Room-Temperature Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ is not Tetragonal: Direct Observation of Magnetoelastic Interactions in Pnictide Superconductors

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Using a local, real-space probe, aberration-corrected scanning transmission electron microscopy (STEM), we discovered room-temperature distortions in the crystal structure of the parent BaFe$_2$As$_2$ and superconducting Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ compounds never before reported. Combining these results with extended x-ray absorption fine structure (EXAFS) for BaFe$_2$As$_2$ suggests that the Fe$_2$As$_2$ substructure is quite rigid but the Ba is weakly bound and displaced within the Fe$_2$As$_2$ substructure. These distortions indicate that the C$_4$ tetragonal symmetry is broken at room temperature in unstrained crystals, lowering the symmetry to orthorhombic (I$2$mm), and that all of the crystals are twinned. The size of the twin domains is small, on the order of a few nanometers, and the variation of the domain size with $x$ correlates with the magnitude of the dynamic Fe moment as gleaned from electron energy loss spectroscopy (EELS) data. While several experiments have so far shown indirect indication of a nematic state, these results represent a remarkable direct observation of the effects of magneto elastic coupling and suggest they likely play a role in the superconducting mechanism.

Understanding the microscopic origin of superconductivity in the iron-based superconductors requires an accurate knowledge of the crystal structure, which is the starting point for developing a theoretical framework. BaFe$_2$As$_2$-based superconductors have been heavily studied both experimentally and theoretically, in large part due to the ability to grow large single crystals that are macroscopically homogeneous. The crystallographic basis of these experiments is derived from diffraction-crystals that are macroscopically homogeneous. The crystallo-

The present work demonstrates that the well-studied “tetragonal”-to-orthorhombic transition, occurring below 140 K in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ for $x \leq 0.055$, is actually a transition from one orthorhombic phase (I$2$mm) to another (Fmmm); the C$_4$ symmetry is already broken at room temperature. The interaction between lattice and spin (or orbital) degrees of freedom results in orthorhombic crystal symmetry at room temperature, and the single crystals are composed of nanometer-size twin domains. This result is only evident by observing the crystal in real space and with sub-Ångstrom resolution, because the material “looks” tetragonal on larger length scales due to averaging over the two types of domains. All structural measurements indeed average over some characteristic volume with length scale $L_v$. If there is variation on a much shorter length scale it will be averaged out. For example, if a slightly orthorhombic crystal is highly twinned on a scale significantly shorter than $L_v$, the true symmetry can be resolved. Aberration-corrected STEM yields real-space images of the positions of atoms or ion-columns in a solid using an electron probe smaller than an atom. In a solid, the electron probe channels down the atomic columns in the direction perpendicular to the plane of the sample, probing a thickness of ~10 nm. However, in the plane of the sample, $L_o$ is on the order of the atom size, much smaller than the characteristic length

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DOI: 10.1002/adma.201404079
of other structural techniques based on x-ray, neutrons, visible light, ultrasound, etc.\cite{12,13}

Tracking the evolution of these structural domains with doping yields a direct and surprising representation of the interplay between spin and lattice degrees of freedom. The domain sizes shrink as the local Fe magnetic moment decreases at low doping concentrations and grow again as the local moment increases around optimal doping due to spin fluctuations beneficial to superconductivity.

Figure 1a shows a typical high angle dark field (HAADF) image in [001] projection of BaFe$_2$As$_2$, which exhibits the usual Z contrast, and from which the atomic column positions are derived by calculating the position of the center of mass for the atomic columns’ intensity, through an iterative algorithm.\cite{14} In Figure 1a, the white spots are columns of alternating Ba and As atoms (here the relative $x,y$ displacements of Ba and As are not determined), while the gray spots represent the positions of Fe atoms. A visualization of the lattice distortion is obtained by plotting the distances between Ba(As) columns and adjacent Fe columns within sets of alternating (100) planes, as shown in Figure 1b–d in the form of surface and line plots. The line plots in Figure 1d are obtained by averaging the surface plots along the [010] for the two sets of planes, (100)$\alpha$ and (100)$\beta$, respectively. Figure 1a shows a domain in which the distance between Ba(As) columns and Fe columns are modulated in one direction, which we refer to as $<100>$, but not in the orthogonal $<010>$ direction. The observed modulation gives rise to crests and valleys in the surface plot. d) Plot of the same Ba(As)–Fe distances for the (100)$\alpha$ planes, now averaged in the $<010>$ direction (blue). The red data points in the same plot are the distance between Ba(As) and Fe for the sets of planes labeled (100)$\beta$ in (b), also averaged in the $<010>$ direction. In the (100)$\beta$ planes the distance between columns has the same magnitude than in the (100)$\alpha$ planes but is shifted with respect to the latter by ½ unit cell.

