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The phase transition of strontium titanate

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The structural phase transition of strontium titanate has played a crucial role in the development of our understanding of structural phase transitions. It was the first system for which experiments showed a soft mode, non-classical exponents, two time scales and two length scales for the fluctuations above T_C. These experiments are reviewed. The first two of these results are now well understood but the last two are in contradiction with the accepted scaling theory of phase transitions. Various suggestions have been put forward and these are reviewed for accounting for these results in terms of defects and imperfections but they are not completely convincing. Further work is needed either to confirm that these suggestions are correct or to develop new explanations.

1. Introduction

The purpose of this paper is to review the development of our understanding of the structural phase transition of $SrTiO_3$. The reason for choosing $SrTiO_3$ is that almost every new development in structural phase transition theory has begun with experiments performed on $SrTiO_3$. It was the first material undergoing a structural phase transition for which the soft modes were clearly measured and this led to the classical era of the study of phase transitions as described in § 2. This is still the starting point in the study of any new material.

Section 3 describes departures from the classical theory close to the transition temperature, T_C, due to the interaction between the different critical fluctuations. Properties have different exponents from those given by the classical theory and, again, these differences were first clearly identified for structural phase transitions by measurements on $SrTiO_3$. The theories of the critical fluctuations depend on the ideas of scaling which postulate that at any temperature close to T_C, the critical fluctuations can be described in terms of a single length scale and time scale. In contrast, experiments on $SrTiO_3$ and other materials have clearly given results which suggest that at least two length and two time scales are needed to describe the critical fluctuations. In § 4 we describe these experiments in detail as their results are clearly inconsistent with the basic assumption of scaling theory. Possible explanations for these results are described in § 5. Nevertheless, after 25 years of study, the structural phase transition in $SrTiO_3$ is still not understood.

2. The classical era

At high temperatures, $SrTiO_3$ has the cubic perovskite structure but, below the phase transition temperature $T_C \approx 105$ K, the structure is distorted by a rotation of

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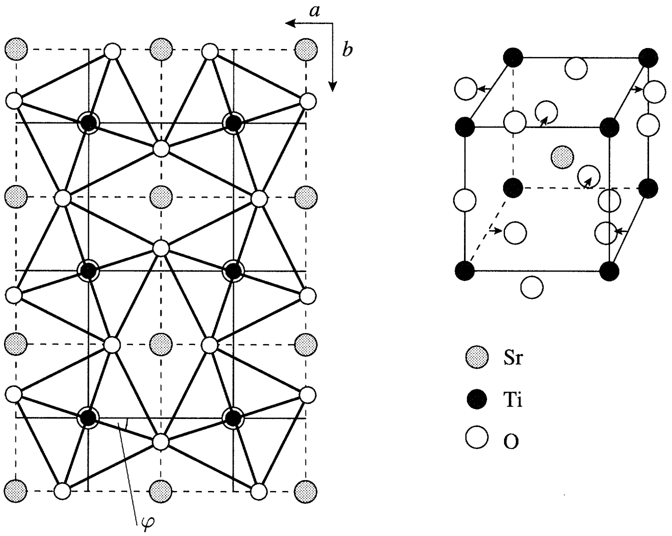

Figure 1. A projection down the cube axis of the distorted phase of $SrTiO_3$, as deduced by Unoki & Sakudo (1967).

the oxygen octahedra about each Ti ion as illustrated in figure 1 (Unoki & Sakudo 1967). The rotation is of opposite sense in neighbouring unit cells and so is described by a wavevector $\boldsymbol{q}_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\boldsymbol{a}^*$ of the high-temperature phase and, although figure 1 shows a rotation about the c-axis, it is equally possible for the rotation to be about the equivalent a- or b-axes.

Before the discovery of the phase transition in $SrTiO_3$, Cochran (1960) and Anderson (1960) had suggested that structural phase transitions might be associated with an instability of the crystal against one of the normal modes of vibration and, furthermore, that as $T \rightarrow T_C$, the frequency of this mode $(\boldsymbol{q}_s j)$ might be expected to vary as

$$\omega^2(\boldsymbol{q}_s j) = c(T - T_C), \tag{2.1}$$

where c is a constant. This mode is known as a soft mode, and soon after the work of Unoki & Sakudo (1967), neutron scattering experiments on $SrTiO_3$ were performed to study the temperature dependence of the appropriate normal mode with a wavevector at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\boldsymbol{a}^*$ zone boundary by Cowley *et al.* (1969) and by Shirane & Yamada (1969). The results of these experiments were in good agreement with one another and, as illustrated in figure 2, provided excellent support for the concept of a soft mode. The experiments not only confirmed the wavevector of the soft mode as suggested by Unoki & Sakudo (1967), but also the pattern of displacements shown in figure 1 and, below T_C, the triply degenerate soft mode is split into two: a singlet for rotations about c and a doublet for rotations about the a- and b-axes.

The success of these ideas then lead to the development of a phenomenological theory for the phase transition of $SrTiO_3$ along the lines developed by Landau (1937). Slonczewski & Thomas (1970) showed that the free energy has the form

$$\begin{aligned} G = G_0 &+ \tfrac{1}{2}a(T - T_C)\boldsymbol{Q}^2 + \boldsymbol{Q}^2 + u(\boldsymbol{Q}^2)^2 + v(Q_1^4 + Q_2^4 + Q_3^4) + e_1(\eta_1 + \eta_2 + \eta_3)\boldsymbol{Q}^2 \\ &+ e_2[\eta_1(2Q_1^2 - Q_2^2 - Q_3^2) + \eta_2(2Q_2^2 - Q_1^2 - Q_3^2) + \eta_3(2Q_3^2 - Q_1^2 - Q_2^2)] \\ &+ e_3(Q_1Q_2\eta_6 + Q_1Q_3\eta_5 + Q_2Q_3\eta_4) + \tfrac{1}{2}\sum_{\alpha\beta} C_{\alpha\beta}\eta_\alpha\eta_\beta, \end{aligned} \tag{2.2}$$

