Structural phase transitions

I. Landau theory

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ABSTRACT

Structural phase transitions can be studied by a variety of techniques; macroscopic fields, X-ray, light and neutron diffraction, and resonance methods. The information which can be obtained by these different techniques about the order parameter and susceptibility at structural phase transitions is described and compared. Landau theory coupled with the 'soft mode' concept provides a simple picture of many structural phase transitions in terms of relatively few phenomenological constants. A review is given of the application of this type of theory to the wide variety of different phenomena which can occur at structural phase transitions. In particular, emphasis is placed on the nature of the fluctuations within Landau–Ginzburg theory and on the role of secondary order parameters. The nature of incommensurate phases and of lock-in phase transitions are discussed using both the conventional lattice dynamical approach and the soft soliton theories. The parameters of the Landau theory can, in principle, be obtained from a microscopic model. We critically discuss the attempts that have been made to develop models for anharmonic crystals, order–disorder systems and various electronic instabilities.

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§ 1.1. Introduction

Structural phase transitions occur when a material changes its crystallographic structure. The first studies of these transitions were measurements of macroscopic properties; specific heat, dielectric susceptibility or thermal expansion, and it was through these measurements that the transitions were discovered and initially characterized. Because the macroscopic properties change at the transition, their study is of importance for the various different applications of these materials: an example is the use of ferroelectrics as piezoelectric components and as pyroelectric detectors. There has also been a great deal of effort devoted to elucidating the nature of structural phase transitions at a more microscopic level. This work began with the
careful determination of the crystal structure of the phases on both sides of the transition. Some of the earliest measurements were performed on BaTiO$_3$ by Megaw (1947), Kanzig (1951) and by Shirane et al. (1955) and most recently by Harada et al. (1970). The results of their investigations are illustrated in fig. I.1, which shows the low-temperature phase of BaTiO$_3$, $T < 393$ K, in which the atoms are displaced away from the centro-symmetric positions they have in the high-temperature cubic phase. In ferroelectric BaTiO$_3$ the static displacements of the atoms in every unit cell of the distorted phase are the same.

![Fig. I.1](image1.png)
The distorted perovskite structure of ferroelectric BaTiO$_3$.

At other structural phase transitions the unit cell in the distorted phase consists of two, four or maybe more unit cells of the high-temperature phase. As an example of this type of phase transition we show, in fig. I.2, the structure of SrTiO$_3$ below the transition at 110 K. In this case the high-temperature perovskite phase is distorted by an anti-phase rotation of neighbouring oxygen octahedra (Unoki and Sakudo 1967).

![Fig. I.2](image2.png)
These measurements showed that at least at some structural phase transitions the atoms in the distorted phase are slightly displaced away from the equilibrium positions of the high-temperature phase. This then led to the suggestion by Cochran (1960) and Anderson (1960), and earlier but largely unnoticed comments by others (Raman and Nedungadi 1940 and Saksena 1940, for example) that these phase transitions might be the result of an instability of the crystal against a particular normal mode of vibration of the high-temperature phase. Since this suggestion, there have been numerous measurements of the so-called ‘soft modes’ associated with structural phase transitions as reviewed for example by Scott (1974) and by Shirane (1974), and at least for these ‘displacive’ phase transitions their existence is well established.

There are other structural phase transitions where the phase transition is associated with an ordering of some variable which is disordered in the high-temperature phase. One example of this ‘order–disorder’ type of behaviour is the ferroelectric phase transition in NaNO₂. In the high-temperature (paraelectric) phase the triangular NO₂ groups have the N ions along either the positive or negative b axis with equal probability, but below 436 K the N ions tend to align in the same direction, as shown in fig. 1.3 (Hoshino and Motegi 1967). Since the reorientation of the NO₂ groups involves very large displacements, particularly of the N ions, these motions cannot be described in terms of small displacements about the equilibrium positions. Consequently in these order–disorder systems ‘soft mode’ ideas are less useful than in the displacive materials. Finally, we mention another type of order–disorder phase transition, namely that occurring in alloys. In fig. 1.4 we show the structure of ordered CuZn (β-brass); above the ordering temperature, 741 K, the Cu and Zn atoms are randomly arranged on the body-centred cubic lattice, but below the transition they take up the regular arrangement shown.

Fig. 1.3

The structure of ferroelectric NaNO₂ (Hishano and Motegi 1967). Diagram taken from Sakurai et al. (1970).
During the 1960s and 1970s our understanding of structural phase transitions progressed rapidly—in a large part owing to the development of experimental techniques which enabled the microscopic properties to be probed more accurately. In particular, the measurements by neutron and Raman spectroscopy and by magnetic resonance techniques have proved to be especially powerful in exposing the richness and variety of phenomena displayed by systems undergoing structural phase transitions.

It is our intention in this, the first of three articles, to describe these developments within the unified framework afforded by the phenomenological theory of Landau (1937); we defer to parts II and III a discussion of those areas where Landau theory has proved to be inadequate. In this review we shall use as examples the phase transitions in BaTiO₃, SrTiO₃, NaNO₂ and β-brass to illustrate the wide range of the phenomena occurring at structural phase transitions. We shall concentrate on providing a unified framework and approach rather than to provide an exhaustive account of the experimental data and theoretical treatments of any particular material. Excellent books using this latter approach have been written by Jona and Shirane (1962) and more recently by Lines and Glass (1977).

Section 1.2 of this article is a review of the notation and the basic lattice dynamical results for the susceptibility and scattering cross-sections of a crystal. In § 1.3 we describe and compare the different experimental techniques which can be used to measure the order parameter and susceptibilities close to a phase transition. We also discuss the advantages of different techniques and illustrate the results with particular regard to the phase transitions discussed above.

The simplest theory of structural phase transitions is Landau's (1937) phenomenological theory, which was developed independently in great detail for BaTiO₃ by Devonshire (1949). We believe that the first stage in the understanding of a structural phase transition is the development of the appropriate Landau theory in terms of various phenomenological parameters. In § 1.4, we describe the application of Landau theory to a very wide range of different structural phase transitions. In view of the recent interest in incommensurate phases, we discuss these in considerable detail.

Landau theory involves a considerable number of parameters which, at the phenomenological level, must be obtained from experimental measurements. In
principle they can also be obtained from a microscopic theory which will then answer such questions as why the undistorted phase is unstable, and what is the transition temperature, \( T_c \). In § 1.5 we review the different microscopic models which have been developed to describe structural phase transitions and to obtain the parameters of a Landau expansion.

§ 1.2. Preliminaries

1.2.1. The Hamiltonian

Below the critical temperature for a structural phase transition the mean position of an atom is displaced from its position in the high-symmetry phase. Consequently the theory of structural phase transitions makes use of the results and notation developed to describe displacements of the atoms from their equilibrium positions. We adopt the notation which is now commonly used in lattice dynamics (Cochran 1973, Cowley 1968). In the high-temperature, high-symmetry phase the mean equilibrium positions of the atoms are \( \mathbf{R}(l \kappa) \), where \( l \) denotes the unit cell and \( \kappa \) the \( \kappa \)th type of \( s \) different atoms within the unit cell, so that \( \mathbf{R}(l \kappa) = \mathbf{R}(l) + \mathbf{R}(\kappa) \). The displacements of the atoms from these equilibrium positions are written \( \mathbf{u}(l \kappa) \), so that the position of the atoms at any instant is \( \mathbf{r}(l \kappa) = \mathbf{R}(l \kappa) + \mathbf{u}(l \kappa) \).

The potential energy of the crystal, \( V \), may then be expanded, formally, as a power series in the displacements, \( \mathbf{u}(l \kappa) \). In the harmonic approximation all of the terms of higher order than second in this expansion are neglected. Within the harmonic approximation the equations of motion for an atom can be diagonalized by introducing a plane-wave representation, when the equations decouple for different wave-vectors, and the resultant dynamical matrices can be diagonalized, to give the frequencies \( \omega(q_j) \) and normalized eigenvectors \( \mathbf{e}(\kappa, q_j) \) for the normal modes. In terms of these normal modes the displacements are written

\[
\mathbf{u}(l \kappa) = \sum_{q_j} (NM_\kappa)^{-1/2} \mathbf{e}(\kappa, q_j) \exp(iq_j \cdot \mathbf{R}(l \kappa)) Q(q_j),
\]

where \( M_\kappa \) is the mass of atoms of type \( \kappa \), \( N \) is the number of unit cells in the crystal and \( Q(q_j) \) is the amplitude of the normal mode, which, since \( \mathbf{u}(l \kappa) \) is real, must satisfy the constraint,

\[
Q(q_j) = Q^*( -q_j). \tag{1.2.2}
\]

In terms of these normal modes the harmonic part of the Hamiltonian becomes

\[
H_2 = \frac{1}{2} \sum_{q_j} [\dot{Q}(q_j)\dot{Q}(-q_j) + \omega(q_j)^2 Q(q_j)Q(-q_j)], \tag{1.2.3}
\]

where

\[
\dot{Q}(q_j) = \frac{dQ(q_j)}{dt} = P(q_j),
\]

the momentum conjugate to \( Q(q_j) \).

In the usual development of lattice dynamics the normal mode coordinates are written in terms of phonon creation and destruction operators;

\[
Q(q_j) = \left( \frac{\hbar}{2\omega(q_j)} \right)^{1/2} (a(q_j) + a^T(-q_j)) \tag{1.2.4}
\]
from which we can obtain the thermodynamic average
\[ \langle Q(q_j)Q(-q_j) \rangle = \left( \frac{\hbar}{2\omega(q_j)} \right)^{2n(q_j) + 1}, \] (I.2.5)
where \( n(q_j) \) is the Bose occupation number, \( n(q_j) = 1/(\exp(\beta\omega(q_j)) - 1) \), and \( \beta = (k_B T)^{-1} \). In most applications classical statistics are adequate when eqn. (I.2.5) becomes
\[ \langle Q(q_j)Q(-q_j) \rangle = (\beta\omega(q_j)^2)^{-1}. \] (I.2.6)

Structural phase transitions occur only in crystals that are significantly anharmonic and for which the strictly harmonic frequencies, \( \omega(q_j) \), may be imaginary. The results of eqns. (I.2.4)-(I.2.6) can, however, be used provided that \( \omega(q_j) \) is interpreted as a suitably renormalized frequency as we shall discuss in § 1.5.1 (Cowley 1964). We shall need to consider the terms in the expansion of the potential energy beyond second order which may be written as
\[ H_A = \sum_{q_1,q_2,q_3} \sum_{j_1,j_2,j_3} V_q(q_1 q_2 q_3) Q(q_1_{j_1}) Q(q_2_{j_2}) Q(q_3_{j_3}) + \ldots. \] (I.2.7)

Structural phase transitions occur only in crystals that are significantly anharmonic and for which the strictly harmonic frequencies, \( \omega(q_j) \), may be imaginary. The results of eqns. (I.2.4)-(I.2.6) can, however, be used provided that \( \omega(q_j) \) is interpreted as a suitably renormalized frequency as we shall discuss in § 1.5.1 (Cowley 1964). We shall need to consider the terms in the expansion of the potential energy beyond second order which may be written as
\[ H_A = \sum_{q_1,q_2,q_3} \sum_{j_1,j_2,j_3} V_q(q_1 q_2 q_3) Q(q_1_{j_1}) Q(q_2_{j_2}) Q(q_3_{j_3}) + \ldots. \] (I.2.7)

At many structural phase transitions the size and shape of the crystal alters. These changes are described by introducing infinitesimal strain parameters, \( \eta_{\beta\gamma} \). The displacement of an atom due to an infinitesimal strain is
\[ u_{\alpha}(l\kappa) = \sum_{\beta} \eta_{\alpha\beta} R_{\beta}(l\kappa). \] (I.2.8)

A comparison of eqns. (I.2.8) and (I.2.1) then suggests that
\[ \eta_{\alpha\beta} = \lim_{\hbar \to 0} \frac{i\eta_{\beta}}{\sqrt{(N\sum_{\kappa}M_{\kappa})}} Q(q_{\beta}, \alpha), \] (I.2.9)
where \( Q(q_{\beta}, \alpha) \) is the acoustic mode amplitude with eigenvector polarized in the \( \alpha \) direction and wave-vector in the \( \beta \) direction. Alas, however, it is not possible to represent any particular combination of strain parameters in terms of the acoustic mode amplitudes; consequently, the terms involving the strains (or long wavelength acoustic modes) must be excluded from the summation over \( q_j \) in eqns. (I.2.3) and (I.2.7) (Born and Huang 1954) and written as further contributions to the hamiltonian, with the form
\[ H_D = \sum_{\alpha\beta} \sum_{\alpha\beta} \eta_{\alpha\beta} \left[ \sum_j V_{\alpha\beta}^{(0)} Q_{\alpha j}^{0} + \sum_{q_{ij}} V_{\alpha\beta}^{(q)} Q_{\alpha j}^{(q)} Q_{\alpha j}^{(-q)} + \ldots \right] + \sum_{\alpha\beta} \eta_{\alpha\beta} \eta_{\beta\gamma} [C_{\alpha\beta\gamma} + \ldots], \] (I.2.10)
where we have written only the three most important terms in the double power series expansion about the equilibrium positions of the high-symmetry phase. The
first term in eqn. (1.2.10) describes the coupling of a strain to a long wavelength optic mode of vibration, while in the second term use has been made of wave-vector conservation. The third term contains the usual elastic constant multiplied by the volume of a unit cell.

At order–disorder phase transitions, as discussed in the introduction (figs. 1.3 and 1.4), the different possible positions of the atoms may be a considerable distance apart. Although it is always possible to express the hamiltonian in a power series in the displacements, the series will be, at best, only very slowly convergent and consequently very difficult to employ in practice. An alternative approach is to introduce a new Ising spin variable which describes the large-scale motions. In the case of NaNO$_2$ the spin variable locates the N atom of each NO$_2$ group in either the positive, $S(l|\kappa) = \frac{1}{2}$, or negative, $S(l|\kappa) = -\frac{1}{2}$, $b$ direction. In the case of NaNO$_2$ there is only one NO$_2$ group in each unit cell so that we may then drop the suffix, $\kappa$, and have a single spin variable $S(l)$ describing the orientation of each NO$_2$ group.

A similar notation may be developed for a binary, $AB$, order–disorder alloy. If the crystal has only one type of site (i.e., one value of $\kappa$) in the high-symmetry phase then we may introduce a spin variable $S(l) = \frac{1}{2}$ if the site $l$ is occupied by an $A$ atom and $-\frac{1}{2}$ if it is occupied by a $B$ atom. This model may also be extended to include more complex alloys and more complex high-temperature phases.

In the case of the $AB$ alloy, the potential energy between atoms at $R(l)$ and $R(l')$ may have different functional forms according to whether both atoms are of type $A$, both are of type $B$, or if there is one of each. Denoting these interaction energies by $\phi_{AA}$, $\phi_{BB}$ and $\phi_{AB} = \phi_{BA}$ the energy of interaction between the two sites may then be written as

$$
\phi(l|l') = \phi_0(l'|l) + 2\phi_1(l'|l) (S(l) + S(l')) + 4\phi_2(l'|l) S(l) S(l'),
$$

(1.2.11)

where

$$
\phi_0 = \frac{1}{4} (\phi_{AA} + \phi_{BB} + 2\phi_{AB}).
$$

$$
\phi_1 = \frac{1}{4} (\phi_{AA} - \phi_{BB}).
$$

$$
\phi_2 = \frac{1}{4} (\phi_{AA} + \phi_{BB} - 2\phi_{AB}).
$$

This is then a general representation of the potential between $l$ and $l'$ irrespective of the occupation of the sites.

The third term of eqn. (1.2.11) gives rise to an interaction between the spin variables at different sites. It is frequently useful to diagonalize this term with the atoms at their mean equilibrium positions to obtain eigenvectors $E(\kappa, qj)$ and eigenvalues $J(qj)$ such that

$$
S(l|\kappa) = \frac{1}{\sqrt{N}} \sum_{qj} E(\kappa, qj) \exp (i q \cdot R(l|\kappa)) S(qj),
$$

(1.2.12)

where $S(qj)$ is the amplitude of the spin normal mode.
I.2.2. Susceptibility

The change in the property of a system when an external field is applied is described by the susceptibility: for example, the dielectric susceptibility gives the change in the dielectric polarization on application of an electric field. More generally, we consider a property of the system described by an operator, $B(r)$, which is dependent upon position, and apply to the system some time-dependent ‘field’ $E(r)$ whose interaction with the system we write as $H' = -A E$ with $A(r)$ some other operator. We may then introduce a position-dependent susceptibility

$$\chi_{BA}(r-r') = \frac{\partial}{\partial E(r')} \left. \langle B(r) \rangle \right|_{E(r')=0}. \quad (I.2.13)$$

Writing the response in the form

$$\langle B(r) \rangle = \text{Tr} \left\{ \exp \left( -\beta (H + H') \right) B \right\} / \text{Tr} \left\{ \exp \left( -\beta (H + H') \right) \right\}, \quad (I.2.14)$$

where $H$ is the hamiltonian of the unperturbed system, the susceptibility follows from eqn. (I.2.13) in the classical limit, as

$$\chi_{BA}(r-r') = \beta \langle B(r) A(r') \rangle. \quad (I.2.15)$$

Since most of our interest is directed towards pure materials (where wave-vector conservation plays an important role), it proves useful to introduce the Fourier transform of this susceptibility,

$$\chi_{BA}(K) = \beta \langle B(K) A(-K) \rangle, \quad (I.2.16)$$

where the operators $B(K)$ are the Fourier transforms of $B(r)$

$$B(K) = \int B(r) \exp (-iK \cdot r) d^3r. \quad (I.2.17)$$

The operators $B(K)$ may be expanded formally in powers of normal mode coordinates $Q(q_j)$ (or, in the appropriate cases, the ‘spin’ coordinates $S(q_j)$): thus we write

$$B(K) = B^0(K) \Delta(K) + \frac{1}{N} \sum_{q_j} B(K, q_j) Q(q_j) \Delta(K + q), \quad (I.2.18)$$

where $B^0(K)$ is the operator for the undistorted crystal. Wave-vector conservation is ensured by the delta function which is defined by

$$\Delta(K) = \sum_{l} \exp (iK \cdot R(l)) = \frac{(2\pi)^3}{N} \sum_{\tau} \delta^{(3)}(K - \tau), \quad (I.2.19)$$

where the summation is over the reciprocal lattice vectors, $\tau$, of the undistorted lattice, while $\delta^{(3)}(K)$ is the normal three-dimensional delta function.

The expressions for the coefficients in the expansion, eqn. (I.2.18), may be found once an expression is known for the operator $B(r)$. For example, if $B(r)$ is the dipole moment operator

$$B(r) = M(r) = \sum_{l} \delta(r - R(l)), \quad (I.2.18)$$

where $Z_\kappa$ is the apparent charge, then

$$M(K, q_j) = \sum_{\kappa} Z_\kappa M_\kappa^{-1/2} e(q_j) \exp (i(K + q) \cdot R(\kappa)), \quad (I.2.20)$$

while $B^0(K) = 0$. 

$$\begin{align*}
\end{align*}$$
Now, returning to the susceptibility function, eqn. (I.2.16), we make use of the expansion (I.2.18) for $B(K)$ and $A(K)$, picking out, in each case, the term in the expansion that is linear in the normal coordinate. The resulting contribution to the susceptibility is

\[
\chi_{BA}(K) = \sum_{q_j} \Delta(K + q)B(K, q_j)A(-K, q_j')\chi(q_j, q_j').
\] (I.2.21)

The importance of this result is that it shows that any one-phonon susceptibility can be obtained in terms of the susceptibility for the normal mode operators,

\[
\chi(q_j, q_j') = \beta \langle Q(q_j) Q(-q_j') \rangle.
\] (I.2.22)

Using the results quoted above, eqn. (I.2.6), for the harmonic crystal with classical statistics, this becomes,

\[
\chi_{h}(q_j, q_j') = \omega(q_j)^{-2} \delta_{j,j'}.
\] (I.2.23)

A similar analysis may be carried through for an order-disorder system. The operator, $B(r)$, is expanded in a power series in the spin operators (or, if necessary a double power series in the spin and displacement operators) with

\[
B(K) = B^0(K)\Delta(K) + \left(\frac{1}{N}\right)^{1/2} \sum_{q_j} B_s(K, q_j)S(q_j)\Delta(K + q) + \ldots,
\] (I.2.24)

where the coefficients $B_s(K, q_j)$ are given in terms of the spin eigenvectors. If the dipole moment associated with the $\kappa$th type of molecular group is $p_\kappa$, then the coefficients in the expansion of the dipole moment operator are given by

\[
M_\kappa(K, q_j) = 2 \sum_\kappa p_\kappa E(\kappa, q_j) \exp(i(K + q).R(\kappa)).
\] (I.2.25)

The susceptibility is then given by eqn. (I.2.21) but with the normal mode susceptibility replaced by

\[
\chi_{\kappa}(q_j, q_j') = \beta \langle S(q_j) S(-q_j') \rangle.
\] (I.2.26)

The susceptibility can be generalized to describe the response of a system to a time-dependent field, $E = \frac{1}{2} E_0 \left( \exp(i\omega t) + \exp(-i\omega t) \right)$. The susceptibility is then dependent upon the frequency $\omega$ as well as the wave-vector $K$ and written $\chi_{BA}(K, \omega)$. The calculation of this frequency-dependent susceptibility is more difficult than that of the static susceptibility described above but is detailed in many texts such as Landau and Lifshitz (1959). Since a time-dependent field may lose energy to the system, the frequency-dependent susceptibility has both real and imaginary parts which are connected by a Kramers-Kronig relation

\[
\chi^R_{BA}(K, \omega) = \frac{1}{\pi} \int \frac{\chi^I_{BA}(K, \omega')}{(\omega' - \omega)^2} \, d\omega',
\] (I.2.27)

and which satisfy the symmetry properties

\[
\chi^R_{BA}(K, \omega) = \chi^R_{BA}(-K, -\omega) \quad \text{and} \quad \chi^I_{BA}(K, \omega) = -\chi^I_{BA}(-K, -\omega).
\]

Since energy must be lost to the system, the imaginary part of the diagonal part of the susceptibility, $\chi^I_{AA}(K, \omega)$, is positive for $\omega > 0$. 

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Finally the dynamic susceptibility can be obtained for one-phonon processes as described above for the static susceptibility. The dynamic one-phonon susceptibility \( \chi(q,j'), \omega) \) can then be calculated explicitly for harmonic normal modes as

\[
\chi^R(q,j', \omega) = (\omega(q,j)^2 - \omega^2)^{-1} \delta_{jj'},
\]

(I.2.28a)

and

\[
\chi^I(q,j', \omega) = \frac{\pi}{2\omega(q,j)} \left[ \delta(\omega - \omega(q,j)) - \delta(\omega + \omega(q,j)) \right] \delta_{jj'}.
\]

(I.2.28b)

### 1.2.3. Scattering cross-sections

The calculation of the cross-section for the scattering of an incident plane-wave beam of particles with wave-vector \( k_1 \) and energy \( E_0 \) into a plane-wave beam with wave-vector \( k_2 \) and energy \( E \) is described by Van Hove (1954). Within the first Born approximation the differential cross-section can be written as

\[
\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_2}{k_1} S(K, \omega),
\]

(I.2.29)

where \( K \) is the wave-vector transfer \( K = k_1 - k_2 \), and \( \hbar\omega = E_0 - E \) is the energy transfer. The Van Hove scattering function, \( S(K, \omega) \), is given by

\[
S(K, \omega) = \sum_\Omega p_\Omega F(K)_{\Omega\Omega} F(-K)_{\Omega\Omega} \delta(\omega - \omega_\Omega),
\]

(I.2.30)

where \( F(K)_{\Omega\Omega} \) is the expectation value of an operator describing the interaction between the initial and final states of the system. It is sometimes more convenient to rewrite eqn. (I.2.30), making use of the Heisenberg representation of the operators:

\[
S(K, \omega) = \frac{1}{2\pi} \int_0^\infty \langle F(K, \tau) F(-K, 0) \rangle \exp(i\omega\tau) d\tau.
\]

(I.2.31)

In the case of X-ray or neutron scattering, the interaction between the particles and the specimen can be expressed in terms of a scattering length \( b_{\kappa} \) as

\[
F(K, \tau) = \sum_{\kappa} b_{\kappa} \exp(iK \cdot r(\kappa, \tau)),
\]

(I.2.32)

where \( r(\kappa, \tau) \) is the instantaneous position of the atoms \( (l\kappa) \). For the scattering of X-rays by rigid atoms of a particular type \( \kappa \), the scattering length \( b_{\kappa} \) is the same for each site \( l \), being equal to the scattering power of each single electron multiplied by the atomic form factor, which is dependent upon the wave-vector, \( K \). For neutrons the scattering length may vary from site to site, owing to the randomness in the isotopic distribution and the spin alignment of the nuclei. This randomness results in incoherent scattering which usually gives rise to a troublesome background: we shall largely neglect it. The coherent scattering reflects the average scattering length \( b_{\kappa} = 1/N \sum_l b_{\kappa} \) and hence includes the interference effects between the different ions. The X-ray or coherent neutron scattering is then given by

\[
F(K, \tau) = \sum_{\kappa} b_{\kappa} \sum_l \exp(iK \cdot r(l\kappa, \tau)).
\]

(I.2.33)
The operator $F(K, \tau)$ can then be obtained by expanding the position coordinate $r(k, \tau)$ in powers of the displacements. When these displacements are transformed into the normal mode coordinates one finds

$$F(K, \tau) = F^0(K) + \left( \frac{1}{N} \right)^{1/2} \sum_{qj} \bar{F}(K, qj) \Delta(K + q) Q(qj, \tau) + \ldots,$$

where $Q(qj, \tau)$ is the instantaneous amplitude of the normal mode coordinate, and the coefficients are given by

$$F^0(K) = \sum_k b_k \exp(iK \cdot R(k)) \exp(-W_k),$$

while

$$F(K, qj) = \sum_k b_k M_k^{1/2} e(K, qj) \exp(i(K + q) \cdot R(k)) \exp(-W_k),$$

where $W_k$ is the Debye-Waller factor. Using these results $S(K, \omega)$ can be divided into a Bragg part, $S^0(K, \omega)$, and a one-phonon part, $S^1(K, \omega)$, where

$$S^0(K, \omega) = N|F^0(K)|^2 \delta(\omega) \Delta(K)$$

and

$$S^1(K, \omega) = \sum_{qj} \Delta(K + q) F(K, qj) F(-K, -qj) \mathcal{S}(qj, \omega),$$

where $\mathcal{S}(qj, \omega)$ is the displacement-displacement correlation function

$$\mathcal{S}(qj, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle Q(qj, \tau) Q(-qj', 0) \rangle \exp(i\omega\tau) d\tau.$$

This displacement-displacement correlation function can be related to the imaginary part of the dynamic susceptibility introduced in the previous section as shown for example by Cowley (1963). The result is that

$$(n(\omega) + 1) \chi^d(qj, \omega) = \frac{\pi}{\hbar} \mathcal{S}(qj, \omega),$$

where $n(\omega)$ is the Bose-Einstein factor. Furthermore the static displacement-displacement correlation function

$$\mathcal{S}(qj) = \int_{-\infty}^{\infty} \mathcal{S}(qj, \omega) d\omega$$

is within the classical approximation, $\hbar \omega \ll k_B T$, related to the static susceptibility, by use of eqn. (1.2.27), to give

$$\beta \mathcal{S}(qj) = \chi(qj).$$

Since all X-ray and many neutron scattering experiments measure the integrated scattering, this relationship is of considerable importance.

These results for the susceptibility and scattering show the one-phonon parts are determined by the normal mode susceptibility multiplied by the appropriate coefficients. Provided, then, that these coefficients can be treated as wave-vector-, frequency- and temperature-independent constants, the behaviour of the suscepti-
ibility or scattering cross-section close to a phase transition will be very similar, irrespective of the probe used to perform the measurements.

A similar analysis can be carried through for an order–disorder system. For example in an \(AB\) alloy the coherent scattering lengths may be \(b_A\) and \(b_B\), which are not usually the same. The structure factor, eqn. (I.2.33), then becomes

\[
F(K, \tau) = \sum_i \sum_\kappa (\vec{b}_\kappa + S(\kappa, \tau) b'_\kappa) \exp(iK \cdot r(\kappa, \tau)),
\]

where \(\vec{b}_\kappa = \frac{1}{2}(b_A + b_B)\) and \(b'_\kappa = b_A - b_B\). The expansion of \(F(K, \tau)\) is now given by eqn. (I.2.34) with \(\vec{b}_\kappa\) replacing \(b_\kappa\). The leading term in the spin variables is given by

\[
\left(\frac{1}{N}\right)^{1/2} \sum_{qj} F_s(K, qj) \Delta(K + q) S(qj, \tau),
\]

where

\[
F_s(K, qj) = \sum_\kappa b'_\kappa \exp(-W_\kappa) E(qj) \exp(i(K + q) \cdot R(\kappa)).
\]

Substitution of eqn. (I.2.44) into eqn. (I.2.31) and repeating the development given above then shows that the cross-section mirrors the behaviour of the spin correlation function given by eqn. (I.2.26).

