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2008 J. Phys.: Condens. Matter 20 425223

(http://iopscience.iop.org/0953-8984/20/42/425223)

J. Phys.: Condens. Matter **20** (2008) 425223 (5pp) doi:10.1088/0953-8984/20/42/425223

Critical slowing down of spin fluctuations in $BiFeO_3$

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Received 19 August 2008, in final form 16 September 2008
Published 30 September 2008
Online at stacks.iop.org/JPhysCM/20/425223

Abstract
In earlier work we reported the discovery of phase transitions in $BiFeO_3$ evidenced by divergences in the magnon light-scattering cross-sections at 140 and 201 K (Singh *et al* 2008 *J. Phys.: Condens. Matter* **20** 252203) and fitted these intensity data to critical exponents $\alpha = 0.06$ and $\alpha' = 0.10$ (Scott *et al* 2008 *J. Phys.: Condens. Matter* **20** 322203), under the assumption that the transitions are strongly magnetoelastic (Redfern *et al* 2008 at press) and couple to strain divergences through the Pippard relationship (Pippard 1956 *Phil. Mag.* **1** 473). In the present paper we extend those criticality studies to examine the magnon linewidths, which exhibit critical slowing down (and hence linewidth narrowing) of spin fluctuations. The linewidth data near the two transitions are qualitatively different and we cannot reliably extract a critical exponent ν, although the mean field value $\nu = 1/2$ gives a good fit near the lower transition.

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

1. Introduction

Near second-order phase transitions there is generally a slowing down of fluctuations in the order parameter [1]. In ferroelectric transitions the spatial regions of correlated polarization (domains) increase in size as the Curie temperature T_c is approached from above and reverse polarization more slowly. This is usually characterized [2] by a power-law dependence of fluctuation time $\tau(T) = bt^{-\nu}$ upon reduced temperature $t = (T - T_c)/T_c$. The correlation length exponent is $\nu = 1/2$ in mean field, $\nu = 1$ in the Ornstein–Zernike model or the [2D] Ising model, and $\nu = 0.64$–0.70 for [3D] Ising or Heisenberg models [3]. Fourier transforming this in terms of a spectral linewidth $\Gamma(T)$, one has for $T > T_c$

$$\Gamma(T) = \Gamma_0 t^{\nu} \qquad (1a)$$

and below T_c,

$$\Gamma(T) = \Gamma'_0 t^{\nu'} \qquad (1b)$$

(primes on exponents conventionally denote the ordered phase $T < T_c$).

In fluids it is usual to define a dynamical structure factor that is proportional to the total scattering intensity to describe such phenomena; and such structure factors have the property that they are proportional to the density–density correlation function. In the hydrodynamic limit in which the wavevector q of the fluctuation is much smaller than the inverse correlation length κ, the linewidth Γ in scattering experiments (Raman or neutron) is proportional to q^2. This is also true for spin–spin correlations in magnets [4]. Thus in the present work the magnon linewidths at a given temperature are not constants but instead $\Gamma_0(q)$ may be a strong function of scattering angle and hence momentum transfer q; this geometrical effect is described in detail, including significant birefringence effects, by Scott [5]. Although originally derived for fluid problems, this q-dependent linewidth result also holds extremely well for spin diffusion in semiconductor spin-flip light scattering [4, 6] and for phason-like fluctuations in quasielastic light scattering in incommensurate insulators [7, 8] both of which have very strong q^2-dependences.

Rather recently unexpected phase transitions in bismuth ferrite were discovered near 140.3 and 201.0 K [9, 10], interpreted as spin–reorientation transitions analogous to those in orthoferrites such as $ErFeO_3$. (Bismuth ferrite is an extremely trendy material with >700 publications on it in the past five years, owing primarily to is ferroelectric–

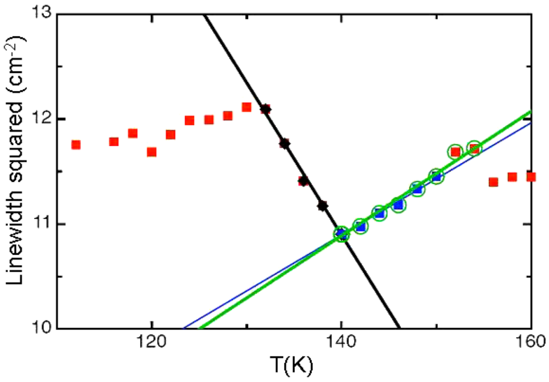

Figure 1. Graph of measured magnon linewidth squared versus temperature for $BiFeO_3$ transition near 140 K. The exponent $\nu = 1/2$ fitted to the curve is not adjustable and is derived assuming the intrinsic width is added in quadrature to the instrumental linewidth. Other fitted parameters are $T_c = T_2 = 140.0 \pm 0.2$ K; $d\Gamma'/dT = 0.07 \pm 0.01$ cm^{-1} K^{-1}; $d\Gamma/dT = 0.03 \pm 0.01$ cm^{-1} K^{-1}; instrumental resolution width $= 3.2 \pm 0.1$ cm^{-1}. Two fits are shown above T_c, including a different number of data points.