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\textbf{Figure 1.} Structural distortion observed in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$: a) plane-view image of undoped BaFe$_2$As$_2$. Similar images were used for the doped compositions. b) Schematic model of the lattice distortions, consisting in a shift of the Fe (blue dots) sublattice with respect to the Ba (orange dots) sublattice in the $<100>$ direction. The black dashed circles indicate the positions where the Ba(As) columns would be in the tetragonal structure. The As–Ba displacement could not be determined. c) Surface plot of the distance between Ba(As) and Fe columns in one set of (100) planes labeled $\alpha$ in (b). Within this set of planes (perpendicular to the plane of the drawing) the distance between Ba(As) and Fe columns alternates between small and large values as function of position along [100] (expressed as number of half unit cells), as indicated by the blue segments in (b). This modulation gives rise to crests and valleys in the surface plot. d) Plot of the same Ba(As)–Fe distances for the (100)$\alpha$ planes, now averaged in the $<010>$ direction (blue). The red data points in the same plot are the distance between Ba(As) and Fe for the sets of planes labeled (100)$\beta$ in (b), also averaged in the $<010>$ direction. In the (100)$\beta$ planes the distance between columns has the same magnitude than in the (100)$\alpha$ planes but is shifted with respect to the latter by ½ unit cell. e) Comparison between the FeAs$_4$ tetrahedra in the tetragonal structure (top), and the FeAs$_4$ tetrahedra in the distorted lattice (bottom) with displacement exaggerated for clarity and assuming As and Ba not displaced in the $xy$ plane with respect to each other. f) 3D tetragonal structure of BaFe$_2$As$_2$.\cite{12,13}
FeAs sublattice. Other words from a shift of the Ba sublattice with respect to the Ba atoms within the cage formed by Fe and As atoms, or in other placements we observe in STEM originate from a movement of the FeAs sublattice with respect to the FeAs layers (Fe–Fe 1 and Fe–Fe 2 ) shown in Figure 2b. The EXAFS results suggest that the dislocations of the As resulting from Ba moving off center would lower the symmetry of the coordination environment of Fe, and alter the Fe–As bond distances and angles. Such changes are expected to directly affect the magnetism in these materials. For example, an increase in the Fe–As bond distance has been linked to an increased local magnetic moment [15] and more localization and interaction among electrons. [16] Moreover, Co substitution in the underdoped regime has been shown to reduce this distance and therefore lower the ordered magnetic moment. [17]