Finally to determine the Raman scattering of laser light requires an expansion of the polarizability of the material in powers of the displacements. Formally the expansion can be written

\[
P_{\alpha\beta}(K) = P_{\alpha\beta}^0(K) \Delta(K) + \left(\frac{1}{N}\right)^{1/2} \sum_{qj} P_{\alpha\beta}(qj) q(qj) \Delta(K + q) \Delta(K + q) + \ldots.
\]

Substituting this expansion into eqn. (1.2.31) yields an expression for the Raman scattering tensor \(I_{\alpha\beta}\), which determines the scattering into a polarization \((\beta\delta)\) from an incident beam polarized in the \((xy)\) direction. The cross-section is thus dependent upon the displacement–displacement or spin–spin correlation functions, as in the case of X-ray and neutron scattering. Unlike the neutron or X-ray scattering case, however, in Raman scattering the wave-vector transfer \(K\) is restricted to be much smaller than a reciprocal lattice vector.

§1.3. Order parameters and fluctuations

I.3.1. Primary order parameters

At a structural phase transition the symmetry of the crystal changes: some of the symmetry operations of the high-symmetry phase, which is usually but not always the high-temperature phase (see §1.4.5), are not symmetry operations of the low-symmetry phase. Above the ferroelectric phase transition of BaTiO₃, fig. 1.1, each Ba and Ti ion is at a site having the full cubic symmetry but in the distorted phase the symmetry at each site is only tetragonal. This breaking, in the low-symmetry phase, of some of the symmetry operations of the high-symmetry phase is the essential characteristic of most phase transitions. (However, cf. §1.4.3.2.)

The displacements of the atoms which are associated with the breaking of the symmetry are characteristic of the distorted phase, and, furthermore, at a
continuous phase transition decrease continuously to zero as the high-symmetry phase is approached. In a single domain of the distorted phase, the displacements in any one unit cell have a definite relationship to those occurring in any other unit cell. In BaTiO₃ the displacements are equal in every unit cell, while in SrTiO₃, fig. 1.2, they are of equal magnitude but are systematically in opposite directions in neighbouring unit cells. This long-range order is characteristic of distorted phases, and suggests that the displacements can be described in terms of the normal modes, or spin variables, introduced in §1.2. This is indeed the case at the majority of structural phase transitions—one exception being the lock-in phase transitions discussed in §1.4.5.

The simplest example of a structural phase transition occurs when the distortions may be described by a single normal mode; the amplitude of the distortion is then given by the order parameter

\[ Q_0 = N^{-1/2} \langle Q(q_{\text{sj}}) \rangle, \]  

where \( q_{\text{sj}} \) is the particular normal mode which describes the atomic displacements in the distorted phase, and the factor of \( N^{1/2} \) is introduced so that \( Q_0 \) is independent of the crystal size.

If the phase transition is continuous the order parameter will approach zero as \( T \to T_c \) and is assumed to be given by a power law;

\[ Q_0 \sim (T_c - T)^\beta, \]  

where \( \beta \) is known as the critical exponent for the order parameter. In classical theories of phase transitions, such as those discussed in §§1.4, and 1.5 the exponent \( \beta = 0.5 \), while in practice \( \beta \) varies between 0.25 and 0.5 as described in part II.

Frequently the possible atomic displacements of the distorted phase cannot be described solely in terms of a single normal mode, but only in terms of linear combinations of \( n \) normal mode coordinates; \( n \) is then known as the number of components of the order parameter (or the order parameter dimensionality) and in the high-symmetry phase all these \( n \) normal modes have the same frequency. We shall write the amplitudes of these normal modes

\[ Q_i = N^{-1/2} \langle Q(q_{\text{sj}i}) \rangle, \]  

and the order parameter in the distorted phase as

\[ Q_i = Q_0 \zeta_i, \]  

where

\[ \sum_i \zeta_i^2 = 1, \]  

and the parameters \( \zeta_i \) determine the structure of the distorted phase, while \( Q_0 \) varies with temperature as described by eqn. (I.3.2).

Both BaTiO₃ and SrTiO₃ are examples of systems where \( n = 3 \). In the case of BaTiO₃ the ordered phase may be characterized by displacements along the \( x, y \) or \( z \) axes, each of which corresponds to a different normal mode, while in SrTiO₃ the oxygen octahedra can rotate about any of three cube axes. In both of these cases the wave-vectors \( q_{\text{sj}} \) are the same for all three values of \( i \); \( q_s = 0 \) for BaTiO₃, \( q_s = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})2\pi/a \) for SrTiO₃. For this type of phase transition \( n \) cannot be larger than 3. Recently, however, there has been considerable interest in incommensurate phase
transitions, where (in cubic materials) the value of \( n \) may, in principle, be as large as 48, as described in §1.4.4.

Although we have introduced the concept of an order parameter through the displacive phase transitions shown in figs. 1.1 and 1.2, the same approach may be used to specify an order parameter in the order-disorder case when

\[
Q_0 = N^{-1/2} \langle S(q_j) \rangle. \tag{1.3.5a}
\]

Thus, for example in the case of NaNO\(_2\), the order parameter gives a measure of the difference between the numbers of NO\(_2\) groups displaced along the positive and negative \( b \) axis.

A more formal description of the order parameter at a phase transition may be given in the language of group theory (Landau and Lifshitz 1959). The density distribution of a crystal \( \rho(r) \) can be expressed as a linear combination of normalized functions, \( \phi \), which transform into one another under the symmetry operations of the group, \( G \), of the high-symmetry phase. It is convenient to choose the functions \( \phi \) so that they divide into a sum of sets of functions which transform only within the set under the symmetry operations. These functions, \( \phi_p^i \), then form the bases of the irreducible representations of \( G \), where \( p \) labels the irreducible representation and \( i \) the number of the functions in that representation. Then amongst the functions \( \phi_p^i \) there is one which is invariant under \( G \), and this describes the structure \( \rho_0(r) \) of the high-symmetry phase. Any distortion \( \delta \rho(r) \) can then be written as

\[
\delta \rho = \sum_p \sum_i C_p^i \phi_p^i, \tag{1.3.5b}
\]

where \( \sum \) omits the term describing the structure of the high-symmetry phase. Now at a continuous phase transition the distortion in structure can be described in terms of only one irreducible representation, \( p = s \), say; the coefficients \( C_s^i \) then describe the structure of the distorted phase.

The displacements of the atoms about their equilibrium positions are a set of functions which transform under the symmetry operations of the group, \( G \). In setting up the normal modes in §1.2 the symmetry of the crystal ensures that each normal mode transforms as a particular irreducible representation of the space group. The functions \( Q(q_j) \) are then proportional to the functions \( \phi_p^i \) introduced above and the coefficients \( C_s^i \) are proportional to the order parameters \( Q_i \). The number of components of the order parameter, \( n \), is then the dimensionality of the sth irreducible representation of the full space group.

1.3.2. Secondary order parameters

The term secondary order parameters is used, alas, in two different ways. In the first instance, it is used to describe distortions (in the low-symmetry phase), which arise at the phase transition, but which do not break as many of the symmetry elements of the high-symmetry phase as are broken by the primary ordering. This concept may, perhaps, be clarified by considering BaTiO\(_3\) and SrTiO\(_3\), for both of which there is a macroscopic strain in the distorted phase in addition to the primary distortion. In the case of BaTiO\(_3\) the point group of the high-temperature phase has the full cubic symmetry, m3m, and the distorted phase has the tetragonal point group 4 mm. If, however, the distortion to a tetragonal structure arose purely from the tetragonal strain, \( \eta_{zz} = (\eta_{xx} + \eta_{yy})/2 \), then the distorted phase would have the symmetry 4/mmm. The point group 4/mmm can be obtained from 4 mm by adding a mirror plane perpendicular to the tetragonal axis. The symmetry of this mirror plane
is broken by the distortions described by the primary order parameter but is not broken by the secondary order parameter, the tetragonal strain.

In the case of SrTiO₃ the symmetry of the low-temperature phase is 4/mmm but contains two formula units in each unit cell, whereas if the only deformation was the strain the point group symmetry would be 4/mmm but there would be only one formula unit in each unit cell. Consequently the primary order parameter breaks the translational symmetry between the two formula units in each unit cell of the distorted phase whereas the secondary order parameter (the tetragonal strain) does not.

Since the distortions produced by a secondary order parameter break the symmetry of the high-symmetry phase they must decrease to zero as \( T \to T_c \). We therefore write the temperature dependence of a secondary order parameter, \( \bar{Q} \), whether it be the strain or another normal mode, as

\[
\bar{Q} \sim (T_c - T)^\beta.
\]

Since the secondary order parameter does not break all the symmetry elements that are broken at \( T_c \), it must, when close to \( T_c \) have a vanishingly small amplitude compared with the primary order parameter; thus one expects that \( \bar{\beta} > \beta \).

The other use of the term secondary order parameter arises when there is more than one normal mode (\( q_j \)) which has the symmetry of the primary order parameter. For example, in BaTiO₃ there are three different frequencies of the transverse optic modes of long wavelength. Although we can choose the mode eigenvectors so that the displacements close to \( T_c \) are given by only one of these modes, as the distortions become larger the pattern of the atomic displacements may alter and this can be represented as a coupling to the other normal modes.

1.3.3. Experimental determination of the order parameter

1.3.3.1. Macroscopic measurements

If the order parameter has wavevector \( q_s = 0 \), a ferrodistortive transition, then its temperature dependence may be determined by macroscopic measurements. For example, in ferroelectric materials the spontaneous polarization, \( P_s \), is proportional to the amplitude of the distortion of a long wavelength infra-red active mode. In the notation developed above

\[
P_s = \frac{1}{v N^{1/2}} \sum_j M(0j)\langle Q(0j) \rangle,
\]

where \( v \) is the volume of the unit cell and the dipole moment operator of the mode is given by eqn. (I.2.20).

If there is only one mode \( j \), eqn. (I.3.1) shows that

\[
P_s = \frac{1}{v} M(0j)Q_0.
\]

showing that a measurement of \( P_s \) determines the order parameter \( Q_0 \). In fig. I.5 we show the measured spontaneous polarization for BaTiO₃ (Merz 1953); note that the phase transition in BaTiO₃ is of first order.

The spontaneous polarization gives a measure of the primary order parameter only if the phase transition is to a ferroelectric phase. If the order parameter
corresponds to a $\mathbf{q} = 0$ mode of even symmetry, then there will be a change in the refractive index or optical polarizability of the crystal, proportional to the order parameter $Q_0$. For example, the optical polarizability is given by eqn. (1.2.46) as an expansion in powers of the normal mode coordinates. If the leading term is non-zero the change in polarizability is given by

$$
\delta P_{s\theta} = P_{s\theta}(0j)Q_0.
$$

if there is only one mode $j$. Harley and MacFarlane (1975) have measured the order parameter in DyVO$_4$ and TbVO$_4$ using the birefringence of the crystal as illustrated in fig. II.15 of part II.

Finally if the primary order parameter is the macroscopic strain, it can be measured macroscopically, or possibly more reliably by using neutron or X-ray diffraction.

Macroscopic techniques have the disadvantage that they can only measure the primary order parameter at ferrodistortive, $\mathbf{q} = 0$, phase transitions, and furthermore require single domain samples to be available. Unfortunately single domain samples can usually be produced only by applying a field to the specimen which may then influence the results. Also close to $T_c$, the susceptibility becomes large, see §I.3.4, and the measurement of a small spontaneous polarization, in the presence of a large dielectric constant is far from being a technically easy experiment.

Secondary order parameters can be measured using macroscopic techniques, but the results for the spontaneous polarization or refractive index may be difficult to interpret. This is because the two-phonon term in the expansion of the dipole moment or polarizability, eqn. (I.2.46), is of the form,

$$
P_{s\theta}^{(2)}(\mathbf{K}) = \frac{1}{N} \sum_{\mathbf{q}_1,\mathbf{q}_2,j_1,j_2} P_{s\theta}(\mathbf{q}_1,\mathbf{q}_2) Q(\mathbf{q}_1,j_1) Q(\mathbf{q}_2,j_2) \Delta(\mathbf{K} + \mathbf{q}_1 + \mathbf{q}_2).
$$

If we approximate $\langle Q(\mathbf{q}_1,j_1)Q(\mathbf{q}_2,j_2) \rangle$ by $\langle Q(\mathbf{q}_j) \rangle \langle Q(-\mathbf{q}_j) \rangle$, then this term will
A. Cowley contribute a term to the change in polarizability
\[ \delta P_{\alpha \beta} \approx P_{\alpha \beta} \left( \mathbf{q}_i - \mathbf{q}_j \right) \mathbf{Q}_0^2. \]

This term may well be of the same order of magnitude as the term arising from the one-phonon contribution of the secondary order parameter $\mathbf{Q}$, which is given, eqn. (I.2.46), by
\[ \delta P_{\alpha \beta} \approx P_{\alpha \beta} \left( \mathbf{0} \right) \mathbf{Q}. \]

Without a detailed knowledge of the polarizability parameters it is impossible to distinguish between these two processes experimentally.

1.3.3.2. Scattering measurements

The theory of the scattering of X-rays and neutrons from crystals was briefly reviewed in §I.2.3. The structure of the crystal is determined by the Bragg reflections, which are dependent upon the infinitely long time part of the correlation function, eqn. (I.2.31). In the long time limit
\[ \langle F(K, t)F(K, 0) \rangle = |\langle F(K, 0) \rangle|^2, \] (I.3.10)
so that the Van Hove scattering function has the form
\[ S^0(K, \omega) = |\langle F(K, 0) \rangle|^2 \delta(\omega). \] (I.3.11)

In the high-symmetry phase these results have already been given by eqns. (I.2.35) and (I.2.37) and enable the structure of the phase to be determined experimentally.

In the distorted phase the scattering can be obtained if the positions $\mathbf{R}(\mathbf{k})$ are replaced by the positions in the distorted structure. It is, however, more instructive to expand the structure factor $\langle F(K, 0) \rangle$ in powers of the displacement as in eqn. (I.2.34). When the expectation value of eqn. (2.34) is taken one obtains
\[ \langle F(K, 0) \rangle = F^0(K)\Delta(K) + \sum_{i=1}^{n} F(K, \mathbf{q}_i, \mathbf{q}_j)\langle Q_i \rangle \Delta(K + \mathbf{q}_i) \] (I.3.12)
where we have neglected, for the present, higher powers in the primary order parameter and all secondary order parameters.

Now if $\mathbf{q}_i$ is non-zero, eqn. (I.3.12) shows that there will be new Bragg reflections present in the distorted phase with an intensity given by $N|F(K, \mathbf{q}_i)|^2\langle Q_i \rangle^2 \Delta(K + \mathbf{q}_i)$. The intensity of these Bragg reflections enables the relative sizes of the different components of the order parameters, the $\langle Q_i \rangle$, to be found while their temperature dependence gives a measure of the exponent $\beta$ describing the temperature dependence of the primary order parameter. The temperature dependence of the new Bragg reflection in the antiferrodistortive phase of SrTiO$_3$ is shown in fig. 1.6 as determined with neutron scattering techniques by Riste et al. (1971).

The behaviour is less straightforward for ferrodistortive phase transitions, $\mathbf{q}_i = 0$. The intensity is given by
\[ S^0(K, \omega) = N\delta(\omega)\left| F^0(K) \right|^2 + \sum F(K, 0, \mathbf{q}_j)\langle Q_j \rangle^2 \Delta(K). \] (I.3.13)

The change in the intensity of these reflections close to $T_c$ is proportional to $\langle Q_i \rangle^2$ because the cross terms cancel, provided that $F^0(K)$ is not zero or strongly
The temperature dependence of the superlattice reflection $\mathbf{K} = \frac{2\pi}{a} (1, 1, \frac{1}{2})$ in SrTiO$_3$ after Riste et al. (1971). The dotted line indicates that $T_c$ for the specimen was $106.1 \pm 0.3$ K.

Temperature dependent. (We discuss the temperature dependence of the Debye-Waller factors in §§ 1.3.5 and 1.4.)

The use of scattering techniques to determine secondary order parameters is subject to the same difficulties as those discussed for macroscopic properties. In the expansion of the structure factor $\langle F(K, 0) \rangle$, eqn. (1.2.38), there are not only linear terms in $Q(q_j)$ but second-, third-, and higher-order terms. The second-order terms will give rise to additional contributions to the scattering with the wave-vector conservation conditions given by $\Delta(K)$ and $\Delta(K + 2q_j)$. The intensity arising from these diffraction effects caused by the primary order parameters, must be included when the amplitude of the secondary order parameters are being deduced from the intensities measured at these wave-vector transfers. Note that, whereas the relative sizes of the one- and two-phonon terms in the expansion of the polarizability are largely unknown, in the case of displacive phase transitions these relative amplitudes for scattering experiments are given exactly in terms of the supposedly known eigenvectors and scattering lengths. It is therefore possible to separate these two effects at least in principle. This advantage of diffraction is frequently rather illusory in practice, because the effects of the two-phonon terms in a diffraction experiment are usually relatively larger than in the polarizability experiment.

At strictly order–disorder phase transitions, such as the $AB$ alloy, there are only linear terms in $S(h\mathbf{c})$ in the expansion of $F(K, \tau)$, eqn. (1.2.43). Consequently the interpretation of the scattering is simpler in these systems than in the displacive materials. In the molecular systems, such as NaN02, however, the situation is more complex because of a coupling between the spin and the displacement variables, so that it again becomes difficult to extract secondary order parameters reliably.

There are two experimental problems in the application of diffraction techniques to the determination of order parameters. Firstly Bragg reflections from real crystals frequently suffer from extinction effects. At antiferrodistortive phase transitions close to $T_c$, the new Bragg reflections of the distorted phase are weak and probably not greatly influenced by extinction, as shown (fig. 1.6) by the agreement between results of experiments on different sizes of crystal; however, as the system is cooled extinction will become more and more important. Extinction provides a particularly difficult problem at ferrodistortive transitions because the crystal will usually break
up into domains changing the extinction effects on the normal Bragg reflections. Changes in these Bragg intensities will not then reflect the order parameter in the way suggested after eqn. (I.3.13).

A second problem (to be discussed in detail in the next section) is that, close to $T_c$, the diffuse scattering is large for small frequency transfers and at those wave-vector transfers at which the Bragg reflections of the distorted phase appear. This is the cause (at least in part) of the high temperature ‘tail’ to the Bragg reflection intensity shown in fig. I.6 (to which we shall devote much attention in III).

The exponent $\beta$, can be accurately obtained only to the extent that the diffuse scattering can be accurately subtracted out. Since the Bragg scattering is a delta function in both energy and wave-vector transfer whereas the diffuse scattering is broad the subtraction is made easier if the experiment is performed with very good resolution in either $K$ or $\omega$. In the case of conventional X-ray scattering it is impossible to energy discriminate against the diffuse scattering, but in principle it is possible to use very good $K$ space resolution. It is possible to energy discriminate using Mössbauer $\gamma$-rays as a source for the scattering and then to perform energy analysis (Darlington and O’Connor 1976) using a similar Mössbauer absorber. It is surprising that this technique has not been applied to measure $\beta$.

By using neutron scattering techniques, the energy analysis is more easily performed. Conventional inelastic scattering techniques give an energy resolution of about $0.1 \text{ meV}$ which is not normally good enough to permit the neglect of the diffuse scattering. The development of new techniques with a resolution of $1 \mu\text{eV}$, such as the backscattering spectrometer (Alefeld et al. 1969) and the spin–echo spectrometer (Mezei 1972) holds out the possibility of eliminating the diffuse scattering more completely. The wave-vector resolution is, however, inferior to that which can be obtained with the best X-ray spectrometers.

I.3.3.3. Resonance methods

The order parameter at a structural phase transition may be determined by using electron paramagnetic resonance, E.P.R., or nuclear quadrupole resonance, N.Q.R. (Müller 1971, Blinc 1971). The E.P.R. method depends upon the presence in the crystal of a magnetic ion. The most suitable ions are those with a half-filled closed shell, Mn$^{2+}$, Fe$^{3+}$, Gd$^{3+}$ or Tb$^{4+}$ because; (i) they are spherically symmetric and so do not introduce local distortions in symmetry and (ii) they have very long E.P.R. relaxation times even at room temperature. One of these ions must then be present in the crystal at a low concentration, say, $10^{18} \text{ cm}^{-3}$; Fe$^{3+}$ is usually present in ‘pure’ SrTiO$_3$ at about this concentration.

The crystal field hamiltonian for a 3d transition metal ion can be expressed as a spin hamiltonian in terms of the normalized magnetic spin operators, $O^m_n$ (Hutchings 1964), which transform in the same way as the corresponding cartesian polynomials;

$$H_{cf} = \sum_{m=-2}^{2} B^m_2 O^m_2 + \sum_{m=-4}^{4} B^m_4 O^m_4.$$ 

The coefficients in this expansion $B^2_2$, $B^4_2$ may then be obtained at least approximately in terms of the ionic charges, bonding and nearest neighbour distances (Hutchings 1964). Typically the $B$-coefficients are about $10^{-3} \text{ meV}$.

In the high-symmetry phase the site symmetry is such that some of the $B^m_i$ coefficients are zero; for example in SrTiO$_3$ with an Fe$^{3+}$ ion replacing the Ti$^{4+}$ ion only the coefficients $B^0_4$ and $B^4_{4}$ are non-zero. In the distorted phase, one (or more) of
the $B$-coefficients becomes non-zero and increases in a manner dependent upon the primary order parameter, $Q_0$, and the secondary order parameter $\bar{Q}$

$$B = A_1 Q_0 + A_2 Q_0^2 + \ldots + A_1 \bar{Q} + A_2 \bar{Q}^2 + \ldots$$  \hspace{1cm} (1.3.14)$$

In the case of Fe$^{3+}$ in SrTiO$_3$, $B_0^2$ is allowed in the distorted phase. However, since the Fe$^{3+}$ ion is situated at a centre of symmetry even in the distorted phase, the coefficient $A_1$ in eqn. (1.3.14) is zero. The secondary order parameter for SrTiO$_3$ is the strain and so $A_1$ is non-zero. Consequently $B_2^0$ for SrTiO$_3$ has two contributions proportional to $Q_0^2$ and to $\bar{Q}$, and as with the macroscopic polarizability it is difficult to distinguish the effects of these two different processes.

In contrast Gd$^{3+}$ ions in SrTiO$_3$ are situated at the Sr$^{2+}$ site, which is not a centre of symmetry in the distorted phase, and so $A_1$ of eqn. (1.3.14) is non-zero (Unoki and Sakudo 1967).

Müller and Berlinger (1971) were, however, able to directly measure the primary order parameter in SrTiO$_3$ using the Fe$^{3+}$ centre. In a single domain specimen of distorted SrTiO$_3$, fig. 1.2, the two Ti$^{4+}$ sites have their environments twisted in opposite senses. Hence, by determining the orientation of the principal axes of the spin hamiltonian for these two types of sites, the rotation angle of the oxygen octahedra could be determined. Using this approach with the Fe$^{3+}$-vacancy centre in SrTiO$_3$ Müller and Berlinger were able to determine the rotation angle in SrTiO$_3$ to $\pm 0.01^\circ$, fig. II.17, but more typically the accuracy of such experiments is $0.1^\circ$.

In an E.P.R. experiment the line width of the resonance is typically about $10^{-4}$ T, and so there will be a splitting once the local distortion of the structure persists for times longer than $10^{-6}$ s. Unfortunately, the E.P.R. method cannot be used when the material is magnetic and it depends on being able to produce material with the necessary impurities situated at known sites in the host material. It also suffers from the disadvantage that there is always a niggling uncertainty as to whether the behaviour near the E.P.R. impurity site is the same as that of the bulk material.

Nuclear quadrupole resonance arises from the transitions between the different nuclear energy levels caused by the interaction between the nuclear quadrupole-moment and the electric field gradient. The electric field gradient may be expanded in a similar manner to the electrostatic potential which determines the E.P.R. spectrum, only the selection rules for the coefficients are different. In particular, if the ion is situated at a centre of symmetry in the high-symmetry phase, the linear term, $A_1$, in eqn. (1.3.14) is zero even in the distorted phase and the $B$ coefficient is proportional to $Q_0^2$. Examples of this behaviour are provided by the work of Borsa (1971), using $^{139}$La and $^{27}$Al resonances in LaAlO$_3$, which undergoes a similar phase transition to SrTiO$_3$.

In materials of lower symmetry the linear term in eqn. (1.3.14) is non-zero and the $B$ coefficients are proportional to the order parameter. This is illustrated by the $^{133}$Cs resonance in CsH$_2$ AsO$_4$ as shown in fig. 1.7 (Bline and Mali 1969).

N.M.R. has the advantage over E.S.R. that it does not necessitate the introduction of an impurity, but the selection rules are such that the $B$ parameters are more commonly proportional to $Q_0^2$ than to $Q_0$ and so cannot be used to determine the exponent $b$. The frequency resolution of the spectrometers is such that the local distortion must persist for $10^{-3}$ s to give a sharp line characteristic of the distorted phase.

Finally the Mössbauer effect may be used to determine the order parameter at a
structural phase transition (Shenoy 1973). At a phase transition the Mössbauer line may split because of a change in the nuclear energy levels caused by the interaction of the nuclear quadrupole moment with the electric field gradient. The selection rules and dependence of the splitting on the order parameter are then the same as those described for N.M.R. experiments. The accuracy of Mössbauer experiments is usually less than that of N.M.R. experiments and furthermore the experiments frequently require that the Mössbauer nucleus be introduced into the material as an impurity.

Fig. I.7

Temperature dependence of the nuclear quadrupole $^{133}$Cs magnetic resonance in CsH$_2$AsO$_4$ after Blinc and Mali (1969).

1.3.4. Static susceptibility

In § 1.2, the susceptibility of a one-phonon process was shown to be dependent upon the coupling between the probe and the phonon (described by the operators such as $B(K, q_j)$ or $F(K, q_j)$) and the one-phonon response functions, $\chi(q_{jj'}^\prime)$, eqn. (I.2.22). In the distorted phase $\langle Q(q_{ji}) \rangle$ is non-zero, so that, at a continuous phase transition, it is reasonable to expect that $\langle Q(q_{ji})Q(-q_{ji}) \rangle$, a measure of the fluctuations of the normal mode coordinate $Q(q_{ji})$, will diverge at $T_c$ giving rise, eqn. (I.2.22), to a divergence of the susceptibility $\chi(q_{ji})$, as illustrated for BaTiO$_3$ in fig. 1.8. We shall therefore study the behaviour of the susceptibility $\chi(q_{ji})$ as the temperature $T \to T_c$ and wave-vector $q \to q_c$ for the particular modes whose expectation values are non-zero in the distorted phase. It is convenient to introduce a notation to describe the fluctuations for the normal modes with wave-vectors close to $q$. We define

$$
\hat{Q}_i(k) = Q(k + q_{si,j}) - \langle Q(k + q_{si,j}) \rangle $$

and

$$
Q_i(k) = Q(k + q_{si,j}).
$$

Note that in the fluctuating parts of the order parameter we have not introduced the factor of $N^{-1/2}$ included in eqn. (I.3.1); the $Q_i(k)$ are proportional to the phonon amplitude.

We introduce a corresponding notation for the susceptibility

$$
\chi_i(k) = \chi(k + q_{si,j}^i,j),
$$

$$
= \beta \langle \hat{Q}_i(k)\hat{Q}_i(-k) \rangle. \tag{I.3.15 b}
$$
In the high-symmetry phase \( \chi_i(k) \) is independent of \( i \) and its divergence is given by scaling theory (cf. Stanley 1971, §II.4.3.5) for \( T \to T_c, k \to 0 \), as

\[
\chi_i(k) \approx C_i t^{-\gamma} D(k^2 \xi^2_x),
\]

where

\[
t = (T - T_c)/T_c,
\]

and \( \gamma \) is the susceptibility exponent which is unity for classical theories, but can be much larger in real systems. The function \( D(x^2) \) is a scaling function, (normalized such that \( D(0) = 1 \)) describing the wave-vector dependence of the susceptibility. \( \xi_x \) is the correlation length in the \( x \) direction. The correlation length diverges at a continuous phase transition, and the divergence is described by the exponent \( \nu \)

\[
\xi_x = f_+ (x^2 t^{-\nu}),
\]

where classical theories yield \( \nu = 0.5 \), but more exact theories again give rather larger values.

There are two special cases of eqn. (I.3.16) of particular importance

\[
\chi_i(0) = C_i t^{-\gamma}, \quad |k| = 0
\]

and

\[
\chi_i(k) = D_0/k_x^2 \eta, \quad T = T_c,
\]

where the exponent, \( \eta = 2 - (\gamma/\nu) \), is zero according to classical theory, and remains small in more refined theory. This exponent is particularly hard to measure and we shall not discuss it further.
In the distorted phase, the symmetry is broken so that the different susceptibility functions are neither independent nor equal. It is, however, possible to choose basis functions from the $Q_i(k)$ in terms of which the susceptibilities are independent. In BaTiO$_3$ with a ferroelectric $c$ axis the dielectric susceptibility in the ferroelectric phase is different for the $a$ and $c$ axes as illustrated in fig. 1.8.

