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FAST TRACK COMMUNICATION

Critical phenomena at the 140 and 200 K magnetic phase transitions in $BiFeO_3$

J F Scott[1], M K Singh[2] and R S Katiyar[2]

[1] Earth Sciences Department, University of Cambridge, Cambridge CB2 3EQ, UK
[2] Department of Physics, University of Puerto Rico, San Juan, PR 00931-3343, USA

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Abstract
We have measured the magnon Raman cross-sections for bismuth ferrite as a function of temperature near the newly discovered magnetic phase transitions near $T_2 = 140.3 \pm 0.2$ K and $T_1 = 201.0 \pm 0.8$ K (Singh *et al* 2008 *J. Phys.: Condens. Matter* **20** 252203) and evaluate the critical exponents ($\alpha = 0.05$ and $\alpha' = 0.09$) characterizing that at 140.3 K and ($\alpha = 0.06$ and $\alpha' = 0.13$) that at 201.0 K. These are $\ll$1, and hence the data fit a logarithmic divergence about as well. The occurrence of divergences in the *electric* susceptibility proportional to the specific heat anomaly in non-ferroelectric transitions due to piezoelectric coupling was first reported by Kizhaev *et al* (1986 *JETP Lett.* **43** 445); in the present paper we apply an analogous theory to magnetoelastic coupling at *magnetic* transitions. This is an application of the basic Pippard relationship between susceptibilities and specific heat (Pippard 1956 *Phil. Mag.* **1** 473) to a magnetoelastic system. The observations are related to the mechanical loss anomalies observed at the same temperatures (Redfern *et al* 2008 *Preprint* cond-mat). Our results support the distorted spin cycloid model of Zalesskii *et al* (2003 *Phys. Solid State* **45** 141) and not the earlier model of Sosnowska *et al* (1982 *J. Phys. C: Solid State Phys.* **15** 4835).

Recently we reported the discovery of two new magnetic phase transitions near 140 and 200 K in bismuth ferrite [1]. We interpret these as spin-reorientation transitions. In close analogy with the well-known orthoferrites (e.g., $ErFeO_3$) these transitions come in pairs; as temperature is cooled, the spins rotate out of a plane at the upper transition temperature T_2 and become orthogonal to the plane at the lower transition T_1 [2]. In $ErFeO_3$ these transitions are at 90 and 103 K; in $BiFeO_3$, at 140 and 200 K. In each case the magnon frequency decreases somewhat (50% in $ErFeO_3$; 5% in $BiFeO_3$). The decrease would be 100% to zero frequency if there were no coupling of magnons to strain; but in $BiFeO_3$ this is particularly large, as shown by the sharp increase in mechanical loss tangent at both transition temperatures [3]. Note that the antiferromagnetic Neel temperature T_N is at much higher temperatures (633 K in $ErFeO_3$ and 643 K in $BiFeO_3$) and hence plays no direct role in the cryogenic phenomena. As the 200 K transition is approached from above, however, frustration among the ordering spins leads to a spin-glass behaviour [4] with an extrapolated freezing temperature of 29.4 K and a cusp in the zero-field-cooled susceptibility at 53 K. Such a spin-glass is unusual and perhaps unique because the system remains acentric in its glassy phase. Fischer and Hertz have emphasized [5] that no published theories are expected to apply to acentric spin-glasses and that such non-centrosymmetric spin-glasses cannot be Ising-like; indeed the critical exponent $z\nu$ describing the spin-glass is experimentally found [4] to be 1.4–1.5, rather than the values 7–9 typical of Ising systems. This value is close to that of 2.0 originally calculated for a mean-field spin-glass by Kirkpatrick and Sherrington [6], but they did not expect [7] that Nature would actually provide a mean-field spin-glass. In the case of $BiFeO_3$ the strong coupling of spins to elastic strain may do just that [3], since strain is always unscreened and hence long-range.

