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Electroclinic response of some ferroelectric liquid crystals

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We report measurements on the temperature variation of the electroclinic coefficient (e) of three members of a homologous series and a commercial ferroelectric mixture. The pure compounds have P/θ ratios which are an order of magnitude larger than that of the commercial mixture. This is reflected in the temperature variations of the electroclinic coefficient. Plots of e^{-1} versus temperature indicate that in all the four cases the Landau theory gives a good description of the critical divergence of e as the S_C^*–S_A transition point is approached. We have made a detailed analysis of the data on one compound using the Garoff–Meyer model to confirm that the critical behaviour for the soft mode is indeed well described by the Landau theory.

1. Introduction

The electrooptic properties of ferroelectric liquid crystals are being studied extensively as these materials have considerable advantages over nematic liquid crystals in display applications. Meyer *et al.* [1] who discovered ferroelectric liquid crystals, later found the electroclinic effect in the smectic A phase occurring at temperatures above the range of stability of the smectic C* phase [2, 3]. The chiral symmetry of the molecules removes the mirror symmetry in the plane containing the transverse polarization caused by an external electric field and the layer normal. This means that the molecules tilt with respect to the layer normal in the orthogonal plane. Garoff and Meyer [3] made a detailed study of the electroclinic coefficient in the well known ferroelectric compound 4-decyloxybenzylidene-4′-amino-2-methylbutyl cinnamate (DOBAMBC) with an emphasis on the critical behaviour of the electroclinic coefficient as the S_C^*–S_A transition point is approached. They discussed the results in the framework of the Landau theory of the S_C^*–S_A transition. There have been a few other studies of the electroclinic coefficient in the intervening period [4–6]. In particular, Dupont *et al.* [5] have emphasized the need to ensure working with relatively small applied electric fields near the S_C^*–S_A transition point to be in the linear regime so that the comparison with the Landau theory is valid. Recently it has also been suggested that the fast linear electrooptic response characteristic of the electroclinic effect may be useful in device applications [7, 8].

We have been investigating the electromechanical effect in cholesteric liquid crystals during the past few years [9–10]. This effect again arises from the chiral symmetry of the cholesteric phase, and depends on the transport of ions through the helical medium. Our experiment to study this phenomenon in samples with fixed boundary conditions [10] consists of detecting the oscillations in the azimuthal angles

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of the director in a sample under an applied AC electric field. The set-up is exactly similar to the one used for measurements of the electroclinic coefficient. Further, several new ferroelectric compounds have been synthesized in our chemistry laboratory [11] and several properties of these materials like polarization, the tilt angle, etc., have been measured [12]. We thought it worthwhile to study the electroclinic effect in these materials. In this paper, we present our measurements and a preliminary analysis of the data on these systems.

2. Theoretical background

Following the Landau theory of Garoff and Meyer [3], the free energy density of a smectic A liquid crystal consisting of chiral molecules can be written in the form

$$F=F_0+\tfrac{1}{2}A(T)\theta^2+\tfrac{1}{2}\chi_P^{-1}P^2-cP\theta-PE-\frac{\varepsilon_\infty}{2}E^2, \tag{1}$$

where F_0 is the ground state free energy of the smectic A phase, θ is the induced tilt angle, $A(T)$ is the temperature dependent Landau coefficient which goes to zero at the (non-chiral) $\mathrm{S_C}$–$\mathrm{S_A}$ transition point. i.e. $A=a(T-T_c)$, P the induced polarization, E the external electric field and c is the electroclinic coefficient coupling P and θ, and ε_∞ is the high frequency dielectric constant (see also [5]). The primary order parameter of the $\mathrm{S_C^*}$–$\mathrm{S_A}$ transition is the tilt angle θ. The secondary order parameter is the polarization P which makes only a relatively small contribution to the free energy density. Thus the susceptibility χ_P is treated essentially as temperature independent. P and θ are independent variables. As such, minimizing F with respect to these, and rearranging, one finds [3]

$$\theta=\frac{c\chi_P E}{\tilde{a}\left(\dfrac{T-T_c^*}{T_c^*}\right)}\quad\text{say,} \tag{2}$$

where T_c^* is the renormalized critical temperature

$$T_c^*=T_c+\frac{c^2\chi_P}{\tilde{a}}, \tag{3}$$

at which the electroclinic effect diverges, and $\tilde{a}=aT_c^*$. The polarization P is given by

$$P=\left(\chi_P+\frac{\chi_P^2c^2}{\tilde{a}\left(\dfrac{T-T_c^*}{T_c^*}\right)}\right)E, \tag{4}$$

i.e. P also diverges as T_c^* is approached.

