## Coupled structural and magnetic antiphase domain walls on BaFe<sub>2</sub>As<sub>2</sub>

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High-resolution scanning tunneling microscopy measurements on the (001) surface of BaFe<sub>2</sub>As<sub>2</sub>, a parent compound of Fe-based high- $T_c$  superconductors, reveal a complex surface with coexisting structural phases. Large areas display a squarelike  $(\sqrt{2} \times \sqrt{2})R45^\circ$  structure with surface-pinned antiphase domains. The domain walls exhibit  $C_2$  symmetry, in contrast with the bulk  $C_{2v}$  geometric structure. We argue that the strong spin-lattice coupling at the surface results in the coexistence of structure and spin antiphase domain boundaries with  $C_2$  symmetry.

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The discovery of high-temperature superconductivity in the Fe-based compounds has generated enormous excitement and activity in the scientific community.<sup>1,2</sup> Similar to cuprates, the ground state of the parent compounds in the Fe-based superconductors is antiferromagnetically (AFM) ordered and the magnetic ordering must be suppressed in order to achieve superconductivity. However, the parent compounds of Febased superconductors are metallic with small magnetic moments<sup>3</sup> compared to a Mott insulating phase with robust large magnetic moments in cuprates. What is so interesting in these materials is the intimate coupling between spin and lattice in the parent compounds.<sup>4–7</sup> For example, a structural transition from the high-temperature tetragonal to the lowtemperature orthorhombic phase is always accompanied by a magnetic transition from the paramagnetic to the collinear AFM ordered state in BaFe<sub>2</sub>As<sub>2</sub>.

This study on a parent compound BaFe<sub>2</sub>As<sub>2</sub> using scanning tunneling microscopy (STM) reveals  $\pi$ -phase shifted domains between  $(\sqrt{2} \times \sqrt{2})R45^{\circ}$  structures. The symmetry of the associated domain walls is lower than the lattice symmetry expected from the bulk or seen by STM within a single domain. We argue that this is a result of the strong coupling between AFM ordered spins and electrons at the surface, which causes the coexistence of an antiphase spin domain boundary with the antiphase structural boundary.

High-quality BaFe<sub>2</sub>As<sub>2</sub> single crystals were grown using the self-flux method.<sup>8</sup> The crystals are platelike with the (001)direction perpendicular to the plate. The lattice parameters at room temperature are a = 3.9635(5) Å and c = 13.022(2) Å. The susceptibility decreases slightly with decreasing temperature down to about 140 K, where it drops more abruptly due to the magnetic and structural phase transitions. Electrical resistivity measured in the *ab* plane shows metallic behavior. At room temperature, it is  $\sim 0.5 \text{ m}\Omega$  cm and drops steeply below  $\sim 140$  K with decreasing temperature, reaching about  $0.15 \text{ m}\Omega$  cm at 2 K. The STM measurements were conducted on a home-built variable temperature STM<sup>9</sup> with a tungsten tip. BaFe<sub>2</sub>As<sub>2</sub> single crystal samples were first precooled to 80 K in an ultrahigh vacuum environment with basic pressure lower than  $5 \times 10^{-11}$  Torr. After the *in situ* cleavage, the sample was immediately inserted into the precooled STM head.

Figure 1(a) shows the geometric structure of the low temperature bulk orthorhombic (a > b) unit cell, including the collinear AFM spin configuration in the Fe layer. These layered crystals can be cleaved, leaving the As-Fe<sub>2</sub>-As layers intact.<sup>10</sup> STM shows that the surface after cleaving at low temperatures consists of both disorder and ordered regions with two different structures. The ordered surface includes a stripelike (1 × 2) structure and a squarelike  $(\sqrt{2} \times \sqrt{2})R45^{\circ}$ structure (tetragonal notation).<sup>11-17</sup> Figure 1(b) is a typical large scale high-bias (1 V) STM image of an extremely flat area with dark defects and faint zigzag lines, which are domain boundaries (which will be discussed in detail later). Applying a small bias (tip closer to sample) produces an atomically resolved image in a region with no defects, which is shown in the inset of Fig. 1(b). This image shows a squarelike lattice with a unit cell  $\sim$ (5.6 Å  $\times$  5.6 Å), which is the  $(\sqrt{2} \times \sqrt{2})R45^{\circ}$  phase in the tetragonal notation.<sup>18</sup> This tetragonal notation is somehow misleading because the surface unit cell is orthorhombic so the symmetry labeling should be  $(1 \times 1)$ , the same as the bulk symmetry. The difference in the  $(1 \times 1)$  unit cell seen with STM and the bulk truncated surface is that there is only one bright protrusion in each unit cell in the STM image, in contrast to two atoms in the  $(1 \times 1)$ unit cell in the bulk, for a complete surface layer of As or Ba [see Fig. 1(a)]. The exact termination for this phase is still controversial.<sup>11,13,18</sup> It could be a half monolayer of Ba, a full layer of Ba, or As with a distortion that makes one of the two surface atoms invisible. Any of these terminations would have the bulk  $C_{2v}$  symmetry. Thus, it makes no difference on the observed broken symmetry addressed in this Rapid Communication.