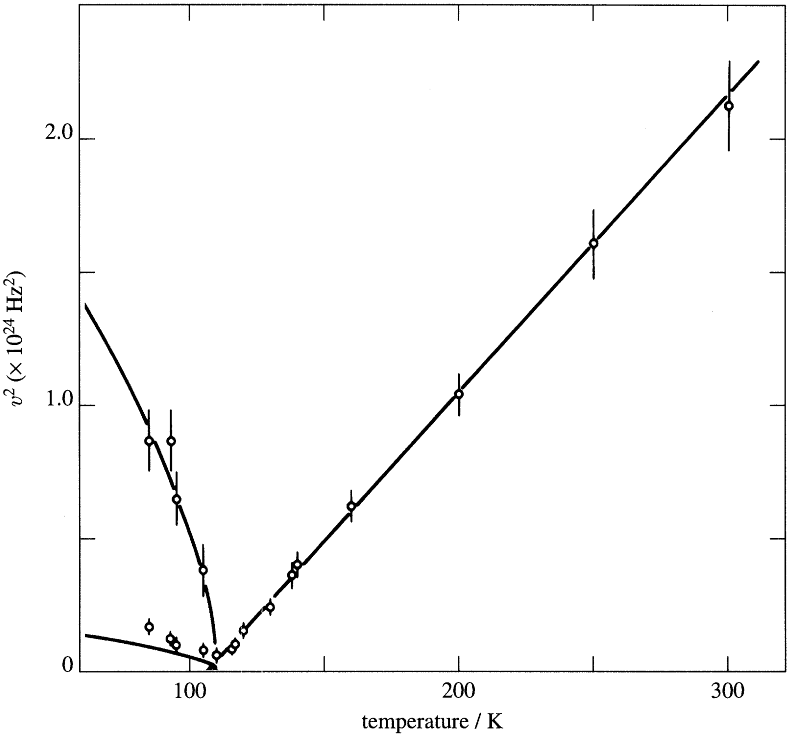

Figure 2. The temperature dependence of the frequencies of the soft mode ($\Gamma_{25}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$) in $SrTiO_3$, both above and below $T_C = 106$ K (from Cowley *et al.* 1969).

where Q_1, Q_2 and Q_3 are the amplitude of the rotations about the *a*-, *b*- and *c*-axes, $\boldsymbol{Q} = (Q_1, Q_2, Q_3)$, the η are the elastic strains in the Voigt rotation, $C_{\alpha\beta}$ are the elastic constants and G_0, a, u, v, e_1, e_2 and e_3 and largely temperature-independent constants.

The free energy function has proved to be very successful at predicting the different low-temperature structures of $SrTiO_3$, and other similar materials, qualitatively describing the phase diagrams under different external stresses (as reviewed by Cowley 1980) and, by choosing the constants appropriately, the quantitative behaviour of many of the properties of $SrTiO_3$. The classical approach to phase transitions consists of obtaining the Landau expression for the free energy and values for its parameters and then calculating the properties neglecting the effects of the fluctuations.

Normally, the constants in the free energy function are adjusted by comparison with the experimental results. In principle, if there is a good understanding of the microscopic interactions, the constants can be calculated in terms of the interatomic force constants. There have been relatively few attempts to carry the programme through but in the case of $SrTiO_3$ a detailed interatomic force model was obtained by Stirling (1972) which was then extended to include anharmonic effects by Bruce & Cowley (1973) who showed that it was possible to obtain the parameters in the free energy with reasonable interatomic forces. The instability in $SrTiO_3$ arises because the interatomic forces give an unusually small frequency for the soft mode resulting from the ideal Sr–O and Ti–O interatomic distances being both incompatible with a single lattice parameter of the cubic structure.

The classical era for $SrTiO_3$ was in the late 1960s and early 1970s and successfully explained many properties in a quantitative way. There is still more work needed to provide a fully convincing calculation of the parameters of the Landau expression in terms of microscopic models. Nevertheless, the development of this approach is the first stage in the understanding of any new structural phase transition.

3. The critical era

The Landau and mean field theories of phase transitions neglect the effect of the fluctuations on the phase transition. These can be included in the theory by the use of the renormalization group theory as described, for example, for structural phase transitions by Bruce (1980). It is not appropriate to describe that development in detail, but it leads to several new concepts. Firstly, as the temperature T approaches T_C, $|t| = |(T - T_C)/T_C| \to 0$, the behaviour of physical quantities depends on exponents. For example, the order parameter below T_C, Q_S, varies as

$$Q_S = Bt^{\beta}, \tag{3.1}$$

where B is a constant and β is a critical exponent. Similarly, the susceptibility for neutron scattering intensity from the soft mode varies as

$$\chi(q_S j) = c|t|^{-\gamma}, \tag{3.2}$$

where c is a constant and γ an exponent. The inverse correlation length of the critical phase fluctuations, K, varies as

$$K = K_0|t|^{\upsilon}. \tag{3.3}$$

The theory then gives these exponents as universal, in the sense that they are the same for all systems having the same dimensionality, d, the same symmetry and the same number of components, n, for the order parameter. In the case of $SrTiO_3$, the universality class is that of the cubic $n = 3$, $d = 3$ system.

Mean field theory gives the exponents as $\beta = \frac{1}{2}$, $\gamma = 1$ and $\upsilon = \frac{1}{2}$, and the measurement of the temperature dependence of the order parameter by Muller & Berlinger (1971) using EPR techniques showed, as illustrated in figure 3, that $\beta = 0.33 \pm 0.02$; clearly different from the mean field result and so demonstrating that Landau theory failed and critical fluctuations did play an important role close to T_C, $|t| < 0.1$. This experiment was the first clear evidence for critical behaviour close to structural phase transitions.

It was a surprisingly long time before measurements were made of the exponents γ and υ. This was because these measurements require the energy integrated scattering and this is difficult to measure reliably for $SrTiO_3$ using neutron scattering because the energy width of the fluctuations is large compared with typical incident neutron energies. The experiment is more easily performed with X-ray scattering techniques but these were not developed until the 1980s. The analysis is also complicated by the cubic anisotropy of $SrTiO_3$ which gives the susceptibility as a function of wavevector $\boldsymbol{q}$ away from $\boldsymbol{q}_S$ as

$$\chi^{-1}_{jj'}(\boldsymbol{q}) = K^2 + (q^2 + fq_j^2)\delta_{jj'} + hq_j q_{j'}(1 - \delta_{jj'}). \tag{3.4}$$

The factor f is particularly important because for $SrTiO_3$, $f = -0.97$ (Stirling 1972) so that the scattering is very anisotropic as a function of wavevector. The reason for this can be seen in figure 1 because there are strong correlations within the *ab* plane for rotations about c but not for correlations between different *ab* planes.