Experimentally, it is necessary to use an AC rather than a DC field to avoid various complications which occur in the latter case. In this case, θ oscillates at the frequency of the applied voltage and one has to include a dissipative contribution to the energy expression. One can then write a phenomenological equation of motion:

$$\eta\dot{\theta}+\tilde{a}\left(\frac{T-T_c^*}{T_c^*}\right)\theta=c\chi_P E, \tag{5}$$

where η is an appropriate viscosity coefficient. If the applied field varies sinusoidally with time, i.e. $E=E_0\exp(i\omega t)$, then θ oscillates at the frequency ω with an amplitude

$$\theta_0=c\chi_P E\Big/\left[\omega^2\eta^2+\tilde{a}^2\left(\frac{T-T_c^*}{T_c^*}\right)^2\right]^{1/2}, \tag{6}$$

and a phase angle

$$\delta=\tan^{-1}\left[-\omega\eta\Big/\tilde{a}\left(\frac{T-T_c^*}{T_c^*}\right)\right]. \tag{7}$$

It is clear from equation (6) that as T approaches T_c^*, because of the viscous term the divergence of θ_0' will be curtailed and the amplitude tends to a saturation value. The relaxation time of the fluctuations of the order parameter θ, viz.

$$\tau=\eta\Big/\tilde{a}\left(\frac{T-T_c^*}{T_c^*}\right), \tag{8}$$

also diverges as T_c^* is approached.

The above results have been obtained in the framework of the Landau mean field theory. Fluctuations can in principle modify the critical index for the divergence of the electroclinic coefficient. Hence, in general, one can replace the reduced temperature $[(T-T_c^*)/T_c^*]$ by $[(T-T_c^*)/T_c^*]^\gamma$ where γ is the critical index, in equations (6) to (8).

3. Experimental results and discussion

A block diagram of the experimental set-up is shown in figure 1. The cell with a typical thickness of 7–10 μm is made of two indium tin oxide coated glass plates. The plates are coated with polyimide and unidirectionally rubbed. The cell is filled with the liquid crystal in the isotropic phase and mounted in an INSTEC HSI-i microscope hot stage and the temperature controlled by INSTEC mK1-i precision temperature controller. The temperature can be controlled and measured to about 10 mK. We measure the sample temperature independently using a platinum resistance thermometer located close to the liquid crystal cell. The hot stage is in turn kept on the stage of a Leitz polarizing microscope (Model Ortholux IIPOL-BK). The sample is slowly cooled from the cholesteric to the smectic A phase. There was a reasonably good overall homogeneous alignment of the compounds for which we report measurements in the present paper. However, one could see a few focal conic defects in the field of view. The

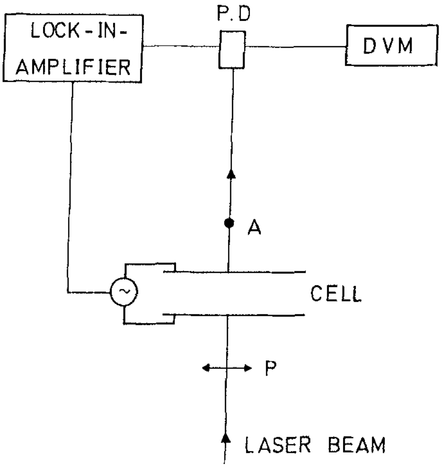

Figure 1. Block diagram of the experimental set-up to measure the electroclinic coefficient.

sample was illuminated with a low power helium–neon laser beam (<0·1 mW). The azimuth of the director was adjusted to be at $\pi/8$ radians with reference to the substage polarizer. The analyser was crossed with reference to the polarizer. The AC output from a lock-in-amplifier (PAR model 5301A) was used as the voltage source to energize the cell. The electrooptic response was monitored using a Hewlett–Packard 'pin' photodiode. The preamplified output of the photodiode was connected both to a DC voltmeter (Keithley Model No. 181) and the lock-in-amplifier to record the DC and f components of the electrooptic signal.