In the distorted phase each of the different susceptibilities is divergent as $T \to T_c$, and the nature of that divergence may be described by eqns. (I.3.16)–(I.3.20) except that the amplitudes $C_+$ and $f_+(x)$ must be replaced by $C_-$ and $f_-(x)$. In all but exceptional circumstances (cf. footnote to Table II.1 in part II) these divergences will be described by the same exponents ($\gamma$ and $\nu$) as characterize the divergences when $T \to T_c^+$. Note, however, that if a continuous symmetry is broken at the phase transition, a more careful treatment of the low-temperature phase susceptibilities is required (§§ I.4.2, I.4.4).

### 1.3.5. Soft modes and the dynamic susceptibility

The imaginary part of the dynamic susceptibility is related to the static susceptibility by the Kramers-Kronig relation, eqn. (I.2.27), according to which

$$\chi^\prime(0) = \frac{1}{\pi} \int_{-\infty}^{\infty} \chi'(\omega')\omega'^{-1} d\omega'$$

The imaginary part of $\chi'(\omega)$ gives the power dissipation of the system, and depends upon the matrix elements coupling the initial and final states of the system and on the density of initial and final states whose energies differ by $\hbar\omega$. The static susceptibility diverges at $T_c$ for $k=0$. Since it is unreasonable to assume that the matrix elements are very temperature dependent, this divergence must reflect a movement in the weight of $\chi'(\omega)$ to smaller $\omega$—the ‘critical slowing down’ discussed by Van Hove (1954).

Dynamic phenomena have played an especially important role in the development of our understanding of structural phase transitions. In particular the appealing concept of a soft mode, introduced independently by Anderson (1960) and Cochran (1960), has frequently proved helpful in describing structural phase transitions, and in illuminating their essential characteristics.

The idea was prompted by the form of the static susceptibility of a harmonic oscillator, given in eqn. (I.2.23) by $\chi_n(q_i)$. Comparing this result with the behaviour of the static susceptibility in the classical theory (eqn. (I.3.19) with $\gamma = 1$) suggests that

$$\omega(q_i)^2 = a(T - T_c), \quad T > T_c.$$  \hspace{1cm} (I.3.21)

Thus, in the soft mode approach, the phase transition is viewed as an instability of the crystal against a particular normal mode, the frequency of which decreases to zero at $T_c$. In the low-symmetry phase the crystal is distorted so as to stabilize this mode, and the distortion is described by a ‘frozen in’ amplitude of this normal mode.

As an illustration of the soft-mode concept the result of inelastic neutron scattering measurements probing the soft mode in SrTiO$_3$ are shown in fig. 1.9. There is clearly a peak in the scattering whose frequency decreases towards zero as $T \to T_c$. In fig. 1.10 we show the square of these frequencies plotted against temperature and the agreement with eqn. (I.3.21) is clearly excellent. Below $T_c$ the triplet soft mode splits into a singlet and a doublet and rises in frequency as described in § I.4.2. Similar results have now been obtained in many materials undergoing structural phase transitions (Scott 1974, Shirane 1974).
Neutron scattering observed at three temperatures from the soft mode in SrTiO$_3$. The Bragg reflection below 110 K is shown on a reduced scale. Below 110 K the triplet soft mode splits into a singlet and a doublet. (From Cowley et al. 1969.)

The temperature dependence of the frequencies of the soft mode in SrTiO$_3$ both above and below $T_c$. (From Cowley et al. 1969.)
Despite these successes, the soft-mode theory is in a strict sense inconsistent. The frequencies of the normal modes in a harmonic crystal are temperature independent. Furthermore soft modes are found to be damped and sometimes even overdamped showing also that the harmonic theory is inadequate. A soft-mode frequency must therefore be interpreted as some type of effective or renormalized frequency as we shall discuss further in §1.5.1.1.

Phenomenologically the damping has been incorporated by approximating the susceptibility by the susceptibility of a classically damped oscillator.

\[ \chi^{-1}(q, \omega) = \omega(q)^2 - \omega^2 - 2i\omega\gamma_0, \]  

(1.3.22)

where \( \gamma_0 \) is the damping constant.

The poles of the susceptibility in the complex \( \omega \) plane are given by

\[ \omega = \pm \left( \omega(q)^2 - \gamma_0^2 \right)^{1/2} + i\gamma_0, \quad \omega(q) > \gamma_0, \]

\[ = i(\gamma_0 \pm (\gamma_0 - \omega(q)^2)^{1/2}), \quad \omega(q) < \gamma_0, \]

(1.3.23)

showing that the soft mode is underdamped when \( \omega(q) > \gamma_0 \) but overdamped when \( \gamma_0 > \omega(q) \). If \( \gamma_0 \) is temperature independent the mode always becomes overdamped as \( T \to T_c \), and the pole of the complex frequency susceptibility approaches the origin of the frequency plane along the imaginary \( \omega \) axis, as shown in fig. 1.11.

The complex frequency plane \( \omega \), showing the motion of the poles as \( T \to T_c \) for a classical oscillator, both (a) undamped and (b) damped, and (c) for a Debye relaxation response.

When the damping becomes very large the mode is overdamped and \( \omega^2 \) may be neglected compared with \( 2\omega\gamma_0 \) in eqn. (1.3.22): the response is then given by

\[ \chi^{-1}(q, \omega) = \omega(q)^2(1 - i\omega\tau_D), \]  

(1.3.24)
Structural phase transitions

where $\tau_D$ is known as the Debye relaxation time and is given by $\tau_D = \frac{2\gamma_0}{\omega(q)^2}$, and so diverges as $T \to T_c$. In this case the pole of the susceptibility in the complex $\omega$ plane is on the imaginary frequency axis, fig. I.11, and the measured response is concentrated at very low frequencies.

A continuous phase transition involves a divergence of the static susceptibility at $T_c$. This is always associated with the approach of a pole of the susceptibility to the origin of the complex frequency plane, as $T$ approaches $T_c$. This pole can be called a soft mode even when it is always heavily overdamped, so that a continuous phase transition always has a soft mode. Alternatively, the use of the term soft mode can be restricted to those cases where the mode shows at least some vestiges of resonant behaviour, the frequency of which decreases as $T \to T_c$. This restriction would confine the use of the term to the displacive class of materials such as SrTiO$_3$ as illustrated by figs. I.9 and I.10. In the order–disorder materials, the modes describing the small oscillations of the atoms or molecules are not strongly temperature dependent as illustrated in fig. I.12 for the optically active modes in NaNO$_2$. The ferroelectric fluctuations in NaNO$_2$ are associated with the relatively slow reorientation of the NO$_2$ groups and, as shown in fig. I.13 by the dielectric susceptibility measurements, the anomalous behaviour of the susceptibility is entirely absent for probe frequencies in excess of $10^9$ Hz. The soft mode in this case is not one of the normal modes of

![Fig. I.12](image_url)

The frequencies of the infra-red active modes in NaNO$_2$ as a function of temperature (Barnoski and Ballentine 1968).
The dielectric susceptibility of NaN\textsubscript{2}O as a function of frequency as measured by Hatta (1968) after Yamada et al. (1968).

vibration describing the small oscillations of the atoms and molecules, but one of the modes described by the spin variables introduced in §1.2.1. Since this hopping is not treated in the harmonic theory of lattice dynamics we prefer to restrict the use of the term 'soft mode' to displacive materials. Alas, since there is not a clear distinction between displacive and order–disorder materials, this inevitably leaves a number of materials, such as KDP, where it is uncertain if a soft-mode description is appropriate.

In this section we have discussed the dynamical susceptibility in terms of phenomenological models which have one or perhaps two simple poles in the complex $\omega$ plane. In §1.5.1, and in part III, we shall discuss a more general approach to this problem. Nevertheless, a characteristic feature of the phase transition is that the dynamical response becomes slower as $T\to T_c$. It is often convenient to describe the fluctuations of the order parameter by a characteristic frequency $\omega_Q$ where

$$\frac{1}{\pi} \int_{-\omega_Q}^{\omega_Q} \frac{1}{\omega} \text{Im} [\chi(q, \omega)] d\omega = \frac{1}{2} \chi(q, 0).$$

On comparing this definition with eqn. (1.2.27), it is clear that $\omega_Q \to 0$ as $T \to T_c$ no matter how complicated the spectral response.
1.3.6. Measurement of susceptibilities

1.3.6.1. Macroscopic measurements

Macroscopic measurements probe the susceptibilities for $\mathbf{K} = 0$, and consequently measure the susceptibility for the primary order parameters only if $\mathbf{q} = 0$. The dielectric susceptibility can be measured by dielectric measurement or by infra-red absorption techniques. The susceptibility can be obtained from eqn. (1.2.21) if both operators $A$ and $B$ are taken to be the dipole moment operator $\mathbf{M}$. If only one mode is temperature dependent then

$$
\chi_{ab}(\omega) = \chi_{ab}^\infty + \frac{1}{\nu} M_a(0f) M_b(0f) \chi(0jj, \omega),
$$

(1.3.25)

where $\chi_{ab}^\infty$ is the dielectric susceptibility of the other modes and the electronic excitations. Static dielectric measurements then give a measure of the soft-mode static susceptibility as illustrated in fig. 1.8 for BaTiO$_3$. Using electrical techniques it is possible to measure the dynamical susceptibility for frequencies up to $5 \times 10^{10}$ Hz as illustrated in fig. 1.13. In principle, a measurement of the infra-red reflectivity gives the dielectric response at higher frequencies and in fig. 1.14, we show the dielectric response of BaTiO$_3$, as measured using these techniques. In practice, however, these techniques are difficult to apply because the range of frequency of most interest in displacive systems is frequently between $10^{11}$ and $10^{12}$ Hz, and this is a very difficult range experimentally. Secondly, the measurements yield the reflectivity, and when the susceptibility is large, the reflectivity is close to unity and large differences in the susceptibility give only very small changes in the reflectivity.

![Fig. 1.14](image)

The reflectivity of BaTiO$_3$ as a function of temperature. (After Ballentyne 1964.)

Ultrasonic measurements at structural phase transitions have been reviewed by Rehwald (1973). When the strain is a primary order parameter, the ultrasonic velocity plays the role of $\omega(\mathbf{q}, j)^2$, and hence the velocity decreases to zero as $T \to T_c$ as shown for KDP (KH$_2$PO$_4$) in fig. 1.15. More frequently the strain is a secondary order parameter and the ultrasonic velocity measures the inverse of their correlation function whose behaviour (to be discussed in more detail in 11.5.1.2) is typified by the results shown in fig. 1.16.
The elastic constants of KDP, $C_{66}^{p}$, and $C_{66}^{e} = C_{66}$ as a function of temperature as measured by Brody and Cummins (1968) using Brillouin scattering techniques.

Ultrasonic experiments also measure the attenuation of the elastic waves; the critical behaviour of the attenuation is discussed briefly in III.3.2.2.

The specific heat may also exhibit singular behaviour near a structural phase transition. In practice the change in the specific heat is frequently very small and difficult to measure accurately as shown in fig. I.17 for SrTiO$_3$.

1.3.6.2. Scattering measurements

By far the most detailed information about susceptibilities can be obtained using the scattering of X-rays, neutrons or light. In the case of X-ray scattering, it is not possible to obtain sufficient energy resolution to measure the dynamic susceptibility; consequently the cross-section for a wave-vector transfer $\mathbf{K}$ is given in the one-phonon approximation by eqns. (1.2.38) and (1.2.42) as

$$
\frac{d\sigma(K)}{d\Omega} = k_B T \sum_{q, \mathbf{j}, \mathbf{j}'} F(K, q, \mathbf{j}) F(-K, -q, \mathbf{j}') \chi(q, \mathbf{j}, \mathbf{j}') \Delta(K + q).$$

(I.3.26)
Velocities of longitudinal and shear waves propagating in a [100] direction in SrTiO₃ from Lüthi and Moran (1970). Key: ○ shows results at 50 MHz; ● at 30 MHz; × at 16 MHz; and + at 10 MHz.

The specific heat of SrTiO₃ near the 110 K phase transition. (After Franke and Hegenbarth 1974.)

If we separate out the term involving the order parameter susceptibilities $\chi_i(k)$

$$\frac{d\sigma(K)}{d\Omega} = \sigma_b(K) + k_B T \sum_{ik} |F(K, q_{sl} + k + j_i)|^2 \chi_i(k) \Delta(K + q_{sl} + k), \quad (1.3.27)$$

where $\sigma_b(K)$ represents the other terms which produce a background scattering. The
experimental results are frequently interpreted by neglecting the $\mathbf{K}$-dependence of the structure factors $F(\mathbf{K}, \mathbf{q}_j)$, when the observed intensity is, after subtraction of the background, proportional to the susceptibility. This approximation is probably reasonably accurate for small $\mathbf{k}$ and can be tested by measuring $\chi_i(\mathbf{k})$ for several different wave-vector transfers $\mathbf{K}$ giving equivalent $\mathbf{k}$.

There are two different techniques which have been used to determine the X-ray scattering cross-section. In both cases it is necessary to use monochromatic radiation to reduce the background. The technique, developed at Orsay by Comès and his collaborators (Comès et al. 1970) employs photographic detection and hence is invaluable for a rapid qualitative survey of the nature of the scattering. In fig. 1.18

Fig. 1.18

The diffuse X-ray scattering in KNbO$_3$: (a) cubic phase at 770 K; (b) tetragonal phase at 520 K; (c) orthorhombic phase at 220 K; and (d) rhombohedral phase at 220 K. Note the disappearance of the streaks of diffuse scattering as the material changes phase. (After Comès et al. 1970.)
we show a typical result obtained for KNbO₃ which undergoes very similar transitions to BaTiO₃. Notice the diffuse streaks joining the Bragg reflections. These show that $\chi_i(k)$ is anisotropic, its value being considerably larger for the wave-vectors, $k$, along the [100] directions than for $k$ along other directions. The other technique involves the use of counters and so in principle provides more quantitative information but is slower. In fig. I.19 we show the diffuse scattering obtained using counter techniques in NaNO₂ by Yamada and Yamada (1966). This technique is capable of very high resolution in wave-vectors $\sim 10^{-4}$ Å⁻¹, and so can be used to give very accurate measurements of the exponents, $\gamma$ and $\nu$. It is rather surprising that there has not been more effort made to exploit this technique in the field of structural phase transitions. (There is, however, some difficulty in constructing accurately controlled temperature environments for specimens for X-ray scattering.)

The diffuse X-ray scattering observed in NaNO₂ at $T_c + 3$ K for scattering for $K = \tau + \zeta_1 a^*$, $K = \tau + 1/8a^* + \zeta_2 b^*$ and $K = \tau + 1/8a^* + \zeta_3 c^*$. The lower part of the figure shows $J(k) = -D(q)$ calculated using the electrostatic approximation. (From Yamada and Yamada 1966.)

It is frequently possible to measure the differential cross-section using neutron scattering, since neutron energies are comparable with the energies of the phonons unlike X-ray photon energies. However, this feature leads to difficulties in the determination of the total scattering cross-section using neutron scattering. In a two-axis spectrometer the neutrons scattered in a particular direction are recorded irrespective of their energy. As shown in fig. I.20 neutrons with different energy transfers have different wave-vector transfers. The integrated intensity is not then an integral over all frequencies for a particular wave-vector transfer, but an integral along a particular path in $(K, \omega)$ space. This will correspond to the true integrated intensity only if the variation in wave-vector transfer $K$, is negligible for all the
frequency transfers occurring in the experiment, \( \omega \). This can be achieved when the energy of the incident neutron beam is very much larger than \( \hbar \omega \). In principle, the accuracy of the integration can be tested by performing a differential scattering experiment in which the spectrometer is controlled so as to obtain a frequency distribution for constant wave-vector transfer, \( \mathbf{K} \), but this requires more complex experimental equipment.

One of the cases where there is no difficulty with the wave-vector dependence in the integration is in order–disorder systems where the energy transfers from the diffuse scattering are negligible. In fig. 1.21 we show the diffuse scattering of neutrons, due to the ordering of Cu and Zn atoms in brass as measured by Als-Nielsen and Dietrich (1967). The scattering becomes more intense as \( T \to T_c \) and also more concentrated in \( \mathbf{k} \)-space.

The differential scattering cross-section is given in the one-phonon approximation by eqn. (I.2.35). If the scattering from the fluctuations in the order parameter are well separated in frequency from the other modes of the same symmetry, then

\[
S^1(\mathbf{K}, \omega) = \sum_\tau |F(\mathbf{K}, \mathbf{k} + \mathbf{q}_\tau)|^2 \Delta(\mathbf{K} + \mathbf{q}_\tau + \mathbf{k}) \mathcal{S}(\mathbf{K}, \omega),
\]

where from eqn. (I.2.4)

\[
\mathcal{S}(\mathbf{K}, \omega) = -\frac{\hbar}{\pi} (n(\omega) + 1) \chi_1^1(\mathbf{k}, \omega).
\]

If \( F(\mathbf{K}, \mathbf{k} + \mathbf{q}_\tau) \) is independent of \( \mathbf{k} \), then the scattering will have the same form at different wave-vectors \( \mathbf{K} \) corresponding to the same \( \mathbf{k} \), and will give a direct measure
The neutrons scattered from $\beta$-brass 8.9 K above $T_c$, and a fit to a Lorentzian cross-section as a function of $k$, or misset from the Bragg peak. (From Als-Nielsen and Dietrich 1967.)

of $\chi_\parallel^2(k, \omega)$ as shown in fig. I.9. If, however, the frequency of the fluctuations in the order parameter is not well separated from the frequencies of the other modes of the same symmetry, the interference terms in eqn. (I.2.38) become important and the shape of the observed spectrum for different but equivalent $K$ become different. We shall examine this point in detail in §1.4.1.

Neutron scattering then provides a very powerful way of studying the critical fluctuations at structural phase transitions. Normal techniques enable an energy resolution of about $5 \times 10^{10}$ Hz and a wave-vector resolution of about $10^{-2}$ Å$^{-1}$. A novel technique employed by Collins and Teh (1973) to measure the differential cross-section for order-disorder alloys was to measure the decay of the fluctuations in real time. This technique is applicable for phase transitions where the characteristic frequency is about $10^{-2}$ Hz.

Raman scattering is restricted to very small wave-vectors $K$ (effectively $K=0$ in most cases) but enables detailed measurements to be made of the frequency dependence of $\chi(K, \omega)$. There are two distinct cases which must be discussed. Firstly there are cases, such as KDP, for which there is a linear coupling between the light and the order parameter fluctuations (the first term in eqn. (I.2.46)). If this is the only mode of importance in the sum over $j$ then the Raman scattering tensor is given by

$$I_{\alpha\beta\gamma\delta} = P_{\alpha\beta}(K_j)P_{\gamma\delta}(-K_j)\mathcal{F}(K, \omega).$$

The results of the Raman scattering in KDP are shown in fig. I.22, and show that the spectral width becomes progressively narrower, as $T \to T_c$, showing the phenomenon of critical slowing down.

This type of result can only be obtained in materials for which the soft mode is Raman active in the high-symmetry phase.

If $q_z = 0$ but the mode is inactive it is possible to break the Raman scattering selection rules by applying an external field to the material and measuring the field.
induced scattering. This technique has been used to make the infra-red-active (but Raman-inactive) modes visible in the Raman scattering from SrTiO₃ and KTaO₃ (Fleury and Worlock 1968).

The two-phonon Raman scattering has a contribution arising from the dependence of the polarizability on

\[ P_{ab} \left( \frac{q}{j}, \frac{q}{j'} \right) Q \left( \frac{q}{j} \right) Q \left( \frac{-q}{j'} \right) \]

Close to the phase transition we consider the particular part of this term for which the normal mode coordinates are those of the order parameters to obtain

\[
P_{ab} \left( \frac{q}{j}, \frac{-q}{j'} \right) Q \left( \frac{q}{j} \right) Q \left( \frac{-q}{j'} \right) \]

If we neglect the wave-vector dependence of the coefficients, this cross-section gives a measure of the frequency-dependent four-point correlation function. In the
interpretation of Raman scattering results this correlation function has almost invariably been approximated by writing

$$\langle Q_i(\mathbf{k}_1,t)Q_i(-\mathbf{k}_1,t)Q_f(\mathbf{k}_2,0)Q_f(-\mathbf{k}_2,0)\rangle \approx 4\langle Q_i(0)\rangle \langle Q_f(0)\rangle \langle Q_i(0,\tau)Q_f(0,\tau)\rangle.$$  

(I.3.32)

The approximation (I.3.32) should be reasonable when $Q_i$ is large, but will fail when it is comparable in size to the fluctuations $Q_i(\mathbf{k})$, i.e. close to $T_c$. With this approximation the Raman scattering becomes $I_{ij,\phi}^{(2)}$,

$$I_{ij,\phi}^{(2)} \approx N\sum_i P_{\phi\#}(\mathbf{q}_{\phi \#} - \mathbf{q}_{\phi \#}) P_{\phi\#}(\mathbf{q}_{\phi \#} - \mathbf{q}_{\phi \#}) \mathcal{F}_{i}(0,\omega)Q_i^2.$$  

(I.3.33)

In fig. 1.23 we illustrate Raman scattering results from SrTiO$_3$ for $T\to T_c$; there is clearly a soft mode whose frequency agrees with that obtained from neutron scattering measurements below $T_c$ (fig. 1.10) showing that Raman scattering provides a valuable way of measuring $\langle a_i(0,\tau)\rangle$ in the distorted phase. The approximation of eqn. (I.3.32) should be reasonable when $\langle Q_i\rangle$ is large, but will fail when the fluctuations in $Q_i$ become comparable with $\langle Q_i\rangle$—i.e. close to $T_c$ (see § III.3.2.2). The analysis of Raman scattering results close to $T_c$, in terms of eqn. (I.3.33) is therefore inappropriate. We suspect that some of the difficulties experienced in the analysis of results close to $T_c$ derive from this erroneous use of eqn. (I.3.33).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Fig_1.23}
\caption{Frequencies of the two soft modes in SrTiO$_3$ below $T_c$ as observed with Raman scattering techniques by Fleury et al. (1968). A is the transverse mode and D the longitudinal mode.}
\end{figure}

I.3.6.3. Local susceptibilities

In § I.3.3.3 we discussed the measurement of order parameters using electron spin resonance and nuclear magnetic resonance techniques. In both cases the method involved determining the resonance frequency of either a particular electron or nucleus in the electric field produced by its environment. This environment is not static but fluctuating, and hence there will be a line width of the resonance which is
determined by the rate at which the spin (electronic or nuclear) can lose its energy. This rate can be calculated and within second-order perturbation theory will depend upon the density of states of the same frequency as the resonance frequency, and the coupling between the spin and these states.

If we extend the expansion eqn. (I.3.14) of the coefficients of the electrostatic potential $B$ to include the fluctuations in the order parameter then, remembering that $B$ is a local quantity,

$$B = \left( \frac{1}{N} \right)^{1/2} \sum_{\mathbf{k}} A_1(\mathbf{k}) Q(\mathbf{k}) + \frac{1}{N} \sum_{\mathbf{k}, \mathbf{k}_2} A_2(\mathbf{k}, \mathbf{k}_2) Q(\mathbf{k}_1) Q(\mathbf{k}_2) + \ldots \quad (I.3.34)$$

where $A_1(0)$ is the $A_1$ of eqn. (I.3.14) and we have assumed that there is only one component of the order parameter. The line width for a resonance frequency $\omega$ is proportional to (Bline 1971)

$$\Gamma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle B(\tau) B(0) \rangle \exp(i\omega \tau) d\tau,$$

where $\omega$ is the resonance frequency and $B(\tau)$ is the operator $B$ at time $\tau$. Substituting the first term of eqn. (I.3.34) for $B(\tau)$ yields

$$\Gamma(\omega) = \frac{1}{N} \sum_{\mathbf{k}} |A_1(\mathbf{k})|^2 \mathcal{S}(\mathbf{k}, \omega), \quad (I.3.35)$$

where $\mathcal{S}(\mathbf{k}, \omega)$ is the one-phonon Van Hove scattering function for the fluctuations. This expression has a sum over $\mathbf{k}$ owing to the local nature of the resonance technique. Nevertheless, an increase in the line width is found close to $T_c$ as illustrated in fig. 1.24 for the $^{133}$Cs N.M.R. resonance in CsD$_2$AsO$_4$ (Bline 1971). Unfortunately, since these experiments determine a sum over $\mathbf{k}$ (for one particular frequency, $\omega$) it is frequently difficult to interpret the results without relying on a particular model for $\mathcal{S}(\mathbf{k}, \omega)$. Furthermore, below $T_c$ the resonance line is split by the distortion and it may be experimentally very difficult to distinguish between the splitting and a line width effect (cf. §III.4.3.2). Finally if $A_1(0)$ of eqn. (I.3.34) is zero, the line width results partly from the two-phonon terms in eqn. (I.3.34) and partly from the terms involving $A_1(\mathbf{k}) \approx k^2$. The line width increase at $T_c$ is then small and in practice almost impossible to interpret quantitatively.

The Debye–Waller factor (eqn. I.2.35) is also a measure of single site properties. To the extent that the motions of the atoms can be described by non-interacting normal modes (i.e. in the displacive limit) then

$$W_\kappa = \sum_{\alpha \beta} \frac{K_\alpha K_\beta}{2} \langle u_\alpha(\kappa) u_\beta(\kappa) \rangle,$$

where the displacement–displacement correlation function is

$$\langle u_\alpha(\kappa) u_\beta(\kappa) \rangle = \frac{1}{M_\kappa} \sum_{\mathbf{q}, j} e_\alpha(\kappa, \mathbf{q}, j) e_\beta(\kappa, -\mathbf{q}, j) \langle Q(\mathbf{q}) Q(\mathbf{q}) \rangle.$$

The normal-mode correlation function is given at high temperatures in terms of $\chi(\mathbf{q}, \mathbf{j})$ by eqn. (I.2.22). Since the susceptibility diverges as $T \to T_c$ for $\mathbf{q} \to \mathbf{q}_c$, $W_\kappa$ will increase as $T \to T_c$. This increase will, however, be less marked than that of the susceptibility $\chi(\mathbf{q}_c, \mathbf{q})$ due to the sum over $\mathbf{q}$ and $\mathbf{q}$ in eqn. (I.3.36).
The behaviour of the Debye–Waller factor in an order–disorder system is different. Consider as an example the N ion in NO₂ which has two positions \( \pm \delta \) for the equilibrium position. In the high-temperature phase, both sites are equally populated so that the Debye–Waller factor is given by \( \cos K \cdot \delta \). In the low-temperature phase the amplitude of the scattering is proportional to \( \cos K \cdot \delta + 2i\langle S \rangle \sin K \cdot \delta \), so that the Debye–Waller factor due to the hopping is given by

\[
\exp (-W_s) = (\cos^2 (K \cdot \delta) + 4\langle S \rangle^2 \sin^2 (K \cdot \delta))^{1/2}.
\]

This shows that the Debye–Waller factor is constant above \( T_c \), and increases below \( T_c \) reaching unity when \( \langle S \rangle = \frac{1}{2} \). Since most real materials are neither strictly order–disorder nor displacive in character, the interpretation of the temperature dependence of Debye–Waller factors is far from unambiguous.

The Debye–Waller factor can be measured, for a particular \( K \), from the amplitude of the Mössbauer \( \gamma \)-rays emitted from a suitable source. In fig. I.25 we show the Debye–Waller factor of \( ^{57}\text{Fe} \) in PbTiO₃ as measured using Mössbauer...
techniques by Bhide and Hegde (1972). The Debye–Waller factor can also be measured using the incoherent scattering of thermal neutrons or from the temperature variation of the intensity of Bragg reflections.

Fig. 1.25

Temperature variation of the Debye–Waller factor in PbTiO₃ as measured from the resonance area of the $^{57}$Fe Mössbauer line by Bhide and Hegde (1972).

§ I.4. PHENOMENOLOGICAL LANDAU THEORY

I.4.1. Single-component order parameters

I.4.1.1. The Landau theory

In 1937, Landau (1937) developed a theory of phase transitions which he applied to structural phase transitions. In this section this theory is applied to a wide variety of different systems, because the first step in the understanding of any new material is the development of the appropriate Landau theory. We begin with the simplest familiar (Landau and Lifshitz 1959) example when the order parameter is a singlet so that there is only one component of $Q_i = Q$ of § I.3 which can then always be chosen to be real. Landau assumes that the free energy of one unit cell of the crystal may be expanded in a power series in this order parameter;

$$G = G_0 + \frac{1}{2} r Q^2 + d Q^3 + u Q^4,$$

(I.4.1)

where the coefficients may be functions of temperature.