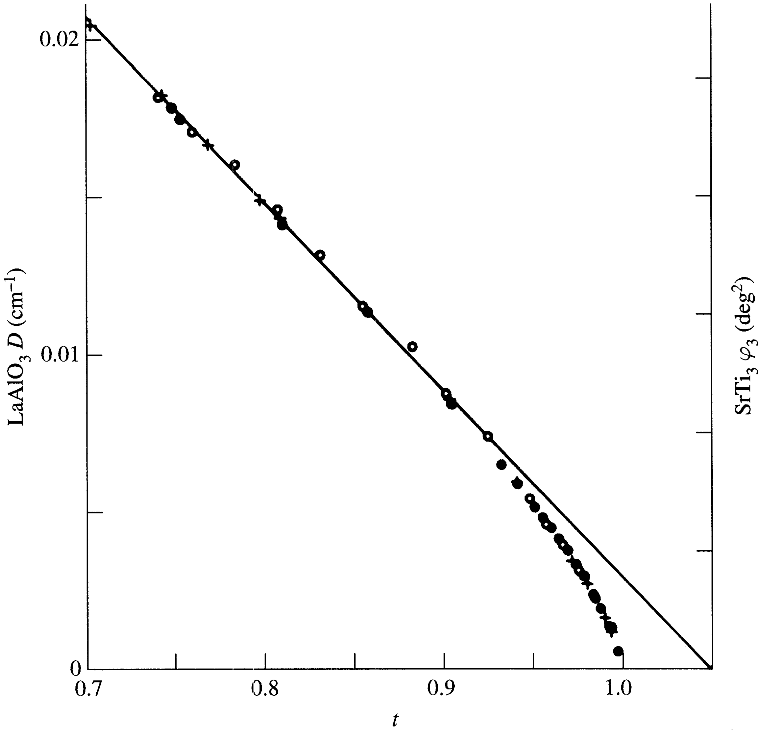

Figure 3. The temperature dependence of the order parameter of $SrTiO_3$ and $LaAlO_3$, as measured with EPR techniques by Muller & Berlinger (1971): +, D $LaAlO_3$:Fe^{3+}; ○, φ $SrTiO_3$:Fe^{3+}; ●, φ $SrTiO_3$:Fe^{3+} − V_0.

X-ray scattering experiments were, however, performed and analysed by Andrews (1986) using a triple crystal X-ray diffractometer on a rotating anode source. The results for K as a function of temperature are shown in figure 4. Those close to T_C will be discussed will be discussed in the next section but for $|t| > 0.04$ he obtained $\gamma = 1.4 \pm 0.1$ and $\upsilon = 0.83 \pm 0.05$, both clearly quite different from the values given by mean field theory. There is no doubt therefore that critical fluctuations alter the temperature dependence of experimental measurable quantities close to T_C.

The theoretical situation for the cubic $n = 3$, $d = 3$ system is also somewhat uncertain. If the cubic terms, v and f_0, are small, Aharony (1976) showed that the system evolved to the isotropic fixed point at which $v = 0$ and $f = 0$, when the exponents would be expected to be $\beta = 0.365$, $\gamma = 1.386$ and $\upsilon = 0.705$ (le Guillou & Zinn-Justin 1980). These results are similar to the experimental values although the differences between the β and υ are at the limit of what might be expected. This success is, however, modified by the calculations of Nattermann (1976) who showed that the isotropic $n = 3$, $d = 3$ fixed point would only describe the behaviour very close to T_C and that, in the presence of the cubic antisotropies, all of the exponents might be larger than those calculated for the isotropic model. Second, if f_0 is close to −1, Bruce (1974) and Nattermann (1976) concluded that the system probably had a first-order transition. Clearly, although critical fluctuations are important in $SrTiO_3$, there is still the need for more theoretical and experimental work to clarify the results. After developing the mean field theory of a phase transition, the next step is the understanding of the critical phenomena, although this has not been accomplished for $SrTiO_3$.

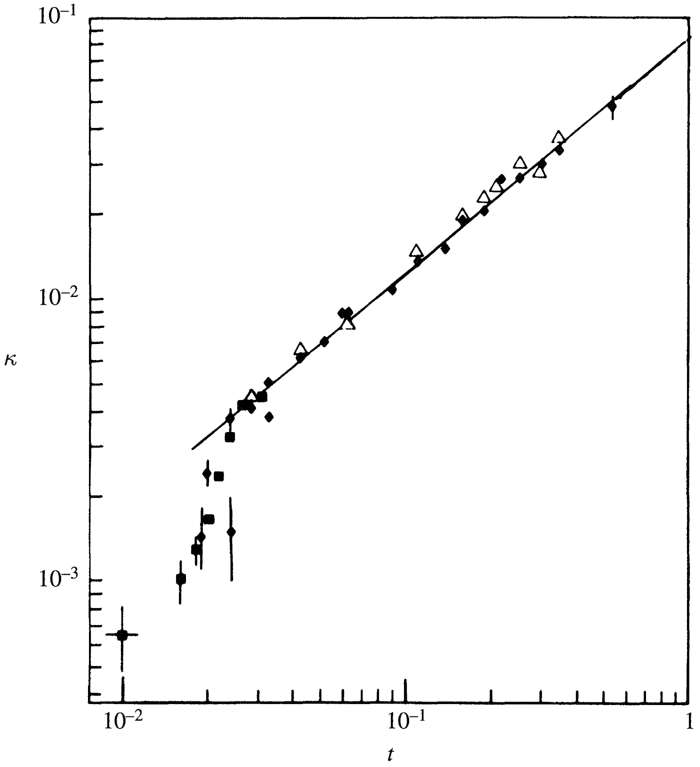

Figure 4. The inverse correlation length K, in units of $2\pi/a$, as a function of temperature (Andrews 1986). The diamonds and triangles are the results of low-resolution measurements and the squares from intermediate-resolution data.

4. Two scales

One of the basic assumptions of both of the theories described above is that, close to the phase transition, there is one length scale and one energy scale and that as $|t| \rightarrow 0$, the former diverges while the latter approaches zero. Experiments have now been performed which question this assumption for both length and energy scales. The first of these experiments was by Riste *et al.* (1971) and repeated in more detail by Shapiro *et al.* (1972). Figure 5 shows the scattering from $SrTiO_3$ 15 K above T_C and, in addition to the inelastic soft-mode scattering, there is a quasi-elastic component. As the temperature is decreased, the quasi-elastic component increases in intensity and is the divergent component at T_C. The data was analysed by assuming a response function such that

$$\chi^{-1}(\boldsymbol{q}j) = \omega_0(\boldsymbol{q}j)^2 - \omega^2 - 2\mathrm{i}\omega\gamma_0 + \frac{\mathrm{i}\omega\tau\delta_0^2}{1-\mathrm{i}\omega\tau}, \tag{4.1}$$

in which the response is that of a simple harmonic oscillator with an additional Debye relaxation term at low energies. The resulting temperature dependence of the parameters is shown in figure 6, where

$$\omega_\infty(\boldsymbol{q}j)^2 = \omega_0(\boldsymbol{q}j)^2 - \delta_0^2. \tag{4.2}$$

In the experiment of Shapiro *et al.* (1972), the energy width of the quasi-elastic peak could not be determined because of the resolution but was less than 0.02 meV.