Measurements were made on four systems, three of which belong to the homologous series, [2*S*, 3*S*]-4′-(2-chloro-3-methylpentanoyloxy)phenyl *trans*-4″-*n*-alkoxycinnamates synthesized in our laboratory [11]. The general structural formula is shown in figure 2. The compounds have two chiral centres and a reasonably high

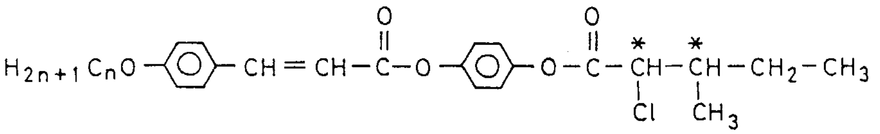

Figure 2. Structural formula of [2*S*, 3*S*]-4′-(2-chloro-3-methylpentanoyloxy)phenyl *trans*-4″-*n*-alkoxycinnamate.

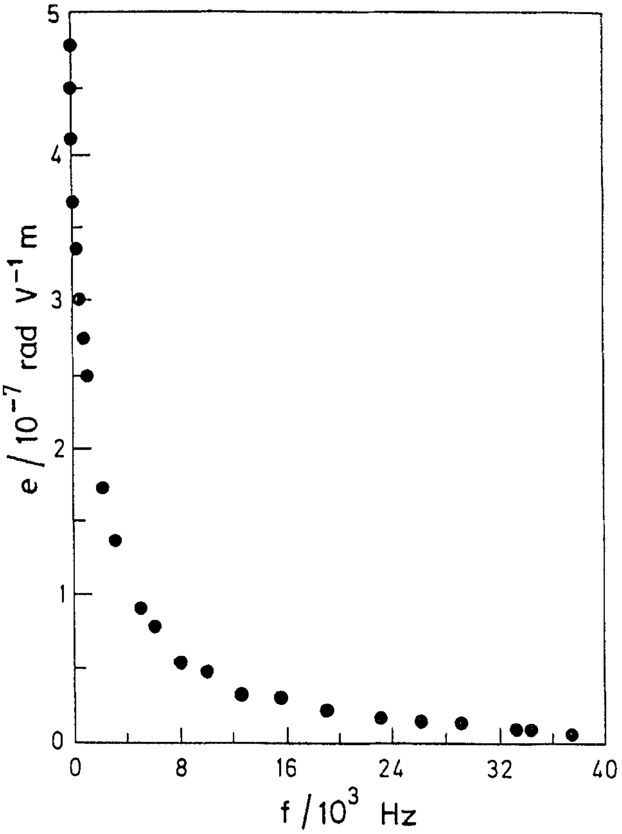

Figure 3. Frequency dependence of the electroclinic coefficient, *e*, of the 8th homologue of the compound whose structural formula is shown in figure 2 at the temperature 66·43°C.

value of polarization in the ferroelectric phase [12]. The studies were made on the 8th, 9th and 10th homologues all of which exhibit the phase sequence isotropic–cholesteric–smectic A–chiral smectic C as the sample is cooled. We have also made measurements on a commercial sample, viz. SCE-6 bought from BDH Ltd.

The data were taken while cooling the samples. The electroclinic tilt angle increases with the applied field (see equations (2) and (6)). As discussed by Dupont *et al.* [5] the electroclinic response becomes a non-linear function of E if the applied field is too large. As the response diverges when the temperature is reduced towards T_c^*, the linear regime shrinks. We have correspondingly reduced the applied voltage to ensure that we are in this regime. The induced tilt angle due to the electroclinic effect is calculated using the relation

$$\theta = \frac{I_f}{4I_0}, \tag{9}$$

where I_f is the amplitude of the photodiode signal at the frequency f of the applied voltage and I_0 is the difference between the DC signals measured as described earlier and that corresponding to zero azimuthal angle. The electroclinic coefficient is given by $e = \theta/E_0$, where E_0 is amplitude of the applied electric field.