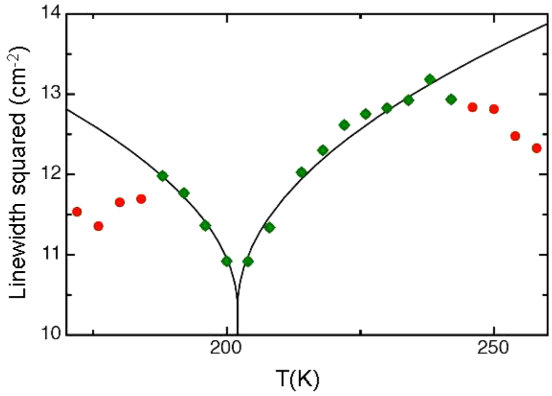

Figure 2. As in figure 1 but for the spin reorientation transition near 201 K. Here the exponent is much less than that at 140 K; in the figure it is constrained to be $\nu = \nu' = 1/4$ assuming that the instrumental and intrinsic widths add in quadrature. These data seem qualitatively different from those in figure 1. Other fitted parameters are $T_c = T_1 = 202.4 \pm 0.5$ K; $d\Gamma'/dT = d\Gamma/dT$; instrumental resolution width $= 3.0 \pm 0.2$ cm^{-1}.

ferromagnetic properties at room temperature.) The critical exponents describing the cross-section divergences of magnon light scattering in this material near these temperatures were fitted, using the Pippard relationship [11], as $\alpha' = 0.11 \pm 0.02 (=1/8?)$ and α = ca $0.06 \pm 0.02 (=1/16?)$; the use of the Pippard relationship was compatible with strong magnetoelastic coupling, demonstrated separately by Redfern *et al* [12]. The values 1/8 and 1/16 are mentioned because at one time they were considered to be the best theoretical estimates for the $d = 3$ Ising model [1b], but unfortunately in the present context it was $\alpha = 1/8$ and $\alpha' = 1/16$ rather than the reverse shown in [10]; in fact it is one of Griffiths' thermodynamic assumptions that $\alpha \geqslant \alpha'$, which disagrees with our earlier data fitting.

In the present paper we would like to try to fit the linewidth narrowing reported near these magnetoelastic phase transition temperatures, and in particular, see if they are mean field with $\nu = 1/2$, or if some other theoretical model (such as Ornstein–Zernike or [3D] Ising) is more applicable. We also try to examine any q-dependence of linewidth by varying the scattering angle; however, this is extremely difficult with opaque samples or micro-Raman instrumentation, because they normally require backscattering geometries.

In these procedures it is important to keep in mind the Levanyuk–Ginzburg criterion [11], which relates the temperature region over which true critical (fluctuation-dominated) exponents may be expected. This varies as the inverse sixth power of the interaction length and hence is expected to be within <1.0 K of the actual transition temperature. At temperatures farther removed, mean field theory is likely to prevail, since the fluctuations are small; i.e., far below the transition temperature $[\langle\phi^2\rangle - \langle\phi\rangle^2]/\langle\phi^2\rangle \ll 1$, where ϕ is the order parameter (in our case, a spin-axis tilt). By comparison the present studies are 1.0–40 K from the transition temperatures and thus apt to be compatible with mean field theory independent of the detailed statistical mechanics involved.

2. Experimental details

Both Cazayous *et al* [13] and Singh *et al* [9, 10] reported magnon linewidth narrowing near 140 and 200 K. Initially Cazayous *et al* found only one anomaly at 140 K [14] and nothing at 200 K, but later studies [13] revealed both transitions with concomitant narrowing. Cazayous *et al* did not initially [14] interpret these phenomena as phase transitions, but later borrowed without attribution the interpretation of Singh *et al* [9, 10, 15] that these were spin–reorientation transitions, as in orthoferrites, and this seems now to be the accepted point of view.