Mapping interatomic distances over large regions (=27 nm × 14 nm) revealed that the shift of the Ba-plane with respect to the FeAs layers does not occur along the same direction everywhere in the crystal but two types of domains form with dimensions of 2–20 nm having the [100] and [010] axes interchanged, as illustrated in Figure 3 for optimally doped Ba(Fe 1–xCox) 2 As 2 . We stress that the displacements we observe are static in nature and not the result of fluctuations in the atomic positions. In fact, the STEM images are acquired during time intervals of tens of seconds and any atomic fluctuation would be averaged within the acquisition time. Figure 3a is a map of the interlattice Fe–Ba(As) column separation along [100]. That is, if Fe and Ba(As) columns projections have coordinates (xFe, yFe) and (xBa, yBa), Figure 3a maps (xBa−xFe) for all the (100)a planes. Figure 3b is in turn a map of the projected interlattice Fe–Ba(As) distance along the perpendicular [010], that is a map of (yFe−yBa) for all Fe and Ba(As) columns. The regions with modulated high and low values (blue stripes) in Figure 3a are regions in which the projected Fe–Ba(As) distance is modulated as in the schematic of Figure 1b, while the mostly green areas are regions for which the projected Fe–Ba(As) distances in this direction are unmodulated and their distribution is random with a standard deviation similar to the uncertainty for this type of measurements. It is easy to see that the unmodulated (green) regions in Figure 3a appear instead modulated with alternating high and low values (blue regions) when the interlattice distances are mapped along [010] (Figure 3b), illustrating that these regions represent domains for which the Fe plane shift occurs along the [010] as opposed to [100]. Another way to illustrate the shift in the Ba and FeAs sublattice is by mapping the displacement of all the Ba columns from the undistorted positions, located at the center of each square defined by the Fe columns. Figure 3c,d shows these maps for the displacement component along [100] and [010], respectively. Displacement of the Ba sites along [100] clearly removes the fourfold symmetry along the c-axis, but retains the mirror plane perpendicular to b and c, and the body-centering. The mirror plane perpendicular to a is lost, but a twofold axis parallel to a remains. Thus this distortion alone reduces the symmetry to the orthorhombic space group I2mm. No additional Bragg reflections are allowed for this lower symmetry structure; however, the reflection intensities from each domain are redistributed as a consequence of the atomic displacements. Whether or not these small intensity differences can be detected in practice would depend in part on the quality of the diffraction data (which is often affected by the malleable bonds (Fe–Fe 1 and Fe–Fe 2 ) shown in Figure 2a are small even at 300 K and indicate that the FeAs sublattice is a stiff structure. In particular, the fact that σ 2 for Fe–As 1 (or As–Fe) is small at 300 K, ≈0.005 Å 2 , means that the static contribution (the displacement that would be measured by STEM) must be significantly smaller. There is much more variation of the Ba–As and Ba–Fe bonds and this variation grows more rapidly with T, as shown in Figure 2b. The EXAFS results suggest that the displacements we observe in STEM originate from a movement of the Ba atoms within the cage formed by Fe and As atoms, or in other words from a shift of the Ba sublattice with respect to the FeAs sublattice.

The EXAFS results cannot exclude that the FeAs 4 tetrahedron might also be distorted, but such a distortion would be much smaller than the size of the STEM measured displacements, 0.1 Å. Indeed, the large displacement of the Ba atoms would likely produce a small distortion in the FeAs layers as well, although it cannot be resolved in our images here. Small displacements of the As resulting from Ba moving off center would lower the symmetry of the coordination environment of Fe, and alter the Fe–As bond distances and angles. Such changes are expected to directly affect the magnetism in these materials. For example, an increase in the Fe–As bond distance has been linked to an increased local magnetic moment [15] and more localization and interaction among electrons. [16] Moreover, Co substitution in the underdoped regime has been shown to reduce this distance and therefore lower the ordered magnetic moment. [17]
nature of these materials). However, the domains are likely too small to be probed independently using conventional diffraction techniques, and the measured intensities would represent the tetragonal average structure. A careful study of the atomic displacement parameters and their temperature dependence obtained from single-crystal neutron diffraction data analyzed using the average structure may show evidence for the displacements, manifested as ellipsoids elongated in the $ab$-plane.

We studied the evolution of the lattice distortions with doping by analyzing crystals with varying content of Co substitutions, and have demonstrated the lattice distortion in both the parent and optimally doped crystals above in Figures 1, 3, respectively. Small Co concentrations ($0 < x \leq 0.04$) disrupt the long-range character of the lattice distortions and shrink the domain size to the point that the distribution of Fe–Ba distances becomes random for $x = 0.04$ (Figure 4c), rendering the structure tetragonal near this doping concentration. However, when approaching optimal doping ($x = 0.06–0.07$) the lattice distortions reappear and the Ba and FeAs lattices are again displaced as in the undoped parent (Figure 4a,b). At much larger doping levels, the domains shrink again (Figure 4d), and the symmetry tends to tetragonal for overdoped, non-superconducting compositions.