A phase is stable only if

$$\frac{\partial G}{\partial Q} |_{Q_0} = 0, \quad \frac{\partial^2 G}{\partial Q^2} |_{Q_0} > 0.$$

(I.4.2)

The high-symmetry phase $\langle Q \rangle = Q_0 = 0$ is then stable only if the linear term in $Q$ in eqn. (I.4.1) is absent and if $r$ is positive. The system is distorted if $r$ is negative.
Furthermore at a continuous phase transition \( G \) must increase with \( |Q| \) at \( T_c, r = 0 \), so that \( d = 0 \) and \( u > 0 \). Landau’s theory is then completed by the further assumption that since \( r \) changes sign at \( T_c \), it can be written as an analytic function of \( T \) near \( T_c \):
\[
r = a(T - T_c),
\]
while the coefficient \( u \) is assumed to be independent of temperature for temperatures sufficiently close to \( T_c \). The free energy of the simplest model then follows as
\[
G = G_0 + \frac{1}{2} a(T - T_c)|Q|^2 + uQ^4.
\]

The stability conditions for the low-temperature phase then give for \( T < T_c \) that the order parameter will have the value
\[
Q_0^2 = \frac{a}{4u}(T_c - T),
\]
while the free energy for the equilibrium displacement is given by
\[
G_s = \langle G \rangle = G_0 - \frac{a^2}{16u}(T_c - T)^2, \quad T < T_c
\]
and consequently the change in specific heat is given by
\[
\bar{C} = -T \frac{\partial^2 G}{\partial T^2} = \frac{a^2 T}{8u}, \quad T < T_c;
\]
\[
= 0 \quad T > T_c.
\]

The susceptibility \( \chi(k = 0) = \left( \frac{\partial^2 G}{\partial Q^2} \right)^{-1} \), is then
\[
\chi(0) = \frac{1}{a(T - T_c)}, \quad T > T_c;
\]
\[
= \frac{1}{2a(T_c - T)}, \quad T < T_c.
\]

These results give, by assumption, that the exponents describing the critical behaviour are \( \beta = \frac{1}{2} \) and \( \gamma = 1 \). In fig. 1.26 we show the free energy for this model both above and below \( T_c \), and in fig. 1.27 the various properties as a function of temperature.

In eqn. (1.4.3) we assumed that \( d = 0 \). This is always the case when there is only one component of the order parameter, but is not necessarily the case for multi-component systems, for example at some elastic instabilities (Cowley 1976a).

When \( d \) is non-zero the transition is of first order and so the expansion of eqn. (1.4.1) is suspect. Nevertheless, in many systems the transition is nearly continuous and the phase transition can be analysed using the Landau expansion. The transition occurs when \( T = T_I \) where
\[
T_I = T_c + \frac{d^2}{2au}.
\]
The free energy $G - G_0$ as a function of the coordinate $Q$ for three models: Model A is the simplest given by eqn. (I.4.3) with $a = 2$, $u = 4$ and $\Delta$ is one in these units. Model B incorporates the cubic term $d$ which was chosen to be 6 when the first-order transition is at $T_c + \Delta$. Model C also has a first-order transition but in eqn. (I.4.9) $a = 2$, $u = -8$ and $h = 6$ when $T_f = T_c + \Delta$.

The order parameter $Q_0$ and inverse susceptibility as functions of temperature for the three models described in fig. 1.26. Note that the inverse susceptibility increases very rapidly for $T < T_f$ for model $C$. 
while the order parameter takes on a value at $T_I$ given by

$$Q_0 = \frac{d}{2u},$$

and below $T_I$ is given by

$$Q_0 = \frac{-3d - (9d^2 - 16ua(T - T_c))^{1/2}}{8u}.$$

(1.4.8)

In figs. I.26 and I.27 we illustrate the properties of this model in more detail. In this case the first-order transition occurs whenever the symmetry allows a non-zero cubic term, $d$. It is therefore a symmetry-driven first-order transition.

A first-order transition also occurs in the simplest model if $u < 0$, but in this case it is a consequence not of the symmetry but of the particular sign of the $u$ coefficient in the Landau expansion. If $u$ is negative, $G$ is unbounded and the expansion must be extended beyond quartic terms. We therefore add an extra term to the free energy, when it is given by

$$G = G_0 + \frac{1}{2}a(T - T_c)Q^2 + uQ^4 + hQ^6 + \ldots,$$

(1.4.9)

where $u$ is now negative and $h$ is assumed to be positive. The transition is of first order and occurs at $T_I$ where

$$T_I = T_c + \frac{u^2}{2ah}, \quad u < 0.$$  

(I.4.10)

The step in the order parameter at $T_I$ is

$$Q_0 = \pm \left( \frac{a(T_I - T_c)}{|u|} \right)^{1/2}$$

while below $T_I$ the order parameter is given by

$$Q_0^2 = \frac{-4u + (16u^2 - 24ah(T - T_c))^{1/2}}{12h}.$$  

(I.4.11)

The properties of this type of first-order transition, of which KDP(KH$_2$PO$_4$) is an example, are illustrated in figs. I.26 and I.27.

I.4.1.2. Coupling to strains

At all structural phase transitions the order parameter is coupled to the elastic strains or possibly other secondary order parameters by terms in the free energy which are linear in the strain and quadratic in the order parameter. In the simplest case we extend the model of the previous section by including the coupling to a single strain parameter, $\eta$. The free energy, given by eqn. (I.4.3), is then extended to include the strains as

$$G = G_0 + \frac{1}{2}a(T - T_c)Q^2 + uQ^4 + \varepsilon Q^2\eta + \frac{1}{2}C\eta^2 + \ldots,$$

(1.4.12)

where $\varepsilon$ is the coupling and $C$ is the appropriate elastic constant. Close to $T_c$ there is no reason to expect that $C$ will be particularly temperature dependent, except by an
unlikely accident. The condition for the material to be stress-free is that \( \partial G / \partial \eta = 0 \), which gives

\[ \eta = -\frac{eQ^2}{C}, \quad (I.4.13) \]

which can be used to eliminate \( \eta \) from eqn. (I.4.12) with the result

\[ G = G_0 + \frac{1}{2} a(T - T_c)Q^2 + \bar{u}Q^4, \quad (I.4.14) \]

where

\[ \bar{u} = u - \frac{e^2}{2C}. \quad (I.4.15) \]

Since eqn. (I.4.14) for \( G \) has exactly the same form as eqn. (I.4.3) except that \( u \) is replaced by \( \bar{u} \), the development goes through unchanged except for the replacement of \( u \) by \( \bar{u} \). Equation (I.4.15) shows that \( \bar{u} \) is less than \( u \); consequently transitions under conditions of constant stress are more likely to be of first order than ones at constant strain.

The elastic strain is proportional to the square of the order parameter, eqn. (I.4.13), and so using eqn. (I.4.4), is expected to be proportional to \( T - T_c \). The susceptibility can be measured in two different ways: at low frequencies the strain will be able to follow the order parameter, \( Q \) and the susceptibility is written \( \chi^0 \), but at high frequencies the strain will be unable to follow and the susceptibility is written \( \chi^\infty \). For \( T > T_c \) both susceptibilities are equal to \( (a(T - T_c))^{-1} \), but for \( T < T_c \)

\[ \chi^0(0) = \frac{1}{2a(T_c - T)} \]

while \( \chi^\infty(0) \) is given by \( \partial^2 G / \partial Q^2 \) with the derivatives evaluated with \( \eta \) held constant when the result is

\[ \chi^\infty(0) = \frac{\bar{u}}{2u(T_c - T)}. \quad (I.4.17) \]

Since \( \bar{u} \) is less than \( u \), \( \chi^\infty < \chi^0 \), although they both diverge at \( T_c \).

It is also necessary to distinguish between the high- and low-frequency response for the elastic constants below \( T_c \). The elastic constant under conditions of constant order parameter, \( Q \), is \( \partial^2 G / \partial \eta^2 = C \), whereas under conditions where \( Q \) can follow the changes in \( \eta \) it is given by \( \partial^2 G / \partial \eta^2 = C - e^2/4u \). Hence, at low frequencies when the order parameter can follow the elastic fluctuations, the elastic constant is predicted to decrease by \( e^2/4u \) at the transition.

In the low-temperature phase there is also a non-zero susceptibility describing the response of the strain to a field which couples to the order parameter, \( Q \). This is given by \( [\partial^2 G / \partial \eta \partial Q]^{-1} = 1/2eQ_0 \), and hence diverges at \( T_c \).

1.4.1.3. Fluctuations in systems with short-range forces

The expansion of the free energy in powers of the order parameter \( Q \) is not sufficient to give a description of the wave-vector dependence of the susceptibility. We now extend the discussion to incorporate the effects of the fluctuations \( Q(k) \).
Formally eqn. (I.4.3) can be extended to give

\[ G = G_0 + \frac{1}{2N} \sum_k R(k)Q(k)Q(-k) + \frac{1}{N^2} \sum_{k,k,k_3} u(k_1, k_2, k_3)Q(k_1)Q(k_2)Q(k_3)Q(-k_1 - k_2 - k_3) + \ldots, \]

where the coefficients in the expansion are wave-vector dependent and use has been made of wave-vector conservation. This expression for the free energy (effective hamiltonian) includes the interactions between the excitations with different wave-vectors and is difficult to solve as discussed in detail in part II. Here the effect of the fluctuations is neglected except for the leading terms. This is then the Landau–Ginzburg theory and is equivalent to neglecting the interactions, the \( u \) term, except when at least two of the \( Qs \) are replaced by the static order parameter, \( Q_0 \).

For the simplest model of a transition \( u(0,0,0) \) is non-zero at \( T_c \), and so we neglect the \( k \) dependence of the anharmonic coefficient \( u \). \( R(0) \) is, however, small at \( T_c \) and so we include in \( R(k) \) the leading terms in an expansion in \( k \). Since if the order parameter has a single component \( q_s \) is a ‘special point’ within the Brillouin zone, there are no linear terms in \( k \). Consequently for an isotropic system with short-range interactions the free ‘energy’ becomes

\[ G = G_s + \frac{1}{2N} \sum_k [a(T - T_c) + fk^2 + 12Q_0^2u]Q(k)Q(-k), \]

where \( G_s \) is the static part of the free energy, eqn. (I.4.5a). The static susceptibility for wave-vector, \( k \), is given by;

\[ \chi(k)^{-1} = [a(T - T_c) + fk^2] \quad \text{for} \quad T > T_c, \]

and by

\[ \chi(k)^{-1} = [2a(T_c - T) + fk^2] \quad \text{for} \quad T < T_c. \quad (I.4.18) \]

It is sometimes useful to define the inverse of these static susceptibilities as the squares of frequencies,

\[ \chi(k)^{-1} = \omega(k)^2, \]

by analogy with the result for a harmonic crystal, eqn. (I.2.23). These frequencies may or may not correspond to the frequencies of resonant normal modes or ‘soft modes’ as discussed in §1.3.5. In terms of these ‘frequencies’ the free energy may be rewritten as

\[ G = G_s + \frac{1}{2N} \sum_k \omega(k)^2Q(k)Q(-k), \quad (I.4.19) \]

where

\[ \omega(k)^2 = a(T - T_c) + fk^2 + 12Q_0^2u. \]

The expansion coefficient \( f \) must be positive at \( T_c \) for the wave-vector of the distorted phase \( q_s \) to be stable, so that to a first approximation it is independent of temperature. These assumptions then give the critical exponents for the correlation function, eqn. (I.3.18), \( \nu = 0.5 \), and \( \eta = 0 \), and the line shape of the scattering as a Lorentzian in wave-vector, \( k \), at fixed temperature. This latter result is consistent with experimental results on, for example, \( \beta \)-brass as shown in fig. I.21.
The temperature dependence of the Debye–Waller factor can be obtained from eqns. (I.3.36) and (I.4.19) for a displacive system as, (Borsa and Rigamonti 1972);

$$\sum_k \chi(k) = K_1 - K_2 |T - T_c|^{1/2}, \tag{I.4.20}$$

where $K_1$ and $K_2$ are constants which depend upon $a$ and $f$. This result shows that the Debye–Waller factor does not diverge at $T_c$ but exhibits a cusp-like behaviour (see, however, §II.5.4.1). A similar behaviour is predicted at other structural phase transitions except when the dispersion relation at small $k$ cannot be expanded in powers of $k$ as we discuss below.

Only in cubic materials is the coefficient of $k$ in eqn. (I.4.19) independent of the direction of $k$. More generally eqn. (I.4.19) becomes

$$\omega(k)^2 = a(T - T_c) + 12Q_0^2u + \sum_{\alpha\beta} f_{\alpha\beta} k_\alpha k_\beta.$$ 

The critical scattering is then Lorentzian in wave-vector, but the width of the Lorentzian depends on the direction of the wave-vector as observed close to the $\alpha-\beta$ transition in quartz by Dorner et al. (1974). The exponent is, however, independent of the direction of $k$, as tacitly assumed in eqn. (I.3.18).

A Lifshitz point (Hornreich et al. 1975) is the point in the phase diagram such that for one or more directions of $k$, the term in $k^2$ in eqn. (I.4.18) has a coefficient $f=0$. This point then separates phase transitions to a phase described by $q_s$ being a ‘special wave-vector’ from phases where $q_s$ is incommensurate with the underlying lattice. These special points are discussed in more detail in §II.5.3.2.

### 1.4.1.4. Uniaxial ferroelectrics

The formal expansion of the $R(k)$ term in powers of $k^2$ in §1.4.1.3 is valid only if there are no long-range forces in the material. The commonest example of a long-range force is the long-range electrostatic force in ferroelectric materials. In these materials the macroscopic electric field associated with the ferroelectric fluctuations makes the response dependent on the direction of the wave-vector; there is a splitting between the longitudinally and transversely polarized modes. Taking account of this electrostatic interaction, and taking the $z$ direction as the unique ferroelectric axis, the free energy is given by eqn. (I.4.19) but with the frequencies given by

$$\omega(k)^2 = a(T - T_c) + \sum_{\alpha\beta} f_{\alpha\beta} k_\alpha k_\beta + g_{\alpha} k_\alpha + 12uQ_0^2, \tag{I.4.21}$$

where the coefficient $g$ is given in terms of the dipole moment operator as

$$g = \frac{1}{\varepsilon_0} |M_z(k)|^2,$$

and is independent of $k$ if the wave-vector dependence of $M_z(k)$ is neglected.

The susceptibility or scattering cross-section, for wave-vectors $k$ in the $x$ and $y$ direction, is similar to that of the isotropic systems discussed above. For other directions of $k$ the limit as $k \to 0$ is not divergent even at $T_c$. This gives rise to a characteristic doughnut shape to the critical scattering, a slice through which is shown in fig. 1.28 as measured in DKDP (KD$_2$PO$_4$) by Skalyo et al. (1970). An analysis of this data enables the parameters $f$ and $g$ to be obtained as shown by Paul et al. (1970).
The critical scattering intensity contours in the (h0l) zone of KD$_2$PO$_4$ from the ferroelectric fluctuations polarized along the z-axis. $T_c$ for the crystal was 221 K. (After Skalyo et al. 1970.)

The singularity in $\chi(k)$ as $k \to 0$ cannot occur in real systems: it is prevented by a more detailed treatment of the electrostatic interactions including retardation or polariton effects, and by the effect of the crystal surfaces (Born and Huang 1954).

The Debye–Waller factor of a uniaxial ferroelectric has an even weaker singularity at $T_c$ than systems with only short-range forces, eqn. (I.4.20). The result was obtained by Meyer and Cowley (1976) as

$$
\sum_k \chi(k) = K_1 + K_2/|T - T_c| \log(K_3|T - T_c|),
$$

(I.4.22)

where the $K$s are constants.

### I.4.1.5. Acoustic mode instabilities

The stability of a crystal against macroscopic strains is most conveniently discussed in the Voigt notation for the strains:

$$
\eta_{xx} = \eta, \eta_{yy} = \eta_2, \eta_{zz} = \eta_3, \eta_{xy} + \eta_{yx} = \eta_6, \eta_{xz} + \eta_{zx} = \eta_5, \eta_{yz} + \eta_{zy} = \eta_4.
$$

The elastic matrix, eqn. (I.2.10), then has the form

$$
H_D = \frac{1}{2} \sum_{\rho\sigma} C_{\rho\sigma} \eta_\rho \eta_\sigma.
$$

The crystal is stable (Born and Huang 1954) only if all the eigenvalues of $C_{\rho\sigma}$ are positive, leading to stability conditions which are dependent upon the particular crystal class (Cowley 1976 a).

The Landau theory of these transitions then follows §I.4.1.1 but with the appropriate eigenvalue of the elastic constant playing the role of the parameter $r$.

Since the point groups of the crystal classes have at most triply degenerate irreducible representations, the order parameter may have one, two or three components.
An example of a one component order parameter occurs for an $\eta_6$, strain in the point groups 42 m, 422 or 4/mmm. The eigenvalue of the elastic constant matrix is $C_{66}$ and the symmetry of the distorted phase is 2 mm, 222, or mmm respectively. The high-symmetry phase will be stable if $C_{66} > 0$ and a phase transition to the distorted phase will occur if $C_{66} < 0$. We therefore assume that $C_{66}/\rho = a(T - T_c)$.

The fluctuations associated with the strains are the acoustic modes of vibration. The velocity of any particular acoustic mode is given by a linear combination of elastic constants, but that combination is dependent upon the polarization and the direction of the wave-vector. In the case of our example, the largest fluctuations close to $T_c$ will arise from the modes with velocities determined solely by $(C_{66}/\rho)^{1/2}$. Since $C_{66}$ is the smallest eigenvalue of the matrix $C_{\rho\alpha}$ every other acoustic mode must have a larger velocity. Now in our example the only acoustic modes with velocities given only by $C_{66}$ are those transverse modes with $\mathbf{k}$ along the [100] or [010] directions and with polarization vectors along [010] or [100] respectively.

The frequencies of the acoustic modes with $\mathbf{k}$ close to the [100] direction are given by

$$\omega(k)^2 = a(T - T_c)k_x^2 + g_1 k_y^2 + g_2 k_z^2 + f_1 k_x (k_y^2 + k_z^2) + f_2 k_y^2 + \ldots,$$

(I.4.23)

and for $\mathbf{k}$ nearly parallel to [010] by a similar expression with $k_y$ and $k_x$ interchanged. This expression shows that the critical fluctuations are confined to particular lines in $\mathbf{k}$ space, whereas they are restricted to planes for uniaxial ferroelectrics.

At some phase transitions there are no acoustic modes with velocities given by the eigenvalue of the elastic constant matrix. In these cases, for example a uniform compression, there are no fluctuations, but they appear in practice to always be of the first order.

1.4.1.6. Interaction between acoustic modes and ferroelectric fluctuations

The macroscopic effects of the coupling between the strains and the electric polarization in ferroelectric materials are described, for example, by Jona and Shirane (1962). In this section we shall emphasize the effect of the coupling on the fluctuations. In materials, like KH$_2$PO$_4$, which are piezoelectric in the high-symmetry phase there is a linear coupling between the strain and the electric polarization. Consequently the order parameter is a linear combination of the strain and polarization. It is convenient, however, to extend the analysis of §I.4.1.1 by explicitly including in the theory both strain coordinates and the polarization. For the case of KH$_2$PO$_4$ we label the polarization along the z axis as $Q_1$ and this is coupled to the strains $\eta_{xy}$. If for simplicity we restrict $\mathbf{k}$ to the x direction then the dielectric fluctuations are coupled only to the transverse modes polarized along [010] and we label them $Q_2$. The quadratic term in the expansion of the free energy is for these modes given by

$$G_2 = \frac{1}{2N} \sum_{ij=1,2} R_{ij}(k_x)Q_i(k_x)Q_j(k_x),$$

where

$$R_{11}(k) = a(T - T_c^z) + f k_x^2, \quad R_{22}(k) = C_{66}k_x^2/\rho,$$

$$R_{12}(k) = R_{21}(k) = kD.$$

Here $D$ is given in terms of the piezoelectric constant $h_{36}$ as $D = h_{36}^2 M_z(0) (\rho v)^{-1/2}$, where $M_z(0)$ is the dipole moment operator of the ferroelectric mode, eqn. (I.2.20).
The effect of the coupling is most readily seen by calculating the dynamical susceptibility within the harmonic approximation. The response to a field which couples only to mode 1 is given by

\[ \chi_1(k, \omega) = \frac{R_{22}(k) - \omega^2}{(R_{11}(k) - \omega^2)(R_{22}(k) - \omega^2) - R_{12}(k)^2}. \]  

(I.4.24)

Now, for small \( \omega \), this expression has the form

\[ \chi_1(k, 0) = \frac{a(T - T_c) + \rho D^2}{a(T - T_c)}. \]

(I.4.25)

The static \( k = 0 \) dielectric susceptibility diverges at the Curie temperature of the free crystal which is a higher temperature than the Curie temperature of the clamped crystal, \( T^* \). At high frequencies, \( \omega^2 \gg R_{22}(k) \), eqn. (I.4.24) reduces to the susceptibility of the clamped crystal—that obtained by neglecting the coupling to the acoustic modes.

Similar results are obtained for the acoustic mode response. At low frequencies the response is given by

\[ \chi_2(k, \omega) = \frac{\rho}{C_6^E - \rho \omega^2}, \]

where

\[ C_6^E = C_6^E - \frac{\rho D^2}{a(T - T_c)}. \]

(I.4.26)

and the change in the velocity arises because the dielectric fluctuations follow the acoustic mode fluctuations and the crystal responds so as to keep the electric field, \( E \), constant. At high frequencies where the ferroelectric fluctuations cannot follow the acoustic response, the latter reduces to \( C_6^E \) and the electric polarization is constant in the crystal. This behaviour is illustrated in KD₂PO₄ where ultrasonic measurements yield the velocity, \( C_6^E \), which decreases to zero at \( T_c \), fig. 1.15, while neutron scattering measurements at frequencies above the dielectric response give the relatively temperature independent, \( C_6^E \) (Paul et al. 1970).

Throughout this section we have assumed that the dielectric fluctuations are intrinsically temperature dependent. The same analysis can be made if we assume in that \( C_6^E \) is temperature dependent, while \( R_{11}(k) \) is relatively temperature independent. This behaviour then corresponds to an elastically driven ferroelectric transition of which lithium ammonium tartrate is an example (Sawada et al. 1977).

In a neutron or X-ray scattering experiment there may be a coupling to both the ferroelectric and acoustic modes, so that the cross-section is given by

\[ S(K, \omega) = Nk_B T \text{Im} \left[ \frac{\{ |F_1(K)|^2 (R_{22}(k) - \omega^2)}{(R_{11}(k) - \omega^2)(R_{22}(k) - \omega^2) - R_{12}(k)^2)} - (F_1(K)F_2(-K) + F_2(K)F_1(-K))R_{12}(k) + |F_2(K)|^2(R_{11}(k) - \omega^2))/(R_{11}(k) - \omega^2)(R_{22}(k) - \omega^2) - R_{12}(k)^2 \right]. \]  

(I.4.27)
where the wave-vector transfer $K = k + \tau$, with $\tau$ a reciprocal lattice vector and $F_1(K)$ and $F_2(K)$ are the structure factors of the modes. Now the unusual feature about this result is that since $R_{12}(k)$ is proportional to $k$, the interference term between the scattering by modes 1 and 2 will change sign with $k$, provided that $F_1(K)$ and $F_2(K)$ do not also change sign. The scattering is then markedly asymmetric in $k$. This effect has been observed in KD$_2$PO$_4$ by Skalyo et al. (1970). In KD$_2$PO$_4$ the ferroelectric fluctuations are overdamped so that inelastic neutron scattering measurements recording the quasi-elastic response gives the scattering by the ferroelectric fluctuations.

Fig. I.29

The critical scattering contours in the (h00) zone of KD$_2$PO$_4$ from the ferroelectric fluctuations polarized along the z axis. $T_c$ for the crystal was 221 K and the upper part shows measurements by Skalyo et al. (1970) and the lower part calculations including the coupling of the ferroelectric and acoustic modes by Cowley (1976 b).
fluctuations. In fig. 1.29 the highly asymmetric critical scattering observed around the \((5, 1, 0)\) lattice point is shown, together with parameter-free calculations of the pattern, performed using the theory illustrated above (Cowley 1976b).

In non-piezoelectric materials the leading coupling between acoustic modes and the ferroelectric fluctuations is proportional to \(k^2\)—there is then no difference above \(T_c\) between the clamped and free dielectric behaviour as shown in § I.4.1.2, and the scattering is almost symmetric in \(k\). There are, however, interesting interference effects between the acoustic and optic modes in the differential scattering cross-section as a function of frequency \(\omega\). These effects are particularly marked if the ferroelectric mode 1 is heavily damped so that its spectral response overlaps the frequency of the acoustic mode 2. In this case the term in eqn. (I.4.27) proportional to \(|F_2(k)|^2\) gives a Lorentzian, centred approximately on \(\omega^2 = R_{22}(k)\); the interference terms, proportional to \(F_1(k)F_2(-k)\), give two contributions—a Lorentzian centred at the same position and a term, asymmetric about that frequency, due to the imaginary part of \(R_{11}(k)\). This asymmetric term gives rise to a characteristic line shape and a shift in the apparent frequency of the peaks in the scattering.

This type of behaviour, which is common to all anharmonic materials, is illustrated particularly strikingly in the uniaxial ferroelectric lead germanate, as shown in fig. 1.30. Near the lattice point \((006)\) the ferroelectric fluctuations have low intensity and only a well-defined transverse acoustic mode is observed. Near the lattice points \((005)\) and \((004)\) both modes scatter strongly and the interference terms give rise to a characteristic asymmetric behaviour at frequencies close to the acoustic

Fig. 1.30

The neutron scattering observed from lead germanate by Cowley et al. (1976). The results show the interference between the acoustic mode and a heavily damped optic mode resulting in the different spectral shapes for the different measurements corresponding to the same wave-vector, \(k\).
mode. Near (005) the interference enhances the high-frequency part of the scattering, and near (004) it has the opposite sign and enhances the low-frequency part. Clearly as with the scattering shown in fig. 1.29 the detailed shape of the scattering is dependent upon the ratio $F_1(K)/F_2(K)$ and so is qualitatively different around different lattice points, $\tau$.

### 1.4.2. Multiple-component order parameters

#### 1.4.2.1. The Landau theory

The order parameter at a structural phase transition may have more than one component (§ 1.3.1): for example, in BaTiO$_3$ and SrTiO$_3$ there are $n = 3$ components. Throughout this section we shall consider the case where the $Q_i$ are real. A necessary condition for this is that the soft-mode wave-vector $q_s$, must satisfy $q_s = \pi/2$ or 0. A sufficient condition can be obtained with the aid of group theory: it is that the antisymmetric square of the order parameters be zero. This condition appears to be the same as the requirement that

$$\nabla_k \omega(q_s + k_j) \bigg|_{k = 0} = 0$$

which is satisfied by modes with $q_s = 0$ and for $q_s = \pi/2$ for the symmorphic space groups, but for the non-symmorphic groups it is not necessarily true. For example, in the diamond structure the longitudinal modes at the [100] zone boundary do not have zero gradient. We shall discuss systems in which the order parameter is complex in §§ 1.4.4 and 1.4.5.

We begin by discussing a system with $n = 2$ components for which the free energy, analogous to eqn. (I.4.3) is

$$G = G_0 + \frac{1}{2} a(T - T_c)(Q_1^2 + Q_2^2) + u(Q_1^2 + Q_2^2)^2 + v(Q_1^2 + Q_2^2)^3 + \ldots$$  \hspace{1cm} (I.4.28)

The symmetry of the order parameter imposes the form of the quadratic term and the third-order term in the $Q$-coordinates must be absent if the transition is continuous. Equation (I.4.28) differs from that of the singlet model eqn. (I.4.3) in that there are two coefficients $u$ and $v$. Equation (I.4.28) reduces to the form of eqn. (I.4.3) if we write $Q_i = \zeta_i Q$ (eqn. (I.3.3)), where the eigenvector is normalized $\sum_i \zeta_i^2 = 1$, when $\tilde{u} = u + v(\zeta_1^4 + \zeta_2^4)$, and $\tilde{u}$ replaces $u$ in eqn. (I.4.3).

The free energy of the ordered phase is a minimum if the constant $\tilde{u}$ is a minimum, eqn. (I.4.5a), and this determines the nature of the ordered phase. There are three cases of continuous phase transitions:

1. $v < 0$ but $v + u > 0$. In this case $\tilde{u} = u + v > 0$ and the ordered phase has one of four domains ($\zeta_1 = \pm 1$, $\zeta_2 = 0$, or $\zeta_2 = \pm 1$, $\zeta_1 = 0$).
2. $v = 0$ and $u > 0$. In this case $\tilde{u} = u$ and the ordered phase may take up any orientation in the space of $Q_1$ and $Q_2$.
3. $v > 0$ and $\tilde{u} = u + v/\sqrt{2} > 0$. In this case there are four ordered domains with $\zeta_1 = \pm 1/\sqrt{2}$, $\zeta_2 = \pm 1/\sqrt{2}$.

These features, a multiplicity of domains and a structure which is dependent upon the particular values of certain of the interactions, are characteristic of all $n > 1$ systems.
The analysis of the model follows exactly as in the \( n = 1 \) system for the order parameter, \( Q_0 \), specific heat, free energy and susceptibility above \( T_c \). Some additional analysis is, however, necessary to obtain the behaviour of the susceptibility below \( T_c \). The static susceptibilities are given by the inverse of the second derivatives of the free energy with respect to \( Q_1 \) and \( Q_2 \), evaluated at the equilibrium state.

