Low-energy, planar magnetic defects in BaFe$_2$As$_2$: nanotwins, twins, antiphase and domain boundaries

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In BaFe$_2$As$_2$, structural and magnetic planar defects begin to proliferate below the structural phase transition, affecting descriptions of magnetism and superconductivity. We study using density-functional theory the stability and magnetic properties of competing antiphase and domain boundaries, twins and isolated nanotwins (twin nuclei) - spin excitations proposed and/or observed. These nanoscale defects have very low surface energy (22-210 mJm$^{-2}$), with twins favorable to the mesoscale. Defects exhibit smaller moments confined near their boundaries – making a uniform-moment picture inappropriate for long-range magnetic order in real samples. Nanotwins explain features in measured pair distribution functions, so should be considered when analyzing scattering data. All these defects can be weakly mobile and/or have fluctuations that lower assessed “ordered” moments from longer spatial and/or time averaging, and should be considered directly.

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I. INTRODUCTION

Fe-based superconductors (FeSCs) provide another avenue to understand unconventional superconductivity.\textsuperscript{1-5} Due to its ease of synthesis, BaFe$_2$As$_2$ is a prototype for these systems, where its low-temperature (T < 140 K) ground state is a striped, antiferromagnetic (AFM) orthorhombic (Fmmm) structure,\textsuperscript{6} often called a spin-density wave (SDW), and which is reproduced in Density Functional Theory (DFT) calculations.\textsuperscript{7} At Neél $T_N$ (140 K), both a magnetic and structural transition occurs to a tetragonal (I4/mmm) paramagnet.\textsuperscript{8} By doping with a transition-metal on the Fe-site or others on Ba- and As-sites, superconductivity (SC) can be achieved, and similarly with pressure.\textsuperscript{9-11}

There are strong connections between the magnetism and SC. Dopant weakens the magnetic state and Cooper pairing is, perhaps, driven by increased magnetic fluctuations out of the ground state.\textsuperscript{12,13} DFT has proven successful in modeling the geometry, magnetic ordering, and electronic structure of FeSCs. The magnetic ground states of LaFeAsO, BaFe$_2$As$_2$, NaFeAs, and FeTe are all correctly predicted.\textsuperscript{7,14-16} Fermi-surface (FS) nesting is apparent from DFT calculations and agrees with angle-resolved photoemission (ARPES), suggesting an itinerant nature.\textsuperscript{17-19} and which is supported from the spin-wave dispersion.\textsuperscript{20,21} Furthermore, DFT explains quantitatively effects of doping on FS nesting, and why Cu doping behaves differently than Co and Ni.\textsuperscript{22} K$_x$Fe$_2$Se$_2$ (isostructural to BaFe$_2$As$_2$) does not have the hole pockets needed for FS nesting,\textsuperscript{23} as DFT finds.\textsuperscript{24}

DFT results for BaFe$_2$As$_2$ show a strong coupling between the structure and magnetism.\textsuperscript{17,20} Planar defects, thus, have been proposed to explain key features in magnetic and transport properties of FeSCs near/below the structural transition. Mazin and Johannes\textsuperscript{25} suggested a model in which low-energy magnetic anti-phase (APBs) and 90° domain (DBs) boundaries proliferate (Fig. 1), which have yet to be tested. So, are structural and magnetic planar defects energetically favorable and what are their properties? To answer, we use DFT to model potentially operative magnetic (structural-induced) defects, both isolated and extended, and explore their stability and properties by varying the structural parameters.

II. BACKGROUND

Defects can be very important in realistic materials, like BaFe$_2$As$_2$. Above $T_N$, the paramagnetic state may be realized by mobile APBs and DBs; below $T_N$, with interlayer coherence, APBs become pinned and DBs thermodynamically inaccessible, possibly explaining sensitivity to interlayer elements, large magneto-resistance, features in the differential resistivity ($dρ/dT$), and invariance of resistivity anisotropy. With orthorhombic distortions ($a > b$), both structural and concomitant magnetic twins (Fig. 2) are observed in BaFe$_2$As$_2$ along (110) with 100-400 nm\textsuperscript{27} up to 10-50 μm\textsuperscript{28} between boundaries. With stress, samples detwin, but twins return upon its removal,\textsuperscript{29} as in YBa$_2$Cu$_3$O$_{7-δ}$,\textsuperscript{30} (110) twins terminate on (110) twins. Twins cause anisotropic scattering near AFM wavevectors, giving 2-dimensional spin fluctuations. Twins also create stripes of increased diamagnetic response,\textsuperscript{31} and nucleate SC at their boundaries.\textsuperscript{32} Recently, Niedziela et al.\textsuperscript{33} found by Rietveld analysis a bigger orthorhombic ratio (O = ($a - b$)/($a + b$)) for local structural fits (O = 1.38%) than global fits (O = 0.78%); they proposed a high density of nano-twins (Fig. 2) account for this discrepancy by its better match to measured pair distribution functions (PDF). We show that displacements at the nano-twin boundary affect spin...
alignment, reducing the average “ordered” moment.

For completeness, we note that, while DFT supports the observed SDW for the parent compound, the Fe moment \((1.6 − 1.9 \, \mu_B)^7,^{34}\) is twice that assessed for the average ordered moment from neutron diffraction \((0.8 − 1.04 \, \mu_B)^{35−37}\). In fact, various experiments assess very different Fe moments. Core-electron spectroscopy\(^{38}\) finds 2.1 \(\mu_B\), like DFT, while \(^{57}\)Fe Mössbauer\(^{39}\) and nuclear magnetic resonance\(^{39}\) find 0.81 \(\mu_B\), as in diffraction assessments. For Fe-based magnets such a large discrepancy between ordered moments from theory and experiment is unusual. Spin-orbit and hybridization (controlled by Fe/As planar spacing) in a DFT+U model explained the small in-plane moments in Fe-pnictides.\(^{40}\) Yet, our DFT moments are reduced \(\sim 10\%\) from spin-orbit, but 50-100\% by slightly reduced Fe-As spacing. DFT predicts correct moments at short times \((\sim 10^{-15} \, s)\) necessary to yield lattice constants that agree with experiment.\(^{26}\) Dynamical mean field theory (DMFT) explains the discrepancy from DFT as a result of dynamical fluctuations at the Fe sites that reduce the observed moment over longer time scales \((\sim 10^{-8} \, s)\),\(^{41}\) and reproduces the trends in reduced Fe moments and renormalized mass across various FeSCs.\(^{42}\) DMFT finds FeSCs are correlated due to intra-atomic exchange from Hund’s coupling \(J\) \((0.3-0.6 \, eV)\)\(^{43−46}\) (which reduces the coherence temperature for Fermi liquid behavior\(^{45}\)), not from especially large \(U\) \((2.8-5.2 \, eV\), as derived from a five band constrained Random Phase Approximation)\(^{44,46−48}\) or proximity to a Mott insulating state. Below the coherence temperature, high electron mobility results in moment screening \((\sim 10^{-9} \, s)\). Notably, this scenario does not consider spatial fluctuations, defects, nor their effect on magnetism near/below the phase transition, as explored in the present work.

### III. METHODS: DEFECTS AND DFT

We use DFT to simulate various magnetic planar defects, i.e., two types of APBs, a 90° DB, twin boundaries, and our modified nano-twin, which are all low-energy excitations of the SDW. Figure 1a and 1b shows two APB boundaries in the Fe-plane – parallel to the \(bc\)- or \(ac\)-planes – and Fig. 1c shows a locally unstrained 90° DB. Figure 2a shows a typical example of an ideal twin. A modified nanotwin with 2-dimensional structural distortion (consistent with that suggested by Niedźwiela et al.\(^{32}\)) is shown in Fig. 2b with a series of static displacements along \(a\)- and \(b\)-axis in the supercell. The undisplaced nanotwin with 1-layer of Fe separating defect planes is really a magnetic stacking fault (SF); a nanotwin supercell has very different boundary conditions than a twin, with different far neighbors and distances between defect pairs; indeed, “ideal twin” supercells formed with 1-layer separation between defect planes (a high density of SFs) has local environments like the nanotwin, except that twin has symmetric relaxations governed by the supercell periodicity, whereas the nanotwin has asymmetric, localized distortions to match the PDF. While we show the defect energies are similar, a nanotwin, due to its boundary condition and supercell, may be considered a fluctuating twin nuclei, which can have low-spin Fe-sites unavailable in the ideal twin supercell.