Both experimental and theoretical works have shown the existence of a significant magneto-elastic coupling in iron-based materials.\textsuperscript{[18]} Therefore, in order to understand the origin of the lattice distortions we measure, it is important to analyze their relationship with the magnetic moment. It is widely accepted that the long-range ordered magnetic moment is completely suppressed for compositions that realize optimal superconductivity (maximum $T_c$). However, the evolution of the local fluctuating Fe magnetic moment with doping has not been investigated in detail. It has been shown by us and others\textsuperscript{[19–23]} that in a family of iron compounds with the same formal oxidation state (3d$^6$, Fe$^{2+}$) and in a similar tetrahedral environment for Fe, there is an empirical linear correlation between the Fe local magnetic moment (LMM) and the ratio of the Fe-L$_3$ and Fe-L$_2$ edge intensities in the electron energy loss spectra (EELS) acquired in the STEM. This relationship finds an explanation in the high sensitivity of the ratio between Fe-L$_3$ and Fe-L$_2$ (L$_{23}$ ratio) to the distribution of 3d electrons among the Fe orbitals (spin states).\textsuperscript{[24,25]} In our case, the relationship between Fe-L$_{23}$ ratio and Fe LMM can be expressed by $y = a\delta + b$ with $a = 0.59 \pm 0.05$, and $b = 1.9 \pm 0.09$; where $y$ represents the L$_{23}$ ratio and $\delta$ the correspondent LMM value.\textsuperscript{[23]} EELS measurements of the Fe LMM by the Fe L$_{23}$ ratios in a STEM have the advantage of

![Figure 3](https://www.advmat.de)
are very well defined for the parent composition and for the 8% doped composition, both of which show large and comparable local Fe magnetic moments. However, for those compositions showing reduced magnitude of local magnetic moment the domains are not well defined, displaying very short coherence in the overdoped compositions, and are nearly absent for compositions in the $x = 0.03$–0.04 range. This behavior clearly illustrates a coupling between spin and lattice degrees of freedom, which is observed here at room temperature, suggesting that electronic instabilities are pervasive in the phase diagrams of pnictides. The initial decrease of the LMM with $x$ increasing from 0 to 0.04 is expected and in agreement with the calculated and experimentally observed reduction of the Fe–As bond distance with increasing Co content.\(^{15–17}\) On the contrary, the electronic states occupied as $x$ increases beyond 0.04 enhance the LMM and its coupling with lattice distortions. As a consequence, these states must not be the same states responsible for the long-range antiferromagnetic ordered phase. We surmise that around the doping composition for which superconductivity emerges, $x \approx 0.03$, electronic orbitals different than those leading to AFM order start to be populated. The different electronic state that develops for $x \geq 0.03$ promotes magnetism of a different kind (than the one promoting long-range order) for which the magnitude of the LMM correlates with the superconducting $T_c$. The large Ba displacements may affect the Fe LMM by distorting the As net, modifying the Fe–As bond distances and angles, or changing the electronic distribution. The direct observation of structural changes in response to doping also indicates that the increased carrier concentration brought about by doping might not be the only factor enabling superconductivity, which would explain why isoelectronic doping can also introduce superconductivity.

The change in behavior in atomic and electronic structure, resulting in recovered atomic displacements and larger LMM starting at around $x = 0.04$ is surprising and indicates profound changes in the electronic structure occurring around this doping level. There are many papers in the literature reporting a reconstruction of the Fermi surface and consequent abrupt changes in physical properties around this composition in Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$.\(^{28–30}\) The different 3$d$ orbitals shift with respect to the Fermi level as a function of doping, and these shifts must alter the dynamic Fe moment and cause the increases for $x > 0.04$ (see schematic in Figure 4 and ref.\(^{23}\)) The observation of a higher fluctuating magnetic moment around optimal doping (maximum $T_c$) qualitatively supports the idea that some magnetic fluctuations are good for superconductivity.

The presence of lattice distortions is not confined to the Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ system. In fact, we have observed similar interlattice modulation in the (Ca$_{1−x}$Pr$_x$)Fe$_2$As$_2$ system;\(^{31}\) although, in this case, we did not investigate as many doping compositions as for the Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ system. In particular, as we found in this study, highly strained, as-grown CaFe$_2$As$_2$ crystals obtained by quenching from high temperature, still show lattice distortion but the size of the domain is nearly vanishing. The LMM of these samples is smaller than in annealed crystals, which show large modulation domains and larger local moment. These findings are consistent with the results on the Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ system when considering that strain (or pressure) in 122 arsenides has a similar influence as
doping on the structural and magnetic phase transitions: an increase in pressure leads to lower $T_s$ and $T_N$.[8,13] In the case of CaFe$_2$As$_2$, which is the most pressure sensitive member of the 122-arsenide family, the quenched, strained crystals show $T_N = 0$ K and therefore can be located at the sharp dip of the $T$-$P$ phase diagram for CaFe$_2$As$_2$ around $P = 0.4$ GPa, where significant Fermi surface reconstruction occurs.[34] In this sense, these crystals are analogous to the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ crystals with $x \approx 0.04$; while the annealed, relaxed CaFe$_2$As$_2$ crystals with maximum $T_N = 170$ K, are analogous to the parent BaFe$_2$As$_2$. In view of these results, we believe that the distortions reported here are common to all iron-based superconductors with the ThCr$_2$Si$_2$ structure, and perhaps those adopting other structure types as well.

