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Polar Nano-Domains in Barium Hexaferrite Revealed with Multislice Electron Ptychography

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Barium hexaferrite ($BaFe_{12}O_{19}$ or BaM) is a commercially-important magnetic material with a ferrimagnetic order below ~720 K. It is also studied as a quantum paraelectric candidate, and hence we are exploring its strain engineering as a possible pathway to creating a room-temperature magneto-electric-coupled multiferroic. The projected crystal structure of BaM along the [100] direction is shown in Figure 1(a) with the unit cell marked with a dashed white line. In its native centrosymmetric version, BaM belongs to the $P6_3/mmc$ space group, and first-principles calculations have shown an unstable phonon mode associated with a displacement of the trigonal bipyramid (TBP) Fe^{3+} ion off the mirror plane on which it lies [1]. This off-mirror plane (OMP) displacement and the TBP coordination of the Fe atom with adjacent O atoms is marked with a brown box in Figure 1(a) and shown in detail in Figure 1(b). Further, Figure 1(c) shows the expected structural transformation of the bipyramid under biaxial compressive strain in the ab-plane, resulting in an increased magnitude of the OMP displacement, shortening the Fe-O bonds in the mirror plane and movement of the apical O atoms further away from the mirror plane.

The competition between the long-range Coulomb interaction, short range Pauli repulsion and quantum fluctuations gives rise to various possibilities for the spatial correlation and dynamics associated with the OMP displacements [2]. Previous work has predicted either: i) hopping of the Fe atom between the bistable sites in a double well potential [3,4] or ii) freezing of the Fe atom in different sites leading to different ferroelectric and anti-ferroelectric ordering with different energies [1]. The relative stabilities of these different states are still unknown. We unravel this puzzle by direct imaging of the electric dipoles and depth sectioning enabled by multislice electron ptychography [5,6].

Previous Mossbauer, X-ray and neutron diffraction studies on single crystals have shown that the Fe-Fe distance between the two bistable sites on either side of the mirror plane is around 36 pm [4,7]. Such a small spacing is beyond the resolution limit of conventional imaging methods even on the state-of-the-art microscopes. However, recent developments in detector technology [8] and multislice ptychography have opened avenues to study material properties at a spatial resolution limited only by the thermal vibrations of the atoms [6]. Hence, the OMP displacements in BaM offer an ideal opportunity to explore the physics of these local dipoles using multislice ptychography. Figure 2(a) and (b) show the high angle annular dark field (HAADF) images down the [100] zone axis of a barium hexaferrite single crystal and a thin film with -1% biaxial compression in the ab-plane respectively. For the single crystal, the TBP site appears as a single feature consistent with the 75 pm point-spread function of the microscope, whereas in the strained film, the two sites can be just resolved visually, suggesting OMP displacements larger than 75 pm. The HAADF images can be directly compared with the multislice ptychography

reconstruction of a barium hexaferrite thin film grown on sapphire (partially-relaxed state) shown in Figure 2(c). The reconstructed image, obtained by summing up the different slices along the beam direction (a-axis), has a much higher spatial resolution, with the two split OMP sites now more clearly resolved. In addition, by tracing out the position of the Fe atoms in the different depth slices, we can track how the occupancy and displacement of the two sites varies along the a-axis. Figure 2(d, e) shows the depth profile along both the green and blue lines marked in Figure 2(c) which includes two oxygen atoms on either side of the TBP site. Such depth sectioning shows that the Fe atoms in this partially-relaxed thin film sample is frozen into one of the two sites, with the occupied site oscillating slowly between above and below the mirror plane as we move along the a-axis. This is clear evidence that with the addition of strain, inversion symmetry is broken microscopically, forming polar domains that are only a few nm in size. The question is whether we can coerce this effect further to form larger domains and create a material that is polar on a macroscopic scale [9].