For nondefected (parent) and defected cells we calculate energy per atom and the associated magnetic moments (bulk is 1.6 \(\mu_B\)). From this we derive the planar defect energy, \(\gamma\), defined as \(\gamma = (E_{\text{def}} - E_0) / d / V\), where \(E_{\text{def}}\) and \(E_0\) are the total energy per atom of the defected and nondefected cell, respectively. \(d\) is the distance between defect planes and \(V\) is the volume per atom. While the energy per atom is helpful, \(\gamma\) is the appropriate comparison for cost of creating the defect interface and its dependence on defect density and defect volume. Note that 2 defect boundaries are created for twins, hence, 2\(\gamma\) is appropriate defect energy.

To do this, we use VASP\(^{49}\) with plane-wave pseudopo-
tential projected augmented wave (PAW) basis \(^{50}\) with an energy cut-off of 380–420 eV. A Monkhorst-pack Brillouin zone integration with a \(16^3\) \(k\)-mesh is used for the SDW \((\text{\textit{F}}\text{\textit{m}}\text{\textit{m}}\text{\textit{m}})\) structure. Smaller \(k\)-meshes are used for supercells depending on the length coverage along each axis.

For APBs, we constructed doubled \((2\times1\times1)\), quadrupled, and octupled supercells to examine excitations, denoted by 2-APB, 4-APB and 8-APB, respectively (Fig. 3). For APBs (Figs. 1a,b), we use measured lattice parameters \(^6\) \((a=5.6146, \ b=5.5742 \text{ and } c=12.9453 \text{ Å})\). For a 90º DB, we set \(\bar{a} = \bar{b} = (a + b)/2 = 5.5944 \text{ Å}\) to reduce local strain effects, and construct supercells similar to the APBs, denoted as 2-DB, 4-DB, and 8-DB. Twin \((4[1+n]\times2\times1)\) supercells \((n=0, 1, \ldots)\) are denoted by \((3 + 4n)\text{-N}\) Fe-layers between defect planes, and have \(4(1 + n)\) unit cells along \(a\) and \(8(1 + n)\times10\) atoms/cell. Nanotwin supercells are denoted 3-N, 5-N, 9-N, and 13-N for Fe-layers between isolated nanotwin pairs; the supercells with the static displacements suggested by Niedziela \textit{et al.} are more complex because the local distortions must be compensated within the cell (Fig. 2b).

**IV. RESULTS**

The energies and moments for APB and DB defects relative to the non-magnetic (NM) state are shown in Fig. 3 (top), and compared to the AFM ground state (SDW). In all cases, Fe moments have two behaviors: a high-spin state (HS in Fig. 1) at sites away from boundaries and a low-spin state (LS in Fig. 1) at/around boundaries. For APB\((bc)\), the LS moment falls substantially to \(0.8 \mu_B\) from \(1.6 \mu_B\), similar to that found by Yin \textit{et al.}\(^{51}\) While for APB\((ac)\), the LS moment decreases only to \(1.54 \mu_B\). The two spin states depend on local magnetic environments (inset Fig. 3). Moments do not vary much with the size of the supercells, but these two structures energetically compete with the ground state SDW \((\leq 9 \text{ meV/atom})\). For 90º DB (Fig. 1c), the HS state has a higher moment of \(1.7 \mu_B\) due to global strain from changed lattice parameters. The LS moment decreases slightly to \(1.57 \mu_B\) near the boundary. This defect requires within 2 \text{meV/atom} excess energy to form compared to the SDW. It is energetically competing with the APB\((ac)\). Both defects are then expected to be present at the same temperature. The local environment does not play a significant role, suggesting simple models such as counting the number of aligned neighbors is not sufficient to characterize the moments.