Twinning on a nanometer scale, as we observe it here is not completely new and is likely associated with an order–disorder phase transition mediated by elastic relaxation. This type of transition is known to occur in many systems like ferroelectrics and metal alloys in which, the distortions generating a stress field and twin domains are the off-center displacement giving rise to the polarization in the former case, and the order of cations in the latter. In the case of ferroelectrics, for example, x-ray absorption fine structure (XAFS) has demonstrated that the local ferroelectric distortions at temperatures of hundreds of degrees above the ferroelectric transition $T_c$ remain almost as large as the distortions at very low temperatures far below $T_c$; although the average structure does not look distorted above $T_c$.[35] Computer simulations have shown that the ordering interaction has a strong tendency to form a tweed structure upon prolonged annealing below the transition temperature, as observed experimentally. However, above the transition temperature, where the crystals are grown, the strain fluctuations produce only embryos of a tweed structure, with very small domain (but the same amount of local distortion).[36] This embryonal state is what we observe. Moreover, on the basis of this argument we can predict that a sufficiently long post-annealing treatment of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ crystals might produce a tweed texture that is observable with long-range probes.

In summary, our experimental results provide a direct observation of the complex interplay between structural distortions, 3d orbital occupancy, and local magnetic correlations as ingredients for an improved microscopic description of Fe-based compounds, including the appearance of superconductivity.

Experimental Section

For this study, we used aberration-corrected high-resolution Z-contrast STEM performed in a Nion UltraSTEM10012 microscope operating at 100 kV and equipped with a Gatan Enfina EEL3[37] spectrometer and also in a Nion UltraSTEM2003[38] microscope equipped with a Gatan Enfinium dual EELS system. Both microscopes included a 5th order Nion aberration-corrector, a cold-field emission gun, and are capable of sub-angstrom resolution. Drift instabilities were minimized due to a unique sample holder design, allowing for interatomic distance mapping with picometer accuracy. Single crystals of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with dimensions of $\approx 8$ mm $\times 6$ mm $\times 0.2$ mm were grown out of FeAs self-flux, similar to ref.[39] Nearly 40 TEM samples were prepared (more than one sample for each crystal) in order to rule out any influence of localized defects. Repeated images were acquired in multiple locations for various samples in conditions of negligible sample drift and with varying scanning directions, and the results were reproduced on both microscopes. Each image was collected from a sample that was thinned to a thickness of about 10 nm. Single crystals were initially cleaved or cut and polished to about 20 $\mu$m in thickness using an Allied High Tech & Multiprep System with Allied High Tech Red Lube Extender as lubricant to avoid any contact with moisture. They were subsequently thinned by Ar ion milling at a voltage of 2 kV, and liquid N$_2$ temperature, with a final cleaning step at 0.5 kV for 10 min. Using voltages below 3 kV was critical for obtaining clean and uniform foils due to the nonbrittle nature of iron-based compounds. Voltages above 3 kV resulted in a thick and inhomogeneous surface amorphous layer. Samples were prepared in plane-view and in cross-section geometry (see Supporting Information for cross-section results). As-prepared TEM samples were heated up to 80 °C in high vacuum (10$^{-3}$ Torr) for several hours in order to remove hydrocarbon contamination from air exposure, and then rapidly loaded in the microscope. Oxygen contamination was not observed, as shown by the absence of the O–K edge at 530 eV.

Details of the sample preparation and methodology for the EXAFS work can be found in ref.[39] and references cited therein.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge fruitful discussion with S. J. Pennycook, and E. Dagotto. The research was supported by the Materials Sciences and Engineering Division Office of Basic Energy Sciences, US Department of Energy. Part of the work was supported by ORNL's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. The EXAFS work is supported under NSF (Grant No. DMR1005568). The experiments were performed at the Stanford Synchrotron Radiation Light Source operated by the DOE Division of Chemical Sciences.

Received: September 4, 2014
Revised: February 20, 2015
Published online:


