Direct imaging of the structural domains in iron pnictides $AFe_2As_2$ ($A=$ Ca, Sr, Ba)

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The parent compounds of recently discovered iron-arsenide superconductors, $AFe_2As_2$ with alkaline earth $A=$Ca, Sr, Ba, undergo simultaneous structural and magnetic phase transitions at a temperature $T_{SM}$. Using a combination of polarized light microscopy and spatially resolved high-energy synchrotron X-ray diffraction we show that the orthorhombic distortion leads to the formation of 45°-type structural domains in all parent compounds. Domains penetrate through the sample thickness in the c-direction and are not affected by crystal defects such as growth terraces. The domains form regular stripe patterns in the plane with a characteristic dimension of 10 to 50 $\mu$m. The direction of the stripes is fixed with respect to the tetragonal (100) and (010) directions but can change by 90° on thermal cycling through the transition. This domain pattern may have profound implications for intrinsic disorder and anisotropy of iron arsenides.

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Until last spring, there was only one class of high transition temperature (high-$T_c$) superconductors - the cuprates [1]. Discovery of superconductivity [2] with $T_c$ currently as high as 56 K [3, 4] in iron arsenide compounds RFeAs(O,F) (abbreviated as R-1111 with $R=$ rare earth), has fueled hopes that a new chemical and physical perspective can shed light on the nature of the high-$T_c$ superconductivity.

Comparison of the cuprates and iron arsenides indeed reveals some similarities. Both classes of compounds have well defined layered structures. Within the layers the transition metals Cu and Fe are arranged on a square lattice and their orbitals make the main contribution to the electronic density of states at the Fermi level [5]. However, the electronic structures of the parent compounds are notably different: the cuprates are magnetically ordered Mott insulators, whereas in the iron arsenides the magnetic transition occurs in the metallic state below $T_M$ and is accompanied by a structural distortion below $T_S$. In both cases the superconductivity appears on doping of the parent compounds, suppressing the magnetic order. The character of the magnetic order is notably different as well. In the cuprates, the magnetism is characterized by a simple antiferromagnetic arrangement of spins in the tetragonal planes [6] and is very anisotropic (close to two-dimensional) [7]. In the iron arsenides, the spins on the iron sites form stripe order in the basal planes, with ferromagnetic spin alignment within the stripes and antiferromagnetic order between stripes both in the plane and perpendicular to the plane [8].

The stripe type of magnetic order is incompatible with the tetragonal symmetry of the crystal. Its formation becomes possible because the crystal undergoes a tetragonal-to-orthorhombic structural transition. This transition precedes magnetic ordering in the parent R-1111 compounds [8] ($T_S > T_M$), whereas both transitions occur simultaneously in $AFe_2As_2$ with $T_S=T_M=T_{SM}$ [3, 10, 11]. It is not yet clear whether magnetism or structural distortion is the driving force behind the transition.

In this paper we show that the orthorhombic structural phase transition leads to the formation of a pattern of structural twin domains. These domains are thin plates with the extended surface parallel to the tetragonal c-axis and they span the entire crystal. We determined that the domains are of the 45° type, with faces corresponding to the (110) and (110) planes in the orthorhombic notation, as expected for the distortion along the orthorhombic a-axis. This is similar to the structural domains formed during growth in the orthorhombic phase of YBa$_2$Cu$_3$O$_{7-\delta}$ [12, 13].

Single crystals of BaFe$_2$As$_2$ and of SrFe$_2$As$_2$ were grown from FeAs flux from a starting load of metallic Ba (or Sr) and FeAs, as described in detail elsewhere [14, 15]. Crystals were thick platelets with sizes as big as 12×8×1 mm$^3$ and large faces corresponding to the tetragonal (001) plane. For polarized optical imaging, the samples were cleaved with a razor blade into rectangular shaped platelets of typically (2-5)×(2-5)×(0.1-0.5) mm$^3$. Single crystals of CaFe$_2$As$_2$ were grown from Sn flux as described elsewhere [16]. The crystals were the same size as crystals of Ba and Sr compounds, but due to both very clean natural growth faces corresponding to (001) and (011) crystallographic planes and difficulty to form a good cleave surface they were used as-grown in the study.

X-ray diffraction measurements were performed to characterize the quality of the single crystals. The absorption length of the high energy (99.6 keV) x-rays from the synchrotron source (beamline 6ID-D in the MUCAT sector at the Advanced Photon Source, Argonne) was about 1.5 mm, which allowed the study of the entire sample volume. With the use of a slit system, the
A regular pattern of domain boundaries oriented in two orthogonal directions is clearly visible in all cases. The contrast of the pattern is highest in the $A=\text{Ca}$ compound, consistent with the largest orthorhombic distortion, equal to 0.67% for $A=\text{Ca}$, 0.55% for $A=\text{Sr}$ and 0.36% for $A=\text{Ba}$. A typical domain width is about 10 $\mu$m. Over large areas, sometimes covering the whole surface of the crystal, domains form stacks of parallel plates. In some areas perpendicular domain sets inter-penetrate. A supplementary material real-time movie shows the evolution of the domain walls in a warming-cooling cycle [24].