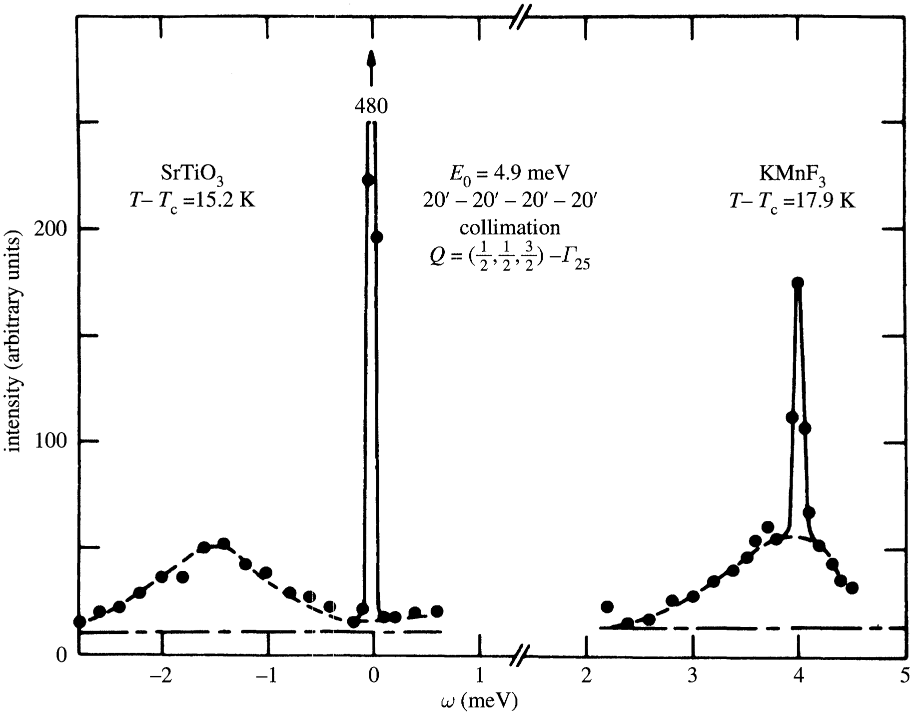

Figure 5. The zone boundary soft-mode scattering in $SrTiO_3$ and $KMnF_3$ showing quasi-elastic, as well as inelastic, scattering (Shapiro *et al.* 1972).

The unexpected feature of these results is that there are clearly two energy scales, the soft mode and the quasi-elastic scattering, whereas scaling theories predict only one scale.

Since the initial measurements, there have been several experiments to measure the energy width of the quasi-elastic scattering; those of Töpler *et al.* (1977) give an energy width of less than 10^{-3} meV. The role of defects of the scattering was studied by Hastings *et al.* (1978), who investigated reduced $SrTiO_3$ containing O vacancies. The results gave an increase in the central peak intensity with increasing defect concentration, but a factor of 200 increase in the defect concentration only produced a factor of three increase in the quasi-elastic scattering at the same reduced temperature.

More recently, Shirane *et al.* (1993) measured the wavevector dependence of the soft mode and quasi-elastic scattering separately and compared the results with the X-ray measurements of Andrews (1986) shown in figure 4. Their results, as shown in figure 7, strongly suggest that the X-ray scattering for $|t| > 0.024$ measures the total neutron scattering; the sum of the soft mode and quasi-elastic scattering and hence that both parts of the inelastic profile are needed to account for the critical scattering discussed in § 3. Finally, quasi-elastic scattering is observed at many other phase transitions from one ordered phase to another slightly distorted, but ordered, phase. In these cases, soft-mode behaviour is to be expected and, in almost all, quasi-elastic scattering is observed over a wide temperature range $|t| < 1.0$.

The evidence for two length scales was first obtained by Andrews (1986), as shown by figure 4. As the temperature became close to T_C, $t < 0.04$, his data for K and χ deviated from the form found at higher temperatures. The measurements shown in

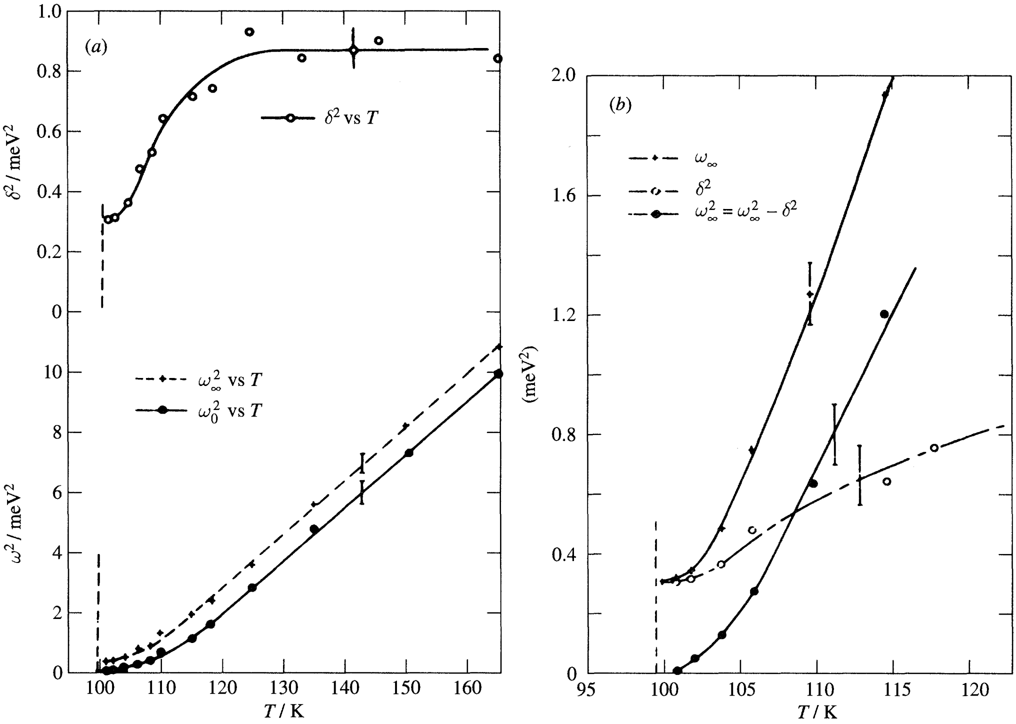

Figure 6. The parameters of the soft-mode spectral function as a function of temperature (Shapiro *et al.* 1972).