The data taken in our laboratory were obtained using a T64000 spectrometer (Horiba Inc.) equipped with a triple-grating monochromator and a Coherent Innova 90 C Ar^+-laser with excitation wavelength of 514.5 nm in a backscattering geometry appropriate for opaque materials. Temperature control was good to ±0.1 K over the time required to measure a spectrum, but absolute temperature is probably accurate to only ±0.5 K, due to sample heating from the laser. The spectral resolution was typically about 1 cm^{-1}. The narrowest magnon linewidth we measured under such resolution was 1.6 cm^{-1}. The data sets in figures 1 and 2 are wider (ca 3 cm^{-1}), but this is due to the measurement of different polarizations for the scattered light, as explained in section 3.1 below.

2.1. Linewidth deconvolution procedure

Over the temperature range studied the apparent magnon linewidths varied from full widths at half maximum of about 4 cm^{-1} to slightly less than 2 cm^{-1}. In order to obtain accurate magnon linewidths it is necessary to deconvolute the intrinsic width from the spectral resolution. This is not a completely trivial undertaking. Usually the intrinsic linewidth is approximately Lorentzian but the instrumental response is more nearly Gaussian. This problem was considered carefully many years ago by Worlock and Fleury [16–18], and we follow their guidelines. Simply put, the question is whether intrinsic and instrumental linewidths add linearly or as squares. Worlock and Fleury found that the instrumental width and intrinsic linewidth added approximately in quadrature, not linearly. The net result is that there is a systematic uncertainty in our quoted values that is somewhat greater than the random statistical error. In order to facilitate the least squares fit to the correlation exponent ν, it was very useful to require the transition temperatures to be the same for data both above and below the transition and thereby to simultaneously fit all the data near each transition; this is tantamount to requiring a second-order transition. If T_c is allowed to be a different free variable for data above and below, as would be the case for a first-order transition, then ν and T_c become more highly correlated in the least squares fitting.

For deconvolution in quadrature one has

$$\Gamma^2(T) = \Gamma_0^2 + B^2 t^{2\nu}, \tag{2a}$$

which can be expanded as

$$\Gamma(T) = \Gamma_0[1+(B^2/\Gamma_0^2)t^{2\nu}]^{1/2} = \Gamma_0[1+(B^2/2\Gamma_0^2)t^{2\nu}+\cdots]. \tag{2b}$$

Note from equation (2*b*) that the exponent characterizing $\Gamma(T)$ near the transition temperature is 2ν and not ν. Thus a linear dependence very near the transition temperatures will actually characterize $\nu = 1/2$ (mean field). Unfortunately the numerical value extracted for ν in this way depends critically upon the exact deconvolution scheme employed, which is one reason we cannot do a least squares fit to ν from existing data. The usual least squares routines result in large uncertainties for ν and high correlations among the fitted parameters, which are not independent; therefore what we do instead is to show in figures 1 and 2 that the mean field value is merely *compatible* with the data.

3. Interpretation of data

As shown in figures 1 and 2, the linewidth data near the two transitions are not qualitatively similar: Those data near 201 K are symmetric above and below the transition temperature and exhibit marked curvature when linewidth is plotted versus temperature. This may relate to the fact that the transition near 201 K has much greater strain coupling than that at 140 K [12]. We note in addition that the magnon linewidth is not T-independent outside of this temperature range; near 230 K there is the onset of a splitting between the zero-field-cooled susceptibility and the field-cooled susceptibility, which has been interpreted as the beginning of spin-glass behavior discussed below. Simultaneously fitting linewidths both above and below the transition temperature yielded $T_1 = 202.3 \pm 0.3$ K, which agrees within a two-standard-deviation error with our value determined earlier from cross-section divergence of 201.0 ± 0.8 K. However, for the lower transition near 140 K the linewidth narrowing is nearly linear with temperature both above and below the transition and hence a least squares fits of the data to equation (1) yielded for this phase transition $\nu = \nu' = 0.42 \pm 0.08$, assuming quadrature linewidth-resolution convolution (a simpler linear deconvolution yields larger values). Within experimental uncertainty these values satisfy the mean field prediction of $\nu' = \nu = 1/2$. This may be compatible with our earlier conclusion that the transitions are magnetoelastic [10]. Strain is usually long-range and unscreened, and so mean field results are not unreasonable *a priori*. It is also compatible with the fitting of the critical exponents α; in our fittings we found that the assumption of logarithmic divergences (equivalent to $\alpha = 0$, which occurs in mean field and more explicitly as logarithmic in [2D] Ising models) gave approximately as good a fit as did power laws with exponents α or $\alpha' = 0.05$–0.11.