For a distorted phase of type I, with \( \zeta_1 = 1 \) and \( \zeta_2 = 0 \) the second derivatives of the free energy yield the susceptibilities,

\[
\chi_1(0) = \left[ \frac{\partial^2 G}{\partial Q_1^2} \right]^{-1} \quad \text{and} \quad \chi_2(0) = \left[ \frac{\partial^2 G}{\partial Q_2^2} \right]^{-1}.
\]

Below \( T_c \) the 'longitudinal' susceptibility is given by

\[
\chi_1(0) = \left[ 2a(T_c - T) \right]^{-1},
\]

the same expression as for the \( n = 1 \) system eqn. (I.4.6), while the 'transverse' susceptibility is given by

\[
\chi_2(0) = -\frac{u + v}{av(T_c - T)},
\]

which since this phase is only stable if \( v < 0 \) is always positive. The terms 'longitudinal' and 'transverse', are used by analogy with the Heisenberg model of magnetism: \( \chi_1 \) describes the fluctuations parallel to the order parameter, and \( \chi_2 \) the fluctuations perpendicular to that direction. For case II, \( v = 0 \) and \( \chi_2(0) \) is infinite for all \( T \leq T_c \). Physically this is because the Hamiltonian has continuous rotational symmetry in \( Q_1 \) and \( Q_2 \) so that it costs no energy to rotate the order parameter. The existence of the infinite susceptibility is then an example of Goldstone's theorem (see, e.g., Wagner 1966).

In phase III, with \( \zeta_1 = \zeta_2 = 1/\sqrt{2} \), the derivatives of the free energy are as follows:

\[
\frac{\partial^2 G}{\partial Q_1^2} = \frac{\partial^2 G}{\partial Q_2^2} = 2a(T_c - T) \frac{u + v}{2u + v},
\]

and

\[
\frac{\partial^2 G}{\partial Q_1 \partial Q_2} = 2a(T_c - T) \frac{u}{2u + v}.
\]

The susceptibility can be brought into a diagonal form as discussed in §1.3.3, by considering the susceptibility for fields along the ordering direction, \( \chi_1(0) \), and transverse to that direction, \( \chi_2(0) \). Then \( \chi_1(0) \) is given by eqn. (I.4.6) or (I.4.29) while

\[
\chi_2(0) = \frac{2u + v}{2av(T_c - T)},
\]

which is necessarily positive when phase III is stable.

This analysis can be repeated for an \( n = 3 \) component system (Slonczewski and Thomas 1970) when the free energy is

\[
G = G_0 + \frac{1}{2} a(T - T_c)(Q_1^2 + Q_2^2 + Q_3^2) + u(Q_1^2 + Q_2^2 + Q_3^2)^2 + v(Q_1^4 + Q_2^4 + Q_3^4).
\]
There are again three possible phases:

I. $v < 0$; the ordered phase is tetragonal (for example $\zeta_1 = \pm 1, \zeta_2 = \zeta_3 = 0$) and $\tilde{u} = u + v$. An ordered phase of this type occurs in BaTiO$_3$ and SrTiO$_3$.

II. $v = 0$; the orientation of the distortion is undefined.

III. $v > 0$; the ordered phase has trigonal symmetry with $\zeta_1 = \pm \zeta_2 = \pm \zeta_3 = \pm 1/\sqrt{3}$ and $\tilde{u} = u + 1/3v$. This phase occurs in LaAlO$_3$ for which the transition is otherwise similar to that occurring in SrTiO$_3$ (Müller et al. 1968).

In all of these phases there is a longitudinal susceptibility given by

$$\chi_L(0) = [2a(T - T_c)]^{-1},$$

and a doubly degenerate transverse susceptibility given, for phase I, by

$$\chi_T(0) = -\frac{u + v}{av(T_c - T)},$$

and for phase III by

$$\chi_T(0) = \frac{3u + v}{2av(T_c - T)}.$$

Finally, we briefly consider the more complicated case of an $n = 4$ system. The most general form of the free energy is then

$$G = G_0 + \frac{1}{2}a(T - T_c) (Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2)$$

$$+ u(Q_1^2 + Q_2^2 + Q_3^2 + Q_4^2)^2 + v(Q_1^2 + Q_4^2 + Q_2^2 + Q_3^2)$$

$$+ w_1(Q_1^2 Q_2^2 + Q_3^2 Q_4^2) + w_2(Q_1^2 Q_3^2 + Q_2^2 Q_4^2)$$

$$+ w_3 Q_1 Q_2 Q_3 Q_4.$$

In real systems not all the fourth-order invariants may be allowed by the symmetry of the problem as we shall discuss later for BaMnF$_4$ and NbO$_2$.

There are five different possible phases of the most general $n = 4$ model and we list in table I.1 a typical $\zeta$ vector, for each phase. The most stable phase is that with the smallest value of

$$\tilde{u} = u + v \sum_i \zeta_i^4 v + w_1(\zeta_1^2 \zeta_2^2 + \zeta_3^2 \zeta_4^2) + w_2(\zeta_1^2 \zeta_3^2 + \zeta_2^2 \zeta_4^2) + w_3 \zeta_1 \zeta_2 \zeta_3 \zeta_4.$$

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\zeta$</th>
<th>$\tilde{u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>(1000)</td>
<td>$u + v$</td>
</tr>
<tr>
<td>II</td>
<td>(1111)</td>
<td>$\frac{1}{2}u + v - \frac{1}{8}(w_1 + w_2) - \frac{1}{4}w_3$</td>
</tr>
<tr>
<td>III</td>
<td>(1100)</td>
<td>$\frac{1}{2}u + v - \frac{1}{4}w_1$</td>
</tr>
<tr>
<td>IV</td>
<td>(1010)</td>
<td>$\frac{1}{2}u + v - \frac{1}{4}w_2$</td>
</tr>
<tr>
<td>V</td>
<td>(1001)</td>
<td>$\frac{1}{2}u + v$</td>
</tr>
</tbody>
</table>
The susceptibilities in the ordered phase may be calculated as discussed, above. In each case one finds a longitudinal susceptibility given by eqn. (I.4.34), and three transverse susceptibilities. These transverse susceptibilities are dependent on the anisotropic coefficients, but unlike the \( n = 3 \) systems, they may not be all equivalent.

1.4.2.2. Coupling to strains

In multi-component systems the coupling to secondary order parameters, such as the strain is more complicated than for \( n = 1 \) systems described in §1.4.1.2. It is necessary to include the different strain components so that for BaTiO\(_3\) and SrTiO\(_3\), for example, there are six components of the strain. The free energy of both of these materials is then given by eqn. (I.4.33) with the addition of an elastic contribution \( G_c \), which is given by (Devonshire 1954, Slonczewski and Thomas 1970)

\[
G_c = e_1 (\eta_1 + \eta_2 + \eta_3) (Q_1^2 + Q_2^2 + Q_3^2) + e_2 [\eta_1 (2Q_1^2 - Q_2^2 - Q_3^2) + \eta_2 (2Q_2^2 - Q_1^2 - Q_3^2) + \eta_3 (2Q_3^2 - Q_1^2 - Q_2^2)] + e_3 (Q_1 Q_2 \eta_6 + Q_1 Q_3 \eta_5 + Q_2 Q_3 \eta_4) + \frac{1}{2} \sum_{\alpha \beta} C_{\alpha \beta} \eta_\alpha \eta_\beta, \tag{I.4.37}
\]

where we used the Voigt notation for the strains. Minimizing \( G + G_c \) with respect to the strains gives

\[
\eta_1 = -\frac{e_1}{C_{11} + 2C_{12}} (Q_1^2 + Q_2^2 + Q_3^2) - \frac{e_2}{C_{11} - C_{12}} (2Q_1^2 - Q_2^2 - Q_3^2),
\]

and

\[
\eta_4 = -\frac{e_3}{C_{44}} Q_2 Q_3.
\]

When these results are substituted back into eqns. (I.4.33) and (I.4.37), the free energy has the same form as eqn. (I.4.33) for the strain-free case except that \( u \) and \( v \) are replaced by

\[
\bar{u} = u - \frac{3}{2} \left[ \frac{e_1^2}{C_{11} + 2C_{12}} - \frac{e_2^2}{C_{11} - C_{12}} + \frac{e_3^2}{C_{44}} \right],
\]

\[
\bar{v} = v - \frac{9}{2} \frac{e_2^2}{C_{11} + C_{12}} + \frac{3}{4} \frac{e_3^2}{C_{44}}.
\]

This result shows that the coupling to the strain modifies the parameters of the Landau theory, as found in §1.4.1.2, and so may drive the transition to be of first order, or change the structure of the distorted phase. As discussed for the \( n = 1 \) system, it is necessary to distinguish between the high- and low-frequency susceptibilities below \( T_c \) (Slonczewski and Thomas 1970). Experimental confirmation of the necessity to distinguish between the high- and low-frequency susceptibilities is provided by Raman scattering and neutron scattering measurements in SrTiO\(_3\). The ratios of the squares of the 'longitudinal' frequencies below and above \( T_c \) is \( 2.4 \pm 0.2 \) (Worlock and Olsen 1971) in excess of the factor 2 which would be expected in the absence of the coupling to strain.

As described in §1.4.1.2, the theory can also be used to predict a jump in the
elastic constant at \( T_c \). This is qualitatively the correct behaviour as shown by the measurements on \( \text{SrTiO}_3 \) illustrated in fig. 1.16. In detail, however, the behaviour is more complex as described in §II.5.2.2.

In this section the temperature dependence of the strain and elastic constants is found to be independent of its symmetry. This is correct only within Landau theory. In a more complete theory discussed in §§II.5.1.2 and II.5.2.2, it is essential to distinguish between strains which are secondary order parameters and break the symmetry of the high-symmetry phase, and strains which have the complete symmetry of that phase. In \( \text{SrTiO}_3 \) an isotropic strain \( \eta_1 = \eta_2 = \eta_3 \) does not break any symmetry operation of the high-symmetry phase, whereas a tetragonal strain, \( \eta_1 = \eta_2 = \eta_1/2 \) does. The latter strains must necessarily be zero above \( T_c \). The former strains need not be zero above \( T_c \) and in a better theory than Landau theory the behaviour of these two types of strains is different.

### 1.4.2.3. Improper ferroelectrics

Improper ferroelectrics are examples of systems for which the secondary order parameter is a ferroelectric distortion. Their properties are reviewed by Dvorak (1974). Since in a ferroelectric material there are different domains corresponding to the different directions of the polarization, there cannot be terms in the free energy of the form \( QQ^2 \), where \( Q \) is the primary order parameter of an \( n = 1 \) system. Improper ferroelectrics can occur only when the primary order parameter has at least two components. The simplest model (Cochran 1971) of an improper ferroelectric is that of an \( n = 2 \) system with a coupling to the ferroelectric polarization of the form \( Q_1 Q_2 \tilde{Q} \), when the free energy is

\[
G = G_0 + \frac{1}{2} \alpha (T - T_c)(Q_1^2 + Q_2^2) + u(Q_1^2 + Q_2^2)^2 + v(Q_1^2 + Q_2^2) + \epsilon Q_1 Q_2 \tilde{Q} + \frac{1}{2} b \tilde{Q}^2, \tag{1.4.38a}
\]

where \( b \) is the inverse dielectric susceptibility which is assumed to be only weakly temperature dependent. Minimization of the free energy with respect to \( \tilde{Q} \) yields

\[
\tilde{Q} = -\frac{\epsilon}{b} Q_1 Q_2, \tag{I.4.38b}
\]

which substituted back into eqn. (1.4.38) yields an equation identical to eqn. (1.4.38) but with \( u \) and \( v \) replaced by

\[
\tilde{u} = u - \frac{\epsilon^2}{4b} \quad \text{and} \quad \tilde{v} = v - \frac{\epsilon^2}{4b}.
\]

If \( \tilde{v} < 0 \), the ordered structure is case I of §1.4.2.1, which then with eqn. (1.4.38) gives \( \langle \tilde{Q} \rangle = 0 \) and the phase is not ferroelectric. On the other hand if \( \tilde{v} > 0 \) the ordered structure is case III and \( \tilde{Q} = \pm (\epsilon/2b)Q_0^2 \) with the plus sign if \( \zeta_1 = -\zeta_2 \) and the minus sign if \( \zeta_1 = \zeta_2 \).

In practice the phase transitions of improper ferroelectrics are of first order (Dvorak 1974), possibly because the interaction \( \bar{n} \) is always less than \( u \), but possibly also because of the effects discussed in §II.5.2.2. There is, however, evidence that \( \tilde{Q} \) is proportional to \( Q_0^2 \) as shown in fig. I.31 for \( \text{Tb}_2 (\text{MoO}_4)_3 \) (Dorner et al. 1972).
The temperature dependence of the strain distortion $\theta$, the spontaneous polarization and of the square of the primary order parameter as measured by the Bragg reflections in the improper ferroelectric $\text{Tb}_2(\text{MoO}_4)_3$. (After Dorner et al. 1972.)

The temperature dependence of the dielectric constant in three improper ferroelectrics. (After Dvorak 1974.)

The development described in § I.4.1.2 can be repeated to show that the dielectric susceptibility in an improper ferroelectric should, within Landau theory, have a step at $T_c$. In fig. I.32, we show measurements of the susceptibility in three improper ferroelectrics. This simple theory describes the results in $(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$, but is less satisfactory for CoI boracite or $\text{Gd}_2(\text{MoO}_4)_3$. In part this undoubtedly reflects the fact that the theory given above is very much too simple to describe real improper ferroelectrics. In particular, there is a coupling between the strain and the primary order parameter and between the strain and the spontaneous polarization, as illustrated in fig. I.31. It is then necessary to distinguish between the clamped and free dielectric constant as described in detail by Dvorak (1974).
The wave-vector dependence of the fluctuations in systems with more than one component for the order parameter can be obtained in much the same manner as was described in detail in § 1.4.1.3 for $n=1$ component systems.

At a transition for which the order parameter is neither an electrical polarization nor an elastic strain, the quadratic term in the expansion of the free energy is

$$G_2 = \frac{1}{2N} \sum_{ij} R_{ij}(k) Q_i(k) Q_j(-k).$$

where

$$R_{ij}(k) = a(T - T_c) \delta_{ij} + f_{ab}(ij) k_x k_y.$$  

The number of coefficients $f_{ab}(ij)$ may be reduced by symmetry so that, for example, in SrTiO$_3$ there are three components of the order parameter corresponding to rotations of the oxygen octahedra about the $x$, $y$, $z$ directions, respectively, and three independent $f_{ab}(ij)$ coefficient. In this case eqn. (I.4.39) can conveniently be rewritten as

$$R_{ij}(k) = \left[ a(T - T_c) + 2(k_x^2 + k_y^2) \right] \delta_{ij} + \lambda h k_x k_y (1 - \delta_{ij})$$

and the coefficients $\lambda$, $f$ and $h$ have been measured for SrTiO$_3$ by Stirling (1972) from the anisotropy in the phonon dispersion relations about the $R$ point, with the results

$\lambda = 216 \pm 20$ (THz Å$^2$),  $f = -0.97 \pm 0.01$,  $h = 0.19 \pm 0.04$

showing a very large degree of anisotropy.

The anisotropy and coupling between the modes in these systems means that the eigenvectors of the matrix in eqn. (I.4.39), are very dependent upon the direction of $k$. A detailed analysis of the form of the susceptibility is then difficult. An unexpected result of this behaviour occurs in the scattering cross-section around the incipient ordering wave-vector, $q_0$, which may not exhibit the full symmetry of the crystal. This is illustrated by the form of the scattering for wave-vector transfers $K$, close to $K_0 = 2\pi/a (3/2, 1/2, 1/2)$ in SrTiO$_3$. At this position the structure factors of the three modes are $F(K, 1) = 0$, $F(K, 2) = F(K, 3) = F$. Because $f$ is close to $-1$ the susceptibility and scattering is large for the $i$th component for wave-vectors along the $i$th direction. Consequently there will be a large scattering observed for wave-vectors $K = K_0 + (0, k, 0)$ and $K = K_0 + (0, 0, k)$ but no corresponding scattering along $K = K_0 + (k, 0, 0)$ because $F(K, 1) = 0$.

### 1.4.2.5. Ferroelectrics

The long-range electrostatic forces modify the form of the fluctuations for small $k$ in ionic materials as explained for uniaxial ferroelectrics in § 1.4.1.4. In the case of cubic ferroelectrics, such as BaTiO$_3$, we choose the $i$th component of the order parameter to give the electrical polarization along the $i$th direction. The expansion of the second term in the free energy is then given by eqn. (I.4.40) but with the additional electrostatic term;

$$R_{ij}(k) = \left[ a(T - T_c) + \lambda (k_x^2 + k_y^2) \right] \delta_{ij} + \lambda h k_x k_y (1 - \delta_{ij}) + \frac{k_i k_j}{k^2}.$$  

The matrix $R_{ij}(k)$ can then be diagonalized for $k \to 0$ to give the ‘frequencies’ of a
Structural phase transitions

longitudinal fluctuation above $T_c$ as $\omega_k^2 = a(T - T_c) + g$ and two transverse fluctuation 'frequencies' as $\omega_k^2 = a(T - T_c)$. If the structure factors of the three modes are proportional to $K_i$, eqn. (I.2.36), then the scattering intensity for large $g$ is given (Cochran 1969) by $|K^2| \sin^2 \theta$ where $\theta$ is the angle between $K$ and $k$ as illustrated in fig. I.33.

![Sketch of constant intensity contour lines as function of wave-vector transfer $K$ for a cubic ferroelectric or for $K$ within the plane of ferroelectric fluctuations for a [2d] ferroelectric. (After Cochran 1969.)](image)

In the case of ferroelectrics with two components polarized in say the $x$ and $y$ directions, there are two transverse fluctuations for $k$ along the $z$ direction, but a longitudinal and a transverse fluctuation for $k$ in the $(x, y)$ plane. For $K$ in the $(x, y)$ plane the scattering has the same form as shown in fig. I.33. Although the tetragonal phase of BaTiO$_3$ is a two-component ferroelectric system, we are unaware of any detailed measurements of the critical scattering.

I.4.2.6. Acoustic instabilities

Nearly all the acoustic instabilities with $n \geq 2$ have cubic terms in the Landau expansion of the free energy, and so are predicted to be of first order. The only example (Cowley 1976a) with $n = 2$ and no cubic terms is an instability against $\eta_4$ and $\eta_5$ in the tetragonal system. The velocities of the acoustic waves are zero at $T_c$ for modes with wave-vector $k$ perpendicular to the [001] direction and polarized along [001] or with $k$ along [001] and polarized transversely. The former set give rise to a similar scattering pattern to that of uniaxial ferroelectrics, while that of the latter set is similar to that of the acoustic instabilities discussed in § I.4.1.6.

I.4.3. Phase diagrams

I.4.3.1. Tricritical points

In § I.4.1.1 the free energy, eqn. (I.4.9), was shown to give rise to a continuous phase transition if $u > 0$, and a first-order transition if $u < 0$. The point $u = 0$ terminates the line (in the space of $u$ and $T$) of continuous phase transitions and is
known as a tricritical point. The Landau expansion of the free energy at this point is
\[ G = G_0 + \frac{1}{2} a(T - T_c)Q^2 + hQ^6, \]
so that the order parameter is given by
\[ Q_0^4 = \frac{a}{6h}(T_c - T) \]
and the susceptibility below \( T_c \) by
\[ \chi(0) = \left[ 4a(T_c - T) \right]^{-1}. \]

The results show that within Landau theory the principal tricritical point exponents have values \( \beta = 1/4, \gamma = 1 \) (to be compared with the Landau results for an ordinary critical point, \( \beta = 1/2, \gamma = 1 \)). It also follows from (I.4.43b) that the ratio of the susceptibility above \( T_c \) to that below \( T_c \) for a constant \( |T - T_c| \) is 4 within the classical tricritical theory—twice the Landau result for an ordinary critical point. A fuller description of tricritical points and a comparison with experimental results is given in §1.5.3.1.

1.4.3.2. Phase transitions without symmetry breaking

In §1.3.1 we emphasized the importance of the concept of symmetry breaking at structural phase transitions. There are, however, phase transitions where (as at the liquid–gas critical point) the symmetry is unchanged. Consider, to be specific, the Landau free energy for an \( n = 1 \) system in an applied field:
\[ G = G_0 + \frac{1}{2} a(T - T_0)Q^2 + uQ^4 + hQ^6 - EQ \]
For \( u > 0 \) there is no phase transition when \( E \neq 0 \). For \( u < 0 \) there is a first-order phase transition for small \( E \), and no phase transition for large \( E \). There exists a critical value of the field \( E_c \) at which the transition is continuous and beyond which no transition occurs. The critical field, and the corresponding transition temperature \( T_c \) are located by the conditions
\[ \left( \frac{\partial G}{\partial Q} \right)_E = \left( \frac{\partial^2 G}{\partial Q^2} \right)_E = \left( \frac{\partial^3 G}{\partial Q^3} \right)_E = 0, \]
as
\[ E_c = 16h \left( \frac{|u|}{5h} \right)^{5/2} \]
and
\[ T_c = T_0 + \frac{6u^2}{5ha} \]
There is no symmetry breaking at the critical point, since (by virtue of the applied field) the coordinate \( Q \) already has the non-zero value
\[ Q_0 = \left( \frac{|u|}{5h} \right)^{1/2} \]
The order parameter for the phase transition must thus be defined as the difference between the two possible values of $Q_0$ characterizing the two phases that coexist on the phase boundary which terminates at the critical point.

This type of behaviour has been observed in $\text{KH}_2\text{PO}_4$ by Eberhard and Horn (1975). At atmospheric pressure the phase transition is first order and shows a temperature hysteresis of 0.025 K. On increasing the applied field the hysteresis decreases and extrapolation of their data suggests that $E_c = 6.5 \times 10^5$ V/m.

1.4.3.3. Competing interactions

One of the characteristic features of an $n > 1$ component system is the possible occurrence of different ordered phases: the $n = 2$ system has an ordered phase, I, with $\zeta_1 = 1$, $\zeta_2 = 0$ and another, II, with $\zeta_1 = \zeta_2 = 1/\sqrt{2}$ whose relative stability is determined by the sign of $v$, §1.4.2.1. More than one phase transition may occur if there are competing interactions one of which favours one of these phases, while another favours the other phase. This type of competition is responsible for the successive phase transitions in $\text{BaTiO}_3$ (Devonshire 1954) and we illustrate the behaviour by extending the free-energy equation, (I.4.33), to include sixth-order terms in the order parameters;

$$G = G_0 + \frac{1}{2} \alpha(T-\Delta\nu)(Q_1^2 + Q_2^2 + Q_3^2) + \alpha(Q_1^2 + Q_2^2 + Q_3^2)^2 + v(Q_1^2 + Q_2^2 + Q_3^2) + h_1(Q_1^2 + Q_2^2 + Q_3^2)^3 + h_2(Q_1^2 + Q_2^2 + Q_3^2) + h_3(Q_1^2 + Q_2^2 + Q_3^2) + Q_3^2(Q_1^2 + Q_2^2 + Q_3^2) + Q_3^2(Q_1^2 + Q_2^2 + Q_3^2).$$  \hspace{1cm} (I.4.44)

The quadratic term and the terms in $u$ and $h_1$ are isotropic and so do not determine the nature of the ordered phase. We shall determine the structure of the ordered phase by using perturbation theory to calculate the energy of the anisotropic terms. Consider three possible structures for which $(Q_1, Q_2, Q_3)$ are given by: I$(1,0,0)Q_0$, II$(1/\sqrt{2}, 1/\sqrt{2}, 0)Q_0$ and III$(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})Q_0$. The contribution of the anisotropic terms to the free energy is

$$G_{\text{AN}}(I) = (v + h_2 Q_0^2)Q_0^2,$$

$$G_{\text{AN}}(II) = \left(\frac{1}{2}v + \frac{1}{4}(h_2 + h_3)Q_0^2\right)Q_0^2.$$

$$G_{\text{AN}}(III) = \left(\frac{1}{3}v + \frac{1}{9}(h_2 + 2h_3)Q_0^2\right)Q_0^2. \hspace{1cm} (I.4.45)$$

If $v < 0$ then phase I will tend to be more stable than phase II or III. If, however, $h_2$ and $h_3$ are negative then they will tend to stabilize phase III rather than phases I or II. Since, however, the $h$-coefficients are multiplied by $Q_0^2$, there may be a temperature at which it is energetically favourable for a transition to occur from the structure favoured by $v$ to that favoured by the $h$-coefficients. If we neglect $h_3$ for simplicity then three transitions are predicted by eqns. (I.4.45) if $v < 0$ and $h_2 > 0$: disordered $\rightarrow$ phase I when $T = T_c$; phase I $\rightarrow$ phase II when $Q_0^2 = -2v/3h_2$; phase II $\rightarrow$ phase III when $Q_0^2 = -6v/5h_2$. Whereas the first transition may be continuous, the second and third transitions are necessarily of first order. It is interesting to note that phase II can never be stable under the action of the parameters $v$ or $h_2$ alone, but can
be stabilized by a competition between these terms. Devonshire (1954) applied this theory in detail to BaTiO$_3$ and was able to show that it explained the occurrence of the three transitions. However, not surprisingly, a satisfactory quantitative description could be obtained only when the parameters were allowed to be temperature dependent.

If the parameter $v$ is positive, phase III is stable below $T_c$ and, if $h_2$ is negative there is a first-order transition to phase I, when $Q_2^6 = -3v/4h$. In this case phase II is never stable. In fig. 1.34 the phase diagrams of these $n=3$ systems are illustrated.

![Phase diagrams for an $n=3$ system with $Q^4$ and $Q^6$ anisotropies.](image)

Another type of competition between different phases arises if a stress or strain is applied to the crystal favouring one of the possible lower temperature phases, rather than the other (Bruce and Aharony 1975).

The effect of a [100] stress on SrTiO$_3$ is to split the degeneracy of the three modes $Q_1$, $Q_2$ and $Q_3$. The free-energy equation, (I.4.33), may then be rewritten as

$$G = G_0 + \frac{1}{2} \{a(T - T_c)(Q_1^2 + Q_2^2 + Q_3^2) + 2p_1 Q_1^2 + p_2(Q_2^2 + Q_3^2)\} + u(Q_1^2 + Q_2^2 + Q_3^2)^2 + v(Q_1^4 + Q_2^4 + Q_3^4),$$  (I.4.46)

where the new terms $p_1$ and $p_2$ are proportional to the stress applied along the [100] direction. In the interests of simplicity we shall assume that $p_1 = -p_2 = p_0$, neglect the strain dependence of $u$ and $v$ and assume $v$ is negative (e.g. SrTiO$_3$). In this case both the applied stress and $v$ favour ordering along the cube axis, $Q_1$, if $p_0 < 0$, and $Q_2$.
or $Q_3$ if $p_0 > 0$. The phase transitions occur when

\[ T = T_0 - \frac{2p_0}{a} \quad \text{for} \quad p_0 < 0 \]

\[ T = T_0 + \frac{p_0}{a} \quad \text{for} \quad p_0 > 0, \]

and there is a first-order transition separating the two ordered phases, as shown in fig. I.35 (a).

Fig. I.35

![Phase diagrams for a $[100]$ stressed $n = 3$ system. (After Bruce and Aharony 1975.) (a) The case $v < 0$ (e.g. SrTiO$_3$). (b) The case $v > 0$ (e.g. LaAlO$_3$).](image)

The behaviour is more complicated if $v > 0$, (as in the case of LaAlO$_3$), because then the applied field favours ordering along the cube axes while $v$ favours the $[1, 1, 1]$ type of ordering. The essential form of the phase diagram may be determined by assuming that the anisotropic terms are small and using perturbation theory to calculate their effects: a more complete treatment is given by Bruce and Aharony (1975). If the order parameter of the ordered phase is written $(Q_1, Q_2, Q_3) = (\cos \theta, \zeta_2 \sin \theta, \zeta_3 \sin \theta)Q_0$ where $\zeta_2^2 + \zeta_3^2 = 1$, then the anisotropic contribution to the free energy is

\[ G_{\text{AN}} = \frac{3p_0}{2} Q_0^2 \cos^2 \theta + v(\cos^4 \theta + \sin^4 \theta(\zeta_2^4 + \zeta_3^4))Q_0^4. \]

Now since $v > 0$ and we wish to minimize $G_{\text{AN}}$, $\zeta_2^4 + \zeta_3^4 = \frac{1}{2}$, and hence we can minimize $G_{\text{AN}}$ with respect to the angle $\theta$ to obtain three solutions:

I. \( \cos \theta = 0, \)

II. \( \cos^2 \theta = \frac{1}{3} - \frac{p_0}{2vQ_0^2} \)

III. \( \sin \theta = 0 \)

Phase I is stable when $p_0 > 2vQ_0^2/3$ and phase III stable when $p_0 < -4vQ_0^2/3$ and an intermediate phase in which the ordering vector is more general is stable for intermediate values of $p_0$. The phase diagram is sketched in fig. I.35 (b).
A similar analysis may be applied to the case of [111]-stressed materials, though the treatment is complicated by the non-orthogonality of the different [111] directions. This time, as one might expect, an 'intermediate' phase occurs when $v$ is negative, as shown schematically in Fig. 1.36. A comparison of these results with experimental data is given in §II.5.3.3.

