The discovery of high-temperature superconductivity in the Fe-based compounds has generated enormous excitement and activity in the scientific community [1, 2]. Not only is this a new class of materials exhibiting some form of unconventional superconductivity but at the first glance the behavior resembles that of the cuprates [3], raising the expectation that the Fe-based superconductors might offer an avenue to understand the inherent pairing mechanism responsible for superconductivity in both systems. The ground state of the parent compounds in the cuprates and Fe-based superconductors is antiferromagnetically (AFM) ordered and it appears that the magnetic ordering must be suppressed in order to achieve superconductivity. Both sets of materials exhibit a superconducting “dome” as a function of either hole or electron doping. However, as more data becomes available for the Fe-based compounds, it is becoming increasingly clear that the members of this family behave rather differently than the cuprates. The AFM ground state of the Fe-based parent compounds is metallic but Mott insulating for the cuprates. The small magnetic moments [4, 5] and the characteristic of electronic structure probed by photoemission measurements [6] indicate that the Fe bands are like an itinerant metal not localized as in the cuprates. While cuprates such as La$_2$−xSr$_x$CuO$_4$ undergo a structural transition [6], there is no evidence for the coupling between structure and AFM ordering. In Fe-based compounds, there is complex coupling between lattice and spin degrees of freedom: a structural transition from a high-temperature tetragonal (HTT) to a low-temperature orthorhombic (LTO) phase is always accompanied by a magnetic transition within a narrow temperature window. It is also known that the application of pressure can drive some of the parent compounds into the superconducting state without chemical doping [7]. Naively, the creation of a surface can be viewed as the application of a uniaxial pressure. In this Letter, we explore the effect on the coupling between spin, lattice and electrons in one of the parent compounds, BaFe$_2$As$_2$, caused by the creation of a surface.

Figure 1 shows the bulk and surface structure for the LTO phase of BaFe$_2$As$_2$. It consists of alternatively stacking Ba and Fe-As layers in bulk (Fig. 1a). The LTO phase (\(< 140\) K) is a collinear AFM ordering with the spin structure shown in Fig. 1a. We know from our previous study [8] that the ordered exposed surface of BaFe$_2$As$_2$ is the As plane and there is no measurable surface reconstruction. If the As atoms were buckled vertically, it would be detected by low energy electron diffraction (LEED) [9]. On the surface, the As atoms (blue) are in the first plane and the Fe atoms (red) in the second plane for the (1×1) (001) surface unit cell with the bulk orthorhombic structure (see Fig. 1b). As shown in Fig. 1b, all As atoms are expected to be identical in the surface unit cell exhibiting C$_{2v}$ symmetry. The mystery is that the high-resolution scanning tunnelling microscopy (STM) image measure of electronic density distribution, only reveals half of As atoms that should be present for a bulk truncated surface (Fig. 1c) [8]. This suggests that there are two inequivalent As sites on the surface not seen in bulk. According to our STM work reported in this Letter, it is plausible that the two inequivalent As sites result from the underneath spin structure through strong orbital-spin coupling. Given the fact that the Fe moments are aligned antiferromagnetically along the longer a axis and ferromagnetically along the shorter b axis [10], the relationship between the “visible” As atoms and the spin structure is illustrated in Figs. 1d (As2) and
FIG. 1: (a) Bulk lattice and spin structures of BaFe$_2$As$_2$ with Fe magnetic moments indicated by red arrows; (b) Schematic view of As terminated surface with underneath Fe layer; (c) As atoms seen by STM (solid circles), the empty circles represent “invisible” As atoms; (d-e) Possible relationship between “visible” (As2 in (d), As1 in (e)) and the spin structure of Fe atoms.

While we cannot determine which of these two configurations has the lowest energy, As1 and As2 are clearly surrounded by different spin environments.