At high temperatures in the smectic A range, the electroclinic relaxation time is very short, but as the temperature is reduced towards T_c^*, it increases sharply (see equation (8)). A typical frequency dependence of the electroclinic coefficient is shown in figure 3 for the eighth homologue at ~ $T_c^* + 0{\cdot}2°$. The detailed temperature dependence of the

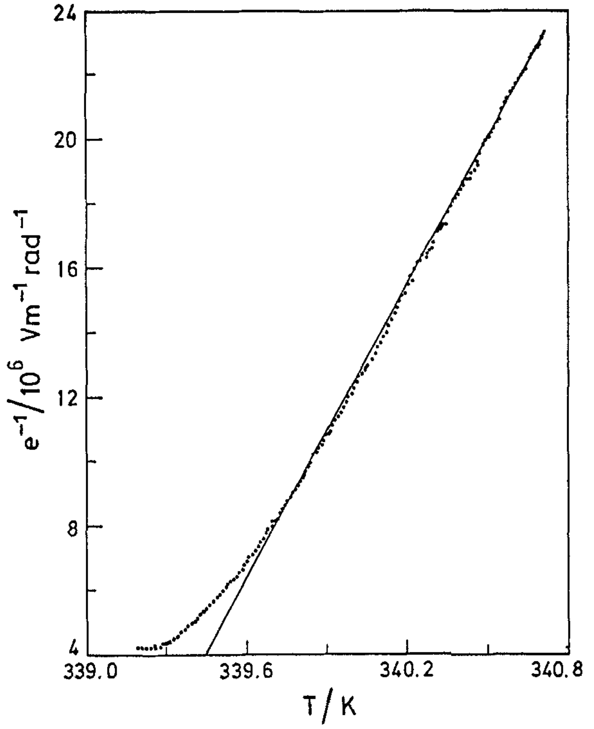

Figure 4. Temperature dependence of the inverse electroclinic coeffcient e^{-1} of the 8th homologue of the compounds whose structural formula is shown in figure 2.

electroclinic coefficient has been measured usually at a frequency $\simeq 1{\cdot}96$ kHz. We measured both the amplitude and phase of the electroclinic signal in a temperature range of ~ 1–$2°$ above T_c^*. As expected from equation (6) the electroclinic coefficient rapidly increases as the S_C^*–S_A transition temperature is approached. The measured phase angle of the signal is slightly less than π radians at temperatures far above T_c^*, and decreases as the temperature is decreased, i.e. the actual phase delay of signal increases as T_c^* is approached. The rate of this variation grows as T_c^* is approached. We have plotted the inverse electroclinic coefficient (e^{-1}) as a function of temperature in figures 4 to 7 for the four systems studied. At temperatures well above T_c^*, the variation of e^{-1} is quite linear as expected from the Landau theory (see equation (2)). As T_c^* is approached and the relaxation time increases, the dissipative contribution becomes important and the electroclinic coefficient saturates (see equation (6)). Correspondingly e^{-1} shows a deviation from the linear dependence on T. The slope of the linear variation depends on the ratio of the coefficient of the first term of the Landau expression, a, and the electroclinic coupling constant, c (see equation (2)). The slopes have the magnitudes $1{\cdot}55 \times 10^7$, $2{\cdot}1 \times 10^7$ and $1{\cdot}6 \times 10^7$ for the 8th, 9th and 10th homologues respectively. As the chemical nature and the smectic A range of all the three homologues are very similar, the slopes have the same order of magnitude. On the other hand, in the case of SCE-6, the slope is an order of magnitude larger, being $1{\cdot}1 \times 10^8$. The (P/θ) value of the 10th homologue of the pure compound is $\simeq 2{\cdot}35 \times 10^{-3}$ C/m^2 in the ferroelectric phase, at $\sim T_c^* - T = 5°$ [12]. For SCE-6, this ratio is $\sim 1{\cdot}3 \times 10^{-4}$ C/m^2 at a similar relative temperature in the S_c^* phase [13]. From equations (2) and (4), $P/\theta \sim c\chi_P$, while the slope of e^{-1} versus T plot is $\sim(\tilde{a}/c\chi_P)$ from equation (2). As P/θ is an order of magnitude larger in the pure compounds compared to SCE-6, the slope is correspondingly smaller.

