Temperature induced phase transition from cycloidal to collinear antiferromagnetism in multiferroic Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ driven by $f$-$d$ induced magnetic anisotropy

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In multiferroic BiFeO$_3$ a cycloidal antiferromagnetic structure is coupled to a large electric polarization at room temperature, giving rise to magnetoelectric functionality that may be exploited in novel multiferroic-based devices. In this paper, we demonstrate that by substituting samarium for 10% of the bismuth ions the periodicity of the room temperature cycloid is increased, and by cooling below $\sim$ 15 K the magnetic structure tends towards a simple G-type antiferromagnet, which is fully established at 1.5 K. We show that this transition results from $f-d$ exchange coupling, which induces a local anisotropy on the iron magnetic moments that destroys the cycloidal order - a result of general significance regarding the stability of non-collinear magnetic structures in the presence of multiple magnetic sublattices.

I. INTRODUCTION

In multiferroic materials spontaneous magnetic order is coupled to ferroelectricity such that the magnetic state may be tuned by an electric field, and vice versa. In these technologically important materials, a polar magnetic structure must be uniquely stabilised by the absence of inversion symmetry in an already ferroelectric phase, or itself break inversion symmetry and induce a coupled electric polarization. Such magnetic structures typically arise through a complex interplay between frustrated magnetic exchange interactions and anisotropies. Of all multiferroic materials, BiFeO$_3$ is arguably the most studied owing to its large electric polarization (over 150 $\mu$Cm$^{-2}$) which is coupled to antiferromagnetism at room temperature - a key requirement for technological application.

BiFeO$_3$ has a rhombohedrally-distorted perovskite crystal structure with polar space group $R3c$. The Fe$^{3+}$ magnetic sublattice is ordered at room temperature ($T_N =$ 640 K), with a predominantly antiparallel alignment of nearest neighbor (NN) spins (G-type) resulting from a net ferromagnetic component induced by spin canting in the basal plane. The crystal and magnetic structure of BiFeO$_3$ may be tuned by doping rare-earth ions onto the bismuth site. In general, lanthanide substitution reduces the average polarizability of the A-site cation, with greatest depolarization achieved with rare-earth ions of small radii. Increasing lanthanide content therefore destabilizes the $R3c$ phase, and drives the crystal structure from polar, to antipolar (reported for $Ln=La$–Sm, and generally PbZrO$_3$-related $\sqrt{2}a_p \times 2a_p \times 2\sqrt{2}a_p$ superstructure except for Bi$_{1-x}$La$_x$FeO$_3$, where the PbZrO$_3$-related structure is stable only in a narrow compositional range and is replaced by an incommensurate phase with Ima$\overline{3}m$ symmetry and finally to non-polar GdFeO$_3$-type $\sqrt{2}a_p \times 2a_p \times 2\sqrt{2}a_p$ superstructure, with each morphotropic phase transition having a profound effect on the ferroelectric and piezoelectric response of the material. For example, holmium substitution gives rise to an enhancement in the remnant ferroelectric polarization at low switching fields, suppression of the spin cycloid towards a canted G-type antiferromagnetic structure was found in Bi$_{1-x}$Dy$_x$FeO$_3$, and a temperature induced 90° spin flop occurs upon doping neodymium. It has been suggested that in certain compositions ferromagnetism may coexist with ferroelectricity - critical progress towards device engineering.
At room temperature Bi$_{1-x}$Sm$_x$FeO$_3$ maintains a single $R3c$ polar phase up to a samarium content of $x \sim 0.15$. The system then transitions to a mixed $R3c$/PbZrO$_3$-related phase for compositions in the range $0.1 < x < 0.18$, and finally a single non-polar GdFeO$_3$-type phase is stabilized for $x \geq 0.18$. Weak ferromagnetism is now well established in the non-polar phase, consistent with a symmetry allowed canting of the G-type antiferromagnetism. Remarkably, weak ferromagnetism with a softened hysteresis has been reported in the polar phase of Bi$_{1-x}$Sm$_x$FeO$_3$ ($x < 0.15$). As in undoped BiFeO$_3$, ferromagnetism is incompatible with the cycloidal magnetic structure, and despite numerous studies the exact nature of this phenomenon remains unclear.

In this paper we demonstrate that the room temperature magnetic structure of Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ is indeed cycloidal, albeit with a lengthened periodicity compared to BiFeO$_3$ in accordance with a reduction in the polarization of the A-site cation sublattice. Furthermore, we show that at low temperatures the magnetic structure transitions from a spin cycloid to a simple G-type antiferromagnet, which is fully established at 1.5 K. This magnetic phase transition can be explained as a result of $f-d$ exchange coupling that induces an easy-axis magnetic anisotropy upon the Fe$^{3+}$ sublattice. This observation opens new routes for manipulating the cycloidal magnetic structure within the ferroelectric phase of BiFeO$_3$.

II. EXPERIMENT

The polycrystalline Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ sample was synthesised via a solid state reaction route as detailed in reference [26,28–32]. Field cooled magnetization versus temperature measurements were performed between 150 and 2 K using an applied field of 5000 Oe in a Quantum Design MPMS. Neutron powder diffraction measurements were performed using the time-of-flight diffractometer WISH at ISIS, the UK pulsed Neutron and Muon Spallation Source. 1 g of powder Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ was placed in a thin 3 mm vanadium can to minimise the effects of samarium absorption. The can was mounted inside a standard helium-4 cryostat, providing sample temperature control in the range 1.5 K to 300 K. Heat capacity data were collected from polycrystalline samples of BiFeO$_3$ and Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ as a function of temperature (cooling from 150 K to 3 K) using a Quantum Design Physical Properties Measurement System. Both samples had a mass of ~5.5 mg, and were prepared by cold pressing and sintering at 750°C for 5 hours.

III. RESULTS AND DISCUSSION

A. Crystal structure

As Bi$_{0.9}$Sm$_{0.1}$FeO$_3$, lies close to the morphotropic phase boundary [33] and also because inhomogeneous samarium doping may lead to phase coexistence, we carried out a neutron powder diffraction study of the crystal structure of our sample. Figure 1a shows data measured at 1.5 K. These data were found to be representative of all data collected in the temperature range 1.5 to 300 K, with the exception of the magnetic diffraction peaks (discussed in detail later), and small changes in the nuclear peak positions in accordance with thermal expansion of the lattice. All nuclear diffraction peaks could be reliably fit by Rietveld refinement of the $R3c$ crystal structure using FULLPROF [36]. The calculated diffraction patterns for both PbZrO$_3$-related and GdFeO$_3$-type structures do not reproduce the data, and there is no qualitative evidence for phase coexistence. Hence, Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ unambiguously adopts the polar $R3c$ crystal structure at all measured temperatures (n.b. we neglect the true monoclinic symmetry of the magnetically ordered system as magneto-elastic coupling is weak). The temperature dependencies of the $a$ and $c$ lattice parameters ($R3c$ in hexagonal setting) are shown in figures 1b and 1c, respectively. The lattice was found to smoothly contract on decreasing temperature, with the largest change observed in the $c$ direction.

B. Magnetic structure

The strongest magnetic diffraction peaks, labelled with an asterix in Figure 1a, were measured in high resolution at 300 K, 30 K, and 1.5 K (Figure 2). At 300 K four reflections were observed - pairs of the six $(1,0,1)\pm$k satellites have common d-spacing forming three peaks in the powder data, and the fourth peak is a superposition of the (0,0,3)\pmk reflections. For the BiFeO$_3$ cycloidal magnetic structure with a circular spin rotation envelope propagating along $(\delta,\delta,0)$, the intensities of the $(1,0,1)\pm$k and (0,-1,1)\pmk peaks (green and pink dashed lines in Figure 2) are predicted to be exactly 75% of the (-1,1,1)\pmk intensity (brown dashed line), as observed. An elliptical distortion of the rotation envelope would lead to a small, almost immeasurable deviation in the relative intensities of these three peaks. The (0,0,3)\pmk peak intensity is dependent only on the magnitude of the ab-plane component of the magnetic moments, and is therefore highly sensitive to the ellipticity of the cycloid (or the degree of out-of-plane spin canting in a collinear G-type AFM phase) when measured relative to the $(1,0,1)\pm$k reflections.