The energy and moments for twins are shown in Fig. 4a. Interestingly, an Fe-atom in a twin has three spin states depending on the local environment. Fe-atoms at the boundary remain in a medium-spin state (MS in Fig. 2a). A LS state occurs on Fe-sites adjacent to the boundary (Fig. 2a). These Fe-sites have the same nearest-neighbor environment as the bulk HS states but differ in the farther neighbors. These defects can form at a few \text{meV/atom}, albeit \(\gamma\) is more critical, see below.

The nanotwin energies and moments versus distortion along \(a-\) and \(b-\)axis (in Å) are shown in Fig. 4(b,c). Similar to twins, there are three Fe spin states: a HS bulk \((1.6 \mu_B)\), a MS \((1.42 \mu_B)\) at the boundary, and a LS \((0.8-1.0 \mu_B)\) in the vicinity of the distorted side of the boundary. The structural perturbations show a stronger effect on the LS moments near defect boundaries, decreasing to as low as \(0.8 \mu_B\). Isolated (fluctuating) nanotwins are equally competitive to form as dense twins but with much reduced moments. Energies are affected mostly by the changed magnetic configurations and very little by spatial distortions. So, magnetic defects drive the short-range structural distortion (not the other way
TABLE I. γ (2γ for twins) for various planar defects (in mJ/m²). Energies (meV/atom) are relative to SDW. γ_{twin} is dominated by d increasing faster than the decrease in (E_{def} - E_0), unlike for APBs or DBs.

| defect type       | supercell | energy (2)γ | γ (mJ/m²) | ∆E (meV/atom) |
|-------------------|-----------|-------------|-----------|---------------|
| APB (bc-plane)    | 2-APB     | 26.5        | 118       |               |
|                   | 4-APB     | 15.0        | 133       |               |
|                   | 8-APB     | 9.0         | 160       |               |
| APB (ac-plane)    | 2-APB     | 5.0         | 22        |               |
|                   | 4-APB     | 2.5         | 22        |               |
|                   | 8-APB     | 2.0         | 35        |               |
| 90° DB            | 2-DB      | 5.0         | 22        |               |
|                   | 4-DB      | 2.7         | 24        |               |
|                   | 8-DB      | 1.3         | 22        |               |
| “twin” (ideal)    | 0-N       | 18.3        | 57        |               |
| “twin” (relaxed)  | 1-N       | 9.9         | 62        |               |
| “twin” (ideal)    | 1-N       | 11.9        | 74        |               |
|                   | 3-N       | 8.2         | 102       |               |
|                   | 7-N       | 6.6         | 165       |               |
| twin (ideal)      | 11-N      | 6.1         | 228       |               |
|                   | 15-N      | 5.0 (max)   | 252       |               |
|                   | 19-N      | 3.7         | 231       |               |
|                   | 23-N      | 3.0         | 222       |               |
|                   | 27-N      | 2.4         | 210       |               |
| nanotwin (undistorted) | 3-N | 9.2 | 86 | |
| (undistorted)     | 5-N       | 6.4         | 80        |               |
|                   | 9-N       | 4.1         | 77        |               |
|                   | 13-N      | 2.5         | 63        |               |
| NM bulk           | n/a       | 28.0        | n/a       |               |

V. DISCUSSION

Twin separation d is also affected by stress. Equilibrium is typically reached when the applied stress is ~ 2γ_{twin}d, which is, however, exceedingly small for isolated twins in BaFe₂As₂. In real samples twins appear in 90° oriented pairs, where (110) twins terminate on (110) twins; this configuration is stabilized by lattice strain arising from disclinations, where the strain is reduced at the cost of increased d. With stress (estimated roughly from a set of disclinations, and orders of magnitude larger than 2γ_{twin}d), samples detwin, but twins would return upon its removal.