At Neel transitions in uniaxial antiferromagnets, Schulhof *et al* have shown [8] that one should see divergences in the magnon cross-sections for light scattering or neutron scattering, concomitant with linewidth narrowing. The narrowing is 'critical slowing down' and reflects the fact that very near the transition temperatures the spin fluctuations become larger in size (coherent length increases with critical exponent ν) and slower in time. Experimentally for MnF_2

they found that the correlation length exponent $\nu = 0.63$, and that the susceptibility exponent γ for longitudinal response was 1.3 whereas that for transverse response, 1.5. The value 1.3 agrees very well with the theoretical 4/3 for a uniaxial antiferromagnet [9]. Their work develops further the earlier theory by Fleury and Loudon [10] that did not assess the role of fluctuations. Similar linewidth narrowing at 140 and 200 K in $BiFeO_3$ has been observed independently by Cazayous *et al* [11] and by Singh *et al* [1], and is typically lowering from 3.90 to 1.95 cm^{-1} near T_1 or T_2, with the latter value instrumentally resolution-limited. These values are similar to those [8] in MnF_2 near $T_N = 67$ K, where Schulhof *et al* find neutron scattering magnon linewidths (dependent upon momentum transfer q) of order 0.1 meV (0.8 cm^{-1}), compared with 1.0 meV (8 cm^{-1}) 4.1 K away from T_N.

We emphasize that the intensity divergences for the magnons in the Raman effect at low temperatures need not relate to the susceptibility exponent γ in the case of $BiFeO_3$. The reason is that the magnons are thought to be electromagnons, by virtue of the fact that there is strong and probably linear coupling between the ferroelectric polarization and the magnetic spins, at least locally [12], and the low-T transitions are very far from the Neel temperature (643 K).

Let us explain the absence of the critical exponent γ in a simple way: if the phase transition in question were ferroelectric, the order parameter would be polarization P and the exponent involved would be $\gamma = 1$, the exponent for the isothermal susceptibility. If it were ferromagnetic or antiferromagnetic, the order parameter would be M or M (sublattice), and the exponent would also be γ, which is ca 4/3 for an Ising model. However, we interpret the transition(s) as spin reorientation (coupled magnetoelastically to strain). In this case the exponent is not γ and cannot be ca 1; instead, the strain coupling allows us to invoke the 1956 Pippard relationship (Pippard–Janovec–Garland [13–16]), which says that specific heat scales as elastic strain, and both scale as the exponent α (not γ). α is ca 0.1 in most statistical mechanics models. We cite the work of Kizhaev *et al* [13] because in 1986 they pointed out that there are indeed dielectric anomalies at non-ferroelectric phase transitions, but since P is not the order parameter (strain is), the divergence goes as exponent α and not γ. Simply put, since the Neel temperature $T(N) = 643$ K is hundreds of degrees above the phenomena we see, the dynamics do not involve γ; if all this happened at $T(N)$, γ would be the key exponent.

In the present case another clue is that the magnon Raman intensity is very strong—much greater than in, for example, MnF_2. This surprisingly strong magnon Raman intensity may come almost entirely from phonon coupling, and Adem and Mostovoy [33] have shown that in such a case the cross-section diverges not as $(T_0 - T)^{-\gamma}$ but as $(T_0 - T)^{-\alpha}$, where α is the critical exponent characterizing specific heat divergence. Such an argument can also be made by applying the early results of Kizhaev *et al* to dielectric anomalies at non-ferroelectric phase transitions [13]. These authors argued that the electric susceptibility would couple to strain and result in a divergence that varies as that of the specific heat, which is an exponent usually labelled α. In the present case the coupling is not

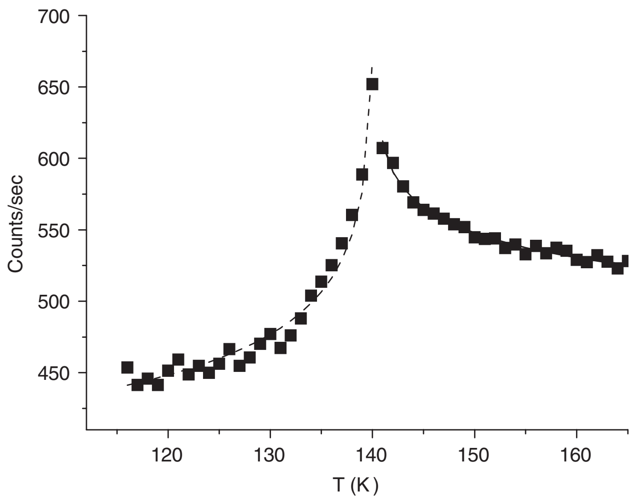

Figure 1. Magnon Raman cross-sections versus temperature above and below the lower spin-reorientation temperature T_2. The solid curve is a fit to a power law: $I(T) = I(0)[T_2/(T_2 - T)]^{\alpha'}$ below and $I(T) = I(0)[T_2/(T - T_2)]^{\alpha}$ where $I(0)$ is the magnon intensity at $T = 0$. The least squares values are $T_2 = 140.3 \pm 0.3$ K, $\alpha = 0.05 \pm 0.01$ and $\alpha' = 0.09 \pm 0.01$.