The 300 K data in Figure 2a was fit by Rietveld analysis using FULLPROF [36]. The propagation vector was determined by the separation of the magnetic peaks,
FIG. 1. (Color online) a) Medium resolution neutron powder diffraction data (WISH detector bank 2) measured from Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ at 1.5 K (black circles). The polar R$3c$ crystal structure (upper tick marks and red line) is fit to the data, showing excellent agreement - the difference pattern is shown as a solid black line at the bottom of the figure. The diffraction patterns calculated for antipolar (PbZrO$_3$-related) and nonpolar (GdFeO$_3$-type) crystal structures are also shown. The magnetic diffraction peaks (lower tick marks) at $d \simeq 4.57$ are labelled with an asterix. b) and c) The temperature dependence of the $a$ and $c$ lattice parameters, respectively, plotted with the same $y$-axis scale.

and refined to $\mathbf{k} = (\delta, \delta, 0)$, $\delta_{300K} = 0.0033(1)$. The magnetic diffraction intensity was scaled to the full nuclear diffraction pattern observed at shorter $d$-spacing, giving moment magnitudes of $m_{LC} = 3.8(1) \mu_B$ and $m_{||c} = 3.1(1) \mu_B$, which corresponds to an average Fe$^{3+}$ magnetic moment of $3.4(2) \mu_B$ and an ellipticity of 0.8 (defined as $m_{LC}/m_{LC}$). The maximum moment, $m_{LC}$, is consistent with that found for undoped BiFeO$_3$, in which $m_{Fe} = 3.75(2) \mu_B$. The propagation vector has shortened with respect to BiFeO$_3$ to a value similar to that observed in Bi$_{0.9}$La$_{0.1}$FeO$_3$ ($\delta = 0.0036(5)$). This lengthening of the cycloidal periodicity upon doping is consistent with a depolarization of the A-site cation sublattice as the canting angle of neighboring magnetic moments is proportional to the crystal polarization. An ellipticity value $< 1$ is also consistent with a reduced polarization, as the competing DM interaction associated with octahedral rotations favors in-plane magnetic moments.

Refinement of the cycloidal model against data measured at 30 K (Figure 2b) showed little change in the propagation vector, $\delta_{30K} = 0.0036(1)$, but gave moment magnitudes of $m_{LC} = m_{||c} = 3.7(1) \mu_B$ - a circular spin rotation envelope. At higher temperatures a reduction of the Fe moments when the spin lies against magnetic anisotropy may be stabilized through entropy, however, at low temperature the system will tend towards a fully saturated moment on every Fe ion.

