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 temperature magnetoelectric multiferroic (ferroelectric, antiferromagnetic), and has some very attractive features such as huge remnant polarization (around 100 $\mu$C/cm$^2$) in both single-crystal [1,5] 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].

BiFeO$_3$ has a rhombohedrally distorted perovskite structure (space group R3c) at room T [11] which is both ferroelectric (with polarization along the (111) 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 [12, 13]. The cycloidal rotation cancels almost all macroscopic magnetization, and hence BFO is antiferromagnetic; upon heating, it becomes paramagnetic at $T_N$=640K [14]. Around 1100K BFO shows a transition from rhombohedral to orthorhombic symmetry [7] or perhaps monoclinic [8], and around 1200K 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 amorphous BFO below 200K. However, three recent works [1, 2, 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 $\approx$ 250K, as can subsequently be seen in earlier data [19, 20]. Furthermore, there is a distinct peak in the zero-field-cooled magnetization around 50K. Below this lower T, the temperature-frequency dependence of magnetic susceptibility indicates a possible spin glass transition, although the authors noticed that the behavior 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 ($\nu_\phi$) was very small (around 1.4), much closer to the value expected in a mean-field system (where $\nu_\phi$=2) than in a classic Ising-type magnetic spin glass ($\nu_\phi$=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 $\approx$200K, one very weak at $\approx$140K. Cazayous et al. reported a strong anomaly at 140K, and only a keen eye might discern a very small anomaly at 200K. 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 or-
Fig. 1: Frequency dependence of the dynamic mechanical modulus and tanδ of BiFeO₃ as a function of T. The large peak in tanδ and concomitant relaxation in modulus on heating through 200K shows significant frequency-temperature dispersion.

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. Dynamic Mechanical Analysis of ceramic BFO bars was performed in a three-point bending configuration using samples that were 2mm wide, 0.5mm thick, and 5mm between knife edges. Force 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 290K (Fig. 1). The Youngs 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, tanδ, indicative of transition from a dynamically relaxed system above 230K to an unrelaxed state below this temperature. There is strong frequency dependence of the mechanical relaxation T, signaling 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 tanδ around 200K 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 to 1.1 eV [24]).

The DMA data also show a very weak anomaly, seen most clearly in the data for tanδ collected at 2Hz (Fig. 2), at 140K. The weakness of the 140K feature and strength of the one around 200K 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.

The dielectric constant was also measured as a function of T and frequency for single crystals and for ceram-
spatial-charge, but nevertheless the position of the anomaly at 140K shows some low-frequency dispersion, probably due to the nature of the low-frequency probes. The dielectric constant (capacitance) in the MHz regime should be carried out on single crystal samples. This suggests that further studies in the 50K, 200 and 230K. The fact that they are subtle may explain why they may have gone unnoticed in spite of extensive research on this 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 200K 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 140K 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 (tanδ<0.1) (Fig. 4) and furthermore (perhaps surprisingly) there is no obvious sign of change in the losses at the critical temperatures, ruling out a conductive artifact.

Both the mechanical and dielectric data show only very weak evidence of the transition at 140K, which suggests that this transition is predominantly magnetic. The transitions above ≈200K, 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 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). In the dielectric data two small discrete anomalies at 200 and 230K are seen while the mechanical relaxation at this temperature is broad and large.

The low-T anomaly in dielectric response at 50K is weak but nonetheless clear, showing that the magnetic order parameter is coupled to 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 have emphasized that no published theories apply to spin glasses lacking an

![Graph 1](image1.png)

**FIG. 3**: Dielectric constant of BiFeO$_3$ at low- $T$, measured at 10kHz.

![Graph 2](image2.png)

**FIG. 4**: Dielectric constant and loss of BiFeO$_3$ at low- $T$, measured at 10kHz.
inversion center, and further, that such glasses cannot possibly be Ising-like.

Our results indicate that BiFeO$_3$ is remarkably similar to the orthoferrite ErFeO$_3$, which has $T_N = 633K$ and spin-reorientation transitions at 90K and 103K [compared with $T_N = 643K$ and spin reorientation transitions at 140K and 200K in BiFeO$_3$]. According to the theory of Koshizuka and Ushioda [27] one might expect the magnon frequency $f$ to drop to zero at $T_{\text{reorient}}$ and the magnon integrated cross section to diverge due to enhanced thermal population $kT/hf$; however Koshizuka and Ushioda report [PRB 22, 5394 (1980)] a smaller (50%) magnon frequency decrease and consequently a cross section increase of only about $\times 5$, and attribute this to phonon-magnon coupling (magnetostriction). Singh et al.'s[2] magnon frequency decrease is only $\approx 5 \%$ and the peak scattering amplitude increases by a maximum of $\times 5$ to $\times 10$ - but the linewidth decreases by at least $\times 5$ (resolution limited). Thus the integrated cross section changes by only a small amount. This is compatible with the strong mechanical losses we see around 200K (and somewhat weaker at 140K) and implies very large striction. This is compatible with respect to linewidth narrowing and peak amplitude divergence with the spin-fluctuation models of Koshizuka and Ushioda and Schulhof et al. [22,27]; however, the linewidth narrowing and peak amplitude divergence imply critical fluctuations not explicit in their original papers.

In summary, we show that the anomalies in bismuth ferrite at cryogenic $T$s can be interpreted as phase transitions at 50K (magnetic, but glassy and with magnetoelastic coupling), 140K (dominantly magnetic), 200K (magnetoelastic), and 230K (magnetic, glassy). 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 behavior, resulting in a rare example of an acentric mean-field spin glass in BFO. It would appear that a new model for non-Ising spin glasses must now be developed if the low-$T$ magnetoelastic properties of BiFeO$_3$ are to be adequately explained.

We are grateful to R Palai and H Schmid who provided ceramic and single crystal samples of BFO.

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