular resolutions were better than 15 meV and 0.15°, respectively, for both measurements. The temperature of the sample was controlled accurately down to 40 or 20 K, respectively, with liquid He cryostats and built-in heaters in both systems.

The detailed band dispersions as measured by ARP are shown in Fig. 2. In the RT metallic state [Fig. 2(a)], the three bands cross Fermi energy ($E = 0, E_F$) at different Fermi momenta (k_F's) of 0.75 (m_1), 0.54 (m_2), and 0.41 (m_3) Å^{-1} in the first BZ [along $k_\perp = 0$ Å^{-1} of Fig. 2(e)]. That is, the three metallic bands have different band fillings, 0.11 (m_1), 0.38 (m_2), and 0.50 (m_3), respectively, as integrated over one BZ, where 1 represents a filled band. The experimental FS topology of the metallic phase [Fig. 2(e)] indicates clearly the dimensional property of each band. The m_3 band with a nearly linear FS is close to an ideal 1D band, while the m_1 and m_2 bands with the wiggling FS's are typical quasi-1D [6]. More quantitatively, the anisotropy of the band structure ($t_{\|}/t_\perp$), the ratio of the band widths along ($t_{\|}$) and perpendicular ($t_\perp$) to the wires, of the m_3 and m_1 (m_2) bands are 72 and 8 (8), respectively, with indeed an order of magnitude difference [1]. This RT band structure is well reproduced by the first-principles calculation based on an established structure model [see Fig. 1(a)] [7]. The theory further indicates that the m_1 and m_2 bands originate mostly from the p_z orbitals of the In atoms but m_3 mostly from the Si-In bonds [7]. The wave functions of the m_1 and m_2 bands have a mirror symmetry along the wire, which are distributed symmetrically on the upper and lower In zigzag chains [Fig. 1(a)], respectively. This indicates that these two quasi-1D bands are closely entangled as a bonding-antibonding pair.

The half-filled m_3 band with a perfect nesting can be directly related to the Peierls instability and the CDW of the In wires. The PLD and charge ordering with a doubled ($\times 2$) periodicity along the wires were observed previously [6] and were detailed very recently [13]. This 1D CDW and PLD would straightforwardly lead to a band gap on m_3 at its own k_F, while the changes of the other metallic bands are not trivially expected. One of the previous ARP studies claimed the gap openings on m_2 and m_3 with rather rigid band dispersions [9]. In contrast, the other study reported the gap openings on m_1 and m_2 with an overall shift of the whole band dispersions. We note that those previous studies sampled only limited k points. This may have prevented the LT band structure from being unveiled fully since the apparent cross section of each band varies significantly over BZ's. [6]

We thus mapped out the LT band structure for the whole BZ (in fact, for a few irreducible BZ's), which is shown partly in Figs. 2(b) and 2(d). The LT ARP data show clearly that *there are only two nearly parabolic bands which are backfolded at the middle of the RT BZ* ($\bar{K}$). Note here that the band backfoldings are very clear, and thus the size of the band gaps can be determined unambiguously: 0.34 (m_3') and 0.04 eV (m_2') below E_F. The band with a larger band gap at LT (denoted as m_3') obviously corresponds to m_3. We also reasonably relate the band with a smaller band gap (denoted as m_2') to m_2. This means that the RT m_1 band disappears or is evacuated and instead the occupancy of m_2 is increased. The band-gap values are consistent with the previous measurement [6] which estimated the gap size from the leading edge shifts of the energy distribution curves. In that way, however, the gap size was slightly underestimated and only the uppermost band gap (that of m_2 as made clear in the present study) was actually probed.

The *double gap structure* [see Fig. 1(f) for a schematic] and the evacuation of m_1 are unexpected observations. What one can easily expect is (i) the gap opening only at m_3 with the other bands basically intact [Fig. 1(d)] or (ii) the gap opening for all three bands at their own k_F's [Fig. 1(e)]. In the former case, the resulting LT system would have both metallic and insulating bands and thus would not be nominally insulating after the phase transition. Even in this case, one may still expect a reduction of the electric carrier density, as observed in some complex CDW systems [5]. The latter case was often observed for multiband superconductors, such as MgB_2 [3] and $2H$-$NbSe_2$ [4], which exhibit a unique phase transition. However, a similar case may not be applicable to a CDW system since the gap-opening mechanism without a corresponding CDW/PLD formation is not provided.

