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FAST TRACK COMMUNICATION

Elastic and electrical anomalies at low-temperature phase transitions in BiFeO3

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Abstract
Our measured dielectric constant and mechanical response of multiferroic $BiFeO_3$ indicate four phase transitions below room temperature. Features correlate with those reported at 50 K (from a peak in the zero-field-cooled magnetic susceptibility) and 230 K (from splitting between field-cooled and zero-field-cooled magnetic data; Singh *et al* 2008 *Phys. Rev.* B **77** 144403), and those at 140 and 200 K (from the magnon light scattering cross section; Singh *et al* 2008 *J. Phys.: Condens. Matter* **20** 25203). The primary order parameter is not the polarization in any of the low-T transitions. Instead, the transition near 200 K shows strong elastic coupling, while that at 50 K is fundamentally magnetic, but magnetostrictively coupled to the lattice. The low-T phase transitions display glassy behaviour. A further anomaly at 140 K interpreted as spin reorientation (Singh *et al* 2008 *J. Phys.: Condens. Matter* **20** 25203; Cazayous *et al* 2008 *Phys. Rev. Lett.* **101** 37601) shows only weakly in dielectric and mechanical studies, indicating that it is predominantly magnetic with little coupling to any of the other order parameters.

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

1. Introduction

Magnetoelectric multiferroics are materials where ferroelectricity and magnetism coexist and are coupled. These materials are attracting increasing interest due to their possible applications as magnetic detectors and multi-state memory devices, as well as for the rich physics behind the fundamental mechanisms for magnetoelectric coupling. Among the materials being most actively studied, $BiFeO_3$ ('BFO') stands out for being the only known room T magnetoelectric multiferroic (ferroelectric, antiferromagnetic), and has some very attractive features such as huge remnant polarization (around 100 μC cm^{-2}) in both single crystal [4, 5] and thin-film form [6, 7] and coupling between the directions of the ferroelectric polarization and the sublattice magnetization [8]. For this reason, BFO has been touted as a possible active material in the next generation of lead-free ferroelectric materials [9] and also as the active layer in magnetoelectric memories based on exchange bias [10].

Although >700 papers have been published on it since 2003, there remain a number of questions and controversies. First, the presence or absence of an antisymmetric linear magnetoelectric effect in the free energy $\alpha_{xy}(T)P_xM_y = -\alpha_{yx}(T)P_xM_y$ remains moot because although it is permitted locally, it is thought to average globally to zero due to the cycloidal incommensurate spin structure proposed by

Sosnowska *et al* [11]. Second, and closely related, this cycloidal spin arrangement has been questioned by Zalesskii *et al* [12], raising uncertainty about the magnetoelectric effect. Third, two new magnetic phase transitions at 140 and 201 K have been inferred from magnon Raman scattering [1–3], and therefore it is unknown what the magnetic symmetries are in the three low-temperature phases $T < 140$ K, 140 K $< T <$ 201 K, and $T >$ 201 K. (However, there has been no independent evidence published yet that these anomalies at 140 and 201 K are true phase transitions and not just some dynamical effects.) Fourth, there are additional anomalies near 50 and 230 K in the field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibilities, and these have been interpreted as evidence for spin-glass behaviour, but such spin-glass effects in bismuth ferrite remain controversial and lack independent support. In the present work we provide measurements of mechanical loss, dielectric constant and loss, and specific heat near the temperatures at which these anomalies occur, which permit some preliminary interpretation of the characteristics of $BiFeO_3$ at low temperatures.

$BiFeO_3$ has a rhombohedrically distorted perovskite structure (space group $R3c$) at room T [13] which is both ferroelectric (with polarization along the $\langle 111 \rangle$ directions) and antiferromagnetic. The antiferromagnetic symmetry is itself very exotic, with a long period (62 nm) cycloidal helix of spins, incommensurate with the lattice periodicity [11, 12]. The cycloidal rotation cancels almost all macroscopic magnetization, and hence BFO is antiferromagnetic; upon heating, it becomes paramagnetic at $T_N = 640$ K [14]. Around 1100 K BFO shows a transition from rhombohedral to orthorhombic symmetry [7] or perhaps monoclinic [8], and around 1200 K it becomes cubic. It is not yet certain which of the two phase transitions is the ferroelectric–paraelectric one. On the other hand, there is evidence that the transition to the cubic phase is accompanied by the onset of a metal–insulator transition [15, 16]. While the high T phase diagram appears to be quite rich, there has been comparatively little reported for the low-T properties, although it has been suggested [17, 18] that spin-glass behaviour occurs in BFO below 200 K. However, three recent works [1–3] indicate further complexity in the low-T nature of BFO.