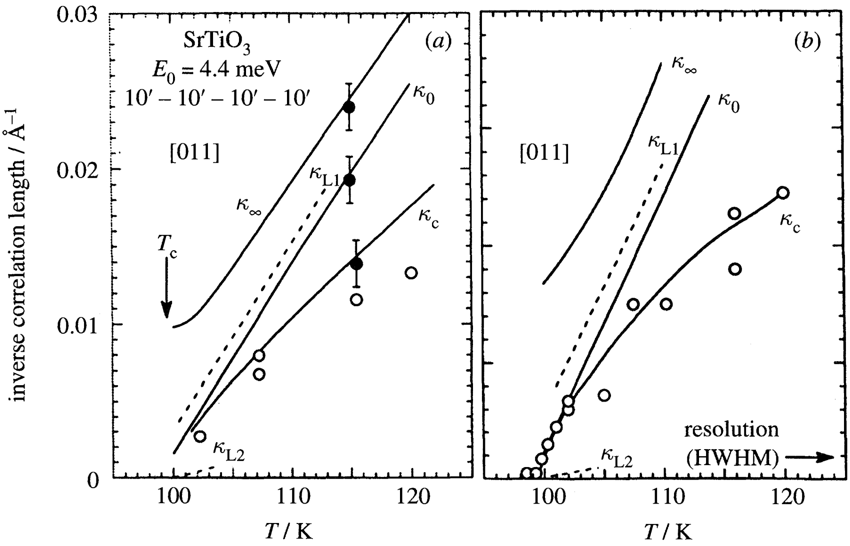

Figure 7. The inverse correlation lengths, K, for the soft modes K_∞, quasi-elastic scattering, K_C and total neutron scattering K_0 along the (*a*) [100] and (*b*) [110] directions and compared with the X-ray results (dotted line) (Shirane *et al.* 1993).

figure 4 were made with an in-plane resolution of about 0.01 Å^{-1} and to study this behaviour in detail the resolution was improved. The results then obtained are shown in figure 8 and there are clearly two components; a broad component and a narrow,

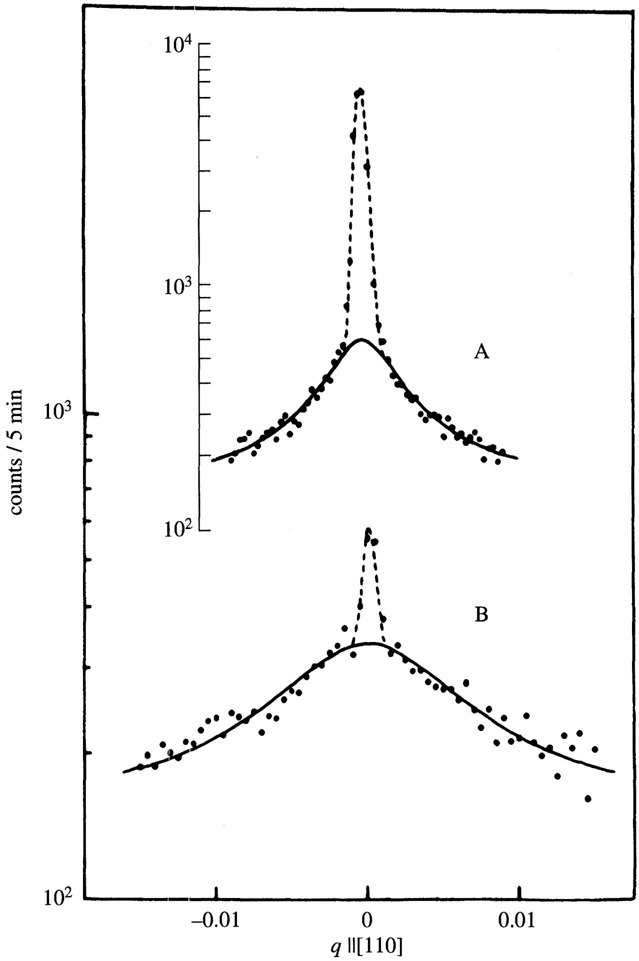

Figure 8. X-ray scattering at (A) $T_C + 0.65$ K and (B) $T_C + 2.45$ K, showing the two length scales (Andrews 1986).

more Bragg-like, component which rapidly increased in intensity as t decreased. Subsequent measurements by Nelmes *et al.* (1988) and by McMorrow *et al.* (1990) have shown that the narrow component is not resolution limited but that its width decreases when the temperature is reduced, as shown in figure 9. Furthermore, the detailed profile of this component cannot be described by a Lorentzian susceptibility, such as equation (3.4), but is described by an isotropic Lorentzian squared form,

$$I_D(\boldsymbol{q}) = \frac{A_D K_D}{(K_D^2 + \boldsymbol{q}^2)^2}, \tag{4.3}$$

and the exponent describing the behaviour of K_D was $v_D = 0.51 \pm 0.09$.

All of these measurements were performed with incident X-ray energies of about 15 keV when the penetration depth is only about 50 µm. Neumann *et al.* (1995) have used much higher energy X-rays, 100 keV with a large penetration depth and found that, when the scattering occurs from the bulk of the crystal, the long length scale component was absent. The second long length scale arises therefore from the near (*ca.* 50 µm) surface region of the crystal.

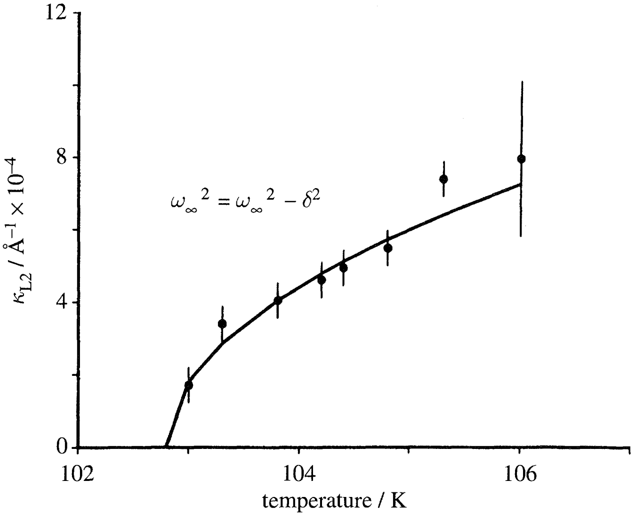

Figure 9. The width, K_D, of the narrow X-ray scattering as a function of temperature. Fits give K_D varying as $K_0|t|^{\upsilon_D}$, with $\upsilon_D = 0.51 \pm 0.09$ (McMorrow *et al.* 1990).