![Fig. 1.36](image)

Phase diagrams for a [111] stressed $n=3$ system. (After Bruce and Aharony 1975.) (a) The case $v<0$. (b) The case $v>0$.

I.4.4. Incommensurate phase transitions

I.4.4.1. The simplest incommensurate phase

As yet we have described only those phase transitions where the order parameters, $Q_i$, are real, but in general they may be complex. Consider a tetragonal material in which the order parameter, $Q_i$, has a wave-vector $q_i = (0, 0, \zeta)$. Then unless the wave-vector is the zone centre or zone boundary, the order parameter $Q_i$ will be complex. Initially it seems surprising that $q_i$ can have a value between 0 and the zone boundary because it is only at these points that symmetry may impose that $V_{q_i} \omega(q_j) = 0$. There is nothing, however, to prevent $V_{q_i} \omega(q_j) = 0$ for an arbitrary point in the zone for some particular combination of interatomic forces. However, in these cases the wave-vector $q_i$ of the minimum in the dispersion relation is not fixed by symmetry and so is usually temperature dependent. Both of these features are illustrated in figs. 1.37 and 1.38 for $K_2SeO_4$ (Iizumi et al. 1977), where we show the measured dispersion relation and the temperature dependence of $q_i$.

In the theory of incommensurate phase transitions the order parameter $Q_1$ is complex and there is necessarily another coupled order parameter, $Q_2$, with wave-vector $-q_i$. Since, however, the atomic displacements, $u(kc)$ are real, eqn. (I.2.1) shows that $Q_1$ and $Q_2$ must be complex conjugates of one another, and it is frequently useful to define new variables to explicitly take account of this condition. The most direct way of doing this is to write

$$Q_1 = \frac{1}{\sqrt{2}} A \exp(i\phi), \quad Q_2 = \frac{1}{\sqrt{2}} A \exp(-i\phi), \quad (I.4.47)$$

where the coordinate $A$ is the amplitude of the distorted wave and $\phi$ is its phase and
Fig. 1.37

The dispersion relation of the soft mode in K₂SeO₄ at various temperatures. (After Iizumi et al. 1977.)

Fig. 1.38

The temperature dependence of \( q_s = \frac{1}{\beta} (1 - \delta) \frac{2\pi}{a} \) in K₂SeO₄ compared with calculation by Iizumi et al. (1977).

both are real. An alternative approach is to introduce new coordinates which are written as

\[
P_1 = \frac{1}{\sqrt{2}} (Q_1 + Q_2),
\]

\[
P_2 = \frac{i}{\sqrt{2}} (Q_2 - Q_1), \tag{1.4.48a}
\]

where \( P_1 \) and \( P_2 \) are again real.

The relationship between these two coordinate systems is

\[
P_1 = A \cos \phi \quad \text{while} \quad P_2 = -A \sin \phi. \tag{1.4.48b}
\]
The free energy of this system is
\[ G = G_0 + a(T - T_c)Q_1Q_2 + 4uQ_1^2Q_2^2, \] (I.4.49)
where the terms in \( Q_1^2, Q_2^2, Q_1^4, \) and \( Q_2^4 \) are absent because they fail to satisfy wave-vector conservation. Substituting eqn. (I.4.47) into eqn. (I.4.48) we obtain;
\[ G = G_0 + \frac{1}{2}a(T - T_c)A^2 + uA^4; \] (I.4.50)
an expression involving the amplitude \( A \) which is identical to the free energy of the singlet system discussed initially, eqn. (I.4.3). We immediately obtain, therefore, that
\[ A_0^2 = \frac{a}{4u}(T_c - T), \quad T < T_c; \] (I.4.51)
and analogous expressions for the specific heat and free energy. The other noteworthy point about eqn. (I.4.50) is that it does not explicitly involve the phase angle \( \phi \). The free energy is therefore independent of the choice of \( \phi \).

In the alternative representation with the order parameters, \( P_1 \) and \( P_2 \), the free-energy equation, (I.4.49), becomes;
\[ G = G_0 + \frac{1}{2}a(T - T_c)(P_1^2 + P_2^2) + u(P_1^2 + P_2^2)^2. \] (I.4.52)
This form of the free energy is identical with that of the \( n = 2 \) system, discussed in §1.4.2.1, except that \( v = 0 \). The phase transition is therefore to a phase of type II, §1.4.2.1, corresponding to \( (P_1, P_2) = A_0(\zeta_1, \zeta_2) \) with the eigenvector \( \zeta \) arbitrary. This continuously variable direction in the \( (P_1, P_2) \) space corresponds to the arbitrary choice of the phase angle \( \phi \) in the other representation.

The analysis of §1.4.2.1 can now be repeated to obtain the susceptibility both above and below the phase transition to give
\[ \chi_L(0) = \chi_T(0) = \left[ a(T - T_c) \right]^{-1}, \quad T > T_c; \] (I.4.53a)
\[ \chi_L(0) = \left[ 2a(T_c - T) \right]^{-1}, \quad T < T_c; \] (I.4.53b)
\[ \chi_T(0) = \infty, \quad T < T_c, \] (I.4.53c)
where \( \chi_L \) is determined by the fluctuations parallel to the ordering vector, \( \zeta \), which are frequently called amplitude fluctuations, and \( \chi_T \) corresponds to fluctuations perpendicular to that direction which have an infinite susceptibility. These fluctuations were called phasons by Overhauser (1971) because they correspond to changes in the phase of the order parameter.

I.4.4.2. More complex incommensurate phases
Not all incommensurate phases have only two components of the order parameter. In order to illustrate the type of behaviour which occurs we examine the properties of two \( n = 4 \) systems. The first corresponds to an incommensurate phase in an orthorhombic crystal with wave-vector \( \mathbf{q}_1 = (\pm \zeta_1, \pm \zeta_2, 0) \) or a tetragonal crystal with \( \mathbf{q}_1 = (\pm \zeta, 0, 0) \) and \( (0, \pm \zeta, 0) \). It is then convenient to introduce two amplitudes
Structural phase transitions

and phases by the requirement that

\[ Q_1 = \frac{1}{\sqrt{2}} A_1 \exp(i\phi_1), \quad Q_2 = Q_1^*, \]

\[ Q_3 = \frac{1}{\sqrt{2}} A_2 \exp(i\phi_2), \quad Q_4 = Q_3^*. \]

The free energy is then of the form

\[ G = G_0 + a(T - T_c)(Q_1 Q_2 + Q_3 Q_4) + 4(u + v)(Q_1^2 Q_2^2 + Q_3^2 Q_4^2) + 8uQ_1 Q_2 Q_3 Q_4. \]

With the aid of the transformation, eqn. (I.4.54), the free energy becomes

\[ G = G_0 + \frac{1}{2} a(T - T_c)(A_1^2 + A_2^2) + u(A_1^2 + A_2^2)^2 + v(A_1^4 + A_2^4), \]

which is independent of the phase angles \( \phi_1 \) and \( \phi_2 \). Now, since eqn. (I.4.56) is identical with the \( n = 2 \) system described in §1.4.2.1, there are three solutions

I. \( v < 0 \) \( A_1 \) or \( A_2 = A_0 \), and the other is equal to zero.

II. \( v = 0 \) \( A_1 + A_2 = A_0 \).

III. \( v > 0 \) \( A_1 = A_2 = A_0/\sqrt{2} \).

The susceptibilities can be obtained in the usual way. For structure I, with say \( A_1 = A_0 \), there is a longitudinal susceptibility corresponding to fluctuations in \( A_1 \) given by

\[ \chi_1(0) = [2a(T_c - T)]^{-1}, \quad T < T_c, \]

while the transverse susceptibility arising from the fluctuations in the phase \( \phi_1 \) is infinite. The susceptibilities of the \( Q_3 \) and \( Q_4 \) modes are degenerate and given by

\[ \chi_3(0) = \chi_4(0) = -\frac{u + v}{2a(T_c - T)}, \quad T < T_c. \]

If the ordered phase is of type III then there is a longitudinal susceptibility given by eqn. (I.4.57), and another amplitude susceptibility corresponding to anti-phase fluctuations of the two amplitudes with a susceptibility given by

\[ \chi_A(0) = \frac{2u + v}{2a(T_c - T)}, \quad T < T_c. \]

and two infinite susceptibilities, corresponding to fluctuations in the phase angles \( \phi_1 \) and \( \phi_2 \). In this system the number of phasons with infinite susceptibility depends on the number of pairs of \( q \) and \(-q\) present in the ordered structure. If there is only one pair, phase I, then there is only one infinite phase susceptibility, but if both modes are present in the ordered structure, two susceptibilities are infinite.

Finally let us consider another case of an \( n = 4 \) system; \( \text{BaMnF}_4 \) which has an ‘a’ face centred orthorhombic structure and an incommensurate phase described by the four order parameters;

\[ Q_1(q_a = (0.39, \frac{1}{2}, \frac{1}{2})), \quad Q_2(q_a = (-0.39, \frac{1}{2}, \frac{1}{2})), \]

\[ Q_3(q_a = (0.39, -\frac{1}{2}, \frac{1}{2})) \text{ and } Q_4(q_a = (-0.39, \frac{1}{2}, \frac{1}{2})), \text{ (Shapiro et al., 1976).} \]
The free energy is now of the same form as eqn. (I.4.55) but with an additional term given by $4w(Q_1^2Q_3^2 + Q_2^2Q_3^2)$. When this is transformed to the form of the free energy given in eqn. (I.4.56), we obtain an additional term $\omega A_1^2A_2^2 \cos(2\phi_1 + 2\phi_2)$. This term has the effect of fixing the relative phases between the two pairs of incommensurate wave-vectors. Consequently for the structure of type I, discussed above, this term splits the degeneracy between $\chi_3(0)$ and $\chi_4(0)$, while for the structure of type III, there is only one infinite susceptibility which arises from fluctuations which preserve $\phi_1 + \phi_2$, while the other phase susceptibility is finite and corresponds to fluctuations in $\phi_1 + \phi_2$. The effect of the Umklapp interaction in BaMnF$_4$ is therefore to reduce the degeneracy of the susceptibilities, and in particular to ensure that there is only one phase mode with an infinite susceptibility. The number of infinite phase susceptibilities is then the number of pairs of wave-vectors in the ordered structure, $n/2$, less the number of phase locking terms. There are always phase locking terms which restrict the number of infinite phase susceptibilities to be a maximum of three.

1.4.4.3. Fluctuations of incommensurate phases

We now extend the analysis, particularly of the simplest incommensurate phase, to include the wave-vector dependence of the fluctuations. The free-energy equation, (I.4.49), is extended to include the wave-vector dependence of the quadratic term in $Q_1Q_2$ when for small $\mathbf{k}$ expanding about the temperature dependent, $\mathbf{q}_0$, gives

$$G = G_0 + \frac{1}{N} \sum_{\mathbf{k}} (a(T - T_c) + f_1(k_x^2 + k_y^2) + f_2(k_z^2)) Q_1(\mathbf{k})Q_2(-\mathbf{k}) + \frac{4w}{N^2} \sum_{k_1,k_2,k_3} Q_1(\mathbf{k_1})Q_2(\mathbf{k_3})Q_1(\mathbf{k_2})Q_2(-\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3).$$  (I.4.58)

The fluctuations can be found by transforming to the $P_1(\mathbf{k}), P_2(\mathbf{k})$ coordinates when for $T > T_c$ the quadratic terms in the $P(\mathbf{k})$ become

$$\frac{1}{2N} \sum_{\mathbf{k}} \sum_{i=1} R_{ii}(\mathbf{k})P_i(\mathbf{k})P_i(-\mathbf{k})$$

with

$$R_{ii}(\mathbf{k}) = a(T - T_c) + f_1(k_x^2 + k_y^2) + f_2k_z^2,$$  (I.4.59)

so that the ‘frequencies’ of the fluctuations described by $P_1(\mathbf{k})$ and $P_2(\mathbf{k})$ are equal and given by

$$\omega_1(\mathbf{k})^2 = \omega_2(\mathbf{k})^2 = R_{11}(\mathbf{k}).$$  (I.4.60)

The corresponding frequencies below $T_c$ can be found by assuming a particular phase for the ordered structure so that $\phi = 0$ in eqn. (I.4.48 b), when the longitudinal or amplitude frequency is given by

$$\omega_L(\mathbf{k})^2 = 2a(T_c - T) + f_1(k_x^2 + k_y^2) + f_2k_z^2$$  (I.4.61)

and the transverse or phase frequency by

$$\omega_T(\mathbf{k})^2 = f_1(k_x^2 + k_y^2) + f_2(k_z^2)$$  (I.4.62)

In fig. 1.39 we illustrate these frequencies close to $T_c$.

The phase frequencies are linear with $k$ below $T_c$ and their slope is independent of temperature in this model.
The dispersion relations for the excitation frequencies of an incommensurate system with a plane-wave ground state. (After Bruce and Cowley 1978.)

Before discussing experimental observations of phasons, it is worthwhile discussing their nature in more detail. An alternative approach for describing the fluctuations of an incommensurate phase is to consider fluctuations in the amplitude and phase. By analogy with the treatment of the fluctuations in the order parameter $Q$ as wave-vector dependent $Q(k)$, we introduce a wave-vector-dependent fluctuation in the amplitude, $A(k)$, and phase $\phi(k)$ so that from eqn. (I.4.47) we obtain for small fluctuations

$$Q_z(k) = \frac{i}{\sqrt{2}} (A(k) \exp(i\phi_0) + iA_0 \exp(i\phi_0) \phi(k))$$

where $\phi_0$ is the phase of the ordered structure. If the ordered structure is chosen as above to have $\phi_0 = 0$, then to leading order in the fluctuations

$$P_1(k) = A(k), \quad P_2(k) = A_0 \phi(k).$$

$P_1(k)$ and $P_2(k)$ can now be identified with the amplitude and phase fluctuations, but the identification is accurate only for leading-order terms in the expansion of the complex exponential, $\exp(i\phi(k))$; once $\phi(k)$ becomes sufficiently large to invalidate this expansion, then the two developments are no longer identical. In particular, the second-order terms in the expansion of $\exp(i\phi(k))$ give a real contribution to the right-hand side of eqn. (I.4.63) which must be incorporated with the $P_1(k)$. This leads to a large correction to the longitudinal susceptibility: in fact we have shown (Bruce and Cowley 1978) that it varies as $1/k$ for small $k$ below $T_c$, cf. eqn. (I.4.53b). This is an exactly analogous problem to the well-known divergence of the longitudinal susceptibility of a Heisenberg ferromagnet below $T_c$ on the coexistence curve (Vaks et al. 1967). In our notation it arises because fluctuations in the direction of the order parameter in $(P_1, P_2)$ space are relatively easy and to second order give rise to fluctuations in the length of any component of that parameter.
The scattering cross-section for X-ray or neutron scattering is readily obtained using the techniques developed in § I.2.3 and the definition of the $P$ coordinates in eqn. (I.4.48). The result is

$$S^1(K, \omega) = \frac{hN}{2\pi(n(\omega) + 1)} \sum_k [\Delta(K + q_s + k)$$

$$\times |F(K, q_s + k)|^2 + \Delta(K - q_s + k)|F(K, -q_s + k)|^2]$$

$$\times \text{Im} [\chi_L(k, \omega) + \chi_T(k, \omega)],$$

(I.4.65)

where $\chi_L(k, \omega)$ and $\chi_T(k, \omega)$ are the frequency dependent susceptibilities of the longitudinal and transverse fluctuations, and the $F$s are the mode structure factors defined by eqn. (I.2.36). Above $T_c$, eqn. (I.4.65) reduces to the usual one-phonon cross-section from the soft mode, but below $T_c$, $\chi_L$ and $\chi_T$ differ so that there are two response functions for each $K$. The scattering cross-section in principle enables both the phase and amplitude modes to be observed as illustrated in fig. 1.39. Alas we are unaware of any neutron scattering measurements which convincingly vindicate the existence of phasons in real incommensurate systems. In $K_3\text{SeO}_4$ (Iizumi et al. 1977) and $\text{BaMnF}_4$ (Shapiro et al. 1976) considerable scattering is observed for the appropriate wave-vector transfers, but it has not, as yet, been possible to distinguish the scattering from the phase modes from that of the normal elastic waves seen emanating from the Bragg reflection of the incommensurate phase. In fig. 1.40 we show experimental results obtained for the one-dimensional conductor, KCP, (Carneiro et al. 1976) and this too definitely shows scattering at low energies close to the incommensurate wave-vector, $2k_F$, but it is not clearly of phason character. In $\text{TaSe}_2$ (Moncton et al. 1975) and $\text{NaNO}_2$ (Sakurai et al. 1970) the transitions are more closely of the order–disorder type and so it is not possible with conventional neutron scattering techniques to determine the dispersion relations.

The amplitude and phase modes can also be observed using light scattering techniques. The polarizability tensor is expanded in powers of the coordinates $Q_1$ and $Q_2$ as

$$P_{a\beta}(K) = \sum_k P^0_{a\beta}(q_s + k, -q_s - k + K)Q_1(k)Q_2(-k + K).$$

Now since the modes can be determined most directly by one-phonon scattering we are interested in the terms in which either $Q_1(k)$ or $Q_2(k)$ takes on its average value. It is useful to expand the polarizability for small $K$ so that

$$P_{a\beta}(q_s, -q_s + K) = P^0_{a\beta} + \sum_\gamma P^1_{a\beta, \gamma} K_\gamma + \ldots$$

and then since $P_{a\beta}(k_1, k_2)$ is symmetric in $k_1$ and $k_2$

$$P_{a\beta}(q_s + K_s, -q_s) = P^0_{a\beta} - \sum_\gamma P^1_{a\beta, \gamma} K_\gamma + \ldots$$

When the polarizability is expressed in terms of the $P$ coordinates and the ordered structure is assumed to have $\phi = 0$ (eqn. I.4.48b) then

$$P_{a\beta}(K) = A_0 P^0_{a\beta} P_1(K) + i A_0 \sum_\gamma P^1_{a\beta, \gamma} K_\gamma P_2(K).$$
Neutron scattering intensity counters for scattering vectors $K = \xi C^* + \tau$ in KCP. (From Carneiro et al. 1976.)

This equation shows that the amplitude fluctuations are observable with Raman scattering techniques, while the phase fluctuations can be observed by Brillouin scattering techniques. The frequencies and line widths of the amplitude mode in $K_2\text{SeO}_4$, measured by Raman scattering techniques (Wada et al. 1977) are shown in
Since the phase modes can be observed in Brillouin scattering they must have the same symmetry as acoustic modes, and will therefore interact with them. This interaction can be evaluated (Bruce and Cowley 1978) by expanding the coupling coefficient between the strain $\eta_{ab}$ and the modes $(q_j)$ and $(-q_j)$,

$$ V_{ab} \begin{bmatrix} q_j & -q_j \end{bmatrix} $$

in eqn. (I.2.10), as was described above for the polarizability. The result is similar; there is a linear coupling between the phasons and the strain parameters which is determined by

$$ iA_0 V_{ab,\gamma} = \frac{\partial}{\partial k_\gamma} V_{ab} \begin{bmatrix} q_j & q_j + k \end{bmatrix}. $$

This coupling is proportional to the order parameter $A_0$, and will modify the velocities of both the phasons and acoustic modes.

Fig. I.41

Raman scattering measurements of the longitudinal or amplitude mode in K$_2$SeO$_4$. Phase (2) is paraelectric, (3) is incommensurate and (4) is a locked-in phase. (After Wada et al. 1977.)

Alas we do not, as yet, know of any direct observation of phasons by either Brillouin or ultrasonic techniques. Bechtle and Scott (1977) have suggested that some anomalies in the intensity of the Brillouin scattering of the acoustic modes in BaMnF$_4$ arise because of coupling to the phasons but this is not yet proven.

Finally, we discuss the effect of the phasons on the Debye–Waller factor of the incommensurate phase. The Debye–Waller factor is determined by the displacement–displacement correlation function for the particular site in the crystal. When wave-vector is conserved this can be expressed in terms of the normal mode
correlation function $\sum_{q_{j}j'} \langle Q(q_j)Q(-q_{j'}) \rangle$ as shown by eqn. (I.3.36). In an incommensurate phase, this correlation function is given by

$$\langle u_{\kappa}(l\kappa)u_{\ell}(l\ell) \rangle = \frac{1}{M_{\kappa}} \frac{1}{N} \sum_{q_{1},q_{2},j,j'} e_{\kappa}(\kappa, q_{1}, j_{1})$$
$$\times e_{\ell}(\kappa, q_{2}, j_{2}) \langle Q(q_{1}, j_{1})Q(q_{2}, j_{2}) \rangle \exp(\iota q_{1} - q_{2}) \cdot R(\kappa).$$  \hspace{1cm} (I.4.66)

We shall now consider the part of the Debye–Waller factor dependent upon the correlation function of the amplitude and phase modes described above. When the transformation is made to the $P_{1}$ and $P_{2}$ coordinates the relevant contribution to (I.4.66) is proportional to

$$\frac{1}{2N} \sum_{\kappa} \left[ (1 - \cos(2q_{s} \cdot R(\kappa)))/(\omega_{\kappa}(\kappa)^{2} + (1 + \cos(2q_{s} \cdot R(\kappa)))/(\omega_{\ell}(\kappa)^{2}) \right] \quad \text{(I.4.67)}$$

where the frequencies are given by eqns. (I.4.60)-(I.4.62). This result is unusual below $T_{c}$ in that it varies with position, $R(\kappa)$. In an incommensurate phase each atom is displaced a different amount and since the fluctuations correspond to fluctuations in that displacement it is to be expected that the Debye–Waller factor varies with position. The intensity of the Bragg reflections corresponding to the underlying lattice $K = \tau$ and to the incommensurate phase, $K = \tau + q_{s}$, have the same Debye–Waller factor determined by

$$\bar{W} = \frac{1}{2N} \sum_{\kappa} \left( \frac{1}{\omega_{\kappa}(\kappa)^{2}} + \frac{1}{\omega_{\ell}(\kappa)^{2}} \right).$$ \hspace{1cm} (I.4.68)

An alternative approach to the scattering properties and the Debye–Waller factor was developed by Overhauser (1971) using the phase variable $\phi(\kappa)$ directly. The component of the Bragg scattering from the $(l\kappa)$th atom is determined by $\langle \exp(iK \cdot u(l\kappa)) \rangle \exp(iK \cdot R(\kappa))$. If we consider only the displacements due to the phase fluctuations then

$$u(l\kappa) = \left( \frac{2}{M_{\kappa}} \right)^{1/2} A_{0} e(\kappa, q_{s}) \cos(q_{s} \cdot R(l\kappa) + \phi_{0} + \phi(l\kappa)),$$ \hspace{1cm} (I.4.69)

where $\phi(l\kappa)$ is the fluctuating part of the phase

$$\phi(l\kappa) = \frac{1}{\sqrt{N}} \sum_{\kappa} \phi(\kappa) \exp(iK \cdot R(l\kappa)).$$ \hspace{1cm} (I.4.70)

The Bessel function expansion for a complex exponential is

$$\exp(i\zeta \cos \psi) = \sum_{n = -\infty}^{\infty} i^{n} J_{n}(\zeta) \exp(i\zeta \psi),$$

and gives

$$\langle \exp(iK \cdot u(l\kappa)) \rangle = \sum_{n = -\infty}^{\infty} i^{n} J_{n}(y) \exp(in(q_{s} \cdot R(l\kappa) + \phi_{0}))$$
$$\hat{} \times \langle \exp(in\phi(l\kappa)) \rangle,$$ \hspace{1cm} (I.4.71)

where

$$y = \sqrt{2A_{0} K \cdot e(\kappa, q_{s})/M_{\kappa}^{1/2}}.$$
The effective Debye–Waller factor for the different terms $d_n = \langle \exp \left( i n \phi(h \kappa) \right) \rangle$ is then given, using eqns. (I.4.70) and (I.4.64), as

$$\exp (-\tilde{w}) = d_n = \exp \left( -\frac{n^2}{2 A_0^2 N} \sum_k \omega_k(k)^2 \right). \tag{I.4.72}$$

This result shows that the Bragg reflections of the underlying lattice, $K = \tau$, are given by the terms in eqn. (I.4.71) with $n = 0$. Since $d_0 = 1$, the phase fluctuations do not contribute to their Debye–Waller factor, while the primary Bragg reflections of the incommensurate phase $K = \tau - q_s$ have a Debye–Waller factor given by $d_1$. This is an unusual Debye–Waller factor because it is independent of $K$ and decreases to zero rapidly as $T \to T_c$ due to the dependence on $A_0^2$. The higher terms in the expansion (I.4.71) correspond to the two-phonon, three-phonon terms, etc., in the expansion of the scattering cross-section as discussed in §1.3.1.

These results are clearly very different from those derived using the expansion in terms of $P_1$ and $P_2$, eqn. (I.4.68), and so we are left with two questions. Firstly why are they so different, and secondly which, if either, is correct? The reason for the difference is that the expansion in $P_2$ and the phase fluctuations, $q$, are only exactly equivalent to first order. Since the Debye–Waller factor is a summation over infinitely many-phonon processes the two expansions give different results because they include terms beyond the first order in a different way. It is clearly physically appealing to use the phase fluctuation model of Overhauser (1971) because the energy is unchanged by a change in the phase, $\phi_0$. Consequently it would seem that eqn. (I.4.72) is to be preferred. Close to $T_c$, however, the fluctuating displacement, $\phi(h \kappa)$, can become large, because the amplitude $A_0$ becomes very small. Our development, however, has treated the fluctuations in $\phi(h \kappa)$ as a harmonic oscillator and this is clearly inappropriate when $\phi(h \kappa) \sim \pi$. Consequently we expect the phase mode contribution to the Debye–Waller factor to be given accurately by eqn. (I.4.72) for $T \ll T_c$, but close to $T_c$ there will be deviations from this behaviour and it will possibly revert more closely to the form obtained in eqn. (I.4.68), which yields the normal Debye–Waller factor for $T > T_c$.

1.4.4.4. Secondary order parameters

At incommensurate phase transitions there is always a coupling between the strain and pairs of order parameters. In the simplest model the coupling is given by $2 \varepsilon Q_1 Q_2 \eta$, which when transformed into the phase and amplitude coordinates becomes $\varepsilon A_0^2 \eta$. Consequently the coupling alters the magnitude of the amplitude and the character of the amplitude fluctuations but has no direct effect on the phase fluctuations. These effects can be treated using the methods outlined in §1.4.1.2, and the results are essentially the same as those obtained there.

In principle it is possible to have an improper ferroelectric in which the primary order parameter has an incommensurate wave-vector, if the irreducible representation of the order parameter is doubly degenerate. In this case the ferroelectric ordering will be accompanied by a particular choice of the relative phases of the two systems (Cochran 1971). Since, however, we are unaware of any real systems of this type we shall not discuss them in more detail.

Of more interest in incommensurate phases are secondary order parameters associated with wave-vectors of the form

$$q_m = m q_s + \tau_m. \tag{I.4.73}$$
where \( m \) is any integer. A simple mean field argument shows that if there is a term in the hamiltonian of the form

\[
V \left( \mathbf{q}_j \mathbf{q}_j - 2 \mathbf{q}_j \right),
\]

then in an incommensurate phase with a distortion of wave-vector \( \mathbf{q}_j \), there will also be a distortion with wave-vector \( 2 \mathbf{q}_j \). Extending this argument shows that distortions will occur for all the wave-vectors given by eqn. (I.4.73). We may expect, however, that increasing \( j \) will involve increasing orders of the anharmonic interactions so that the amplitudes of these distortions decrease rapidly as \( j \) increases. Despite this it is necessary to consider if these secondary distortions can influence the qualitative features discussed above.

The free energy of the system within a completely general Landau theory may be written (Kwok and Miller 1966)

\[
G = G_0 + \sum_n \sum_{j_1, \ldots, j_n} V_n \left( \mathbf{q}_{j_1} \cdots \mathbf{q}_{j_n} \right) \langle \mathbf{Q}(\mathbf{q}_{j_1}) \rangle \cdots \langle \mathbf{Q}(\mathbf{q}_{j_n}) \rangle \Delta(\mathbf{q}_{j_1} + \cdots + \mathbf{q}_{j_n})
\]

where the \( \mathbf{q}_m \) belong to the set given in eqn. (I.4.73) and the \( V_n \) coefficients may be temperature dependent. Now consider a change in the phase of the distorted waves to

\[
\langle \mathbf{Q}(\mathbf{q}_{j_m}) \rangle_\phi = \exp \left( im\phi \right) \langle \mathbf{Q}(\mathbf{q}_{j_m}) \rangle,
\]

then the free energy of the new phase is

\[
G_\phi = G_0 + \sum_n \sum_{j_1, \ldots, j_n} V_n \left( \mathbf{q}_{j_1} \cdots \mathbf{q}_{j_n} \right) \exp \left( i(m_1 + \cdots + m_n)\phi \right)
\]

\[
\times \langle \mathbf{Q}(\mathbf{q}_{j_1}) \rangle \cdots \langle \mathbf{Q}(\mathbf{q}_{j_n}) \rangle \Delta(\mathbf{q}_{j_1} + \cdots + \mathbf{q}_{j_n}).
\]

But if \( \mathbf{q}_m \) is truly incommensurate, wave-vector conservation implies that \( m_1 + m_2 + \cdots + m_n = 0 \). Consequently \( G_\phi = G \) and the free energy of the incommensurate state is unchanged by the transformation (I.4.74). This then suggests that the phason behaviour, namely \( \chi_T(k) \to \infty \) as \( k \to 0 \), will occur even when the effects of these secondary order parameters are included. An explicit example has been detailed by us elsewhere (Bruce and Cowley 1978).