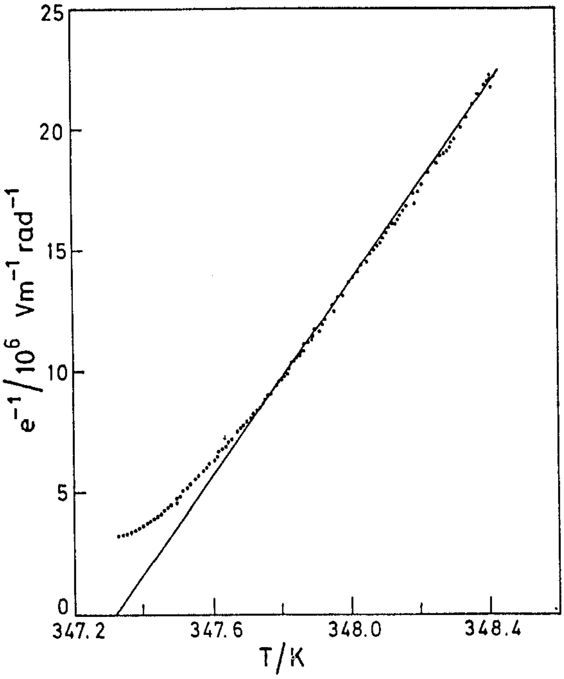

Figure 5. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of the 9th homologue.

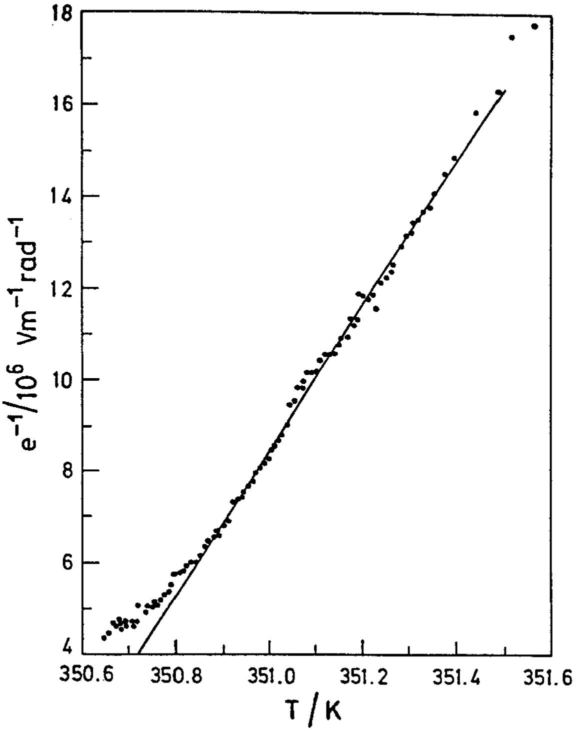

Figure 6. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of the 10th homologue.

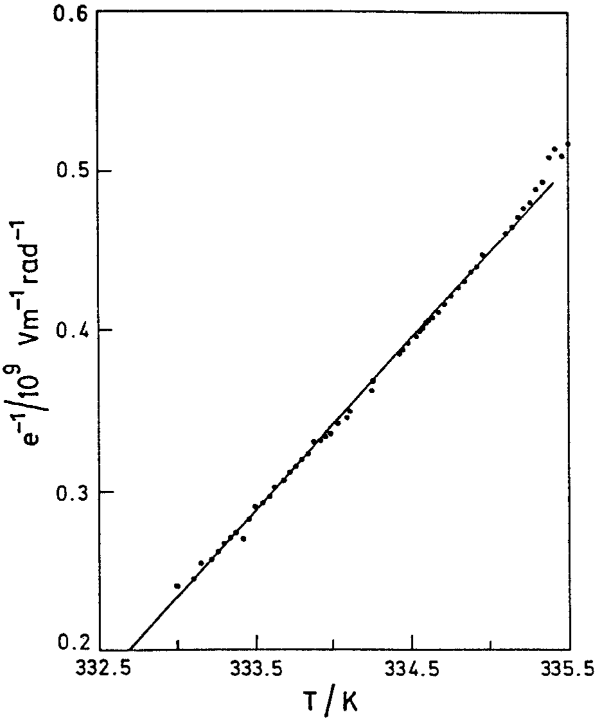

Figure 7. Temperature dependence of the inverse electroclinic coefficient, e^{-1} of SCE-6, a ferroelectric mixture made by BDH Ltd.