The data measured at 1.5 K is in stark contrast to that at 30 K and 300 K. Only two peaks were observed, which index with the same families of reflections as at higher temperatures but with $|\mathbf{k}| = 0$ (i.e. the six $\{1,0,1\} \pm \mathbf{k}$ reflections become equivalent), and corresponds to the collinear G-type antiferromagnetic structure. The G-type model was refined against the full 1.5 K data set (nuclear + magnetic) with reliability factors $R_{nuclear} = 1.77\%$, $R_{magnetic} = 0.31\%$, $R = 3.53\%$, and $R_w = 4.60\%$. The iron moments were found to be of magnitude $3.82(3) \mu_B$ and inclined $32(2)\degree$ from the $c$-axis. The direction of the moment projected onto the $ab$-plane exactly determines the ground state symmetry, however, this could not be determined by powder diffraction. The magnetic space group of the cycloidal phase is $Cc1'$($0, b, 0)$, in which threefold symmetry and two $c$-glides are broken with respect to the parent symmetry, R$3c$. The incommensurate cycloid breaks translational symmetry in the hexagonal basal plane, and propagates...
orthogonal to the remaining glide plane. In the commensurate tilted G-type structure the threefold symmetry is also broken, as well as at least two of the three glides, but translational symmetry within the basal plane is restored. If the antiferromagnetic component of the magnetic moments lies parallel to a glide plane (i.e. in a plane orthogonal to the cycloidal rotation plane) then that glide remains and the magnetic spacegroup is $Cc$, which also allows a ferromagnetic component orthogonal to the glide plane that may couple to the axial octahedral rotations via the second DM interaction discussed in the introduction. If the antiferromagnetic component of the moments is not parallel to the glide plane the ground state symmetry is reduced to triclinic $P\bar{1}$, and any moment configuration is allowed by symmetry. Whilst we cannot empirically differentiate between $Cc$ and $P\bar{1}$ scenarios, we continue on the assumption that the higher symmetry structure is stablized, as drawn in Figure 3.

A phase transition from cycloidal to collinear antiferromagnetism can be observed in the temperature dependence of the magnetic propagation vector (Figure 4b), which shows a trend similar to that observed for other incommensurate to commensurate magnetic phase transitions. The transition was found to be concomitant with an increase in the sample magnetisation, consistent with symmetry-allowed spin canting of the G-type magnetic structure (Figure 4a). The average magnetic moment (Figure 4c) was found to be invariant within error throughout the measured temperature range, whereas the ellipticity of the spin rotation envelope (Figure 4d) monotonically increased on cooling below $\sim 150$ K in favour of a larger magnetic moment component parallel to the hexagonal c-axis.

C. Magnetic anisotropy and f-d coupling

The origin of the temperature dependent ellipticity and the low-temperature transition to a collinear antiferromagnetic structure can be explained by the presence of a uniaxial $Fe^{3+}$ magnetic anisotropy parallel to the c-axis. If, at low temperature, the DM energy associated with octahedral rotations became larger than that of the ferroelectric polarization, a collinear magnetic structure would be favored. However, this anisotropy strictly aligns magnetic moments within the basal plane, which is incompatible with the observed change in ellipticity and the direction of the magnetic moment in the collinear phase (a structure with in-plane magnetic moments was modelled and shown as a blue line in Figure 2c). In a different $Fe^{3+}$-based multiferroic also containing rare-earth ions, $NdFe_3(BO_3)_4$, it was demonstrated that hybridization between 4f and 3d magnetism leads to the anisotropy local to the Nd$^{3+}$ ions being inherited by the essentially isotropic $Fe^{3+}$ ions.

In orthoferrite SmFeO$_3$ (the $x = 1$ end member of the Bi$_{1-x}$Sm$_x$FeO$_3$ series), only the weak ferromagnetic component of the canted AFM iron magnetic structure
couples to the rare-earth sublattice, by symmetry. However, in the rhombohedral phase of Bi$_{1-x}$Sm$_x$FeO$_3$, the point symmetry of the Fe$^{3+}$ site (3) allows the full AFM component of the iron magnetic moments to interact with their nearest neighbor samarium ions. With this in mind, let us consider a plausible microscopic mechanism that may lead to the observed low temperature transition. A Sm$^{3+}$ dopant ion replaces a Bi$^{3+}$ ion with a single nearest neighbor Fe$^{3+}$ separated from it by $(0,0,z)$ with $z \approx 0.22$. We consider the dominant $f$-d exchange contribution between these neighboring sites. If we assume that the site symmetry of the ions is as in pure BiFeO$_3$ - namely point group 3 - then the symmetry allowed exchange, regardless of origin, must take the form $J^x S^x + J^y S^y$, $J^z S^z$ and $J^x S^y - J^y S^x$ where $J^\alpha$ are the operators acting within the $J = 5/2$ Sm$^{3+}$ multiplet and $S^\alpha$ act within the high spin ($S = 5/2$) state space of the Fe$^{3+}$. The three couplings are, respectively, $J_L$, $J_\|$, and $J_{DM}$, and isotropic exchange corresponds to the case $J_L = J_\|$ and $J_{DM} = 0$.