The process of domain formation shows pronounced hysteresis with temperature, and the direction of the dominant lamellae pattern can change by 90 degrees from one run through $T_{SM}$ to another. This is notably different to the case of YBCO, where the domains are “pinned” by the defects even after a process of deoxidation-reoxidation [17].

The lamellae are not affected by the macroscopic crystal defects. As can be seen in the bottom-right corner in the top panel in the Fig. 1 for the Ca compound, the crystal under study has terraces on the sample surface (running at an angle to the figure frame and shown in inset at room temperature), with a step size of the order of 20 $\mu$m along the $c$-axis. On crossing the terraces, the lamellae lines perfectly match at different levels. This clearly shows that the domain walls are extended along the $c$-axis, as expected for a tetragonal-to-orthorhombic distortion. We should emphasize that the domain boundaries are very smooth and regular, revealing the very high forming stepwise translations of the sample perpendicular to the incident beam. The entire sample was scanned in both directions and no impurities, misoriented grains or diffuse signals from disordered material were detected. Therefore, from the x-ray study we conclude that the entire sample is a high-quality single crystal.
FIG. 2: (Color online) High resolution optical image of pure BaFe$_2$As$_2$ above (left) and below (right) the temperature of the coupled structural/magnetic transition, $T_{SM}=135$ K. A pattern of domain walls is formed below $T_{SM}$ due to formation of twin boundaries (top row). Second row of panels shows schematics of the displacements of atoms in the tetragonal lattice (above $T_{SM}$) during structural transition, leading to orthorhombic distortion and formation of domain walls. In the orthorhombic phase the unit cell of the lattice doubles in size in the $a-b$ plane, new unitary vectors $a_O$ and $b_O$ become of different length ($a_O > b_O$), and rotate by approximately 45 degrees. The third row shows sketches of the expected transformation of the X-ray diffraction pattern during domain formation. The bottom row shows actual X-ray data and zooms of (200) and (220) reflections (insets).
of (220) spots shows that the domains extend along c-crystalllographic direction through the whole sample thickness. This shows that domains are true bulk phenomenon.

A recent transmission electron microscopy (TEM) study of domain boundaries in 122 parent compounds found domains which were notably smaller in size than in our study, typically 100 to 400 nm \cite{18}. Even smaller, about 40 nm, domains were reported for the Ca compound above $T_{SM}$. In our study we can not resolve the domains of this size, however, in big sample areas where domains themselves were not spatially resolved, passing through $T_{SM}$ clearly changed the brightness of the image. We do not see any change in the contrast of high quality single-domain areas of Ca-122 samples grown from Sn flux on warming above $T_{SM}$. Since the crystals used in the TEM study were grown from self-flux, which for the Ca compound are of lower quality \cite{19}, this difference can be caused by sample preparation technique. Indirectly, this is supported by the comparison of the sharpness of the resistivity jump at $T_{SM}$, measured in our sample \cite{20} and Ref. \cite{18}. On the other hand sample milling required for TEM can lead to notable stress in the sample, which can be another cause of the difference.

The anisotropy of the electronic structure is believed to be an important parameter for understanding superconductivity in iron arsenides \cite{21, 22}. Measurements of the anisotropy of electrical resistivity in parent compounds found systematically small values of anisotropy $\rho_{c}$, both above and below $T_{SM}$ and the slight anisotropy decreases on passing the transition. Since domains penetrate the whole sample along the $c$-axis, it is reasonable to assume that they will affect less the current flow along the $c$-axis, and thus $\rho_{c}$ measurements. Measurements of in-plane resistivity, $\rho_{a}$, on the other hand, should represent an average of $\rho_{a}$ and $\rho_{c}$, similar to twinned crystals of YBCO \cite{23}. In addition, the value of in-plane resistivity can be notably increased by boundary scattering. Since rapid decrease of resistivity is observed in the Sr and Ba 122 parent compounds below $T_{SM}$, this suggests that domains are rather transparent for electrons.

In conclusion, the parent compounds of iron arsenic superconductors reveal clear pattern of twin domains below the temperature of tetragonal to orthorhombic transition. The domain walls run at approximately 45° to the orthorhombic lattice and span the whole sample along $c$-axis direction.

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