The first of these [1] reports the magnetic properties of BFO single crystals at low temperatures. It was found that the field-cooled and zero-field-cooled magnetization became different at temperatures below ≈250 K, as can subsequently be seen in earlier data [19, 20]. Furthermore, there is a distinct peak in the zero-field-cooled magnetization around 50 K. Below this lower T, the temperature–frequency dependence of magnetic susceptibility indicates a possible spin-glass transition, although the authors noticed that the behaviour was unusual in that susceptibility increases with increasing frequency. It was also reported that the critical exponent describing the slowing down of the glassy dynamics ($z\nu$), was very small (≈1.4), much closer to the value expected in a mean-field system (where $z\nu = 2$) than in a classic Ising-type magnetic spin glass ($z\nu = 7$–10) [21]. On this basis, it was suggested that the spin-glass transition may be coupled to a long-range order parameter responsible for its mean-field behaviour.

Later, two contemporaneous and independent Raman studies reported electromagnon Raman spectra in BFO [2, 3]. Singh *et al* [2] noted two anomalies in the Raman frequency, intensity, and linewidth: one strong at ≈200 K, one very weak at ≈140 K. Cazayous *et al* reported a strong anomaly at 140 K, and a keen eye might also discern a very small anomaly in their data at 200 K. It is interesting that the strength of the anomalies was so different. However, in more recent work they found both transitions with equal magnon cross section divergences by changing their scattering geometry, showing that the differences are not sample-dependent but orientation-dependent. Two separate spin reorientation transition temperatures might be expected since the spins begin to rotate out of a plane at the upper one, while at the lower one the spins have rotated fully 90°, so that they are orthogonal to the original plane. Singh *et al* [1] data are compatible (in respect of both peak intensity divergence and linewidth narrowing) with the original study of spin fluctuations in uniaxial antiferromagnets by Schulhof *et al* [22]. They found that fluctuations along the uniaxial direction diverge and exhibit critical slowing down (spectral narrowing) approaching T_c, with critical exponents $\nu = 0.63$ and γ (susceptibility) $= 1.24$ for the longitudinal fluctuations and $\nu = 0.63$ and $\gamma = 1.47$ for the transverse fluctuations. Note that the transverse fluctuations are not truly divergent but extrapolate to a divergence ≈2 K below T_c.

2. Experiment and results

In order to understand further the nature of these low-T anomalies, we have studied them from the point of view of the two other order parameters of this multiferroic material: ferroelasticity and ferroelectricity.

2.1. Dynamic mechanical analysis

Dynamical mechanical analysis of ceramic BFO bars was performed in a three-point bending configuration using samples that were 2 mm wide, 0.5 mm thick, and 5 mm between knife edges. Forces between 30 and 630 mN were applied dynamically, generating strains of the order of 10^{-4}, at frequencies between 0.6 and 18 Hz and Ts between 120 and 290 K (figure 1). The Young's modulus and loss angle (indicative of a mechanical dissipative process, such as domain wall friction [23]) show stiffening of ≈10% upon cooling accompanied by a simultaneous peak in dissipation, $\tan\delta$, indicative of transition from a dynamically relaxed system above 230 K to an unrelaxed state below this temperature. There is strong frequency dependence of the mechanical relaxation T, signalling either a true glassy transition or else a defect-related relaxation. The limited range of frequencies accessible in our measurement makes it difficult to compare Vogel–Fulcher (glassy freezing) and Arrhenius (thermal activation of defect states) models for the response. None the less, analysis of the frequency dependence of the peak in $\tan\delta$ around 200 K is consistent with an activation energy of 0.59(9) eV which is smaller than that expected for mechanical relaxation due to oxygen vacancies in perovskite oxides (typically around 0.7–1.1 eV [24]).