For our STM investigation, we use high-quality BaFe$_2$As$_2$ single crystals that were grown using self-flux method \[12\]. The measurements were conducted on a home-built variable temperature STM with a tungsten tip. Single crystalline BaFe$_2$As$_2$ was firstly pre-cooled to 80 K in an ultra-high vacuum environment with basic pressure lower than $5 \times 10^{-11}$ Torr. After the in-situ cleavage, the sample was immediately inserted into the pre-cooled STM head. Fig. 2a displays a typical STM topographic image with atomic resolution. In addition to the (1\times1) surface structure, there are white spots either forming zigzag lines (small and clear) or randomly distributed (large and fuzzy). The large and fuzzy white spots can be manipulated by the tip, which are likely Ba atoms as discussed previously \[8\]. Similarly, there are dark spots, some of which are randomly distributed and the others are aligned with white spots in the zigzag lines. Importantly, there are always “dark” spots (see Figs. 2a, 2c) (impurities/defects/“invisible” As sites) at every corner, wherever the zigzag lines change the direction. Large-scale topographic images (not shown) prove that the zigzag lines form closed loops. Fig. 2b shows that the periodicity is the (1\times1) surface structure of orthorhombic bulk, except that we only see half of the As atoms in the surface plane. Through careful calibration including possible thermal drift-induced error, piezo scanner asymmetry and hysteresis by using Fourier-Transform(FT)-STM (see the inset of Fig. 2b), we are able to identify \(a\) and \(b\) directions of the orthorhombic unit cell which are labelled in Fig. 2b.

Given the scenario outlined above (strong orbital-spin coupling), we examine in detail the zigzag lines – domain walls. In solids, the origin of domains can be geometric, magnetic or electronic. Using the FT-STM, we find that all domains in the image have the same \(a\) and \(b\) directions so there is no rotation of the lattice when crossing a domain wall. This allows us to exclude the possibility that the domains are caused by a structural misorientations in the bulk. What we see are surface electronic domains, which can be verified by looking at the bias dependence. Fig. 2c shows the topography taken with a
high positive bias voltage (483 mV). Compared to that taken at 23 mV (Fig. 2a), the domain boundaries have switched from bright to dark. However, we do not see the switching of “visible/invisible” As atoms when changing polarity in the low bias region, as predict by the theory [11]. Because the atomic resolution is lost, whether the switching occurs at high bias is unknown. It should also be mentioned that Fig. 2a can be reproduced after changing the bias voltage from 483 mV back to 23 mV. Therefore the features seen in Fig. 2c are not due to the change of tip or sample condition. The domain boundaries seen by STM are primarily electronic in origin.

Figures 3a and 3b show two different domains with two boundaries in each. There are two boundaries with one along ~45° and another along ~-45° (Fig. 3a) or ~135° (Fig. 3b) with respect to a direction. As can be seen in either figure the change in the (1×1) domains, when crossing a boundary, is an inversion of dark to bright in As, i.e., there is a half electronic unit cell shift across the boundary lines as indicated by lines with arrows in Figs. 3a and 3b. Such an inversion would not occur if the boundary is created simply due to the crystal structural dislocation with half unit cell shift. In our picture, there is no structural change across this boundary and the boundary is actually a spin domain wall. While all the bright white spots residing on both boundaries have elliptical shape, a closer examination reveals that the white spots along the -45° direction are more rounded and the ones in 45° direction more elongated. If one examines the symmetry carefully it is clear that the domains exhibit $C_2$ symmetry. Rotating the image in Fig. 3b by 180° transforms the 135° boundary into a -45° boundary which is identical to the -45° boundary in Fig. 3a, as expected if the boundary direction is unchanged. If we further reflect the rotated image about the a axis, what was the -45° boundary becomes a 45° boundary, which does not look like the original 45° boundary shown in Fig. 3a. Thus, the boundary symmetry is $C_2$ not $C_{2v}$. This is consistent with the theoretical proposal that $C_2$ symmetry is induced by the magnetic ordering [10].

The line profile $Z(x)$ in Figs. 3c and 3d presents a quantitative comparison on the boundaries shown in Figs. 3a and 3b, respectively. While it is expected that $Z(x)$ oscillates with the same periodicity along both directions, the amplitude for the spots in 45° direction (red lines) is more than double compared to that along -45° direction (blue lines). This proves that there are two types of boundaries, reflecting the fact that, when spin configuration is included, the symmetry is reduced from $C_{2v}$ to $C_2$. Fig. 3e demonstrates how the spin structure changes across the boundary, assuming that the spin structure in Fig. 1d produces bright As atoms. All of our observations indicate that there is an electronic order at the surface that reflects coupling between orbitals and spins. Using this model, it is natural to explain the half electronic unit cell shift between adjacent domains by adopting a π phase shift of the spin order along both AFM a axis and FM b axis when crossing boundaries. The spots seen at the boundaries are enhanced local density of states due to the orbital overlap between two “visible” As atoms. As illustrated in Figs. 3f and 3g, the boundary along 45° direction results in brighter spots compared to that along the 135° direction, when taking into account of spin contribution. This is consistent with our experimental observation (Figs. 3c and 3d). The spin structure shown in Fig. 3e suggests that there is a spin flip across the surface boundary creating an anti-phase (Pi-phase) spin domain wall.