While these measurements have been performed on $SrTiO_3$, similar results have been obtained for almost all crystals for which the critical scattering has been measured with X-rays and with a resolution of about 0.001 Å^{-1}. Of particular interest are the results on $RbCaF_3$ (Gibaud *et al.* 1987) and on the magnetic phase transitions of Ho (Thurston *et al.* 1993) and of Tb (Gehring *et al.* 1993).

Finally, the intensity of the X-ray scattering depends on the surface preparation as shown first by Darlington & O'Connor (1976) and more recently by Andrews (1986), and the narrow component is more intense for polished surfaces than when the scattering is from crystals with etched and annealed surfaces.

Finally, in this section, the experimental evidence concerning the two energy and two length scales found from scattering experiments close to phase transitions is summarized.

(a) Two energy scales.

(i) At phase transitions, there are both soft modes and quasi-elastic scattering with very different energy scales for most structural and magnetic transitions between two ordered phases.

(ii) The quasi-elastic neutron scattering has a very slow energy scale $<$ 0.01 meV.

(iii) The neutron scattering profiles are well described by a low-frequency Debye relaxation (equation (4.1)).

(iv) Both the inelastic and quasi-elastic components of the neutron scattering experiments are measured by X-ray scattering techniques and contribute to the critical scattering away from T_C.

(v) The quasi-elastic peak is observed for $t < 1$.

(vi) The quasi-elastic peak is enhanced by introducing defects, but much more slowly then linearly with the concentration of defects.

(b) Two length scales.

(i) Two components to the energy integrated scattering have been observed at most structural and magnetic phase transitions in crystals which have been studied with adequate resolution, 0.001 Å.

(ii) The narrow component corresponds to a length scale more than 10 times longer than the shorter component.

(iii) The critical exponents for the two length scales are different with the shorter length scale being broadly consistent with those expected from critical phenomena theories.

(iv) The long length scale component is described by an approximately isotropic Lorentzian squared.

(v) In $KMnF_3$ and $RbCaF_3$, which undergo slight first-order phase transitions, the narrow component is centred at the Bragg reflection of the strained low-temperature phase rather than the unstrained high-temperature phase.

(vi) The scattering arises 'near', within 50 μm, the surface and its intensity depends on the surface preparation.

5. Possible theories

There have been many theories developed to account for the existence of two time scales, as reviewed by Bruce & Cowley (1980). The two main classes of theories are explanations which describe the effects as arising from the intrinsic dynamics of a system close to a phase transition and those which postulate that defects are needed to produce the long time scale. We shall briefly describe both of these approaches.

The first approach begins with the weakly anharmonic model of the atomic dynamics and looks for a mechanism which can produce a long time scale. As pointed out by Feder (1971), a long time scale can be produced by thermodynamic fluctuations which can only respond on times related to thermodynamic equilibrium. It is, of course, well known that the isothermal and adiabatic responses of systems can be very different and the suggestion is that the central peak arises from a similar difference in the nature of the fluctuations. The difficulty with this approach is that the order parameter fluctuations in $SrTiO_3$ above T_C do not couple linearly to the thermodynamic fluctuations because of wavevector conservation, and so the approach requires the order parameter to couple to both the thermodynamic fluctuations and to another order parameter fluctuation.

This nonlinear coupling may then produce a slow relaxation in addition to the soft-mode inelastic response. This theory was developed particularly by Murata (1975) using the theory of anharmonic interactions and then by Bausch & Halperin (1978) using renormalization group techniques. The conclusion from these calculations is that for displacive systems with a soft mode, there is indeed a deviation close to T_C in the response from that of a damped simple harmonic oscillator, and that this deviation is of the form of additional quasi-elastic scattering. Nevertheless, the width of the quasi-elastic response is not very different from the energy of the soft modes and the quasi-elastic contribution occurs only close to T_C. Both of these are inconsistent with the experimental data, § 4: (a)(i), (ii) and (v).

At order–disorder transitions, there are two time scales. If the local potential energy function has two well-defined minima, one time scale is associated with the motions within one of the minima, while the other is associated with hopping between the two wells. This behaviour is typical of order–disorder transitions in alloys when one time scale is associated with the small atomic vibrations and the other with motions of atoms between different lattice sites. At these transitions, there is no reason to expect a soft mode for the atomic vibrations. The potential energy curve for the zone boundary soft mode does not have two distinct minima at high temperatures. Nevertheless, as the transition is approached, there will be large clusters within which the average value of the oxygen rotations might be considerable. The soft mode is then identified with small vibrations within the clusters and the quasi-elastic scattering with hopping of the clusters between different orientations of the oxygen rotations. This cluster picture has considerable support from studies of one-dimensional models (Krumhansl & Schrieffer 1975; Aubry 1975) which show both small motions and slower motions of domain walls. Unfortunately, this analysis cannot be taken over directly to three-dimensional systems with non-zero phase transition temperatures. There is, however, evidence from EPR measurements (von Waldkirch *et al.* 1976) that the distribution functions of atomic positions at T_C is not a symmetric Gaussian, but two peaked, with peaks each with a rotations angle of 0.22°, but since the average fluctuation angle is *ca.* 2° (Meyer *et al.* 1978), the distribution is not of the order–disorder form with two separate peaks. In conclusion, this approach leads to a similar conclusion to that of the anharmonic lattice theory and, indeed, they are possibly different ways of trying to describe the same physics. Deviations from the simple soft mode are expected close to T_C but the difference in energy scales and the range of temperature over which they occur is much less than that observed experimentally.