In contrast, in the present case, the electrons of the third band (m_1) with the smallest occupation are depleted and are presumably transferred into the neighboring band (m_2). Then, the occupancy of m_2 becomes very close to half filling, which could make the $\times 2$ CDW/PLD act effectively for a gap opening. The increased occupancy of m_2 and the depletion of m_1 are confirmed over the whole BZ; the m_1 band disappears in the whole BZ and the band maxima of m_2 almost overlap with those of m_3 [Fig. 2(f)].

The interband charge transfer is likely since the m_2 and m_1 bands are closely entangled, as indicated in the theory [7]. Since these two states have a good mirror symmetry with respect to a mirror plane along the wire, the charge transfer would break the symmetric charge distribution between the two In zigzag chains of a wire [see Figs. 1(a) and 1(b)]. Such a charge rearrangement of the two In zigzag chains was indeed observed in a recent STM measurement at LT [13]. We further suggest that the interband charge transfer is a way of adapting the new lattice potential imposed by the PLD. This interband-charge-transfer scenario can thus explain the observed double gap structure straightforwardly, where the energy gain by the CDW/PLD formation can be maximized. Here, what is important is that the band filling of m_1 (0.11) and m_2 (0.38) in total is nearly 0.5, which leads to a half-filled band for the restructured band (m_2').

Another important observation is that the m_2' band at LT still has a quasi-1D character, as shown in Figs. 2(f) and 3(a). Hence, there is a possibility that the band-gap size may vary over the k space. We thus measured the position and size of the gap in more detail along the interwire direction ($k_\perp$), as summarized in Fig. 3. While the m_3' band at LT is backfolded nearly at the same $k_\parallel$, the gap position of m_2' changes systematically following the FS topology of the RT m_2 band [see the

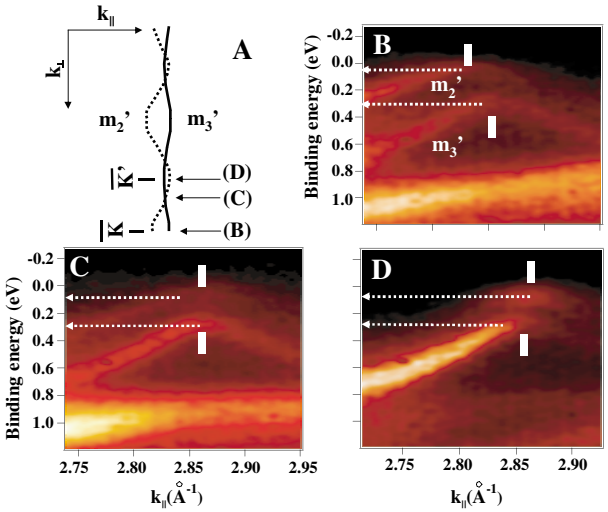

FIG. 3 (color online). Measured energy bands (b)–(d) along the In wires ($k_\parallel$) at 45 K at different $k_\perp$'s indicated in (a). The band backfolding position and the size of the band gap of m_2' vary over $k_\perp$, as indicated by the white bars and dashed arrows, respectively, in contrast with those of m_3'.

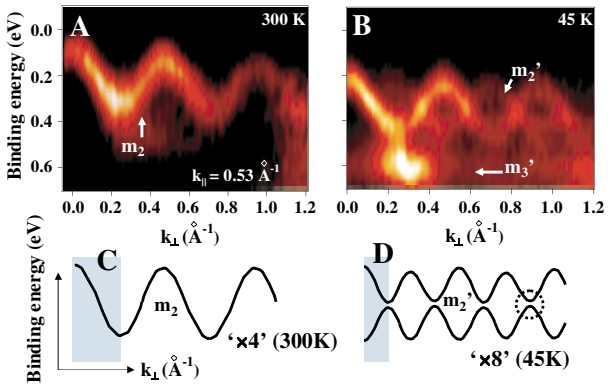

FIG. 4 (color online). Measured dispersions of the m_2 band along the interwire direction ($k_\perp$) at the metallic state (a) and the insulating CDW state (b) at $k_\parallel = 0.53\ \text{Å}^{-1}$, which are schematically drawn in (c) and (d). The first BZ's of the $\times 4$ and $\times 8$ orders are indicated by the shaded rectangles in (c) and (d), respectively.

dashed lines in Fig. 3(a)]. More interestingly, the band-gap size of m_2' also varies: about 90 meV below E_F when the gap is close to the $\times 2$ zone boundary (ZB) [Figs. 3(c) and 3(d)] and 40 meV when it is away from the ZB [Fig. 3(b)]. This strongly suggests that the gap opening of m_2' is also closely related to the $\times 2$ CDW/PLD induced by the Peierls instability.