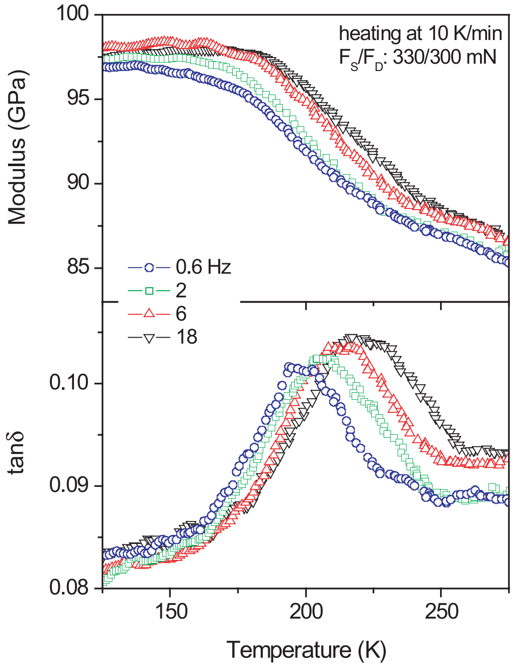

Figure 1. Frequency dependence of the dynamic mechanical modulus and tan δ of BiFeO$_3$ as a function of T. The large peak in tan δ and concomitant relaxation in modulus on heating through 200 K shows significant frequency–temperature dispersion.

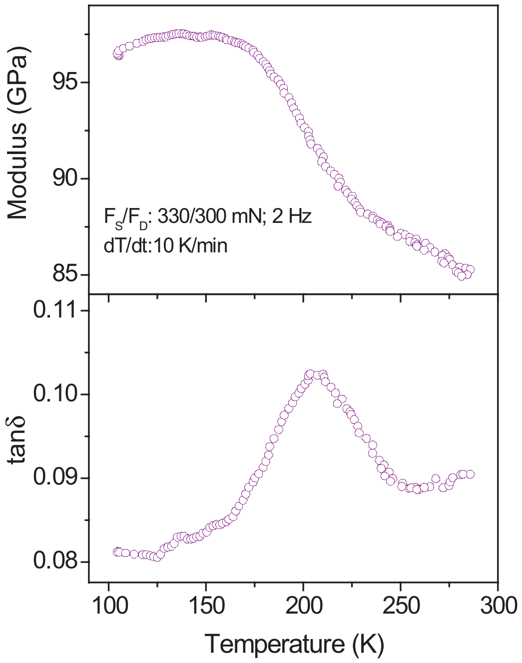

Figure 2. The mechanical modulus and tan δ of BiFeO$_3$ measured at 2 Hz. A small anomaly in tan δ can be seen at 140 K.

The DMA data also show a very weak anomaly, seen most clearly in the data for tan δ collected at 2 Hz (figure 2), at 140 K. The weakness of the 140 K feature and strength of the one around 200 K contrasts markedly with the relative scale of the features seen at these Ts in the electromagnon spectra, which may indicate variable coupling between strain and the primary order parameter at the lower-T anomaly.

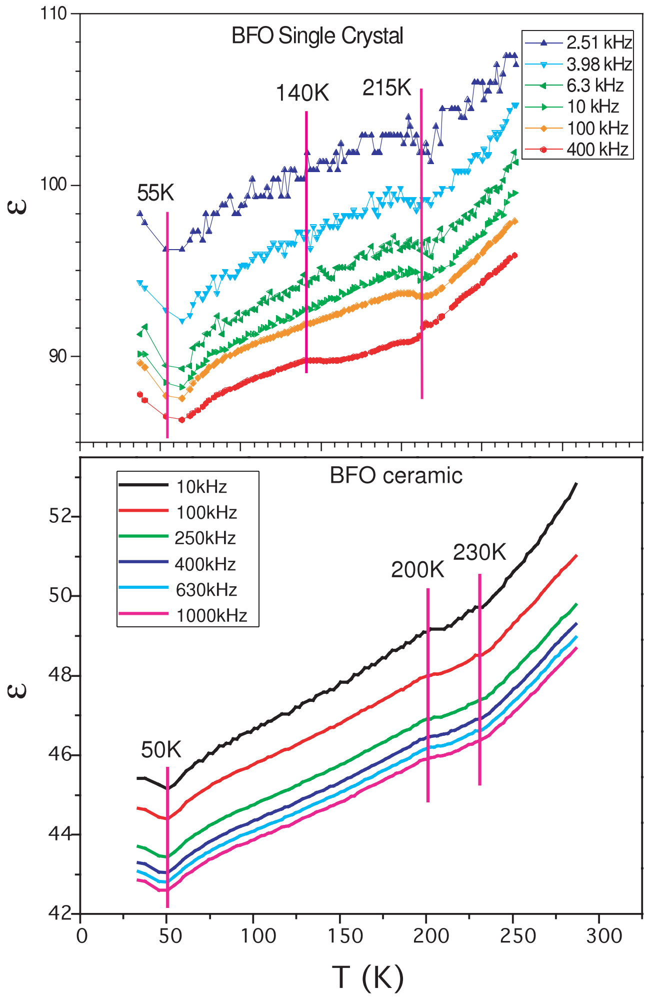

Figure 3. Dielectric constant of BiFeO$_3$ at low-T. A small anomaly at 140 K can be seen in the single crystal data at the highest frequency.