The puzzle is why the electronic topography seen with STM mirrors the spin structure, considering that the Fe layer looks like an itinerant metal. Recent theoretical [13, 21] and experimental studies [6, 22, 23] on the electronic structures of iron-based compounds suggest that orbital degree of freedom emerges in this multiband system with intimate coupling to lattice, charge and spin. It was proposed that the ferro-orbital Fe (3d$_{xz}$) order leads to the structural and magnetic phase transitions [13, 14]. As a result [16], electrical conduction is higher in the AFM a direction than that in the FM b direction as observed experimentally [22]. The recent laser angle-resolved photoemission spectroscopy and band calculations [6] indicate that the two Fermi surface pockets centered at Γ point (α1 and α2) have a predominant Fe 3d$_{xy}$ orbital component which is polarized by AFM order [18]. As argued in Ref. [24], most of the detected electronic contribution by STM comes from the Γ centered α1 and α2 pockets. In such circumstances, it becomes obvious that the STM image includes not only the local electronic topography but also information about magnetic structure.

The first-principles calculation of the surface predicts two different As surface atoms created by the imbalance in chemical valances due to missing Ba atoms [11]. If this were the case, one would not expect the difference (intensity) between two boundaries shown in Fig. 3. Our understanding is that the calculation did not take into account the impact of magnetic ordering to the electronic structure. However, there is no doubt that the surface, especially the As-terminated surface, of BaFe$_2$As$_2$ is quite different from the bulk. The key is how this difference is reflected in the physical properties at or near the surface, and how the surface may affect the bulk. We have focused on the As-terminated (1×1) structure because it corresponds to the bulk orthorhombic phase. But a (1×2) (tetragonal notation) surface reconstruction [26, 31] has also been observed and associated with the tetragonal bulk structure exhibiting $C_{2v}$ symmetry. In these materials, these two structures seem to coexist at the surface [28, 30] through out the phase diagram of Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ [25]. Naively, this would indicate that there are patches of tetragonal surface structure coexisting with orthorhombic phase. What
is needed is a measurement of orthorhombicity as a function of doping and temperature. It may well be that the (1×1) surface structure loses its orthorhombicity as a function of temperature or doping, eventually turning into a $C(\sqrt{2} \times \sqrt{2})R45^\circ$ surface reconstruction of a tetragonal bulk. We already know that the measured superconducting gap using STM is well behaved as a function of $x$ in both surface structures 

FIG. 3: (a-b): Two 56 Å × 56 Å low-bias constant-current STM topographies ($V_{bias} = 23$ mV, $I_{tip} = 200$ pA) showing boundary structures at 80 K. The arrows with dash lines in (a-b) indicate the half electronic unit cell shift in $a$ and $b$ direction respectively. The black rectangular box in (b) shows the size of bright spot on boundary: length/width = 3/2 measured from this image; (c-d): the line profiles for red and blue line in (a) and (b) respectively; (e) A model for domain walls. Here the blue solid circles denote the “visible” As atoms in the LTO surface unit cell, and the red arrows indicate the magnetic moments of Fe atoms; Solid yellow ellipses represent spins and their orientations. Positive and negative signs most close to white spot (the overlapped two As atoms) represent impurities/defects/“invisible” As sites. (f-g): Two types of boundaries breaking $C_{2v}$ to $C_2$ symmetry. The light-blue clouds denote the polarized Fe 3d$_{xz}$ orbitals. Red arrows represent spins and their orientations. Positive and negative signs in small circles indicate the phase of orientation. Note that each ellipse along 45$^\circ$ direction (g) includes 4 negative signs most close to white spot (the overlapped two As atoms) by the boundary; while each along 135$^\circ$ boundary direction includes 4 positive signs (f).

In summary, the imaged domains and domain walls seen by STM are shown to be primarily electronic in origin with strong electron/spin (orbital-spin) coupling, which is clearly reflected by the $C_2$ symmetry. The intimate coupling between the spin and electron orbitals at the surface enable us to observe the electronic structure that mirrors the bulk spin structure. This offers great opportunities for the investigation on the orbital-spin coupling. It also opens a new chapter in the long-standing issues of interplay between superconductivity and magnetism which may only be present at the surfaces (or under pressure) of this new class of superconductors.

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