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Neutron diffraction study of the BiFeO₃ spin cycloid at low temperature

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Abstract
The reported observation of two anomalies in the intensity of the magnon Raman peaks of BiFeO₃ at 140 and 200 K (Singh et al. 2008 J. Phys.: Condens. Mater 20 252203; Cazayous et al. 2008 Phys. Rev. Lett. 101 037601) led to the hypothesis that such anomalies might originate from a spin reorientation transition. In order to test this hypothesis, we have used temperature-dependent neutron diffraction to track the evolution of the magnetic configuration in single crystals of BiFeO₃. Our results indicate that there is no average reorientation of the spins. This suggests that the magnon anomalies may instead be related to the freezing of modes that do not alter the average projection of the spins over the plane of the cycloid, as also reported for multiferroic TbMnO₃ (Senff et al. 2006 J. Phys.: Condens. Mater 18 2069).

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Bismuth ferrite BiFeO₃ is by far the most studied magneto-electric multiferroic material, on account of having both the ferroelectric and magnetic ordering temperatures well above room temperature. Its high ordering temperatures [1, 2] combined with very large polarization [3–6] and coupling between the polarization and magnetic easy plane [7–9] have made this material the most promising candidate for magneto-electric spintronic devices, leading to a very intense study of its properties. This notwithstanding, there still remain important questions about its phase diagram, as emphasized in a recent monograph about this material [10]. One of the unknowns concerns the magnetic behaviour of BiFeO₃ at low temperatures.

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The double peak around the \( \{ \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \} \) reflection is due to the magnetic spin cycloid. It is demonstrated by their excellent functional properties as a perovskite pseudo-cubic framework. The single crystals were grown at temperatures below the ferroelectric critical temperature, \( T_c \), by a flux growth technique, as detailed in [6]. Because they are grown just below \( T_c \), the crystals tend to be either monodomain or have very few large domains. The high quality of the samples is demonstrated by their excellent functional properties as detailed in previous reports [4, 6]. Importantly for the purpose of this paper, these were also the samples examined in the reports of low temperature magnon anomalies [21, 22].

Magnetic ac susceptibility measurements were performed on a larger single crystal with several magnetic domains using a Quantum Design SQUID. These single crystal samples were kindly donated by Professor Hans Schmid, from the University of Geneva, and were made by himself and Rivera using the flux growth method [27].

In order to study the behaviour of the spins, we performed neutron diffraction experiments at the single crystal diffractometer CRG-D15 of the Institut Laue Langevin in Grenoble. The instrument, provided with a closed-cycle cryostat, was used in the four-circle configuration at a wavelength of 1.173 Å. The resolution of the diffractometer is 0.3° FWHM for the Bragg peaks of a standard sample in the angular range of our measurements. The diffraction experiments involved analysing the diffraction peak corresponding to a purely magnetic reflection. The position and intensity of the magnetic peaks were monitored from 2 K to room temperature, thus covering the range of the observed magnon anomalies. All indices in this article will refer to the perovskite pseudo-cubic framework.

3. Results and discussion

As mentioned in section 1, on a local level BiFeO\(_3\) is essentially a G-type antiferromagnet; that is, each Fe spin is surrounded by six antiparallel spins on its nearest neighbours along the principal Cartesian axes [1, 28]. This antiferromagnetic configuration results in a doubling of the magnetic unit cell so that magnetic reflections appear for \( \{ h, k, l \} = \{ 1/2, 1/2, 1/2 \} \). We verified that all such reflections existed, as shown in figure 1. On the other hand, BiFeO\(_3\) also has an antiferrodistortive arrangement of oxygen octahedral rotations that leads to a doubling of the crystallographic unit cell. Accordingly, the \( \{ h, k, l \} = \{ 1/2, 1/2, 1/2 \} \) reflections are not purely magnetic, but contain also information regarding the nuclear positions of the oxygens, which complicates the analysis. However, there is a further feature that is purely magnetic: the spin cycloid. BiFeO\(_3\) has a spin cycloid with a long period of \( \sim 63 \) nm, whereby the sublattice magnetization (and the weak canting moment) rotates within a plane defined by the ferroelectric polarization and the propagation vector (i.e. the magnetic ‘easy plane’) [29, 7, 9]. This periodic spin cycloid shows up as a superlattice reflection (satellite peaks) around some magnetic peaks, as shown in the top curves (blue) of figure 1.
The direction (in reciprocal space) of the intensity modulation corresponds to the propagation direction of the spin cycloid, and the scattering amplitude (i.e. the satellite peak intensity) depends on the projection of the spins onto the plane perpendicular to the scattering vector (i.e. the magnetic 'easy plane'). Thus, for example, if the polarization is along [1,1,1] and the spin cycloid propagates along the [1,-1,0] direction, satellites will appear as intensity maxima in \((1/2, 1/2, 1/2) \pm (\tau, -\tau, 0)\), where \(\tau = 2\pi/\lambda\), with \(\lambda\) being the period of the cycloid. It is worth noting, finally, that for any given ferroelectric domain, there are, in principle, three possible symmetry-allowed directions for the propagation of the cycloid. For the specific example of polarization along [1,1,1], one can in principle find satellites along \((1/2, 1/2, 1/2) \pm (\tau, -\tau, 0), (1/2, 1/2, 1/2) \pm (\tau, 0, -\tau)\) and \((1/2, 1/2, 1/2) \pm (0, \tau, -\tau)\). However, in practice, only one cycloid per ferroelectric domain is usually found [7].