piezoelectric between electric susceptibility and strain, but is magnetoelastic, between magnetic susceptibility and strain. That is, these two transitions are 'magnetoelastic transitions' and the main order parameter may be strain. But the result is the same as with Kizhaev's model:

$$\partial \Delta \chi_m / \partial T = -(\Delta C / T_C) \partial^2 T_C / \partial H^2 \quad (1)$$

where $\Delta \chi_m$ and ΔC are the most singular parts of the magnetic susceptibility and specific heat; T_C, the non-ferroelectric transition temperature; and H, magnetic field. The fact that specific heat C diverges as the elastic coefficients do at a phase transition is often known as the Pippard relationship [14] and was developed further by Garland [15] and Janovec [16]. (Note that [13] incorrectly attributed their large fitted values of α in $KMnF_3$ to dimensionality, but it was later shown by Scott [17] to be due to defects.) The similarity of the present work to that of Kizhaev *et al* is that they showed that the electric susceptibility diverges with exponent α when the order parameter for the structural transition is not polarization; we show that the magnetic response scales as α at a magnetic transition when the order parameter is not the magnetization (i.e., not a Neel or Curie temperature).

The fits to experimental data are shown in figure 1 for the transition near 140 K and in figure 2 for that near 200 K. Since the theory makes predictions for only integrated cross-sections, we intentionally ran the data with relatively wide slit widths, giving a spectral resolution of a 3–4 cm^{-1}. This integrates out the linewidth narrowing [18], which was observed [11, 1] to decrease from 3.9 cm^{-1} to <2.0 cm^{-1} as the transition temperatures were approached. Data above and below T_0 were not forced to fit the same T_0 but were empirically found to be equal; this is equivalent to requiring a second-order transition. Data were taken only every 1.0 K. This is not generally sufficient for precise evaluation of critical exponents;

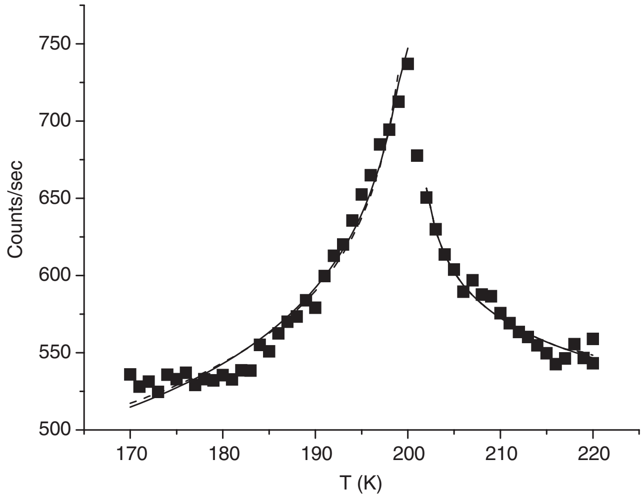

Figure 2. Magnon Raman cross-sections versus temperature above and below the upper spin-reorientation temperature T_1. The least squares values are $T_1 = 201.0 \pm 0.8$ K, and $\alpha = 0.06 \pm 0.003$, and $\alpha' = 0.13 \pm 0.004$.

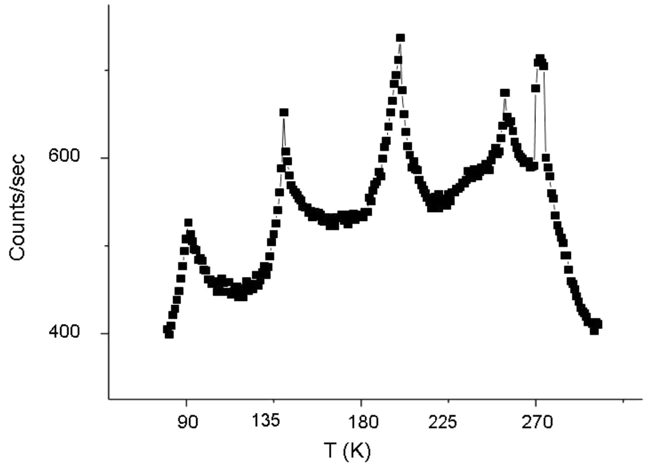

Figure 3. Magnon Raman intensities for all polarization components, showing evidence for two additional magnetic transitions near 90 and 250 K. The peak at 273 K is an artefact due to moisture freezing in the cryostat.