These secondary order parameters break the same symmetry operations of the high-temperature phase as the primary wave-vector, \( \mathbf{q}_j \). They are therefore secondary order parameters of the second type discussed in § 1.3.2. From a somewhat pedantic point of view, eqn. (I.4.73) defines a set of \( \sim N^{1/3} \) possible components of the order parameter with different values of \( \mathbf{q}_m \), in the same direction, corresponding to different components of the same set of order parameters. A different type of combination of this set of order parameters is employed in the next section to discuss lock-in phase transitions.

1.4.5. Lock-in phase transitions

1.4.5.1. Phase-locked phases

In §§1.4.1 to 1.4.3 we discussed the properties of phase transitions for which symmetry imposed \( \nabla_\mathbf{q} \omega(\mathbf{q},j) = 0 \). We shall now discuss the properties of commensurate phases for which \( \nabla_\mathbf{q} \omega(\mathbf{q}) \) is not necessarily zero. For example, a
tetragonal material for which \( \mathbf{q}_s = (0, 0, \zeta) \) and \( \zeta = 2\pi/pc \) has a commensurate wave-vector but if \( p > 2 \) the gradient is in general non-zero. The additional terms in the free-energy equation, (I.4.49), are given by an Umklapp term involving \( p \)th order anharmonicity so that

\[
G = G_0 + a(T - T_c)Q_1 Q_2 + 4aQ_1^2 Q_2^2 + 2^{p-1} V(Q_1^p + Q_2^p).
\]  

(I.4.75)

When this expression is transformed to the amplitude and phase coordinates

\[
G = G_0 + \frac{1}{2}a(T - T_c)A^2 + u A^4 + V A^p \cos p\phi.
\]  

(I.4.76)

This expression depends upon \( \phi \) and so the phase of the distorted wave is one of the \( p \) different choices of \( \phi \) which will minimize eqn. (I.4.76). Strictly speaking within Landau theory, and for \( T \approx T_c \), only the values of \( p = 3 \) and \( 4 \) are of interest. When \( p = 3 \) there are cubic terms in the free energy and so the transition is necessarily of first order, § I.4.1.1, while when \( p = 4 \) the Umklapp term has the form \( A^4 V \cos 4\phi \). Consequently the amplitude of the distorted wave is given by

\[
A_0^2 = \frac{a(T_c - T)}{4(|\mathbf{A}|)}
\]

and the phases of the different possible domains of the distorted wave are \( \phi_0 = 0, \pi/2, \pi, 3\pi/2 \) if \( V \) is negative and \( \pm\pi/4, \pm 3\pi/4 \) if \( V \) is positive. The longitudinal susceptibility can be obtained below \( T_c \) as

\[
\chi_L(0) = \left(2a(T_c - T)\right)^{-1},
\]

while the transverse or phase susceptibility is given by

\[
\chi_T(0) = -\frac{u - |\mathbf{V}|}{4|\mathbf{V}|a(T_c - T)},
\]  

(I.4.77)

which can be written in terms of the amplitude, \( A_0 \), to give the transverse frequency as

\[
\omega_T(0)^2 = (p^2|\mathbf{V}|A_0^{-2}).
\]  

(I.4.78)

These results show that the interaction locks the phase of the distortion so that the susceptibility of the phase mode is finite and of magnitude inversely proportional to that interaction.

Since there is no reason to expect that the phonon dispersion relation will have a minimum exactly at \( \tau/p \), even if it is close to that wave-vector, a continuous phase transition will normally give an incommensurate phase with \( \mathbf{q}_s \) close to \( \tau/p \). This will be followed at a lower temperature by a lock-in phase transition to the commensurate phase with wave-vector, \( \tau/p \), as discussed below.

In NbO\(_2\), however, the transition is apparently directly from a disordered phase to a commensurate phase described by a wave-vector \( \mathbf{q}_s = (3/2, 3/2, 1) \) in reciprocal lattice units (Pynn and Axe 1976). Finally, when \( \mathbf{q}_s \) is commensurate, there are only a finite set of the secondary order parameters with different wave-vectors, and these are then secondary order parameters of the first type because they do not break all the symmetry elements. In NbO\(_2\), for example, the secondary order parameters have \( \mathbf{q}_1 = (1/2, 0, 0) \), or \( (0, 1/2, 0) \) or \( (0, 0, 0) \), none of which break all the translational symmetry elements which are broken by the distortion with \( \mathbf{q}_s = (3/2, 3/2, 1) \).
I.4.5.2. Soft solitons

In the preceding section we have shown that Umklapp terms in the free energy lock the phase of the distorted wave for commensurate wave-vectors $q_\alpha$ and hence lower the free energy. We now consider the tetragonal system discussed in §§1.4.4.1 and 1.4.5.1 but with a phase transition described by an incommensurate wave-vector $q_s$, which is close to the commensurate wave-vector $q_0 = \tau/p$. The quadratic term in the expansion of the free energy is

$$G_2 = \frac{1}{N} \sum_k [a(T - T_c) + f k^2] Q_1(k) Q_2(-k), \quad (I.4.79)$$

where

$$k = q - q_s \quad \text{and} \quad \delta_0 = q_0 - q_s.$$

The system undergoes a phase transition at $T_c$ to an incommensurate phase, whose free energy is given (neglecting the higher Fourier components of the distortion) by eqn. (I.4.5a), as

$$G_{\text{inc}} = G_0 - \frac{a^2}{16 \nu} (T_c - T)^2. \quad (I.4.80)$$

The free energy of the commensurate phase with $p = 4$ is

$$G_{\text{com}} = G_0 - \frac{a^2}{16 \nu} (T_{co} - T)^2. \quad (I.4.81)$$

where $T_{co}$ is the phase transition temperature that the commensurate phase would have had if the incommensurate phase did not occur first, $T_{co} = T_c - \frac{2 \delta_0^2}{a}$ and $V$ is the lock-in energy, eqn. (I.4.76). For temperatures greater than $T_c$ the free energy (I.4.80) is smaller than (I.4.81) and the incommensurate phase is stable, but at $T_L$ these equations predict a first-order transition to the commensurate phase where

$$T_L = T_c - \frac{2 \delta_0^2 \nu}{|V| a}.$$

This analysis demonstrates the essential qualitative features of a lock-in phase transition. There is a competition between the quadratic term in the free energy (the frequency dispersion relation energy) which favours ordering at $q_s$, and the Umklapp interaction energy which favours a commensurate ordering, $q_0$. At high temperatures the second term dominates, but at lower temperatures, $A_0$ becomes large, and the interaction term dominates.

Although the above analysis contains the essential physics, it neglects some interesting and novel features of these phase transitions. These arise because the interaction energy responsible for the lock-in also makes the secondary order parameters very large, and neglecting them as we have done so far in this section is invalid (Moncton et al. 1975).

The effect of the secondary order parameters is most easily calculated by rewriting the free energy in a continuum form as an integral over position, $r$. In principle we should introduce a position dependent amplitude $A(r)$ and phase $\phi(r)$; in practice, however, the analysis is more tractable if we assume $A(r) = A_0$. This phase-modulation-only approximation is justified because the phase or transverse susceptibility is much larger than the amplitude or longitudinal susceptibility, eqn. (I.4.53),
and consequently it is much easier to create local distortions of the phase than of the amplitude. The free energy, eqns. (I.4.76) and (I.4.79), in a real-space representation then becomes (Bruce et al. 1978).

\[
G = G_0 - \frac{a^2}{16\pi} (T_c - T)^2 + \frac{fA_0^2}{Nv} \int G(r) dr.
\]

(I.4.82a)

where \(v\) is the volume of the unit cell and the position dependent free energy is

\[
G(r) = \frac{1}{2} (\nabla \phi(r) - \delta_0)^2 - \nu \cos p\phi(r),
\]

(I.4.82b)

where

\[
\nu = VA_0^{-2}/f
\]

If the vector \(\delta_0\) is along the \(z\) axis, eqn. (I.4.82) is minimized when \(\phi(r)\) is a function only of \(z\) and the phase dependent part of the free energy becomes (for a crystal of length \(L\))

\[
G_{\phi} = \frac{1}{L} \int G(z) dz - \delta_0 \vec{k} + \frac{1}{2} \delta_0^2 - \nu,
\]

(I.4.83a)

where now

\[
G(z) = \frac{1}{2} \left( \frac{d\phi}{dz} \right)^2 - \nu [\cos p\phi(z) - 1],
\]

(I.4.83b)

and

\[
\vec{k} = \frac{1}{L} (\phi(L) - \phi(0))
\]

(I.4.84)

is the effective wave-vector for the incommensurate phase. The problem of finding the nature of the incommensurate phase is then reduced to finding the forms of \(\phi(z)\) which minimize eqns. (I.4.83). McMillan (1976) solved this problem by writing \(\phi(z)\) as a Fourier series

\[
\phi(z) = \delta z + \sum_n H_n \sin (pn\delta z),
\]

and then solving numerically for the coefficients \(\delta\) and \(H_n\). More elegantly, Bak and Emery (1976) observed that the functions for which the integral in eqn. (I.4.83a) is an extremum satisfy the sine–Gordon equation

\[
\frac{d^2\phi(z)}{dz^2} = p \nu \sin p\phi(z),
\]

one solution of which is the soliton or domain wall (Scott et al. 1973)

\[
\phi(z) = \theta(z) \equiv \frac{4}{p} \tan^{-1} (\exp (p \nu^{1/2}z)),
\]

(I.4.85)

which separates a region with \(\phi(z) = 0\), say, from one in which \(\phi(z) = 2\pi/p\). Substituting this solution back into eqn. (I.4.83) gives the energy of a single domain wall as \(1/L \int G(z) dz = 8 \nu^{1/2}/p\). Consequently the free energy of a regular array of \(M\)
solitons with spacing $b$ can be found, taking account of their long distance repulsion, as (Bak and Emery 1976)

$$
\frac{G_{\phi}}{fA_0^2} = \frac{M}{L} \frac{8V^{1/2}}{p} \left[ 1 + 4 \exp \left( -p V^{1/2} b \right) \right] - k\delta_0 - \tilde{V} + \frac{\delta_0^2}{2}.
$$

Now using the fact that $\tilde{V} = 2M\pi/pL = 2\pi/pb$ the free energy becomes

$$
\frac{G_{\phi}}{fA_0^2} = \frac{M}{L} \left( \frac{8V^{1/2}}{p} - \frac{2\pi\delta_0}{p} \right) + \frac{4M}{L} \frac{8V^{1/2}}{p} \exp \left( -p V^{1/2} L/M \right) - \tilde{V} + \frac{\delta_0^2}{2}. \quad (1.4.86)
$$

The first term is the free energy of $M$ non-interacting solitons and if $4V^{1/2} > \pi\delta_0$ this is positive and the commensurate phase with $M = k = 0$ is favoured. If, however, $4V^{1/2} < \pi\delta_0$ a state with non-zero $k$ and $M$ exists which is the incommensurate phase. Thus, there will be a continuous transition from the commensurate to incommensurate state when $4V^{1/2} = \pi\delta_0$, which using the relationship between $V$ and the bare interaction $V$, occurs when

$$
A_0 = \frac{\pi^2 \delta_0^2 f/16 V}{p - \frac{1}{2}}.
$$

For larger temperatures, smaller $A_0$, $M$ steadily increases but is limited by the interaction term in eqn. (1.4.86). This interaction has an exponential dependence on $1/M$ so that the temperature dependence of the order parameter, $M$, is given by

$$
\frac{2\pi M}{pL} = \tilde{V} = \frac{2\pi V^{1/2}}{L} \log \frac{\pi\delta_0}{16 V^{1/2}} \frac{1}{4}. \quad (1.4.87)
$$

This form is very difficult to distinguish experimentally from the discontinuity of a first-order phase transition as shown in fig. I.42.

![Fig. I.42](image)

Sketch of the order parameter $k$, units $\delta_0$, against reduced temperature for a lock-in phase transition. (After McMillan 1976.)

The nature of the structure of the phase function $\phi(z)$ in the incommensurate phase is given by

$$
\phi(z) = \phi_0 + \frac{2\pi m}{p} + \theta(z - mb), \quad (1.4.88)
$$
where $m$ is the closest integer to $z/b$. This structure was calculated by McMillan (1976) for the case of $p=3$ and is illustrated in fig. I.43.

This type of phase transition is quite different from those discussed earlier, because the order parameter is not the amplitude of a single Fourier component of the atomic displacements but is the number of domain walls, each of which is well localized in space. This can occur for an incommensurate phase because of the large number of possible order parameters for an incommensurate phase, as discussed in §1.4.4.4. Whenever there is a very large number of order parameters, there is always the possibility of forming linear combinations, such as domain walls, with unexpected or non-perturbative characteristics.

![Fig. I.43](image)

The structure of the phase function $\theta(x) = \theta(z)$ close to a lock-in phase transition with $p=3$. (After McMillan 1976.)

The scattering cross-section from a distorted wave described by $2A_0 \cos (q_0 z + \phi(z))$ can be calculated within the one-phonon approximation using the methods of §1.2.3. The Fourier transform of the distortion is given by

$$F_\sigma(K) = F_+(K) + F_-(K),$$  \hspace{1cm} (I.4.89)

where $K$ is the $z$ component of $\mathbf{K}$, and

$$F_-(\mathbf{K}) = \frac{A_0}{2a} \int \exp \left( i(K-q_0)z - \phi(z) \right) dz,$$  \hspace{1cm} (I.4.90)

which on substituting for $\phi(z)$ from eqn. (I.4.88) becomes

$$F_-(\mathbf{K}) = \frac{bA_0}{2a} f(K-q_0) \exp \left( -i\phi_0 \right) \sum_{m=1}^M \exp \left( i(K-q_0)mb - i\frac{2\pi}{p}m \right),$$

where $f(K)$ is the form factor of the soliton

$$f(K) = \frac{1}{b} \int_{-b/2}^{b/2} \exp \left( iKz - \theta(z) \right) dz.$$  \hspace{1cm} (I.4.91)
The summation over \( m \) yields the total number of domain walls \( M \) provided that the wave-vector \( K \) is given by

\[ K = T_I = q_0 + \frac{2\pi}{b} \left( \frac{1}{p} + l \right), \]  

(I.4.92)

where \( l \) is any positive or negative integer. The location of these Bragg reflections is illustrated schematically in fig. I.44.

Fig. I.44

![Sketch of the Bragg reflections from an incommensurate phase with a soliton ground state.](image)

Now in real systems the distortion of the atoms is the amplitude multiplied by the eigenvector of the soft mode and the crystal is a lattice, not a continuum. If, however, the phase \( \phi(z) \) is varying only slowly within each unit cell then the intensity of the Bragg reflections can be shown to be given by

\[ I(K) = \frac{N^2 A_0^2}{4} |F(K, q_0)|^2 \sum_l \left[ (\Delta(K + T_I) |f(K + q_0 - \tau)|^2 
+ \Delta(K - T_I) |f(K - q_0 - \tau)|^2 \right], \]  

(I.4.93)

where \( \tau \) is a reciprocal lattice vector of the underlying lattice and \( \Delta(K) \) is given by eqn. (I.2.19).

In principle the form factor of the soliton, eqn. (I.4.91), depends on the detailed structure of the soliton, but if the spacing between them, \( b \), is much larger than the thickness, \( 1/p V^{1/2} \), then they may be approximated as phase step functions, when

\[ f(K - q_0) = f(T_I) = \left[ \pi \left( \frac{1}{p} + l \right) \right]^{-1} \sin \left( \pi/p \right) \exp \left( -i\pi/p \right). \]  

(I.4.94)

The relative intensities of the Bragg reflections calculated using this form factor are shown in fig. I.44.

The relative intensities of the Bragg reflections calculated using this form factor are shown in fig. I.44.
Using the form factor eqn. (1.4.94), the sum over $I$ in eqn. (1.4.93) can be performed to give the integrated intensity of these Bragg reflections. This is found to be identical with the intensity of the Bragg reflection of the commensurate phase. Consequently on approaching the lock-in phase transition, the many Bragg reflections of the incommensurate phase become closer and closer together in $\mathbf{K}$ as the number of solitons decreases, but their integrated intensity remains constant.

The phase excitation spectrum of a system of solitons has been calculated by us elsewhere (Bruce and Cowley 1978). In view of the fact that there are no direct measurements with which to compare these results we only briefly comment on the properties. There are two types of phase excitations. The first of these corresponds to oscillations of the solitons about their mean positions. Since the solitons are a regular array in one dimension, $z$, and interact only with nearest neighbours, the dispersion relation for these excitations is given by the usual expression for the excitations of a one-dimensional chain. A detailed calculation gives these frequencies as

$$\omega_p(k)^2 = 8f_p^2 V \exp(-p^2V^{1/2}b)(1 - \cos(k_z b)) + f(k_x^2 + k_y^2).$$  \hspace{1cm} (1.4.95)$$

This dispersion relation is illustrated in fig. 1.45, and for small $k_z$, $\omega_p(k)$ is linear in $k$ due to the translational invariance of the soliton array. The velocity of the phasons decreases as their separation $b$ increases, and as $T \to T_L$ varies as $(T - T_L)^{1/2}$. The scattering cross-section of these excitations can be evaluated and also decreases to zero as $T \to T_L$ because the number of solitons is decreasing.

The other type of excitation consists of fluctuations in the phase of the essentially commensurate regions of the crystal. These excitations have nearly the same dispersion relation and scattering cross-section as the phase excitations of the commensurate phase discussed in §1.4.5.1, as shown in fig. 1.45.
This type of lock-in phase transition occurs in TaSe$_2$ (Moneton et al. 1975), TaS$_2$ (Nakanishi et al. 1977) and in TTF-TCNQ (Comès et al. 1976). The theory accounts qualitatively for the strong satellites observed in TaSe$_2$ and TaS$_2$, but in all cases the transitions are not continuous but of first order, in contradiction with the prediction of the soliton theory.

There are two main defects of the theory (Bruce et al. 1978). Firstly, there is a coupling to the macroscopic strains. Inclusion of this coupling shows that it leads to different effects dependent upon whether or not the strain can follow the phase soliton profile. This is dependent upon whether there are acoustic modes of the correct symmetry to describe the changes in the strains with distance. In our example, $\partial \eta_{zz}/\partial z$ is given by the longitudinal acoustic modes propagating along the $z$ axis and so $\eta_{zz}$ strains can follow the phase solitons and give rise to a change in the effective interaction, a modified $V$ (Bak and Timonen 1978). In contrast there cannot be $\partial \eta_{yy}/\partial z$ components because there are no acoustic modes propagating along $z$ corresponding to $\eta_{yy}$ strains. Consequently there can only be a macroscopic $\eta_{yy}$ strain, which leads to a term in the free energy which is proportional to $M^2$ and negative; exactly analogous to the negative contribution to $u$ discussed in §I.4.3.1 for conventional phase transitions. In the soliton case, however, eqn. (I.4.86) shows that there is not an intrinsic positive term proportional to $M^2$, so this coupling to the strain necessarily drives this transition to be of first order. We are of the opinion that this latter type of coupling may always occur in real systems.

Secondly, if the soliton thickness is only a few lattice constants, it will be energetically favourable for the solitons to be centred on a particular position within the unit cell. The spacing between the solitons will then be an integral number of lattice spacings so that $b = Ja$, and the wave-vectors of the Bragg reflections will be given by

$$T_I = q_0 \left( 1 + \frac{1}{J} (1 + pI) \right).$$

Under these conditions the system will undergo a sequence of first-order transitions between these different commensurate states until it eventually reaches the primary commensurate phase with $T_I = 2\pi/\alpha p$. This sequence of first-order transitions is sometimes known as a Devil’s staircase (Aubry 1977).

The lattice may also produce a very large lock-in energy even though it does not favour any particular $J$. This may then have a large effect on the phase excitations of the system, as the phasons or soliton modes, fig. 1.45, will then have a gap which can be very large compared with the dispersion in the energy.

Throughout this section we have assumed that there are only two components of the order parameter for the commensurate phase $\pm q_0$. In practice the lock-in phase transition in TaSe$_2$ has three pairs of wave-vectors and so there is the possibility of three different types of solitons with interactions between them. As yet comparatively little work has been done on these more complicated systems. Nakanishi and Shiba (1977) suggest that the phase transitions are of first order. Bak (1978) argues that the interaction energy between the different sets of solitons gives rise to a term in the free energy which is proportional to $M^2$. If this interaction energy is negative, attractive, the transition is always of first order. If it is repulsive then there will probably be a transition to a phase with only one set of these solitons frozen into the crystal followed by another first-order transition to a phase with all three sets of solitons.
Long period structures also occur in alloy systems; for example, Oriani and Murphy (1958) showed that in CuAu there was a structure with long periodicity between 650 and 690 K. At 650 K this undergoes a lock-in phase transition to the well-known ordered CuAu structure. The structure with the long periodicity consists of ordered regions of ordered CuAu, of about 5 unit cells in length, separated by domain walls from the next phase. This transition was discussed in terms of an instability of the crystal against domain walls by Inglesfeld (1972). A similar structure has been postulated by Pynn (1978) for the structure of the ε-phase in Zr and Ti alloys. In his model the ε-phase in Zr₀.₅Nb₀.₅ consists of the bcc structure distorted by a commensurate wave-vector,

\[ q₀ = \frac{2\pi}{a} \left( \frac{2}{3}, \frac{2}{3}, \frac{2}{3} \right). \]

The three different domains corresponding to this deformation are then separated by domain walls which are pinned by the local fluctuations in the concentrations of Nb and Zr atoms and so are varying distances apart.

I.4.5.3. Lock-in without soft solitons

There are lock-in phase transitions to those wave-vectors for which the dispersion relations \( \omega(q) \) are necessarily symmetric about \( q₀ \). In these cases the linear term in \( Vq(\phi) \) in eqns. (I.4.82 a, b) is absent and so the theory developed in § I.4.5.2 must be reworked. In the neighbourhood of one of these more symmetric wave-vectors the dispersion relation can be written in the form

\[
\omega(q)² = \omega(q₀)² + f₁ \left[ -δ₀²k_z² + \frac{1}{2}k_z² \right] + f₂(k_x² + k_y²)
\]

which exhibits a minimum for \( k_z \) along the z axis at the point \( k_z = ± δ₀ \). Bruce et al. (1978) have discussed this type of phase transition using the type of approach developed in the previous section. The equation, analogous to the sine–Gordon equation is a fourth-order differential equation, which does not, to our knowledge, have a simple analytic solution. The solutions were, however, studied numerically by looking, in particular, for a solution of a soliton-like character. Such solutions were found but the energy of these solutions is such that the commensurate phase is unstable against the formation of an incommensurate phase with a nearly plane-wave structure before it is unstable against the formation of these soliton-like structures. Accordingly a first order phase transition is predicted.

There are several examples of this type of lock-in phase transition. NaNO₂ (Yamada et al. 1968) has an incommensurate phase with a wave-vector \( q_s \sim 2\pi/8 \) and a lock-in transition to a ferroelectric phase. The transition is of first order and no harmonics of the incommensurate wave-vector have been observed. In thiourea (McKenzie 1975) a similar phase transition is again first order and occurs at 180 K, while weak first harmonics (about 2% of the primary distortion) were found.

I.4.5.4. Improper lock-in transitions

Some lock-in phase transitions are associated with the onset of ferroelectricity, as found in K₂SeO₄ (Iizumi et al. 1977) and (ND₄)₂BeF₄ (Iizumi and Gesi 1977). In
these cases the lock-in terms in the free energy are of the form

$$2^{p+1} W(Q_1^p + Q_2^p) \bar{Q},$$  \hspace{1cm} (I.4.97)

where $\bar{Q}$ is the ferroelectric secondary order parameter.

In an incommensurate phase with wave-vector $q_s$ terms of the form of eqn. (I.4.97) will necessarily give rise to distortions of the secondary order parameter with a wave-vector $\pm q = \pm (pq_s + \tau)$. This gives rise to a lock-in energy only if $\pm q$ are the same wave-vector when there will be a constructive interference between these two distortions resulting in a lower energy for the resulting commensurate phase. Of course, there will also be the possibility of lock-in due to terms of the form

$$2(p+1) V'(Q_1^{2p} + Q_2^{2p}),$$

for these wave-vectors. This term is usually non-zero but has frequently been neglected in the theory of these materials.

When a plane-wave ground state for the incommensurate phase is assumed the theory can be evaluated as given in detail by Iizumi et al. (1977) for $K_2\text{SeO}_4$, and the analysis is very similar to the treatment of secondary order parameters in §1.4.3 and of lock-in phase transitions at the beginning of §1.4.5.2. Since, however, the dispersion relation is not symmetric about $q_s$, this analysis requires further development to examine if soliton-like structures can modify the behaviour. This approach has been developed by Bruce et al. (1978) and soliton-like structures may occur in the phase of the distorted wave. Since, however, the coupling is through a secondary order parameter the free energy includes a negative term in $M^2$, where $M$ is the number of solitons. Consequently, as discussed in §1.4.5.2, the transition is always of first order because there is no positive term in $M^2$ in the soliton interactions.

Shiba and Ishibashi (1978) have also analysed this problem using a Fourier series expansion of the distortions $Q_1$, $Q_2$ and $\bar{Q}$. They find a continuous transition with properties very similar to that of soliton theory given in §1.4.5.2. We believe this is because their numerical work is not sufficiently accurate.

The lock-in transitions in both $K_2\text{SeO}_4$ (Iizumi et al. 1977) and $(\text{ND}_4)_2\text{BeF}_4$ (Iizumi and Gesi 1977) are of first order. In the former case, $p=3$, relatively strong first harmonics of the primary distortion were observed, while in the latter case, $p=2$, no harmonics have as yet been reported.

§1.5. MICROSCOPIC THEORIES

In this section we review the different microscopic models which may be used to calculate the phenomenological parameters of Landau theory. The statistical mechanics of the models is discussed in only the most elementary way, but we focus on the extent to which the models provide a more microscopic picture than Landau theory. Alas the very success of Landau theory in correlating experimental data means that any microscopic model with a few parameters may well be able to fit a large amount of data, but the model may or may not be a correct microscopic description. We therefore examine the different models critically and find that very few can be said to be a justifiable microscopic and quantitative description.
I.5.1. The weakly anharmonic crystal models

I.5.1.1. The soft mode

In crystals with large and temperature independent band gaps, such as SrTiO$_3$, structural phase transitions of the displacive type are almost certainly correctly described by the anharmonic crystal model. The theory of the weakly anharmonic crystal was developed in the early 1960s by Maradudin and Fein (1962) and by Maradudin and Flynn (1963) as reviewed by Cowley (1963). It was applied to ferroelectrics by Silverman and Joseph (1963) and by Cowley (1964).

The basic result is that the one-phonon susceptibility or scattering cross-section can be obtained from the expressions for a harmonic crystal if the harmonic frequencies $\omega(q_j)$ are replaced by

$$\tilde{\omega}(q_j, \omega) = \omega(q_j)^2 + \sum (q_j, \omega),$$

where $\Sigma(q_j, \omega)$ is the anharmonic part of the self-energy and depends on the frequency, $\omega$, used to study the mode in an experiment.

There are three contributions to the self-energy to lowest order in the anharmonicity as shown in fig. 1.46. The first contribution arises from the thermal strain, $\eta_{\alpha\beta}$, and is obtained from eqn. (I.2.10) as

$$\Sigma^T(q_j) = 2 \sum_{\alpha\beta} V_{\alpha\beta} \left( q_j - q_j \right) \eta_{\alpha\beta}^{T}.$$  

This contribution can be obtained from measurements of the strain dependence of the frequencies of the mode and a knowledge of the thermal strain. Recently Samara et al. (1975) have shown that $\Sigma^T(q_j)$ decreases with increasing temperature for all the ferroelectrics they studied, while it increases for all other types of transition. We are unaware of any reason to expect this to be a universally correct observation.

![Diagram of anharmonic contributions](image1.png)

Diagrammatic representation of the anharmonic contributions to (a)-(d) the self-energy of a normal mode and (e)-(g) the quartic term in the Landau expansion of the free energy.
Structural phase transitions

The second contribution to the self-energy in fig. 1.46 arises from the quartic terms in the anharmonic expansion and contributes, using eqns. (1.2.5) and (1.2.7),

$$\Sigma^4(q) = 6\hbar \sum_{q_{ij}} V \left( \begin{array}{c} q - q_{1j} - q_{1j} \\ q_{ij} - q_{1j} - q_{1j} \\ q_{ij} - q_{1j} - q_{1j} \end{array} \right) \frac{(2n(q_{ij} + 1))}{\omega(q_{ij})},$$

(1.5.3)

which at high temperatures $\hbar \omega(q_{ij}) \ll k_B T$ is proportional to $T$. This term usually gives a contribution to the self-energy which increases with increasing temperature.