As said, the magnetic scattering amplitude depends on the projection of the magnetic moments onto the plane perpendicular to the scattering vector. Thus, in the case of a spin reorientation, the spins will either change their magnetic easy plane altogether (perhaps swapping to another one of the three symmetry-allowed planes), or at least change the size of their projection over the original easy plane (e.g., if they go from a purely cycloidal to a conical configuration, the easy plane projection will decrease and so will the satellite peak intensity). Either way, the integrated intensity of the satellite peaks will either decrease (if the transition is from cycloidal to conical) or disappear (if the transition is from one cycloid plane to a different one). Such spin reorientation transitions, then, should show up as sudden changes in the intensity of the magnetic satellite peaks. In order to test whether this is the case, we have measured the scattered intensity around the \(\{h, k, l\} = \{1/2, 1/2, 1/2\}\) reflections. From figure 1 it can be seen that there are clear satellites around the \(\{1/2, 1/2, 1/2\}\) peak. We therefore monitored the \(\{1/2, 1/2, 1/2\}\) peak as a function of temperature from 18 to 320 K. The scans are shown in figure 2.

The period of the cycloid was determined from the reciprocal distance between the satellite peaks, and is 62.5 nm. The period changes only marginally—if at all—from 18 K up to room temperature, as shown in the top panel of figure 3. The rather constant value of the period as a function of temperature is in good agreement with previous results for BiFeO₃ ceramics reported by Przesnioslo et al [14]. Finally, and most importantly for the purpose of this work, the integrated intensity under the satellite peaks of the \(\{1/2, 1/2, 1/2\}\) reflection was also monitored as a function of temperature. Should there be any change in the size of the projection of the spins over this scattering plane, the integrated intensity should also change. As can be seen in the bottom panel of figure 3, there is no noticeable change. The results, then, appear quite unambiguous: whatever the anomalies at 140 and 200 K are, they do not affect the average projection of the spins over the cycloid propagation plane. This rules out either a spin-flop or a transition from cycloidal to a conical modulation.

In order to relate our measurements to the macroscopic properties of BiFeO₃, magnetic ac susceptibility measurements were also carried out on a single crystal (see figure 4). Measurements were performed at 100, 450 and 1000 Hz; with the sample parallel and perpendicular to the excitation field (4 Oe in all cases), without applied dc field and under a
principle be invoked for BiFeO$_3$. The cycloid itself is caused by the magnetoelectric coupling between the canting moment and the ferroelectric polarization; given that both $T_{\text{Neel}}$ and $T_\text{c}$ are very high, both the ferroelectric polarization and magnetic canting moments should already be almost saturated at room temperature, and thus they can hardly change as the sample is further cooled. Also, the spin reorientations observed in rare earth orthoferrites such as ErFeO$_3$ and NdFeO$_3$ are thought to be related to magnetic interactions between the Fe and the rare earths [30]. Bismuth is not a magnetic ion, and thus the mechanism for spin reorientation in orthoferrites cannot in principle be invoked for BiFeO$_3$.

It has also been noted that at temperatures near 140–150 K the oscillator strength of the magnon changes considerably, suggesting a mode softening scenario rather than a macroscopic spin reorientation [31]. Our own observation that the time-averaged projection of the spins over the cycloid plane does not change with temperature is consistent with this view. Here it is also illustrative to compare BiFeO$_3$ with another magnetoelectric multiferroic that also has an incommensurate spin cycloid, TbMnO$_3$. Senff et al show (figure 4 of [26]) that there are several different magnon modes intrinsic to long period cycloid structures. Some of these affect the magnetization along the cycloid axis; but others do not (e.g. a sliding mode of spins moving around the cycloid axis). The present neutron studies establish that the former cannot be unstable in BiFeO$_3$ at cryogenic temperatures, but leave open the possibility that the latter can. These possibilities certainly merit further study: as Senff et al note, such oscillations should be universal features of all multiferroics with a long period spin cycloid, and this of course includes BiFeO$_3$. The critical slowing down of magnon oscillations is also supported by the observation of linewidth narrowing in the magnon spectra of BiFeO$_3$ [20], while the existence of spin fluctuations is consistent with the considerable diffuse scattering of the satellite peaks, as seen in reciprocal space maps [7].

In summary, then, our results show that there is no reorientation of the average spin configurations, ruling out both a spin-flop between symmetry-allowed cycloid planes and a transition from purely cycloidal to conical orders. The results suggest instead that the magnon instabilities correspond to the kind of oscillations postulated by Senff for long period spin cycloids, which do not affect the average spin projection.

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Figure 4. (Color online) Real (top panel) and imaginary (bottom panel) contributions to the magnetic ac susceptibility of BiFeO$_3$, showing no clear anomalies at low temperatures.
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