Real-space observation of the unidirectional charge density wave
and the structural phase transition in BaNi$_2$As$_2$

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ABSTRACT

Here we use low-temperature scanning tunneling microscopy to study the pnictide superconductor, BaNi$_2$As$_2$, which goes through a tetragonal to triclinic phase transition at ~136 K. In the triclinic phase, we observe the quasiparticle interference and the unidirectional charge density wave (CDW) with $Q = 1/3$ on the Ba surface of BaNi$_2$As$_2$. On the NiAs surface, apart from the unidirectional CDW, there are structural-modulation-induced chain-like superstructures with distinct periodicities. These complex chain-like structures can be along different lattice directions, which forms two domain structures. The unidirectional CDW appears more prominent in the NiAs domain where it is perpendicular to the chain-like superstructures. In the tetragonal phase, the $Q = 1/3$ unidirectional CDW disappears on both the Ba and the NiAs surfaces, and the NiAs surface appears as the ordered atomic chains with the $1 \times 2$ periodicity. Our results provide important insights for the interplay among the structural modulation, the unidirectional CDW and the nematicity in this class of materials.
Unconventional superconductivity is often accompanied by other electronic orders, such as charge density wave (CDW), spin density wave (SDW), and nematic orders. Understanding the interplay between superconductivity and the intertwined orders remains one of the major issues in the research of quantum materials [1-3]. The CDW in cuprates and nematic fluctuations in iron-based superconductors have been intensively studied [4-8], and the CDW and nematicity have also been observed in the superconducting magic-angle graphene [3]. Although it has been widely believed that these electronic orders have strong interrelation with superconductivity, their precise role in superconductivity has not been fully understood. Recently, several CDW states and the nematic order have been reported in the BaNi$_2$As$_2$-related superconducting materials [9-17], which makes them a new platform for studying the interplay between superconductivity and the intertwined orders.

BaNi$_2$As$_2$ is a nickel-based and nonmagnetic pnictide superconductor ($T_c \sim 0.7$ K) [18-21]. At room temperature, it shares the same tetragonal phase as the 122-family Fe-based superconductor, BaFe$_2$As$_2$ [18, 22, 23]. Upon cooling, BaNi$_2$As$_2$ first enters the incommensurate CDW state with the wavevector $Q = 0.28$ below ~150 K, then undergoes the first-order structural transition from the tetragonal to the triclinic crystal structure at ~136 K. In the triclinic phase, the system exhibits a slightly incommensurate CDW with $Q = 0.31$, then locks into a unidirectional commensurate CDW with $Q = 1/3$ [9, 10]. The very recent angle-resolved photoemission spectroscopy (ARPES) results also show the spectral evidence for the unidirectional-CDW-induced band folding in BaNi$_2$As$_2$ [13]. Near the triclinic phase transition, the elastoresponse measurements in BaNi$_2$As$_2$ indicate the diverging of the nematic susceptibility in the $B_{1g}$ channel, and the Sr substitution can gradually suppress the nematic order, which may be the reason for the six-fold increasement of the superconducting $T_c$ in the Ba$_{1-x}$Sr$_x$Ni$_2$As$_2$ system [11]. As increasing the Sr substitution, the triclinic phase transition temperature decreases, and a new CDW with $Q = 1/2$ emerges [10]. Until now, in the BaNi$_2$As$_2$ system, the microscopic information about the structure, the unidirectional CDW and the nematicity remains unknown.

In this Letter, we report a low-temperature and variable-temperature scanning tunneling microscopy/spectroscopy (STM/STS) study on BaNi$_2$As$_2$. In its triclinic phase, we find the unidirectional CDW on both the Ba- and the NiAs-terminated surfaces. On the NiAs surface, we observe the chain-like complex structures with several distinct periodicities, and we investigate the interplay between the chain-like structures and the unidirectional CDW on the NiAs surface. The unidirectional CDW disappears in the tetragonal phase, and the NiAs surface changes to show the ordered atomic chains with a doubling $1 \times 2$ periodicity. Our study provides detailed microscopic information about the complex structure and the unidirectional CDW in BaNi$_2$As$_2$, which should be important for understanding the nematic properties in this class of materials.

Single crystals of BaNi$_2$As$_2$ were synthesized by the self-flux method which is similar as the procedure described in Ref. [24]. The triclinic phase transition at ~136 K could be seen in the temperature-dependent electrical resistivity measurements (see Supplemental Material, Fig. S1 [25]). The low-temperature (4.3 K and 77 K) and the variable-temperature STM experiments were carried out with a Unisoku low-temperature STM. BaNi$_2$As$_2$ single crystal samples were cleaved at
77 K and then transferred into the STM head for measurements. Chemically etched tungsten tips were used for the STM measurements. STS measurements were done by using the standard lock-in technique with 3 or 5 mV modulation at the frequency of 914 Hz.