It is interesting to note that the coefficients Γ_0 and Γ_0' (not exponents) of linewidth versus temperature above and below $T_2 = 140.3$ K in equations (1*a*) and (1*b*) differ by almost precisely a factor of 2.0 (larger below). This is reminiscent of the behavior of reciprocal dielectric constant near second-order ferroelectric transition temperatures, which often also have a difference of 2.0 in slope (theoretically predicted if strain is absent). Note that according to [12] the transition at 201 K is dominated by strain, whereas that at 140 K is relatively strain-free, in accord with this suggestion.

As a more general and probably more important point, the linewidth narrowing shows qualitatively that these are real phase transitions. Alternative models involving defects can indeed create purely dynamic anomalies that are not true phase transitions, such as oxygen vacancy effects [19], and many such anelastic effects due to impurities or defects are well known at low temperatures. A good example relevant to the present study in the temperature range near 200 K in oxides is that due to oxygen relaxation in the high-T_c superconductor YBCO [20]. These are often studied via internal friction. However, none of these defect or impurity mechanisms can cause magnon linewidth narrowing near specific temperatures.

Maximilien Cazayous kindly provided numerical magnon linewidth data to us from his experiments [13]. His data points have similar widths as ours, but they are rather sparse as a function of temperature and hence do not permit evaluation of critical exponents. We tried to superpose them on our data, but they were run with different spectral slit widths and geometries, and incorporating them into our figures would therefore have involved adjustable parameters.

3.1. Linewidth dependence upon scattering angle and birefringence

Any quantitative q-dependence of the linewidths reported here will have to await further study. The micro-Raman technique we employed on these opaque samples did not permit sufficient intensity for quantitative work except at scattering angles near 180°. Larger specimens might permit 45° or 90° scattering studies, as well as grazing incidence, in the near future; and thin specimens might allow near-forward scattering. Typically one can vary q by an order of magnitude with such experiments in transparent materials [5–8].

The wavevector q probed in light scattering is given (for 'extraordinary' incident light polarized along the polar axis and collected 'ordinary' light polarized orthogonal to that axis) by

$$q^2 = [\omega_L(n_e - n_0) + \omega n_0]^2 + 2\omega_L(\omega_L - \omega)n_e n_0(1 - \cos\Theta) \tag{3}$$

where ω_L and ω are the radial frequencies of the incident laser light and of the magnon; n_e and n_0, the extraordinary and ordinary indices of refraction of the specimen; and Θ, the scattering angle. Wavevector (momentum) conservation requires that since the wavevector of incident and scattered light are each approximately $K = \omega_L n$, with $\omega_L = 2\pi \times 20\,486\ \mathrm{cm}^{-1}$ (488.0 nm blue laser light) and $n = 2.62$, then $q = 2.1 \times 10^5\ \mathrm{cm}^{-1}$ for 90° angle scattering but $3.0 \times 10^4\ \mathrm{cm}^{-1}$ for 45° scattering and a few $\times 10^3\ \mathrm{cm}^{-1}$ for small angles. Note that the sign of the first term ($n_e - n_0$) can be reversed by reversing both incident and scattered light polarizations (e.g., xz and zx polarizabilities), so that q can also be varied without changing angle. If the first term in equation (3) is negligible, due to the negative sign of ($n_e - n_0$), then the linewidth will vary very nearly as q^2; whereas if it is positive (or zero, with both incident and scattered light having the same polarization), the linewidth will be more independent of q. In $BiFeO_3$ we know that $(n_e - n_0) = -0.13$ at wavelengths of ca 550 nm is negative and unusually large [5c]. In qualitative agreement with this, we find that rotating the polarizers changes the magnon linewidths at a given temperature in our experiments by approximately a factor of 2, typically from 3.2 to 1.6 cm^{-1}.

Although the existing linewidth data do not include enough scattering angles to afford close comparisons with this theory, it is provided to alert other investigators that comparisons of linewidths will generally not be possible unless scattering angles and birefringence effects are identical. The birefringence effects measured in our preliminary studies suggest that equation (3) is involved.

3.2. Thermodynamic inequalities

Certain relationships are well known among the critical exponents at any continuous phase transition. These are thermodynamically exact as inequalities [21] and are satisfied as equalities under the assumptions of scaling theory. Some of these involve only the exponents α and α' determined in our earlier work together with values of ν' and ν determined in the present paper. Our earlier results [10] for α and α' were very near the fractional values 1/8 and 1/16 respectively often invoked [1] for [3D] Ising models.