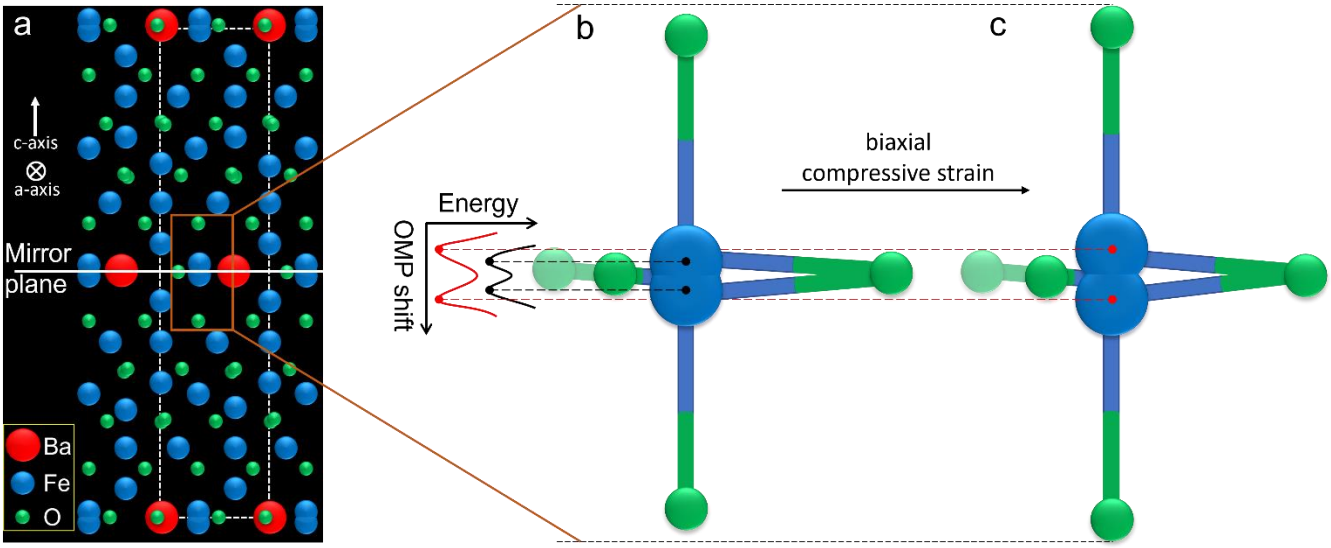

Figure 1. (a) Crystal structure of barium hexaferrite projected along the [100] direction – the unit cell is marked with a dashed white line and the mirror plane marked with a solid white line. The Fe atom lying on the mirror plane and associated with the unstable phonon mode is enclosed in the brown box. (b) shows the trigonal bipyramid coordination and the off-mirror plane displacement of this Fe atom (blue) into two possible sites. The structural transformation of the bipyramid under compressive strain is shown in (c) and is associated with an increase in the magnitude of the OMP displacement, shortening of the Fe-O bonds in the mirror plane and movement of apical O atoms away from the mirror plane. A sketch of the possible double well potential-energy landscape as a function of the OMP displacement for both the strained (red) and unstrained (black) cases is also shown.

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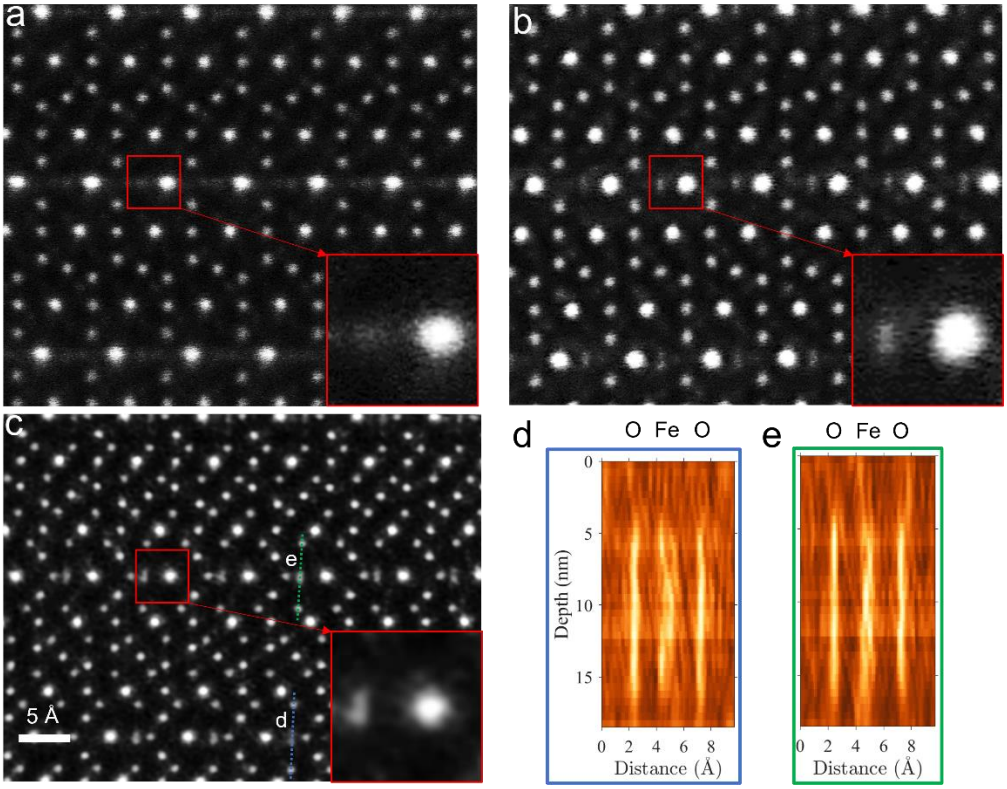

Figure 2. HAADF images for barium hexaferrite (a) single crystal and (b) -1% strained thin film with one of the TBP Fe sites and the adjacent Ba atom magnified in the inset. The split sites appear as a single feature in (a) whereas it can be just visually distinguished in (b). Multislice ptychography reconstruction of a partially relaxed BaM thin film is shown in (c) where the two sites are well resolved, and the lighter O atoms are also visible. The depth profiles along the two dashed lines in (c) are shown in (d) and (e), where one can see that the Fe atom is frozen into one of the bistable sites, with the occupied state varying slowly between above and below the mirror plane along the a-axis.

References:

[1] PS Wang and HJ Xiang, Phys. Rev. X **4**(1) (2014), p. 1. doi: 10.1103/PhysRevX.4.011035
[2] SE Rowley et al., Sci. Rep. **6** (2016), p. 1. doi: 10.1038/srep25724
[3] J Fontcuberta and X Obradors, J. Phys. C Solid State Phys **21** (1988), p. 2335.
[4] HB Cao et al., APL Mater. **3**(6) (2015), p. 1. doi: 10.1063/1.4922934
[5] AM Maiden, MJ Humphry and JM Rodenburg, J. Opt. Soc. Am. A **29**(8) (2012), p. 1606. doi: 10.1364/josaa.29.001606
[6] Z Chen et al., Science **372**(6544) (2021), p. 826. doi: 10.1126/science.abg2533
[7] G Albanese, A Deriu and D Cabrini, Hyperfine Interact. **70**(1) (1992), p. 1087. doi: 10.1007/BF02397518.
[8] H Philipp et al., arXiv:2111.05889 (2021).
[9] The authors acknowledge funding from DOE-BES # DE-SCOO02334, NSF DMR-1719875, DMR-1539918, NSF-MRI-1429155, and PARADIM-MIP DMR- 2039380.