Figure 2(a) shows a low-bias (23 mV) atomically resolved image, but with a larger field of view than that presented in the inset in Fig. 1(b). The randomly distributed (large and fuzzy) spots were previously reported as Ba atoms.<sup>18</sup> Note, in addition to the clear ( $\sqrt{2} \times \sqrt{2}$ )*R*45° ordered structure, there are periodic white blobs forming zigzag lines. Also, there are dark spots, which appear to be randomly distributed and are most likely defects (including vacancies) on the surface, but the zigzag line changes direction at a dark spot. When the bias voltage is increased to 483 mV [or 1 V as in Fig. 1(b)] there is a

## (a) (b) 15mm 15

FIG. 1. (Color online) (a) Bulk lattice and spin structures of BaFe<sub>2</sub>As<sub>2</sub> with Fe magnetic moments indicated by orange arrows. (b) Constant-current ( $V_{\text{bias}} = 1.0 \text{ V}$ ,  $I_{\text{tip}} = 100 \text{ pA}$ ) STM topographic image on (001) surface of BaFe<sub>2</sub>As<sub>2</sub> at 80 K. The inset is a zoom-in, low-bias (23 mV) image (5 nm × 5 nm) exhibiting a squarelike  $(\sqrt{2} \times \sqrt{2})R45^{\circ}$  structure.

dramatic change in the contrast in the STM image, as shown in Fig. 2(b). Under these higher-bias voltages atomic resolution is lost but the zigzag lines become dark, while the dark defects seen in the low-bias image remain dark. The large-scale images show that the zigzag lines form closed loops which separate the surface into different regions, i.e., domains. A contrast reversal as seen at the domain walls means that the origin of the image is primarily electronic, since STM only "sees" charge density. This observation is not due to a change of the tip or sample condition because the contrast reversal is reproducible by changing the bias from 23 to 483 mV and back to 23 mV.

Figures 3(a) and 3(b) show two images of different domain walls that change directions at a defect. In each image there are two boundaries along different diagonal directions, one ~45° and the other ~-45° [Fig. 3(a)] or ~135° [Fig. 3(b)] with respect to the *a* direction. As can be seen in both figures, the adjacent  $(\sqrt{2} \times \sqrt{2})R45°$  domains are shifted by half an orthorhombic unit cell, as indicated by arrows, i.e., an antiphase domain wall. All of the bright white blobs residing on both boundaries have an elliptical shape, but a closer examination reveals that the white blobs along the -45°



FIG. 2. (Color online) Two typical constant-current ( $I_{tip} = 200 \text{ pA}$ ) STM topographic images with different positive bias voltages on the squarelike ( $\sqrt{2} \times \sqrt{2}$ ) $R45^{\circ}$  (001) surface at 80 K: (a) A 35.5 nm × 35.5 nm image at low bias (23 mV) and (b) 70 nm × 70 nm image at high bias (483 mV), respectively.

## PHYSICAL REVIEW B 86, 060512(R) (2012)



FIG. 3. (Color online) (a), (b) Two 5.6 nm × 5.6 nm low-bias constant-current STM topographies ( $V_{\text{bias}} = 23 \text{ mV}$ ,  $I_{\text{tip}} = 200 \text{ pA}$ ) showing boundary structures at 80 K. The arrows with dashed lines indicate the half unit cell shift in the *a* and *b* directions, respectively. (c), (d) Line profiles along domain boundaries shown in (a) and (b). Green and red colors represent two types of domain walls in terms of shapes and intensity. (e) A schematic structure model of the closed domain surrounded by another domain. The thin lines indicate the orthorhombic (1 × 1) unit cells. Solid and open circles represent "visible" sites and "invisible" sites in STM images, respectively. Four domain walls (45°,  $-45^\circ$ ,  $135^\circ$ ,  $-135^\circ$  refer to a longer *a* axis) are shown by blue thick lines, connected by dark holes (defects). On each domain wall, there are two ellipses which represent the bright blobs seen on the domain wall in STM image.

direction are less elliptical. A quantitative difference is seen in the line profiles along these two boundary directions as shown in Figs. 3(c) and 3(d), respectively. The line profile oscillates with the same periodicity along both directions, but the amplitude for the blobs in the  $45^{\circ}$  direction (red lines) is about double compared to that along the  $-45^{\circ}$  direction (green lines). We emphasize that such a difference is not due to anisotropic tip effect as the same result is obtained by different tips in different regions.

If one examines the symmetry carefully it is clear that the domain walls exhibit only  $C_2$  symmetry. Rotating the image

in Fig. 3(b) by 180° transforms the 135° boundary into a  $-45^{\circ}$  boundary which is identical to the  $-45^{\circ}$  boundary in Fig. 3(a), as expected if the boundary direction is unchanged. But if we reflect Figs. 3(a) and 3(b) about the structural mirror plane *ac* and *bc* plane [see Fig. 1(a)], respectively, the 45° boundary is different from the  $-45^{\circ}$  boundary in Fig. 3(a) and the 135° boundary is different from the 45° boundary in Fig. 3(b). This means that the mirror symmetry is broken at the domain wall.

In bulk, the simplest structural domain wall would be a twin boundary, where the directions of a and b are swapped. We were able to determine that the directions of a and b do not change across the boundaries, as indicated in Fig. 2(a). If the directions of a and b were changed so that a was vertical in the upper domain and horizontal in the lower domain, there would be a mismatch in the alignment of the vertical columns along the domain wall, since  $a \neq b$ . To illustrate this, one may assume that, at the point on the domain wall farthest to the left in Fig. 2(a), the vertical column on the upper domain is aligned halfway between the two columns on the lower domain. Since this is an antiphase domain boundary there is a  $\pi$  phase change between the two sides. In this situation, if one moves over *n* vertical columns to the right in the upper domain, the distance traveled is  $n \times b$ . On the other hand, the corresponding position on the lower domain is  $(n - \Delta)a$ , where  $\Delta a$  is the mismatch alignment due to a > b. Using the definition of the orthorhombicity,  $\delta = (a - b)/(a + b) \approx$ (a - b)/(2a), the value of the mismatch  $\Delta$  can be determined:  $\Delta = 2n\delta$ . For the antiphase domain walls when  $\Delta = 0.5$ , the bright columns on the top will be aligned to the bright columns on the bottom. For the measured orthorhombicity of the bulk (~0.4%), this happens when n = 62. However, if we use the enhanced orthorhombicity reported for the surface ( $\sim 2\%$ ),<sup>19</sup> only  $\sim 12$  vertical columns are required to align the vertical columns in the upper and lower domain. The complete domain, partially shown in Fig. 2(a), contains more than  $\sim$ 123 vertical columns. A comparison of the match between the columns in the two domains from the extreme left to the extreme right shows no change, i.e., the two domains are not a result of twinning. Therefore, the domains reported here are not bulk twin boundaries but instead surface antiphase boundaries between two domains of the reconstructed surface.

While excluding the possibility of twin domain boundaries, can the structural mismatch cause the domain walls with reduced symmetry? Figure 3(e) shows a pure structure model. To make the picture as simple as possible, the domain inside the closed boundary contains only ~12 (1 × 1) orthorhombic unit cells. The phase of the inside domain is shifted by  $\pi$ , both the rows and columns, with respect to the outside domain. We will refer to this as a structural antiphase domain but there is no bulk structural boundary associated with this surface domain wall. These surface structural boundaries maintain  $C_{2v}$  symmetry, so that the line profiles for the four boundaries in Fig. 3(e) would be identical. This demonstrates that a pure structure model cannot explain our observation.

We recall that both structural and magnetic transitions occur concomitantly in  $BaFe_2As_2$ .<sup>5</sup> Therefore, spin arrangement has to be taken into account in any model, due to strong spin-lattice coupling. Spin, as angular momentum and torque, is known as a pseudovector (or an axial vector), opposed to a true or polar vector such as velocity.<sup>20</sup> The property of a pseudovector is that



FIG. 4. (Color online) (a) Mirror symmetry operation on spin (pseudovector) and velocity (polar vector) for a vertical mirror plane (out of page) shown by the dashed lines. (b) Structural antiphase, spin single-phase domain model: Bulk spin structure domain with no spin phase change crossing structural boundary. The black arrow indicates the magnetic moment on Fe atoms and its direction. (c) Coupled structural and spin antiphase domain model: Bulk spin structure domains with  $\pi$  phase change across domain walls. The green and red colors represents two types of domain walls.