The other class of theories for describing two energy scales depends on the presence of symmetry breaking defects. The quasi-elastic scattering is then associated with the local distortion occurring around the defect and the energy width with the inverse hopping time (if any) of the defect. The theory of the scattering when defects are introduced has been discussed by Axe *et al.* (1974) and by Halperin & Varma (1976). If the symmetry breaking defects are static, they introduce a distortion about each defect which produces elastic scattering proportional to the square of the host wavevector dependent susceptibility; this is known as Huang scattering. The behaviour of this random field type of system was discussed by Imry & Ma (1975) and has been the subject of extensive theoretical effort and experiments on magnetic systems (see, for example, Cowley *et al.* 1989). The conclusions from this work are, however, unclear for $SrTiO_3$ because it is a cubic $n = 3$, $d = 3$ system. In an Ising $n = 1$ system, on cooling in the presence of random fields, theory predicts a phase transition to a long-range ordered state but with different exponents from those of the homogenous system, but experimentally it is found that there are very long, if not infinite, relaxation times and long-range order is not established. For isotropic $n = 3$, $d = 3$ systems, Imry & Ma (1975) predict that random fields will destroy the long-range order. The situation for the cubic $n = 3$, $d = 3$ system is unclear but probably, in practice, long-range order will be destroyed by the random fields. Since there is long-range order below T_C in $SrTiO_3$, either the number of random fields is small or the defects producing the random fields are mobile.

If the defects are mobile, the theory is different because, on average, the defects are symmetry conserving and the results are modelled by the random bond model. For systems with random bonds, the critical phenomena is the same as that of the pure system (Harris 1974) provided that the specific heat exponent, α, is greater than 0.

The experimental results in $SrTiO_3$ could therefore be described if there were defect sites which for long times were displaced away from the symmetric position at temperatures well above T_C, say 200 K. The energy width of the scattering is then determined by the rate of hopping between the different off-centre positions and the static critical exponents would be the same as those of the pure systems.

This type of theory is consistent with the experimental results described in the previous section for $SrTiO_3$. The difficulty is that the nature of the defects is unknown. The intensity of the central peak is much the same for different nominally pure crystals and for crystals grown by different techniques. The introduction of defects increases the intensity of the quasi-elastic scattering less rapidly than the concentration of defects, although the defects introduced may be of a type which does not contribute to the scattering. The relative intensity of the soft mode and of the quasi-elastic scattering is similar for other very different systems which is difficult to understand if the scattering depends on the properties of the particular defects.

In conclusion, the two energy scales found for $SrTiO_3$ by scattering experiments are not understood. The large difference of the energy scales is inconsistent with present theories of the critical phenomena while, if they arise because the crystals have defects, neither the nature of the defects is known nor why their number and effects are so similar in widely differing materials.

The experiments suggesting that two length scales are needed to describe the critical fluctuations have been performed more recently than those showing that two energy scales are needed and so the theories are less developed and even less satisfactory. The first suggestion arose because the phase transitions of some of the materials showing these effects, $RbCaF_3$ and $KMnF_3$ are of first order while, as discussed above, it has been suggested that $SrTiO_3$ might have a first-order transition. There are then two types of fluctuations corresponding to the two minima in the potential energy and they can have different length scales. Imry & Wortis (1978) then suggested that, in the presence of defects, both phases might be locally stable. Subsequently, the two length phenomena have been found in materials for which the transitions are not of first order and so this explanation seems no longer to be appropriate, at least without further modification.

The phenomena has been shown to occur in the 'near' surface region and so one possibility is that it is surface induced. At the surface of a crystal, the top few atomic layers can undergo a reconstruction leading to different atomic forces than in the bulk. It is then possible that the surface will transform at a higher temperature than the bulk and that, as the temperature is lowered, the phase transition will propagate further and further into the bulk. Detailed theories of this effect have been worked out for smooth surfaces and, once the transition has propagated further than the distorted planes, its dependence on depth depends on the bulk correlation length (Binder 1984). Since the long length scale is found to be isotropic and very long, 1000 Å, and very different from the bulk, this type of theory cannot explain the results.

There have been two proposals which overcome this difficulty by proposing that there are extended defects in the 'near' surface region which produce a new length scale. Altarelli *et al.* (1995) suggested that the defects might produce random bond disorder which decays with distance like $|r|^{-\alpha}$. Weinrib & Halperin (1983) then showed that, if $\alpha < d$, the critical phenomena is different from that of the pure system with exponent $v_D = 2/\alpha$ for point defects and presumably T_C is slightly different from that of the pure system. Altarelli *et al.* (1995) suggest that in the 'near' surface region there are dislocations which produce the necessary long range correlations with $\alpha = 2$. This approach fails to explain the Lorentzian squared profile or why the scattering is roughly isotropic if the dislocations arise due to the surface preparation.

The second proposal is that random fields are created in the 'near' surface region by the surface preparation (Harris *et al.* 1995). In this case, the distorted field around each random field produces a Lorentzian squared profile but the usual Huang theory discussed above gives the same length scale for the distortion around a defect as for the fluctuations of the bulk. Harris *et al.* (1995) argue that the observed difference in length scale might arise if the defects were extended although this is unclear. It is also unclear if the defects are extended why the scattering is isotropic. Although these defect theories explain why the results depend on the surface preparation, they do not explain why similar results are observed for insulators and metals and for different types of phase transition.

An alternative explanation is based on the observation that the strain and the surface both appear to play a role. Near the surface of a crystal, the strain fields represented by the surface waves are free in the sense that there is no restoring force and that these waves can couple to the fluctuations in the order parameter. The theory of phase transitions with a coupling of the fluctuations to the strains was discussed by Wegner (1974) and by Bergman & Halperin (1975). They showed that the effect of the strains could only penetrate into a crystal by a distance determined by the correlation length and hence concluded that the phase transition of a bulk (infinite) crystal would only be affected by strains at T_C. This is not the case for the 'near' surface region probed by X-ray experiments. The coupling to the free surface waves allows these fluctuations to be 'free' instead of 'clamped' and, since the interactions between 'free' fluctuations is weaker than that between 'clamped' ones, they will have a larger T_C than the bulk T_C. Consequently, the 'near' surface behaviour will consist of these 'free' fluctuations with a much larger length scale than the bulk 'clamped' ones. Alas, we have been unable to evaluate the detailed consequences of this proposal. Qualitatively, it can explain the two length scales; 'near' surface 'free' fluctuations and bulk 'clamped' fluctuations. The coupling to surface waves makes the free fluctuations dependent on the surface roughness. The nearly isotropic behaviour arises because the penetration depth of surface waves is the same as their wavelength along the surface. Finally, since the theory depends on the interaction between the fluctuations, it explains why the phenomena is only observed for $t < 0.05$. It predicts that the effects should not be observed if there is no coupling between the order parameter and the strain and if the phase transition is well described by mean field theory.

