Response to Comment on “Epitaxial BiFeO$_3$ Multiferroic Thin Film Heterostructures”

In this response, we report the results of additional experiments that bear on the issues raised in the comment by Eerenstein et al. (1) and suggest some additional possible reasons for the results they have obtained.

In Wang et al. (2), we reported on the ferroelectric and magnetic properties of BiFeO$_3$ (BFO) epitaxial thin films. Our results demonstrated a thickness dependence in these properties, and we suggested that a likely explanation of these effects was that heteroepitaxial strain induced a monoclinic distortion, relaxing gradually with increasing thickness. Detailed x-ray studies (3) have shown evidence for such a monoclinic structure, as well as no evidence for secondary phases. The out-of-plane lattice parameter for the BFO layer progressively increases as the thickness is decreased, consistent with the expected effect of epitaxial constraint.

In contrast to all prior studies, our epitaxial BFO thin films showed a large spontaneous polarization. We considered the hypothesis that this change could be directly attributed to the epitaxially induced change in structure. Our theoretical discussion also included the possibility that the large polarization in thin films could be the result of a change in the switching mechanism in thin films compared to the bulk (4), a change that could be related to other differences as well as to epitaxial strain. Another possibility, originally suggested by Teague et al. (5), is that high leakage in the bulk samples, somehow reduced in the films, could have prevented prior researchers (over the past four decades) from observing the large value of spontaneous polarization in BFO. These latter proposals are consistent with various subsequent measurements of high polarization of BFO in thin film form (6–8).

Our report (2) also included larger values for the magnetization of very thin films (thickness less than ~100 nm), again different from the previously reported magnetic properties of the bulk material. We have continued to investigate the magnetic behavior of the films; Fig. 1A summarizes our recent magnetic measurements from a series of films with systematically varying thickness. In contrast to our original measurements, which were carried out using a vibrating sample magnetometer (VSM), we have now been able to measure our films using a more sensitive, higher resolution superconducting quantum interference device (SQUID) magnetometer (Fig. 1B), which was not accessible to us at the time of preparation of the original paper. Measured using this instrument, the very thin films show a magnetic moment of about 70 to 80 electromagnetic units (emu)/cm$^3$ (corresponding to a magnetization of about 0.5 $\mu_B$/formula unit), which progressively decreases as the film thickness is increased to above 120 nm. Although smaller than in the original report, this value is still much greater than those reported by Eerenstein et al. (1).

In these samples, detailed transmission electron microscopy studies of both planar and cross sections did not reveal any second phases. Piezoimaging with an atomic force microscope (AFM) has clearly shown the presence of piezoelectric domains down to at least 30-nm thickness, although the degree of leakage goes up with decreasing thickness. X-ray diffraction studies have revealed no secondary phases; we have used Rutherford backscattering and energy dispersive x-ray spectroscopy to analyze the cation composition and intensity of the spectrum from the 30-nm-thick film has a distinct magnetic signal, which progressively decreases as the film thickness is increased. The position of the three peaks also reveals the mixed oxidation state of the sample by comparison with a known sample (Fe$_3$O$_4$).

Fig. 2B compares the normalized XMCD spectrum of the 30-nm BFO film to that of a Fe$_3$O$_4$ film. Several key points emerge from this comparison. First, using the Fe$_3$O$_4$ spectrum as a fingerprint, we can clearly identify the peak at ~709.5 eV as the Fe$^{2+}$ peak, consistent with our x-ray photoelectron spectroscopy results. Second, this peak progressively vanishes as the thickness is increased (Fig. 2A). Third, the total intensity of the spectrum from the 30-nm BFO film is approximately 15% of that from the Fe$_3$O$_4$ film, which suggests that the total moment is also approximately 15% of Fe$_3$O$_4$. Finally, the ratio of the three peaks in Fig. 2B is not the same as that in Fe$_3$O$_4$, for which detailed studies have revealed a ratio of 1:1:1 for the Fe$^{2+}$(oct):Fe$^{3+}$(tet):Fe$^{3+}$(oct). What is interesting, and puzzling, is that the +2 state vanishes at thicknesses higher than

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**Fig. 1.** (A) Magnetic response from BFO films grown on 001 STO with different thickness. (B) Comparison of VSM and SQUID results on the 100-nm BFO/SRO/STO (001) sample used in (2). Care was taken to remove any silver spots on the substrate by grinding with emery paper.
The magnetization should be of XMCD spectrums of Fe$_3$O$_4$ and the BFO film. 

The most likely origin of Fe$^{2+}$ in the thin films is the presence of oxygen vacancies, which are typically quite common in perovskites. Our films were grown under relatively reducing conditions, compared with those of Eerenstein et al. (1), and thus favored the formation of Fe$^{2+}$. In the absence of Fe$^{2+}$, our observations (that is, at thicknesses >120 nm) and theoretical analysis (10) suggest that the magnetization should be ~8 to 10 emu/cm$^3$, consistent with the observations of Eerenstein et al. (1).

With the presence of Fe$^{2+}$ in the films, a large number of possible models could be invoked to explain the extra observed moment. We summarize the most plausible here.

One possibility is a ferrimagnetic arrangement in which the moments of the Fe$^{2+}$ ions are aligned oppositely to those of the Fe$^{3+}$ ions, leading to a net magnetic moment. Eerenstein et al. (1) suggest that an oxygen count of 2.75 (instead of 3) would be required to produce our experimentally observed moment of 0.5 μB/Fe. This would be the case for high-spin Fe$^{2+}$, but the oxygen deficiency required to produce the observed moment would be much lower if low-spin Fe$^{2+}$ were present. We suggest that such a ferrimagnetic arrangement may be unlikely; even if Fe$^{2+}$ and Fe$^{3+}$ were to couple ferrimagnetically locally, they would need to also have long-range ordering or the moments from locally ferrimagnetic regions would cancel out. An alternative possible mechanism is a gradual increase in the canting angle as the thickness is reduced, which could be driven by increasing distortions resulting from epitaxial strain, oxygen vacancies, or both. Clearly, this aspect is scientifically very interesting and requires further experimental and theoretical study.

Fig. 2. (A) XMCD results for the 30-nm, 90-nm, and 120-nm BFO/STO (001) samples. (B) Comparison of XMCD spectrums of Fe$_3$O$_4$ and the BFO film.
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