At temperatures below the scale of the ground to first excited crystal field energy gap (applicable to the current study), one must consider the effective exchange, which is the "bare" exchange described above projected onto the Sm$^{3+}$ crystal field ground state. It is therefore important to consider the possible single ion anisotropy of samarium. The site symmetry constrains the 4$f$ to consider the possible single ion anisotropy of samarium. For example, the spin cycloid in BiFeO$_3$ shows a Debye-Einstein model simultaneously fit to both the lower panes $c(T)/T^2$ is plotted in order to accentuate the variation at lower temperatures). The red line shows a Debye-Einstein model simultaneously fit to both BiFeO$_3$ and Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ data sets. Here, it was assumed that phonon excitations form the dominant contribution to the specific heat of BiFeO$_3$, as concluded by ab-initio studies (n.b. the magnon contribution to the specific heat for a collinear AFM and cycloidal magnetic structure would be expected to exhibit the same temperature dependence as the phonon contribution, except for a small magnon gap). The fitted model is in excellent quantitative agreement with the BiFeO$_3$ data. Furthermore, the number of atoms in the sample refined to 91(1)% of the theoretical value, and the average frequency of the Einstein modes refined to 2.7(2) THz, which is in good agreement with the frequency of the first optical phonon mode measured by Raman scattering (∼2.2 THz) and found through ab-initio calculations (∼2.5 THz). In Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ the specific heat was found to deviate from the Debye-Einstein model at low temperature.

The competition between single-ion anisotropy and spin cycloids stabilized by the DM interaction in non-centrosymmetric crystals was previously discussed theoretically for isostructural PbVO$_3$ and BiCoO$_3$. Here V$^{4+}$ has a 3d$^1$ spin configuration that forms an isotropic Kramers doublet. On the other hand, Co$^{3+}$ has a non-Kramers, anisotropic 3d$^6$ electronic configuration. As in BiFeO$_3$, ab-initio calculations predict a spin cycloid in PbVO$_3$. In contrast, single-ion anisotropy in BiCoO$_3$ partially destroys the cycloid and induces a magnetic structure of predominantly collinear AFM domains accompanied by cycloidal domain walls of width 10 unit cells. This description is qualitatively consistent with our data measured on Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ in the G-type AFM ground state, where the magnetic diffraction peaks with a Q component parallel to the magnetic propagation vector were found to be approximately 2% broader than those measured in the cycloidal phase, which is indicative of finite size effects in the collinear AFM ground state.

In addition to Bi$_{0.9}$Sm$_{0.1}$FeO$_3$, we have investigated the rhombohedral phases Bi$_{0.9}$Eu$_{0.1}$FeO$_3$ and Bi$_{0.9}$Tb$_{0.1}$FeO$_3$ finding that, unlike the samarium substituted case, they exhibit no low temperature transition in the magnetic structure. These results are consistent with our understanding of the mechanism driving the low temperature transition in Bi$_{0.9}$Sm$_{0.1}$FeO$_3$: Eu$^{3+}$ is nonmagnetic ($J = 0$), and Tb$^{3+}$ ($J = 6$) is magnetic yet it is non-Kramers in a low symmetry environment so the crystal field ground state may, in principle, be a nonmagnetic singlet - both scenarios being consistent with the absence of a low temperature transition.