Yet another point of the band structure along the interwire direction ($k_\perp$) is related to the extra $\times 8$ ordering. The In wires form a long-range order of 8×2 rather than 4×2 at LT. This interwire order is natural and common for quasi-1D CDW systems due to the interwire coupling inherent to the quasi-1D band dispersion [1] or to the Coulomb interaction of CDW's [14]. The periodicity doubling along the interwire direction ($\times 4 \rightarrow \times 8$) causes m_2' to be folded back at the new ZB of $k_\perp = 0.12\ \text{Å}^{-1}$, as shown in Fig. 4. In contrast, the m_3' band does not show the backfolding because it is nearly ideal 1D and is not dispersive along $k_\perp$. However, the possible gap opening of m_2' at the new ZB [see the dashed circle in Fig. 4(d)] is not clearly confirmed in our experiment. The size of the band gap at the $\times 8$ ZB must be smaller than what we can experimentally measure. This indicates that the extra $\times 8$ potential across the wires is much smaller than the $\times 2$ potential along a wire, as is naturally expected. Note that the main m_3 band for the CDW along the wire has an ideal 1D character and is not expected to provide a significant source of the interwire coupling. This may suggest that the obvious $\times 8$ interwire order is not directly related to the CDW or m_3 but only to m_2. This may lead to partly decoupled behavior of the $\times 2$ and $\times 8$ orders as suggested in a recent x-ray diffraction experiment [15]. Such behavior is not straightforwardly expected in a quasi-1D CDW system with only a single band.

In addition to the major changes in the electronic bands discussed above, more subtle changes are also observed: (i) the flattening of the bands around their minima as noticed in Figs. 2(b) and 2(d) and (ii) the shift of the band minimum for m_3 by about 50 meV [see the dashed lines in Figs. 2(a) and 2(b)]. These are not yet clearly understood and cannot fully be accounted for by the uncorrected surface photovoltage shift [9].

In summary, we investigated the temperature-dependent band structure of an unconventional (quasi-) 1D metallic system of the self-organized In wires on Si(111), the Si(111)(4×1)-In surface. This system was reported to undergo a metal-insulator transition due to the inherent instability of a 1D metal, the Peierls instability, but has a complexity of the triple metallic bands. Through an extensive angle-resolved photoemission study, we observed a clear gap opening for the half-filled ideal 1D band, which is thought to be mainly responsible for the Peierls instability. In addition, two other *quasi-1D* metallic bands were found to evolve into a single band to open a unique and k-dependent gap. Clear evidence of the $\times 8$ interwire order was also observed in the LT band structure, especially for the quasi-1D branch of the multi-band structure. Our results introduce a novel gap-opening mechanism for a multiband Peierls system, where the interband interaction through a direct charge transfer is working.

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[1] G. Grüner, *Density Waves in Solids* (Addison-Wesley, Massachusetts, 1994).
[2] J. R. Schrieffer, *Theory of Superconductivity* (Perseus Books, Reading, MA, 1983).
[3] S. Souma *et al.*, Nature (London) **423**, 65 (2003); S. Tsuda *et al.*, Phys. Rev. Lett. **91**, 127001 (2003).
[4] T. Yokaya *et al.*, Science **294**, 2518 (2001).
[5] J. Schafer *et al.*, Phys. Rev. Lett. **87**, 196403 (2001).
[6] H.W. Yeom *et al.*, Phys. Rev. Lett. **82**, 4898 (1999).
[7] J.-H. Cho *et al.*, Phys. Rev. B **64**, 235302 (2001).
[8] H.W. Yeom *et al.*, Phys. Rev. B **65**, 241307 (2002).
[9] O. Gallus *et al.*, Eur. Phys. J. B **20**, 313 (2001).
[10] J. R. Ahn, H.W. Yeom, H. S. Yoon, and I.-W. Lyo, Phys. Rev. Lett. **91**, 196403 (2003).
[11] J. N. Crain *et al.*, Phys. Rev. Lett. **90**, 176805 (2003).
[12] O. Bunk *et al.*, Phys. Rev. B **59**, 12 228 (1999).
[13] S. J. Park, J. R. Ahn, H.W. Yeom, and I.-W. Lyo [Phys. Rev. Lett. (to be published)].
[14] A. Liebsh, Phys. Rev. Lett. **91**, 226401 (2003).
[15] C. Kumpf *et al.*, Phys. Rev. Lett. **85**, 4916 (2000).