We first investigate the triclinic BaNi$_2$As$_2$. Cleaving the BaNi$_2$As$_2$ single crystals results in both the Ba- and NiAs-terminated surfaces. Figure 1(c) shows the constant-current STM topography taken on the Ba surface of BaNi$_2$As$_2$, where we can clearly see the stripe-like unidirectional pattern (see Supplemental Material for more bias-voltage dependent STM topographies, Fig. S2 [25]). The inset in Fig. 1(c) shows its Fourier transform (FT) image, which shows that the periodicity of the stripe-like pattern is three times the length of the lattice constant. This indicates that there is indeed a unidirectional commensurate CDW with the wavevector $Q = 1/3$ on the Ba surface. In Fig. 1(c), we can also see the ring-like standing wave patterns around the atomic defects, which is due to the quasiparticle interference (QPI) of the electronic states.

In order to extract the electronic band dispersion from the QPI, we perform the energy-resolved differential conductance ($dI/dV$) maps. Figure 1(d) shows the typical $dI/dV$ map taken with ~30 mV bias voltage (see Supplementary Materials for more $dI/dV$ maps, Fig. S3 [25]). The QPI pattern can be obtained by performing FT to the $dI/dV$ maps. Figure 1(e) is the FT image of the $dI/dV$ map shown in Fig. 1(d), where there are two main sets of inequivalent scattering wavevectors: $q_1$ and $q_2$. As the first approximation for understanding the scattering wavevectors, we perform an autocorrelation of the constant energy contours, which neglects the spin or orbital matrix elements during the scattering [26]. Considering the size of the scattering wavevectors in Fig. 1(e), we only plot the autocorrelation of the four small Fermi pockets around Γ point in the constant energy contours [the red circles shown in Fig. 1(b)] [27]. As shown in Fig. 1(h), the autocorrelation pattern can nicely reproduce the main scattering modes shown in Fig. 1(e). The $q_1$ wavevector indicates the scattering along the Γ-Y direction, and the $q_2$ wavevector corresponds to the scattering along the Γ-M direction [Fig. 1(b)]. By plotting the energy dispersion of the $q_1$ and $q_2$ wavevectors, we observe an electron-like band crossing the Fermi level with the band bottom at ~150 meV, which is consistent with the α band in the previous ARPES measurements [27]. In the $dI/dV$ spectrum [Fig. 1(f)], the bottom of the α band appears as a peak located at ~150 mV.

We next turn to the NiAs surface of BaNi$_2$As$_2$. We observe two different NiAs surfaces, and Figure 2(a) shows the STM topography taken near the boundary of these two NiAs surfaces (Domain-I and Domain-II). Figures 2(b) and 2(c) are the zoom-in STM topographies taken on these two surfaces, respectively. We can see the chain-like modulation patterns with distinct periodicities on both Domain-I and Domain-II NiAs surfaces, and the chain directions on these two domains are perpendicular with each other [Figs. 2(b) and 2(c)]. According to the very recent first-principles calculations, the rebonding of the As anions in the NiAs layer of BaNi$_2$As$_2$ can induce complex structural instabilities, such as As dimers, trimers or even more complex bonding arrangements [28]. This could explain the chain-like supermodulations on the NiAs surface with several different periodicities. Similar chain-like complex superstructures have also been reported in the triclinic IrTe$_2$ which is due to the rebonding of Te [29].
As shown in Fig. 2(c), in addition to the chain-like superstructures, the unidirectional CDW pattern can be clearly seen on the Domain-II NiAs surface, and it is perpendicular with the chain-like modulation pattern. In order to clearly reveal the periodicities of the chain-like modulations and the unidirectional CDW on these two NiAs surfaces, we perform FT to the STM topographies [Figs. 2(d) and 2(e)]. Figures 2(f) and 2(g) are the linecut profiles taken along the colored arrows in Figs. 2d and 2e, respectively. From the red curve in Fig. 2(g), we can see the strong wavevector corresponding to the \(Q = 1/3\) unidirectional CDW on the Domain-II surface. As shown by the red curve in Fig. 2(f), the chain-like superstructures indeed consist of several periodicities, and the \(1 \times 3\) wavevector can also be seen. This indicates that the unidirectional CDW also exists in the Domain-I area and it is parallel with the chain-like superstructure direction [Figs. 2(d) and 2(f)]. This makes the unidirectional CDW less visible in the STM topography taken on the Domain-I surface [Fig. 2(b)]. We also find that the \(dI/dV\) spectra are similar on these two NiAs surfaces (see Supplementary Materials, Fig. S4 [25]), which is also consistent with the conclusion that the unidirectional CDW exists on both NiAs surfaces.

Having identified the unidirectional CDWs on the Ba and the NiAs surfaces of the triclinic BaNi\(_2\)As\(_2\), the next question is what is the relationship between the unidirectional CDWs on the Ba and the NiAs surfaces. Figure 3(a) shows the STM topography taken at the step edges between the Ba surface and the Domain-I NiAs surface. The insets are the zoom-in STM topographies taken on the Ba and Domain-I NiAs surfaces, and Figs. 3(b) and 3(c) are their FT images. We can see that the unidirectional CDWs on the Ba and Domain-I surfaces are parallel with each other. When the underneath NiAs is the Domain-II NiAs surface, the unidirectional CDW on the Ba surface is also parallel with the unidirectional CDW on the underneath Domain-II NiAs surface [Figs. 3(d)-(f)]. Our data indicates that no matter the unidirectional CDW on the underneath NiAs surface is parallel or perpendicular with the chain-like superstructures, the unidirectional CDW on the top Ba layer always has the same direction as that on the NiAs surface.