its mirror image is equal in magnitude but flipped in direction because a pseudovector has a chirality. Figure 4(a) illustrates this feature for three different spin directions with respect to the mirror plane. The mirror images of a polar vector such as velocity are also shown. The first case is the most general situation where the spin vector is in an arbitrary direction with respect to the mirror plane. It is easy to see from this picture what happens when the spin is perpendicular to the mirror plane (case 2) or parallel (case 3). Given the bulk AFM structure of  $BaFe_2As_2$  as shown in Fig. 4(b), it is obvious that there is no mirror symmetry for either of the structural mirror planes: horizontal (along the a axis) or vertical (along the baxis). First-principles calculations show that, at the surface, the lowest energy configuration has the same spin structure as the bulk.<sup>21</sup> Therefore, the model shown in Fig. 4(b) is well justified to represent the surface situation. Inspection of this single-phase spin domain shows that the symmetry has been reduced to  $C_2$ .<sup>22</sup> The top-left wall is the same as the bottom-right wall but different from the other two (which are identical to each other). Rotation by 180° takes the top-left wall into the bottom right, and the bottom left into the top right, but there is no mirror symmetry, i.e.,  $C_2$  symmetry. Still, there are several experimental facts that would seem to rule out this single-phase spin domain picture. First, the STM images of a region without a wall for both ordered structures have  $C_{2v}$  symmetry. Second, there is no evidence in the literature from angle-resolved photoemission measurements of detwinned samples that the spin/charge coupling breaks the mirror symmetry.<sup>23</sup> Finally, although we know that the spin ordering breaks mirror symmetry, the spin configuration itself on domain walls is identical to the one within the clean domain. For example, it is hard to believe the white blob on the 45° domain wall can be different from the one on the  $-45^{\circ}$ domain wall since the surroundings show an almost identical spin configuration.

One plausible scenario is that the spin antiphase domain wall coexists with the structural antiphase domain wall due to enhanced spin-lattice coupling at the surface. Figure 4(c) shows such a coupled spin and lattice domain wall. The essential ingredient in this picture is that the spin ordering is locked to the structure or vice versa through the spin-lattice coupling. In Fig. 4(c), the nearest four spins of Fe atoms are always pointing inward to the "visible" solid blue circle sites in any domain (the other possible case not shown here is that the spins are always pointing outward to the "invisible" site). As a result, when crossing structural antiphase domain walls, there is an accompanying antiphase shift of spin ordering.

Given the coupled (locked) structural-magnetic domain model, it is possible to explain many of the experimental observations. The half orthorhombic unit cell shift between adjacent structural domains is accompanied by an antiphase shift of the spin order along both the AFM a axis and FM b axis when crossing boundaries. Right at the walls where adjacent antiphase spin domains meet, the spins of Fe atoms cannot fit into either domain, and thus are frustrated with no clear spin orientations [see the missing arrows along the walls in Fig. 4(c) compared to Fig. 4(b)]. The blobs seen at the

## PHYSICAL REVIEW B 86, 060512(R) (2012)

boundaries are the enhanced local density (occupied near the Fermi energy) of states due to the orbital overlap between two bright protrusions from adjacent domains. The fluctuating magnetic moments on the Fe atoms on the domain walls create two types of spin vortex arrangements around the white blobs. The red color on the  $(45^{\circ} \text{ and } -135^{\circ})$  boundaries in Fig. 4(c) have right-hand spin chirality (indicated by the oriented circle in the bottom-right blob), while on the green colored blobs on the  $(135^{\circ} \text{ and } -45^{\circ})$  boundaries have left-hand chirality (indicated by the oriented circle in the bottom-left blob). Specifically, the different chirality can be described as spin toroidal moment chirality.<sup>24</sup> Through the orbital-spin coupling, the parity of the spin arrangement can give rise to a deference in electronic structure which results in the different distributions of electron density of states at the domain walls as seen by STM. However, to understand the nature of this coupling will require a determination of the exact structure of the surface coupled with a theory that includes the enhanced spin/lattice coupling at the surface.

Both static and dynamic antiphase spin domains have been discussed theoretically.<sup>25,26</sup> In the bulk these domains seem to be dynamic. Mazin and Johannes proposed that these fluctuating domain boundaries can provide an explanation for many experimental observations that otherwise seem to be incongruent.<sup>25</sup> Apparently, as these experiments show, the surface can stabilize these dynamic fluctuations at an antiphase domain boundary. Nevertheless, it is impossible to tell how deep into the bulk this surface-driven magnetic antiphase boundary penetrates through STM measurements.

In summary, we have shown that the surface gives us an opportunity to explore a balance between spin and structure in BaFe<sub>2</sub>As<sub>2</sub>. An antiphase structural domain wall between different regions of the reconstructed surface stabilizes an antiphase spin domain wall, resulting in an observed reduction in the symmetry from  $C_{2v}$  to  $C_2$ . There appears to be an enhanced spin-charge-lattice coupling at the surface. This is further supported by the recent measurements of the temperature dependence of the phonon modes at the surface of BaFe<sub>2</sub>As<sub>2</sub>, which display a gigantic enhancement in the spin/lattice coupling in the low temperature AFM orthorhombic phase.<sup>27</sup>

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COUPLED STRUCTURAL AND MAGNETIC ANTIPHASE . . .

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- PHYSICAL REVIEW B 86, 060512(R) (2012)
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