6. Finale

$SrTiO_3$ has played a central role in the study of phase transitions. Some of the experiments have provided the best evidence for the concept of the soft mode and for the existence of critical phenomena. More detailed experiments have, however, revealed two unexpected but probably unrelated results; the existence of two length and two time scales for the fluctuations. We have reviewed the theories put forward for these effects and at present none is wholly satisfactory. Some postulate defects but the nature of the defects has not been identified in any material, even though similar experimental results are found in many systems.

Possibly, these results imply that we need to rethink the ideas of scaling and phase transitions. It is certain, however, that more work is needed both experimentally and theoretically to explain these experimental results before we can be certain that our understanding of phase transitions is correct.

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References

Aharony, A. 1976 *Phase transitions and critical phenomena* (ed. C. Domb & M. S. Green), vol. 6, p. 357. New York: Academic.

Altarelli, M., Nu, M. D. & Papoular, M. 1995 *Phys. Rev. Lett.* **74**, 3840.

Anderson, P. W. 1960 *Fizika Dielectrikov* (ed. G. I. Skanavi). Moscow: Acad. Nauk SSR.

Andrews, S. R. 1986 *J. Phys.* C **19**, 3721.

Aubry, S. 1975 *J. Chem. Phys.* **62**, 3217.

Axe, J. D. & Shirane, G. 1974 *Phys. Rev.* B **8**, 1965.

Bausch, R. & Halperin, B. I. 1978 *Phys. Rev.* B **18**, 190.

Bergman, D. J. & Halperin, B. I. 1975 *Phys. Rev.* B **13**, 2145

Binder, K. 1984 In *Phase transitions and critical phenomena* (ed. C. Domb & M. S. Green), vol. 8, p. 1. New York: Academic.

Bruce, A. D. & Cowley, A. R. 1973 *J. Phys.* C **6**, 2422.

Bruce, A. D. 1974 *J. Phys.* C **7**, 2089.

Bruce, A. D. 1980 *Adv. Phys.* **29**, 111.

Bruce, A. D. & Cowley, A. R. 1980 *Adv. Phys.* **29**, 220.

Cochran, W. 1960 *Adv. Phys.* **9**, 387.

Cowley, R. A., Buyers, W. J. L. & Dolling, G. 1969 *Solid St. Commun.* **7**, 181.

Cowley, R. A. 1980 *Adv. Phys.* **29**, 1.

Cowley, R. A., Shirane, G. & Yoshizawa, H., Uemura, Y. J. & Birgeneau, R. J. 1989 *Z. Phys.* B **75**, 303.

Darlington, C. N. W. & O'Conner, D. A. 1976 *J. Phys.* C **9**, 3561.

Feder, J. 1971 *Solid St. Commun.* **9**, 2021.

Gehring, P. M., Hirota, K., Majkzak, C. F. & Shirane, G. 1993 *Phys. Rev. Lett.* **71**, 1087.

Gibaud, A., Ryan, T. W. & Nelmes, R. J. 1987 *J. Phys.* C **20**, 3833.

le Guillou, J. C. & Zinn-Justin, J. 1980 *Phys. Rev.* B **14**, 4030.

Halperin, B. I. & Varma, C. M. 1976 *Phys. Rev.* B **14**, 4030.

Harris, A. B. 1974 *J. Phys.* C **7**, 1671.

Harris, Q. J., Feng, Q., Birgeneau, R. J., Hirota, K., Shirane, G., Hase, M. & Uchinokura, K. 1995 *Phys. Rev.* B **52**, 15420.

Hastings, J. B., Shapiro, S. M. & Frazer, B. C. 1978 *Phys. Rev. Lett.* **40**, 237.

Imry, Y. & Ma, S. K. 1975 *Phys. Rev. Lett.* **35**, 1399.

Imry, Y. & Wortis, M. 1978 *Phys. Rev.* B **19**, 3580.

Krumhansl, J. A. & Schrieffer, J. R. 1975 *Phys. Rev.* B **11**, 3535.

Landau, L. D. 1937 *Phys. Z.* **2**, 26.

Meyer, G. M., Nelmes, R. J. & Hutton, J. 1978 *Proc Int. Conf. on Lattice Dynamics* (ed. M. Balkanski), p. 652. Paris: Flammarion.

McMorrow, D. F., Hamaya, N., Shimomura, S., Fujii, Y., Kishimoto, S. & Iwasaki, H. 1990 *Solid St. Commun.* **76**, 443.

Muller, K. A. & Berlinger, W. 1971 *Phys. Rev. Lett.* **26**, 13.

Muller, K. A. & von Waldkirch, T. 1976 In *Local properties at phase transitions* (ed. K. A. Muller & A. Rigamonti), p. 134. Amsterdam: North-Holland.

Murata, K. K. 1975 *Phys. Rev.* B **11**, 462.

Natterman, T. 1976 *J. Phys.* C **9**, 3337.

Nelmes, R. J., Hatton, P. D. & Vass, H. 1988 *Phys. Rev. Lett.* **60**, 2172.

Neumann, H. B., Rutt, U., Schneider, J. R. & Shirane, G. 1995 *Phys. Rev.* B **52**, 3981.

Riste, T., Samuelson, E. J., Otnes, K. & Feder, R. 1971. *Solid St. Commun.* **9**, 1455.

Shapiro, S. M., Axe, J. D., Shirane, G. & Riste, T. 1972 *Phys. Rev.* B **6**, 4332.

Shirane, G. & Yamada, Y. 1969 *Phys. Rev.* **177**, 858.

Shirane, G., Cowley, R. A., Matsuda, M. & Shapiro, S. M. 1993 *Phys. Rev.* **48**, 15 595.

Slonczewski, J. C. & Thomas, H. 1920 *Phys. Rev.* B **1**, 3599.

Stirling, W. G. 1972 *J. Phys.* C **5**, 2711.

Thurston, T. R., Helgesen, G., Hill, J. P., Gibbs, D., Gaulin, B. D. & Simpson, P. J. 1994 *Phys. Rev.* B **49**, 15 730.

Topler, J., Alefeld, B. & Heidemann, A. 1977 *J. Phys.* C **10**, 635.

Unoki, H. & Sakudo, T. 1967 *J. Phys. Soc. Jap.* **23**, 546.

Weinrib, A. & Halperin, B. I. 1983 *Phys. Rev.* B **27**, 413.

Wegner, F. J. 1974 *J. Phys.* C **7**, 2109.