The Josephson inequality [22] expressed as a hyperscaling equality below and above T_c

$$d\nu' = 2 - \alpha' \tag{4}$$

$$d\nu = 2 - \alpha \tag{5}$$

(where the dimensionality of the system is d) is satisfied for our values within their experimental uncertainties, although the small values of α and α' imply for $d = 3$ non-mean-field values of ν and ν' of approximately 0.63–0.65. Note that this Josephson (in)equality is also compatible with mean field if that is taken as having $d = 4$ marginal dimension (for which $\nu = 1/2$ and $\alpha = 0$). Therefore in the present case the mean field approximation ($\alpha = \alpha' = 0$ or logarithmic and $\nu = 1/2$) cannot be ruled out (recall that a logarithmic divergence fitted the cross-sections $I(T)$ nearly as well [10] as did $\alpha = 0.06$, which is always true for very small $\alpha \ll 1$ since in that case $\mathrm{d}I/\mathrm{d}T$ is nearly the same for $I(T) = A \log t$ as for $I(T) = At^{-\alpha}$). We note parenthetically that the values given here do however rule out the [2D] Ising model, which has $\alpha = 0$ (logarithmic), close to that observed, but $\nu = 1$. Defect models [23] also fail utterly, giving $\alpha > 1$ and $\nu < 0$.

Relatively few other thermodynamic inequalities involve both ν and α. However, one that involves α is

$$d\gamma' = (2 - \eta)(2 - \alpha') \tag{6}$$

(which is obtained by combining a Fisher inequality [24] and the Rushbrooke inequality [25]); more pertinent is

$$(2 - \eta)\nu = \gamma, \tag{7}$$

which is a second Fisher inequality [24].

Note that the relationship equation (6) above T_c explicitly involves the dimensionality of the system, whereas equation (7) below T_c does not. These relations could be tested for the spin reorientation transitions in $BiFeO_3$ if the isothermal magnetic susceptibility could be measured precisely, giving γ and γ'; the pair correlation exponent η is small (0.03–0.04 in [3D] Ising or Heisenberg; zero classically) and hence negligible to a first approximation. The exponent β characterizing the order parameter near the Néel temperature (T_N = ca 643 K) is known to be approximately 0.43 from birefringence [5c, 26] and 0.37 from Mossbauer hyperfine splittings [27], but β is unknown near the spin reorientation transitions, and γ is unknown near T_N.

In the approximation that $\eta = 0$ (or $\eta \ll 2$), one also has from the Buckingham–Gunton inequality [24]

$$d\nu = 2(\beta + \nu) \qquad \text{or equivalently } (d - 2)\nu = 2\beta, \tag{8}$$

which could prove useful with additional data on β near 140 or 201 K (if $d = 2$ the approximation $\eta \ll 2$ leading to equation (8) fails and hence instead $\beta = \eta/2 = 1/8$ for the [2D] Ising model).

4. Conclusions

Critical narrowing been evaluated from magnon light scattering linewidths near the spin reorientation transitions in bismuth ferrite at 140.3 and 201 K. However, instrumental response and other technical issues prevent us from evaluating reliably the critical correlation length exponents ν and ν'. For temperatures a few degrees from the 140 K transition they are compatible with a mean field model with $\nu = \nu' = 1/2$, but even this conclusion numerically is dependent upon the deconvolution procedure to extract linewidths from instrumental resolution. These mean field values are also reasonably compatible with our recent evaluations of α and α' as $\ll 1$. Although these results are not sufficient to establish a statistical mechanical model of the transitions (Ising or Heisenberg in two or three dimensions or possibly mean field), they do show real phase transitions, not dynamic effects due to defects, with real critical slowing down of spin fluctuations.

4.1. A long-range spin glass?

Further more precise data and quantitative modeling would be interesting because spin-glass behavior in $BiFeO_3$ is also observed in this temperature regime [28], and the conventional wisdom [29] is that magnetic spin glasses in acentric ferroelectric materials cannot be Ising-like. An Almeida–Thouless AT-line will be shown for this system in a separate publication [30], which varies as predicted with applied magnetic field as $H^{2/3}$; this further implies that it cannot be a short-range Ising spin glass [31–33] but may be mean field [34, 35], in agreement with the present suggestions.

Acknowledgments

This work was supported in Puerto Rico by DOD Grant Nos W911NF-06-1-0030 and W911NF-06-1-0183 and at Cambridge by the EPSRC EP/F001630/1 and EP/CO14561/1 and by the EU FP-6 STREP 'Multiceral' program. We thank Dr Maximilien Cazayous and Professor David Sherrington for helpful discussions and Drs Gustau Catalan and Julia Herrero Albillos for data fitting.

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