After characterizing the triclinic BaNi\(_2\)As\(_2\), we increase the temperature to be above the phase transition temperature (\(-136\) K) and study the tetragonal BaNi\(_2\)As\(_2\). Figures 4(a)-4(c) show the STM topographies on the Domain-II NiAs surface taken at 120 K, 140K and 150 K, respectively, and Figures 4(d)-4(f) are their FT images (see Supplemental Material for the temperature dependent STM data on the Domain-I NiAs surface, Fig. S5 [25]). As increasing the temperature to be above the phase transition temperature (\(-136\) K), the \(Q = 1/3\) unidirectional CDW disappears on the NiAs surface [Figs. 4(d) and 4(e)]. Figures 4(e) and 4(f) also indicate that in the tetragonal phase, the NiAs surface becomes more ordered and the atomic-chain superstructure with \(1 \times 2\) periodicity starts to emerge at 150 K (see Supplemental Material for STM data taken at 160 K, Fig. S6 [25]). In the ordered superstructures, the two nearest As atomic chains have slightly different height. For the Ba surface, although the \(Q = 1/3\) unidirectional CDW also disappears at 140 K and 150 K, no clear superstructure feature can be seen [Figs. 4(g) and 4(h)]. Since the atomic-chain structures with \(1 \times 2\) periodicity only appear on the NiAs surface, they are likely a structural reconstruction induced by the rebonding of the As anions on the NiAs surface [28].
Finally, we discuss the incommensurate CDW that has been reported in the previous x-ray scattering measurements on BaNi$_2$As$_2$ at the temperature between ~130 K to ~150 K [9, 10, 14, 15]. This incommensurate CDW can be suppressed by Sr substitution [10, 30]. In the FT images of the STM topographies taken at 140 K, no clear incommensurate CDW is observed on the NiAs and Ba surfaces [Figs. 4(b) and 4(g)]. One possible reason could be that the incommensurate CDW is disturbed and weakened by the electric field from the STM tip. Similar effect has been observed in the impurity-pinned incommensurate CDW in 2H-NbS$_2$ system [31].

In conclusion, in the triclinic BaNi$_2$As$_2$, we directly observe the unidirectional CDW with $Q = 1/3$ on both the Ba and NiAs surfaces. Due to the rebonding of the As anions, the complex chain-like superstructures appear on the NiAs surface. When BaNi$_2$As$_2$ is in the tetragonal phase, the $Q = 1/3$ unidirectional CDW disappears on both the Ba and the NiAs surfaces, and an ordered atomic-chain superstructure with $1 \times 2$ periodicity emerges on the NiAs surface. Our results are important for fully understanding the complex structure, unidirectional CDW and nematicity in this class of materials.

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Figure 1

Figure 1. (a) Crystal structure of BaNi₂As₂ in the tetragonal and triclinic phases. (b) Schematic of the Fermi surface contours of the triclinic BaNi₂As₂ which are based on the previous ARPES data [27]. (c) Constant-current STM topography taken on the Ba surface of BaNi₂As₂. The inset shows its Fourier transform (FT) image. (d) dI/dV map taken on the Ba surface with −30 mV. (e) The FT image of the dI/dV map in (d). (f) The typical dI/dV spectrum taken on the Ba surface. The inset shows the dI/dV spectrum with smaller energy range. (g) Linecuts along the directions shown by the colored arrows shown in (e) as a function of energy. (h) Autocorrelation of the Fermi surface contours consisting only of the α pockets near the Γ point. The STM data shown in this figure are taken at T = 4.3 K.

Figure 2

Figure 2. (a) Constant-current STM topography taken near the boundary between the Domain-I and Domain-II NiAs surfaces. (b) and (c) Zoom-in STM topographies on the Domain-I (b) and Domain II (c) NiAs surfaces. The white arrows indicate the directions of the atomic chains. (d) and (e) The FT images of (b) and (c). (f) Linecut profiles along the red and blue arrows shown in (d). (g) Linecut profiles along the red and blue arrows in (e). The data shown in this figure are taken at T = 4.3 K.
**Figure 3.** (a) Constant-current STM topography taken near the step edge between the Ba surface and Domain-I NiAs surface. The up-left inset shows the zoom-in STM topography taken on the Ba surface. The bottom-right inset is the zoom-in STM topography taken on the Domain-I NiAs surface. (b), (c) The FT images for the STM topographies shown in the insets of (a). (d)-(f) The same as (a)-(c), but they are taken near the step edge between the Ba surface and the Domain-II NiAs surface. The STM data shown in this figure are taken at $T = 77$ K.

**Figure 4.** (a)-(c) Constant-current STM topographies taken on the Domain-II NiAs surface at 120 K (a), 140 K (b), and 150 K (c). (d)-(f) The FT images of the STM topographies in (a)-(c). (g) and (h) Constant-current STM topographies taken on the Ba surface at 140 K and 150 K, respectively.