Twins cause anisotropic scattering near AFM wavevectors, giving 2-dimensional spin fluctuations, and create stripes of increased diamagnetic response. While twin separation depends on local defects and stress, it is expected to get a peak in the magnetic susceptibility χ(q) at q = 2π/d, where d is the average twin-twin separation where 2γ saturates. The direction of q is perpendicular to twin boundaries (i.e., 45° to reciprocal-space k⊥- and k∥-axes, where x (y) is along a- (b-) axis). While the twins dictate the magnetic correlation length, we suggest that small, low-energy excitation can further depress average moments by spatial and temporal averaging, beyond those due to dynamic fluctuations.
Figure 6. (Color online) $d$-orbital and spin-projected DOS of an undistorted nanotwin on HS (black, heavy line) and LS (red, light line) Fe-sites, with majority (minority) DOS plotted on positive (negative) vertical axis. Fermi energy is indicated by vertical dashed line. $x$, $y$, and $z$ directions correspond to $a$, $b$, and $c$ respectively.

Nanotwins (Fig. 2b) with no local distortion are like an isolated, ideal defect pair, not a dense set of twins. To understand the effect of short-ranged structural distortion, we have studied a 1-N ideal twin with(out) relaxation in $ab$-plane for only those atoms near the boundary, more localized than in the nanotwin supercell. The planar defect energy with(out) relaxation is $62$ ($74$) $mJ/m^2$. Relaxations along $a$- and $b$-axis lie within $0.9\%$ of ideal, close to the best fit to measured PDF, so the twin and nanotwin are very similar in energy and local structure. Unlike for ideal twins, the nanotwin surface energy decreases to its limiting value as the nanotwin-nanotwin distance grows (Table I), and it is much lower in energy than extended twins. Thus, a nanotwin may be considered a fluctuating twin nuclei, which has many more LS sites (Fig. 4) not available in a twin supercell, with moments as low as $0.8 \mu_B$ near the defect, similarly to the assessed values in BaFe$_2$As$_2$. Our calculations support Niedziela et al.’s suggestion that nanotwins constitute an important fluctuating excitation in BaFe$_2$As$_2$.

Because the local magnetic configurations play the key role in determining the spin states of Fe, we calculated the site- and $l$-projected density of states (DOS) to understand the electronic-structure origin. Figure 6 shows the Fe $d$-projected DOS for HS and LS states. For the bulk (HS) states, the major contribution at Fermi energy $E_F$ arises from Fe $d_{xz}$ and $d_{yz}$, also evidenced from ARPES. All the other orbital components exhibit a pseudo-gap near $E_F$. For LS-Fe compared to HS-Fe, all the projected DOS are shifted towards $E_F$. The most pronounced effect occurs for $d_{xz}$ and $d_{3z^2-r^2}$ character, where majority states for LS fall into a pseudogap for $d_{xy}$, but are peaked for $d_{3z^2-r^2}$. Although the change of these orbital states is dominated by in-plane Fe-spin configurations, small contributions also arise from the hybridization with As $p_x$ and $p_y$ orbitals (out of the Fe-plane), eventually altering the FS. The large difference in the near $E_F$ (majority) DOS between the HS and LS state points to the orbital dependent electronic origin for quenched moments.

VI. SUMMARY

In summary, we studied competing low-energy, magnetic planar defects in BaFe$_2$As$_2$. The favorable defects are APB(ac), 90°DB, and nanotwins, but twins (which are observed) are favorable through the mesoscale. The most pronounced reductions in Fe-moment are near the boundaries of APBs(bc) and nanotwins. We find that isolated closely-spaced twins (twin nuclei) are energetically favorable and correspond to a recently proposed nanotwin suggested to match the pair distribution function from scattering experiment. Nanotwins are energetically insensitive to microscopic displacements near the boundary, in contrast to sensitivity to the As $z$ coordinate. APBs along $bc$-planes and $ac$-planes are not equally favorable, an anisotropy not anticipated in the Mazin and Johannes model. These defects can reduce the Fe moment from spatial averaging, an environmental dependence which is not included in DMFT. Assessing these defects and their dynamics can affect magnetism, which can be evaluated via Monte Carlo simulations, and which are planned.

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