however, the data were taken with a focussed laser beam on an opaque sample. Under these conditions absolute temperature is accurate to only ca ±1 K, and relative temperature to only a few tenths of a degree. Additional, more precise studies are warranted. However, the present results, fitted to a power law

$$I(T) = I(0)[T_2/(T - T_2)]^{\alpha}, \quad (2)$$

where $I(0)$ is the magnon intensity at $T = 0$, give least squares values of $T_2 = 140.3 \pm 0.2$ K; $\alpha = 0.05 \pm 0.01$; and $\alpha' = 0.09 \pm 0.01$. Since the absolute value of these exponents are both $\ll 1$, and it is known that power laws for exponents $\ll 1$ closely approximate logarithmic divergences, we then refitted the data to a logarithmic divergence:

$$I(T) = A + B \log[T_2/(T_2 - T)]. \quad (3)$$

This also worked both above and below T_2, with the same fitted value of $T_2 = 140.3$ K. In figures 1 and 2 a dashed line is given fitting equation (3) and a solid line to equation (2); however, the fits are so close that it is not easy to distinguish the difference. For the 140 K transition the coefficient B was 24 counts s^{-1}.

The fits to the intensity data near $T_1 = 200$ K are shown in figure 2. Independently fitting data below and above 200 K yielded for $T < T_1$: $T_1 = 201.8 \pm 0.8$ K and $\alpha' = 0.14 \pm 0.01$; for $T > T_1$, $T_1 = 200.2 \pm 0.8$ K and $\alpha = 0.7 \pm 0.1$. If we then constrained T_1 to be the same value for data above and below, we obtained $T_1 = 201.0 \pm 0.8$ K, $\alpha' = 0.13 \pm 0.004$ and $\alpha = 0.06 \pm 0.003$. We do not regard these numerical values as sufficiently reliable to infer relationships to models (Ising or Heisenberg in different dimensions), particularly because of the temperature dependent background in the data, but they are probably adequate to infer that the exponents are small (ca 0.1) and perhaps smaller above the transitions than below.

Parenthetically we note that the linear magnetoelectric effect (spin-flop in an applied electric field) recently reported by Lebeugle *et al* [12] is symmetry forbidden, assuming that the generally accepted cycloidal structure is correct (α_{12} is nonzero locally but its effect spatially averages to zero). It is clear that many experiments, such as these studies of spin-flop induced by electric field, need to be redone in the other three magnetic phases. In particular, one needs to determine the magnetic space groups below 140 K, between 140 and 200 K, and between 358 and 643 K = T_N.

There have been many recent studies of magnetism in bismuth ferrite and some evidence for spin-glass behaviour below ca 200 K [19–24] prior to our recent work [4]; and the modulated spin structure at low temperatures in bismuth ferrite has been reexamined. A number of papers from Russia have not been cited often [25–28] but provide useful information on the temperature evolution of the cycloid structure and sometimes disagree with the generally accepted 1982 model of Sosnowska. The 2006 paper by Sosnowska's group reconsiders whether there are changes in the cycloid spin arrangements at low temperatures [29], and if the 'Zalesskii model' is correct; however, although their conclusions show that the cycloid ordering at room temperature does indeed become distorted at 4 K, in accord with Zalesskii's model, it does not indicate where the phase transition occurs, and these subtleties remain suitable for more refined studies in order to reconcile x-ray, neutron, and magnetic resonance data. The present results show clearly that although Sosnowska's basic cycloid [30] may remain throughout the cryogenic range, her exact model cannot possibly give all four observed magnetic phases and is therefore correct for, at most, one. Qualitatively we clearly support the Zalesskii model. The situation becomes even more complicated when all polarizations are monitored. In this case (figure 3), one finds another pair of low-temperature magnetic transitions, near 90 and 240 K. Cazayous have reported [31] that the two pairs of transitions may be related to two different sets of magnons in the incommensurate model of de Sousa [32]. We discuss this in a separate paper. For the present we note only that the cross-section divergence at each transition appears similar.

The basic observation that the magnon Raman intensity divergence is characterized by a very small exponent (0.05–0.06 above and 0.09–0.12 below) is a complete surprise, without precedent or predictions. We explain this by invoking the Pippard relationship for magnetoelastic phenomena near phase transitions, in analogy with the model of Kizhaev *et al* for dielectric coupling to strain at non-ferroelectric transitions. Although it is well known that both α and α' are zero (logarithmic) in the (2D) Ising model and very small (0.125) in the (3D) Ising model, this appears to be coincidental, since as discussed above, acentric spin-glasses such as $BiFeO_3$ cannot be Ising-like [5].

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