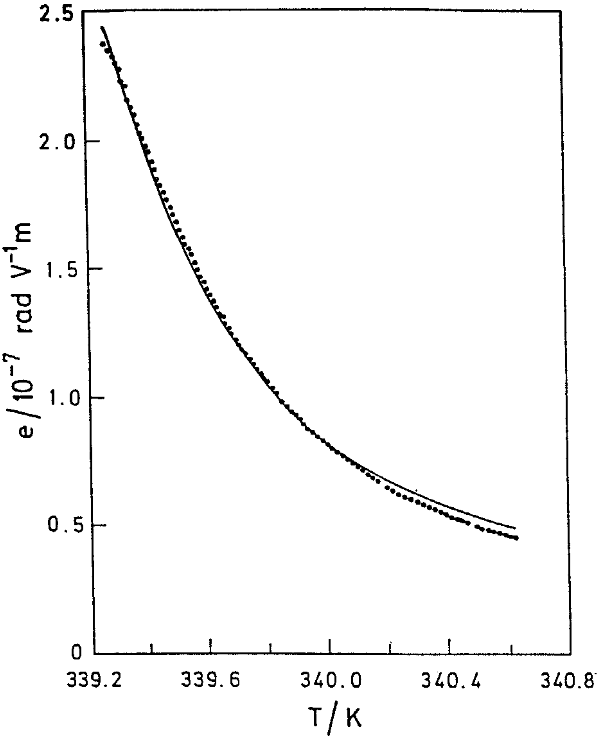

Figure 8. Divergence of *e* in the 8th homologue as T_c^* is approached. The continuous line is the theoretical variation given by equation (6).

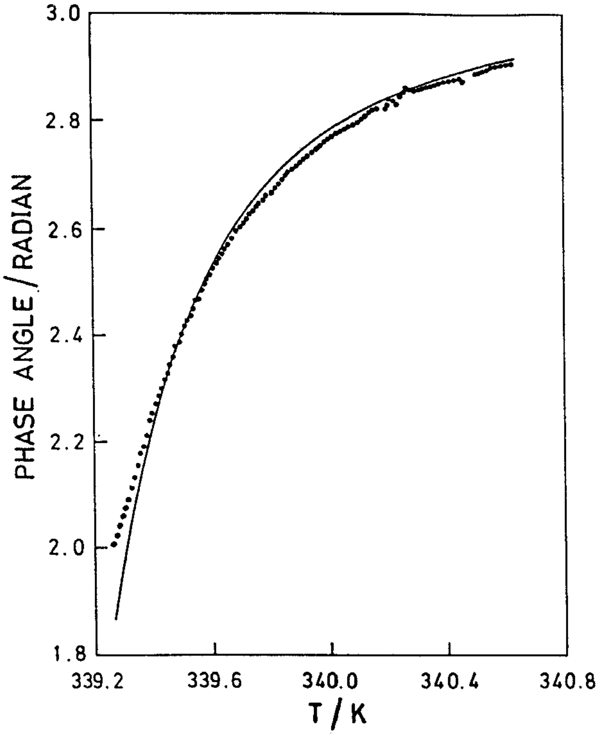

Figure 9. Temperature variation in the phase angle of the electroclinic signal in the 8th homologue. The continuous line is the theoretical variation given by equation (7).

We have fitted our data on the amplitude and phase of the electroclinic signal of the eighth homologue to equations (6) and (7). Following Garoff and Meyer [3], we use a temperature dependent viscosity

$$\eta=\eta_0 \exp(B/T), \tag{10}$$

where B is an activation energy in temperature units.

We adjusted the 6 parameters listed below to get an overall minimum in the χ^2 values for both the amplitude and the phase of the electroclinic signal

δ_b (the background phase angle far above T_c^*): 3·098 rad.

$B=1971\,\mathrm{K}$, $T_c^*=339{\cdot}17\,\mathrm{K}$, $\eta_0\omega/\tilde{a}=2{\cdot}475\times10^{-6}$,

$c\chi_P/\tilde{a}=2{\cdot}135\times10^{10}$ and $\gamma=1{\cdot}0$.

While the fit is not very good, as there are systematic deviations in both the parameters (see figures 8 and 9) it is very clear that γ cannot be significantly different from the mean field value. This is in agreement with other measurements on this index [3, 5]. We should also note that our compound slowly deteriorated with time, and we have not taken into account this factor in the present calculations. We are now improving our experimental set-up and hope to explore the critical behaviour of this soft-mode in greater detail.

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