Resonant ultrasonic spectroscopy of BiFeO$_3$ from ca 5 to 1000 K will be reported elsewhere [29]. These show strong anomalies near 1 MHz at 140 K, and in this sense are complementary to the low-frequency (several Hz) DMA measurements reported here, which give strong effects near 201 K but only weak ‘shoulders’ at 140 K. In addition, the RUS measurements confirm a glassy viscous state of between 30 and 50 K; note that the Vogel–Fulcher freezing temperature was previously estimated by Singh *et al* as 29.4 K and a peak in the magnetic susceptibility found at 50 K. Kleemann *et al* [30] have demonstrated ageing of magnetization in this spin-glass temperature regime.

2.2. Dielectric measurements

The dielectric constant was also measured as a function of T and frequency for single crystals and for ceramics (see figure 3). The single crystals were cut with faces perpendicular to {110} pseudocubic planes. The dielectric constant shows subtle but unambiguous anomalies around 50, 200 and 230 K. The fact that they are subtle may explain why they may have gone unnoticed in spite of extensive research on this

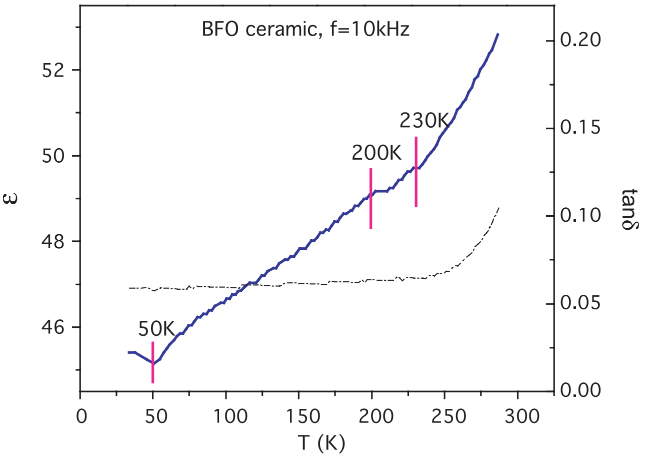

Figure 4. Dielectric constant and loss of $BiFeO_3$ at low-T, measured at 10 kHz.

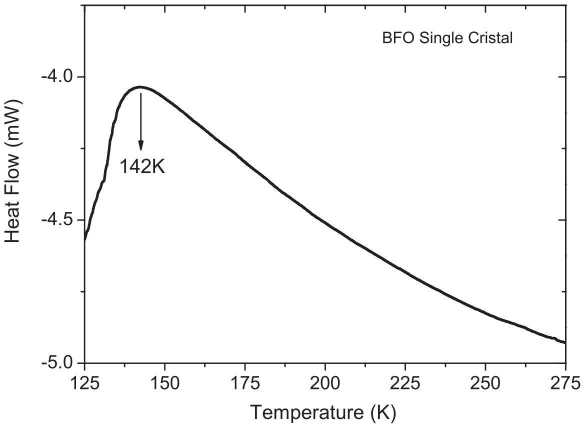

Figure 5. Differential thermal analysis of $BiFeO_3$ at low-T, showing an exothermic phase transition.

compound in recent years. It also indicates that the primary order parameter in these transitions is almost certainly not the polarization, and that they reflect indirect coupling to the primary order parameter. While a single broad peak, strongly dependent on frequency, is seen around 200 K in DMA, two resolved anomalies (independent of frequency) are seen in the dielectric data.

We note that there is no strong evidence of the anomaly at 140 K except at the highest frequency used (400 kHz). This suggests that further studies in the MHz regime should be carried out on single crystal samples; it may be that this transition is insensitive to low-frequency probes. The dielectric constant (capacitance) shows some low-frequency dispersion, probably due to space–charge, but nevertheless the position of the anomalies appears to be relatively frequency-independent, contrary to the glassiness observed in the magnetic and mechanical data. It is also worth mentioning that, although the space charge increases the dispersion and the dielectric losses, these remain low ($\tan\delta < 0.1$) (figure 4) and furthermore (perhaps surprisingly) there is no obvious sign of change in the losses at the critical temperatures, ruling out a conductive artefact [25].