D. Specific heat

Figure 5 shows the specific heat capacity $c(T)$ measured from both BiFeO$_3$ and Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ samples (in the lower panes $c(T)/T^2$ is plotted in order to accentuate the variation at lower temperatures). The red line shows a Debye-Einstein model simultaneously fit to both BiFeO$_3$ and Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ data sets. Here, it was assumed that phonon excitations form the dominant contribution to the specific heat of BiFeO$_3$, as concluded by ab-initio studies (n.b. the magnon contribution to the specific heat for a collinear AFM and cycloidal magnetic structure would be expected to exhibit the same temperature dependence as the phonon contribution, except for a small magnon gap). The fitted model is in excellent quantitative agreement with the BiFeO$_3$ data. Furthermore, the number of atoms in the sample refined to 91(1)% of the theoretical value, and the average frequency of the Einstein modes refined to 2.7(2) THz, which is in good agreement with the frequency of the first optical phonon mode measured by Raman scattering (∼2.2 THz) and found through ab-initio calculations (∼2.5 THz). In Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ the specific heat was found to deviate from the Debye-Einstein model at low temperature.
FIG. 5. (Color online) Specific heat capacity measured from both BiFeO$_3$ and Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ polycrystalline sintered pellets (black points). The bottom panes show the specific heat divided by $T^2$, in order to accentuate low temperature features. The data were fit with a Debye-Einstein model (red line).

(see Figure 5 lower-right pane and Figure 6), indicating an additional contribution to the sample's entropy at low temperature due to the samarium substitution. In the rare-earth substituted system Nd$_{2-x}$Ce$_x$CuO$_4$, a Schottky anomaly was observed at low temperature due to a splitting of the Nd ground state doublet in the presence of $f$-$d$ exchange between Nd and Cu. Furthermore, at certain doping levels the low temperature side of the Schottky peak was found to exhibit a linear temperature dependence which was later found to originate in a degree of disorder within the system inherent to the doping, which effectively broadens the Nd doublet splitting. These exact features were observed in our heat capacity data on Bi$_{0.9}$Sm$_{0.1}$FeO$_3$.

The inset to Figure 6 shows the anomalous contribution to the heat capacity divided by temperature, having subtracted the Debye-Einstein model. Two key parameters may be directly extracted from the data. Firstly, the onset temperature of the anomaly was found to be $\sim$ 17 K (labelled $T_{f-d}$ in Figure 6), which provides an indication of the $f$-$d$ exchange energy. This is in excellent agreement with the neutron diffraction results. Secondly, the integrated anomaly in $\Delta c(T)/T$ provides a measure of the change in entropy, $\Delta s$. For a two level system $\Delta s = N k_B \ln(2)$, where $N$ is the number of contributing atoms in the sample. Here, $N$ was found to be equal to 0.08 atoms per formula unit - in good agreement with the nominal substitution level of 0.1. Together, both quantities provide strong evidence for $f$-$d$ exchange coupling between samarium and iron magnetic moments at low temperature.

IV. CONCLUSIONS

In summary, we have shown that Bi$_{0.9}$Sm$_{0.1}$FeO$_3$ is isostructural with BiFeO$_3$, and shares the same room temperature cycloidal magnetic structure. The real space periodicity of the cycloid was found to lengthen upon samarium substitution - consistent with the depolarization of the nominally bismuth sublattice. Furthermore, we show that at low temperatures the magnetic structure transitions from a spin cycloid to a simple G-type antiferromagnet. The G-type structure is fully established at 1.5 K, and results from an easy-axis magnetic anisotropy induced upon the Fe$^{3+}$ sublattice through $f$-$d$ exchange coupling. This result opens new routes for modifying the cycloidal magnetic structure of BiFeO$_3$ and, more generally, it is relevant to understanding the stability of non-collinear magnetic structures in the presence of local anisotropy that may be inherited through interactions between multiple magnetic sublattices. In future studies it would be useful to experimentally determine the crystal electric field spectrum on the samarium site using inelastic neutron scattering, in order to elucidate the fine details of the magnetic anisotropy present in this system.

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