2.3. Thermal measurement

In order to confirm the phase transition at 140 K and show that it is not just a dynamic effect, we have carried out differential thermal analysis (DTA) on our samples. As shown in figure 5, these reveal a strong specific heat anomaly near 140 K, although surprisingly, none near 201 K.

2.4. Ferromagnetism

Finally, we note that magnetic hysteresis is observed in these samples below 10 K [31]. This suggests that the spin-glass phase is not the $T = 0$ ground state but occurs at temperatures above 10 K but below ca 230 K. On the other hand, the hysteresis may not be intrinsic: Lebeugle *et al* [5] observe that small magnetic hysteresis can be explained by just 1% mol of paramagnetic Fe^{3+}, and that it disappears with sample leaching in HNO_3.

3. Discussion

Both the dielectric data and low-frequency (ca 1 Hz) mechanical loss show only very weak evidence of the transition at 140 K, which suggests that this transition is predominantly magnetic, although it appears strongly in resonant ultrasonic measurements near 1 MHz and in thermal analysis (DTA).

The transition at 50 K and those above ≈200 K, on the other hand, have now been observed in different samples (single crystals and ceramics) and with five different techniques (magnetization, susceptibility, Raman, impedance and mechanical spectroscopy). If either is due to defects, they are of a very pervasive but undetectable nature: XRD studies did not detect any impurities or second-phases in any of our samples. Furthermore, the mechanical response seems very large to be caused by to defects alone, suggesting instead that the primary order parameter may be a structural one, coupled weakly to the polarization (hence the dielectric anomaly) and to the magnetization (hence the electromagnon and magnetization anomalies). The magnon linewidths narrow near 140 and 201 K [26], implying that there is critical slowing down of spin fluctuations; this cannot be explained by defects or other extrinsic effects. In the dielectric data two small discrete anomalies at 200 and 230 K are seen while the mechanical relaxation at this temperature is broad and large.

The low-T anomaly in dielectric response at 50 K is weak but nonetheless clear and reproducible in different samples; its correlation with an anomaly in the magnetic susceptibility [1] indicates coupling between the magnetic order parameter and the polar one. Since the latter is a long-range order parameter, this coupling may account for the apparent (and very unusual) mean-field nature of the low-T spin-glass transition. We note also that if this material is indeed a spin glass, it would be acentric. Fischer and Hertz [27] have emphasized that no published theories apply to spin glasses lacking an inversion centre, and further, that such glasses cannot possibly be Ising-like.

Our results suggest that $BiFeO_3$ may be similar to the orthoferrite $ErFeO_3$, which has $T_N = 633$ K and (spin reorientation?) transitions at 90 and 103 K, compared with $T_N = 643$ K and spin reorientation transitions at 140 and 200 K in $BiFeO_3$. According to the theory of Koshizuka and Ushioda [28] one might expect the magnon frequency f to drop to zero at $T_{\mathrm{reorientation}}$ and the magnon integrated cross section to diverge due to enhanced thermal population kT/hf; however Koshizuka and Ushioda report [28] a smaller (50%) magnon frequency decrease and consequently a cross section increase of only about 5×, and attribute this damping to phonon–magnon coupling (magnetostriction). Singh *et al* [2] magnon frequency decrease is only ≈5% and the peak scattering amplitude increases by a maximum of 5× to 10×—but the linewidth decreases measurably (resolution limited). Thus the integrated cross section changes by only a small amount. This is compatible with the strong mechanical losses we see around 200 K (and somewhat weaker at 140 K) and implies very large striction[4].

In summary, we show that the anomalies in bismuth ferrite at cryogenic temperatures can be interpreted as phase transitions at 50 K (magnetic, but glassy and with magnetoelectric coupling), 140 K (dominantly magnetic), 200 K (magnetoelastic with small coupling to polarization), and 230 K (magnetic; glassy and also weakly coupled to polarization). The coupling between magnetic, electric and elastic order parameters varies according to the length scale of the transition dynamics in each case: dipolar and strain coupling leads to the possibility of long-range correlations dominating the spin-glass behaviour, resulting in a rare example of an acentric mean-field spin glass in BFO. Supporting this is the observation of an Almeida–Thouless line at finite magnetic fields [31], which should not be present for short-range Ising-like spin glasses. It would appear that a new model for non-Ising spin glasses is required if the low-T magnetoelectric properties of $BiFeO_3$ are to be adequately explained.

Acknowledgments

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