The third contribution shown in fig. 1.46 arises from the cubic anharmonicity and yields

$$\Sigma^3(q, \omega) = -4.5\hbar \sum_{q_{1j}, q_{2j}} \left| V \left( \begin{array}{c} q \\ q_{1j} \\ q_{2j} \end{array} \right) \right|^2 \times \left[ R(\omega(\omega(q_{1j})))^{-1} [R(\omega) + i\pi S(\omega)] \right],$$

(1.5.4)

where

$$R(\omega) = (n_1 + n_2 + 1)(\omega_1 + \omega_2 + \omega)^{-1} - (\omega - \omega_1 - \omega_2)^{-1}$$

$$+ (n_1 - n_2)(\omega - \omega_1 + \omega_2)^{-1} - (\omega + \omega_1 - \omega_2)^{-1}$$

and

$$S(\omega) = (n_1 + n_2 + 1)(\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2))$$

$$+ (n_1 - n_2)(\delta(\omega + \omega_1 - \omega_2) - \delta(\omega - \omega_1 + \omega_2)),$$

where $\omega_1 = \omega(q_{1j})$, etc. This term has both real and imaginary parts which depend on the frequency $\omega$. The static real part $\Sigma^3(q, 0)$ is negative and increases in magnitude as the temperature increases. The imaginary part is odd in $\omega$ and so at low frequencies can be written as proportional to $\omega$.

The change in the free energy of the crystal/unit cell due to a static distortion, $Q(q)$, is given by (Cowley 1964)

$$G = G_0 + \frac{1}{2} \tilde{\omega}(q, 0)^2 Q(q)Q(-q).$$

(1.5.5)

This result shows that the free energy of the distorted crystal is determined by the same frequencies as the static susceptibility. They may therefore be equated with the frequencies of eqn. (1.4.16) as

$$\omega(k) = \tilde{\omega}(k + q, 0),$$

The calculation of the static frequencies, $\tilde{\omega}(q, 0)$, is then a calculation of the parameters of the quadratic term in the Landau expansion, eqn. (1.4.1). The Landau theory is recovered if $\tilde{\omega}(q, 0)^2 = 0$ at $T_c$, and is positive for higher temperatures; the change in $\tilde{\omega}(q, 0)$ with temperature gives the parameter $a$.

These results imply firstly that the harmonic frequencies are imaginary, so that the crystal is only stabilized by the anharmonic terms. Secondly the Landau theory is obtained only if the anharmonic self-energy is analytically well behaved at $T_c$. The former is the case if the terms in the summations over $(q_{ij})$ in eqns. (1.5.3) and (1.5.4) for which $(q_{ij})$ are the soft modes make a negligible contribution to these summations. Strictly, this approximation is invalid close to $T_c$, as discussed in detail in paper II, but Landau theory is valid if these terms are relatively small which is probably the case for temperatures not too close to $T_c$. 
At low frequencies we can make use of the low frequency expansion of $E(q_s, \omega)$ to give

$$\tilde{\omega}(q_s, \omega)^2 = \omega(q_s)^2 + E(q_s, 0) - 2i\omega \gamma_0,$$

where $\gamma_0$ is a constant. This gives the one-phonon response function as a classical oscillator, eqn. (1.3.22), but is only valid for the range of $\omega$ for which it is possible to replace $E(q_s, \omega)$ by its low-frequency expansion. We shall discuss this further in paper III, but briefly eqn. (1.5.4) suggests that it is valid for frequencies $\omega < a$ typical acoustic mode zone boundary frequency provided that in eqn. (1.5.4) there are not many terms for which $\omega(q_{1,j_1}) = \omega(q_{2,j_2})$.

The higher order terms in the Landau expansion can be obtained in a similar way as shown schematically in fig. 1.45 for the quartic term. Since the leading terms in these expressions are independent of temperature, the Landau theory approximation, that $u$ is independent of temperature, is clearly a reasonable approximation close to $T_c$. Weakly anharmonic perturbation theory provides explicit expressions for the parameters of Landau theory in terms of the anharmonic interactions and normal modes. There is, however, still a quantitative problem because in most simple materials, the anharmonic corrections to the frequencies are a few per cent for temperatures up to the Debye temperature. We need therefore to understand why the corrections are larger in materials undergoing structural phase transitions and to do so with reasonable interatomic interactions. In the next section we describe attempts to do this for SrTiO$_3$.

1.5.1.2. Models of SrTiO$_3$

There have been many attempts to develop microscopic models to describe the behaviour of SrTiO$_3$. Since, however, we are concerned in this section to examine if the behaviour of SrTiO$_3$ can be obtained using reasonable values of the interatomic forces we shall discuss only the most detailed model used, which happens (!) to have been developed largely by Bruce and Cowley (1973). Stirling (1972) measured the phonon dispersion relations for SrTiO$_3$ and fitted these to obtain the parameters of a shell model for the interatomic forces in SrTiO$_3$. This model which had short-range Ti-O and Sr-O interatomic forces and much weaker forces between neighbouring oxygen atoms, provided an accurate description of the frequencies and eigenvectors of the normal modes in SrTiO$_3$. The model was then extended to include the third and fourth derivatives of the interatomic forces between the Ti-O and Sr-O atoms. The third and fourth derivatives of the Sr-O potential and the third derivative of the Ti-O potential were fitted to the anharmonic terms in the Landau theory of the 110 K transition in SrTiO$_3$ as developed in §§1.4.2 and 1.4.3 and initially by Słonczewski and Thomas (1970). With these three parameters it was possible to obtain reasonable values of the Landau parameters and to calculate the different contributions to the self-energy of the soft mode. In fig. 1.47 we show the frequency dependence of $\Sigma^3(q_s, \omega)$ at 300 K. It shows considerable structure but for $\omega < 3$ THz, the real part is well approximated by a constant and the imaginary part is almost linear in frequency as required for the classically damped oscillator to be an accurate description of the soft mode. The different contributions to the self-energy of the soft-mode are shown as a function of temperature in fig. 1.48. As expected the thermal strain contribution is small, and $\Sigma^3$ and $\Sigma^4$ are both large and to a large extent cancel. It is clearly inappropriate to calculate one of these contributions without also including the others. The agreement between experiment and
The temperature dependence of the $q=0$ modes also involves the fourth derivative of the Ti–O force. When this was obtained from the observed temperature dependence its value turned out to be large and furthermore the other properties which depend upon it, such as the non-linear dielectric constant, were not given accurately by the model. Recently Migoni et al. (1976) have suggested that the strong two-phonon Raman scattering arises in a shell model from a very anharmonic shell-core coupling and further that this coupling contributes to the temperature dependence of the ferroelectric mode in perovskites. This may explain why our calculations of those effects which depend upon the fourth derivative of the Ti–O forces were unsatisfactory, but as yet Migoni et al. have not included the other anharmonic effects in their theory.

Although further calculations will no doubt be performed for SrTiO$_3$, we believe that these results have shown that anharmonicity is the origin of the temperature dependence of the soft modes in these materials. Furthermore the anharmonic parameters for the interatomic forces are very much the size to be expected from work on alkali halides. We are left then with the basic question as to why the effect of the anharmonicity is so much larger in SrTiO$_3$ than in, say, KBr. In SrTiO$_3$ the mean

Fig. 1.47

$\Sigma^3(q', \omega)$ of the $R_{2g}$ mode as a function of $\omega$ for SrTiO$_3$ at 300 K (after Bruce and Cowley 1975).

The real part is a dotted line and the imaginary part a solid line.
The different contributions to the self-energy of the $R_{13}$ soft mode in SrTiO$_3$. The dashed line gives $\Sigma^4$, dotted line $\Sigma^3$, fine dashed line $\Sigma^2$, and the solid line $\Sigma^1$. The circles are experimental results. (After Bruce and Cowley 1975.)


<table>
<thead>
<tr>
<th>Quantity</th>
<th>Units</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order parameter, $Q^2/T_c - T$</td>
<td>$10^{-5}$ A$^2$K$^{-1}$</td>
<td>0.165</td>
<td>0.167</td>
</tr>
<tr>
<td>Raman frequency ratio, $\omega^2/\omega_r^2$</td>
<td></td>
<td>9.4</td>
<td>9.25</td>
</tr>
<tr>
<td>Ratio of Raman frequency to frequency above $T_c$, $\omega^2_{\omega(qj)^2}$</td>
<td>2.4</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td>$dT_c$/$dp$</td>
<td>$10^{-2}$ K bar$^{-1}$</td>
<td>0.17</td>
<td>0.178</td>
</tr>
<tr>
<td>$dT_c$/$dp_{(111)}$</td>
<td>$10^{-2}$ K bar$^{-1}$</td>
<td>0.33</td>
<td>0.294</td>
</tr>
<tr>
<td>Thermal expansion at 300 K</td>
<td>$10^{-6}$ K$^{-1}$</td>
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</tr>
<tr>
<td>Elastic distortion, $\eta$/$T_c - T$</td>
<td>$10^{-5}$ K$^{-1}$</td>
<td>0.83</td>
<td>0.77</td>
</tr>
<tr>
<td>Gruneisen $\gamma$</td>
<td>$10^5$</td>
<td>5.67</td>
<td>5.17</td>
</tr>
<tr>
<td>Change in soft-mode self energy between 110 and 450 K</td>
<td>THz$^2$</td>
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<td>4.86</td>
</tr>
<tr>
<td>Soft-mode damping constant $\gamma_0$ at 110 K</td>
<td>THz</td>
<td>0.1</td>
<td>0.06</td>
</tr>
<tr>
<td>Line width of $q=0$ optic modes at 85 K and 47 K</td>
<td>THz</td>
<td>0.09</td>
<td>0.08</td>
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<tr>
<td></td>
<td>0.15</td>
<td>0.17</td>
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The reflectivity of SrTiO$_3$ compared with measurement of Spitzer et al. (1962). (After Bruce and Cowley 1975.)

Frequency of the normal modes is about 8 THz, so that the self-energy effect for the soft mode at 450 K, fig. 1.47, is only about 8% of the mean frequency squared. This is comparable to the anharmonic self-energy in alkali halides at these temperatures. Consequently in SrTiO$_3$ the anharmonic effects are not large, but the harmonic frequencies of the self mode are very small. Possibly this arises because perovskites have three types of ion and only one free parameter, the lattice constant. It is then very likely that one of the atoms is only a loose fit in its site and so can easily be displaced from its high-symmetry position. This type of argument would seem to be nearly as far as we can go in explaining why many perovskites exhibit structural phase transitions.

1.5.2. Order-disorder systems

1.5.2.1. The time-dependent Ising model

A spin representation for describing order-disorder systems was introduced in §1.2. We shall now discuss the calculation of the parameters of the Landau theory for this model and the time-dependent properties using the theory of Glauber (1963) and as developed by Suzuki and Kubo (1968). In their model each spin interacts with a heat bath, which induces spontaneous spin flips. It is then assumed that each spin relaxes back towards its local equilibrium configuration with a time constant, $\tau_0$, which in the simplest form of the theory is independent of the configuration of the neighbouring spins.

In the interest of simplicity we consider a system with one spin in each unit cell, $S(l) = \pm \frac{1}{2}$, when the hamiltonian of the system in an external field $E(l)$ can be
obtained from eqn. (1.2.11) as

\[ H = 2 \sum_{ll'} \phi_2(ll')S(l)S(l') - \sum_l E(l)S(l), \]

where we have assumed that \( \phi_1(l) \) is included in the external field. The local molecular field on the site \( l \) is

\[ E_m(l) = E(l) - 4 \sum_{ll'} \phi_2(\text{1}l') \langle S(l') \rangle \]

and hence within the simplest time-dependent model the equation of motion is

\[ \tau_0 \frac{d}{dt} \langle S(l) \rangle = -\langle S(l) \rangle + \frac{1}{2} \tanh \left( \frac{\beta E_m(l)/2}{k_B T} \right). \tag{1.5.6} \]

The solution of this equation is well known. The susceptibility above \( T_c \) is obtained by expanding the tanh function to leading order when, after a Fourier transformation,

\[ \chi(q, \omega) = \chi(q) \left( 1 + i \omega \tau(q) \right)^{-1}, \quad T > T_c, \tag{1.5.7} \]

where the static susceptibility is

\[ \chi(q) = \frac{1}{4(k_B T - J(q))}, \]

and the interaction \( J(q) \) is given by

\[ J(q) = -\sum_{ll'} \phi_2(ll') \exp\left( i \mathbf{q} \cdot (\mathbf{R}(l) - \mathbf{R}(l')) \right). \]

The relaxation time is given by

\[ \tau(q) = \tau_0 (1 - \beta J(q))^{-1}. \tag{1.5.8} \]

The static susceptibility, eqn. (1.5.7), shows that the phase transition will occur for the wave-vector \( q_s \), for which \( J(q_s) \) is a maximum and at the temperature \( T_c \) such that \( k_B T_c = J(q_s) \). The Debye relaxation form has a relaxation time, \( \tau(q) \), which for \( q = q_s \) diverges as \((T - T_c)^{-1}\).

We can obtain the parameters of the Landau theory for these systems by comparing these results for the susceptibility with those obtained in § 1.4, and also by comparing the expressions for the order parameter, \( Q_0 = N^{-1/2} \langle S(q_s) \rangle \) for \( T < T_c \). The latter is obtained from eqn. (1.5.6) by expanding the tanh to third order terms to give

\[ Q_0^2 = -\frac{3(2k_B T - J(q_s))k_B^2 T^2}{4J(q_s)^3}, \]

when we can identify the parameters of the Landau theory as

\[ R(k) = 4(k_B T - J(q_s + k)), \tag{1.5.9} \]

and close to \( T_c \)

\[ u = \frac{4}{3} k_B T_c. \tag{1.5.10} \]
Structural phase transitions

Consequently the parameters of Landau theory can be obtained with this model once $J(q)$ is known, and the relaxation time $\tau_0$. A feature of this model which is simpler than the weakly anharmonic crystal model is the way in which the same interaction $J(q_s)$ determines both $T_c$ and $\alpha$, whereas in the other model there is no direct relationship between them.

1.5.2.2. The tunnelling model

In the introduction we described an order-disorder system by using a spin variable $S(l)$ which, for example, described the orientation of the NO$_2$ molecular groups. In some systems quantum-mechanical tunnelling between the two wells lifts the degeneracy of the two orientations and the wavefunctions are either the symmetric or antisymmetric linear combinations. This type of two level system can always be described by an $S=\frac{1}{2}$ spin system but the spin is now a vector. In this case the $S^z$ component describes the location of the ion and the $S^x$ component the tunnelling between the sites. A careful discussion of the derivation of the effective spin hamiltonian for the KH$_2$PO$_4$ system has been given by Tokunaga and Matsubara (1966) and is reviewed by Blinc and Zeks (1974). In the simplest case the hamiltonian of the tunnelling model with one spin/unit cell is

$$H = 2\sum_{ll'} \phi_2(ll')S^z(l)S^z(l') + \sum_l (2\Omega S^y(l) - E(l)S^z(l))$$ (I.5.11)

where $\Omega$ is the tunnelling integral, and we have assumed that the external field couples only to the $z$ component of the spin.

This hamiltonian can be solved within the molecular field approximation as described in the last section and by Blinc and Zeks (1974). The molecular field is a vector

$$E_m(l) = \langle -2\Omega, 0, -4\sum_{l'} \phi_2(ll') \langle S^z(l') \rangle + E(l) \rangle$$

and the static susceptibility becomes

$$\chi(q) = \frac{1}{4(\Omega \coth \beta \Omega - J(q))}$$ (I.5.12)

This shows that a phase transition occurs when $\coth \beta \Omega = J(q_s)/\Omega$, and that the ordered phase is described by the wave-vector $q_s$ for which $J(q)$ is a maximum. This result reduces to that of § 1.5.2.1, namely $k_B T_c = J(q_s)$ where $\Omega$ is small, and as the tunnelling integral becomes larger there is a decrease in $T_c$. This explanation for the transition temperature being much lower in KH$_2$PO$_4$ than in KD$_2$PO$_4$ was the original motivation for the development of the tunnelling model (Blinc 1960).

The parameters of the Landau theory are given by

$$\omega(k)^2 = R(k) = 4(\Omega \coth \beta \Omega - J(q_s + k)),$$ (I.5.13)

which close to $T_c$ becomes

$$R(k) = 4 \left[ \frac{\beta \Omega}{\sinh (\beta \Omega)} \right]^2 k_B(T - T_c) - J(q_s + k) + J(q_s),$$ (I.5.14)

showing that the parameter $\alpha$ depends on the tunnelling integral.

The quartic parameter, $\alpha$, in eqn. (I.4.1) can be found by calculating the temperature dependence of the order parameter using the molecular field theory.
The result, after some algebra, is that

$$u = \frac{2J^3(q_0)}{\Omega^2} \left[ 1 - \frac{\beta_c J(q_0)}{\cosh^2 (\beta \Omega)} \right]$$

(I.5.15)

which reduces to the result (I.5.10) in the $\Omega \rightarrow 0$ limit.

These results show that expressions for the Landau parameters may be obtained from the tunnelling model. The effect of the tunnelling is to decrease $T_c$ and $a$, and to increase $u$.

In addition to these static results, the tunnelling model has also been used to calculate dynamical properties. Within the random phase approximation the Heisenberg equations of motion for the spins lead to a tunnelling frequency for $T > T_c$ (Brout et al. 1966, Blnic and Zeks 1974) given by

$$h^2 \omega_T(k)^2 = 4\Omega(\Omega - J(q_0 + k) \tanh (\beta \Omega)).$$

(I.5.16)

For $k=0$ this frequency decreases to zero as $T' - T_c$, but is given by a different expression to the 'frequencies' of the Landau theory, eqn. (I.5.13). These tunnelling frequencies are quantum mechanical in origin and not the same as the Landau frequencies. This is because in the tunnelling model the spin is a vector and the tunnelling corresponds to the application of a field in the $x$ direction. This causes a part of the spin to align along $x$, with a consequential reduction in the fraction which aligns along $z$, and hence in the susceptibility which depends directly only on the $z$ component.

Before proceeding it is interesting to compare the tunnelling model with the Glauber model discussed in the previous section. In both models a mechanism is put forward by which the particle at site $l$ changes its spin. In the Glauber model, this is by contact with a heat bath when a thermal fluctuation permits the particle to surmount the potential barrier between the two spin values, while in the tunnelling model the particle tunnels through the barrier quantum mechanically. Clearly the former process will tend to be the dominant process at high temperatures and with heavy molecular groups, while the latter will be the more likely at low temperatures and if only light atoms are moving at the transition. This is the case at a number of orientational transitions.

I.5.2.3. Spin–phonon interaction

In order–disorder materials there is often a coupling between the spin and the displacements of the atoms. For example, in NaN02, the force on a displaced Na ion is clearly dependent upon the orientation of the neighbouring NO2 groups (fig. 1.3). The interaction can be expanded as a double power series in the spins and the displacements, but we assume (although it is certainly not always valid) that only the leading term is important,

$$H_I = \sum_{a l l'} W_a(l' l) u_a(l) S(l'),$$

(I.5.17)

where for simplicity we are not including tunnelling effects in this section, and $W_a(l')$ gives the change in the force on atom $l$ when the $l'$ orientation is altered.

If the motion of the displacements is very much more rapid than that of the spins the displacements will take up average positions which are dependent on the
particular spin coordinates. These average positions are most readily found by rewriting the interaction in terms of Fourier coordinates

$$H_I = \sum_{\mathbf{q}} W(\mathbf{q}, \mathbf{j}) \hat{Q}(\mathbf{q}, \mathbf{j}) S(-\mathbf{q}),$$  \hspace{1cm} (I.5.18)

when the instantaneous equilibrium positions of the displacements are given by

$$\hat{Q}(\mathbf{q}, \mathbf{j}) = -\frac{W(\mathbf{q}, \mathbf{j})}{\omega(\mathbf{q}, \mathbf{j})^2} S(\mathbf{q}),$$  \hspace{1cm} (I.5.19)

and the normal modes of vibration are now oscillations about these displaced positions, but in this approximation their frequencies are unchanged.

Using eqn. (I.5.19) to eliminate the $Q(\mathbf{q}, \mathbf{j})$ in the Hamiltonian for $H_I$ and the phonon Hamiltonian, leads to an effective interaction between the spins which in Fourier space is given by

$$J(\mathbf{q}) = J(\mathbf{q}) - \frac{1}{8} \sum_{\mathbf{j}} \frac{|W(\mathbf{q}, \mathbf{j})|^2}{\omega(\mathbf{q}, \mathbf{j})^2}. \hspace{1cm} (I.5.20)$$

Unfortunately, this result is not completely correct because $J(\mathbf{q})$ is derived from the interactions between different sites $l$ and $l'$. An interaction between a spin and itself cannot contribute to the ordering of the spins and consequently that part of the phonon modulated interaction must be subtracted from the effective interaction. The correct result (Kanamori 1960) is

$$J(\mathbf{q}) = J(\mathbf{q}) - \frac{1}{8} \sum_{\mathbf{j}} \frac{|W(\mathbf{q}, \mathbf{j})|^2}{\omega(\mathbf{q}, \mathbf{j})^2} \cdot \frac{1}{8N} \sum_{\mathbf{q}, \mathbf{j}} \frac{|W(\mathbf{q}, \mathbf{j})|^2}{\omega(\mathbf{q}, \mathbf{j})^2}. \hspace{1cm} (I.5.21)$$

The effect of the spin–phonon coupling is then to lead to a modification of the interaction between the spins. This is of particular importance in that the acoustic mode part of eqn. (I.5.21) may lead to a long-range interaction between the spins which falls off only as $1/R^3$ (Sugihara 1959).

Another consequence of the coupling is that the susceptibility or scattering is now a coupled phonon–spin problem. For example, the scattering cross-section from the spin variables, eqn. (I.2.45), is now modified to give an effective structure factor

$$\bar{F}_s(\mathbf{K}, \mathbf{q}, \mathbf{j}) = F_s(\mathbf{K}, \mathbf{q}, \mathbf{j}) - \frac{W(\mathbf{q}, \mathbf{j})}{\omega^2(\mathbf{q}, \mathbf{j})} F(\mathbf{K}, \mathbf{q}, \mathbf{j}),$$

showing that there will be an interference between the scattering from the spin and the phonon modes.

Much of the theory discussed in this section was developed initially for coupled spin–phonon problems in magnetism. It was applied to order–disorder systems by Sakurai et al. (1970) and by Yamada et al. (1972) and to the tunnelling model by Kobayashi (1968).

Finally, in this section we have assumed that the normal modes of vibration could follow the spin coordinates. This is not possible for the long wavelength acoustic modes and in the tunnelling model may not be possible for other modes. The dynamics can then only be discussed once the dynamical response of both spin and normal mode systems is known and their coupling will give rise to effects similar to those described for coupled acoustic and optic modes in §I.4.1.5.
I.5.2.4. Applications to real systems

Throughout this article NaN\textsubscript{2} has been used as an example of an order–disorder system. The first application of the order–disorder theory to NaN\textsubscript{2} was by Yamada and Yamada (1966) to explain their diffuse X-ray scattering measurements (fig. I.19). The NO\textsubscript{2} groups have a dipole moment which may be aligned along the positive or negative b axis (fig. I.3). They calculated the dipolar interaction between the rigid dipoles and found that this part of $J(q) = -D(q)$ gave a contribution with a maximum very close to the wave-vector of the incommensurate phase, and a transition temperature only 50% higher than the observed one (fig. I.19). When they introduced short-range forces between neighbouring dipoles they were able to produce a very good agreement with their experimental results with only three parameters specifying the three nearest neighbour forces.

Unfortunately further developments have questioned the validity of this agreement. In the ferroelectric phase of NaNO\textsubscript{2} the Na are displaced from the mid-points between the NO\textsubscript{2} ions (Kay 1972). This means that in addition to the direct dipole—dipole interaction there is also a phonon-modulated interaction as described in the previous section. When Sakurai et al. (1970) used models describing the normal modes of NaNO\textsubscript{2} to include this extra interaction between the NO\textsubscript{2} groups, they were no longer able to obtain a stable incommensurate phase. The situation is therefore unsatisfactory.

The dynamics of the ordering in NaNO\textsubscript{2} was studied by Hatta (1968) using dielectric measurements (fig. I.13). These results are well described by the model described in §1.5.2.1 with a relaxation time, $\tau_0$, given by Eyring’s reaction rate theory as

$$\tau_0 = \frac{2\pi \hbar}{k_B T} \exp \left( \frac{U_B}{k_B T} \right),$$

where $U_B$ is the potential barrier between the two positions of the NO\textsubscript{2} groups. Assuming that $U_B$ is weakly dependent upon temperature but approximately $7k_B T_N$ and taking $J(q)$ from the work of Yamada and Yamada (1966) described above, Yamada et al. (1968) obtained a good description of the experimental results as shown in fig. I.13.

The ammonium halides crystallize in the CsCl structure, and the tetrahedral NH\textsubscript{4} molecule has two possible orientations depending upon which four of the neighbouring halide ions are closest to the H atoms. These two orientations can be described by a spin variable as introduced in §1.2. The distorted phase of NH\textsubscript{4}Br and NH\textsubscript{4}I is the $\gamma$-phase which has an antiferrodistortive arrangement of the spins described by a wave-vector $q_\gamma = \left( \frac{1}{2}, \frac{1}{2}, 0 \right) 2\pi/a$. On the other hand NH\textsubscript{4}Cl and NH\textsubscript{4}Br at low temperatures form the $\delta$-phase which is a ferrodistortive phase, $q_\delta = 0$.

The direct interaction between the NH\textsubscript{4} ions is an octupole–octupole force and the corresponding $J(q)$ was calculated by Nagamiya (1943). The result is shown in fig. I.50 and favours the ferrodistortive phase. The X-ray structure determination of NH\textsubscript{4}Br by Terauchi et al. (1972) showed that the Br ions become displaced at the transition. Consequently Yamada et al. (1972) developed the theory using the spin–phonon approach described in §1.5.2.3. Although the resulting theory inevitably involved a large number of parameters, it did show that the spin–phonon coupling favoured an antiferrodistortive ordering as illustrated in fig. I.50. The total effective exchange interaction $\tilde{J}(q)$ might then favour either ferrodistortive or antiferrodistortive distortions dependent upon the size of these two terms.
The exchange interaction between spins in the ammonium halide NH$_4$Br after Yamada et al. (1972). The direct interaction is given by $\cdots$, the spin-phonon by $\cdots \cdots$, and the total effective coupling by $\cdots \cdots$.

Another mechanism favouring the antidistortive structure was proposed by H"{u}ller (1972), who suggested that the octupole on the NH$_4$ ion produced an electronic dipole on the neighbouring halide which then produced an electric field on the other NH$_4$ ions. This is clearly similar to the phonon mechanism except that the phonon mechanism produces an ionic dipole instead of an electronic dipole. At present the relative magnitude of these different effects is still uncertain, as reviewed by Vaks and Schneider (1976).

Possibly even more successful has been the theory of the phase transitions in methane. There are several phase transitions at which the different methane molecules within the unit cell order in position. James and Keenan (1959) suggested that the force was an octupole—octupole force and this gives the correct structure (Press 1972), and the anisotropy of the critical scattering (H"{u}ller and Press 1972). Although the agreement with experiment is not perfect, it is sufficiently satisfactory to suggest that the nature of the force between the methane molecules is largely understood.

In other molecular materials such as N$_2$ the form of the intermolecular interaction and the effect of the electrostatic forces in polarizing the ions is less well understood. For some recent work on the problem of obtaining a potential for N$_2$, we refer to the work of Kjems and Dolling (1975) and of Raieh and Gillis (1977).

Finally we comment on the validity of the tunnelling model for describing the KH$_2$PO$_4$ (KDP) class of materials. The original motivation behind the development of the tunnelling model was the ease with which it explains the large isotope effect ($T_c$ for KH$_2$PO$_4$ is 123 K, and is 220 K for KD$_2$PO$_4$) since the change in mass will clearly make a large difference to the tunnelling integral. This was supported also by the results of dynamical Raman scattering experiments which showed for KH$_2$PO$_4$ an overdamped mode but with a considerable spectral width (fig. 1.22), while for KD$_2$PO$_4$ the spectral width was at least an order of magnitude smaller (White et al. 1970). This is in agreement with the predictions of the tunnelling model if $\Omega$ is much larger for KH$_2$PO$_4$ than for KD$_2$PO$_4$, although the simple model fails to explain why
the mode is overdamped. These successes were also supported by the result of the measurements of the decrease in the transition temperature with increasing pressure by Samara (1971) and of an underdamped soft mode at high pressure by Peercy (1973). These results were assumed to arise because the H–H distance decreased with increasing pressure and hence the overlap integral rapidly increases.

The difficulties for the theory are that all the atoms move in the ferroelectric motion (Skalyo et al. 1970), consequently there is a strong coupling between the hydrogen tunnelling and the other normal modes. Although this can in principle be included using the theory of Kobayashi (1968), this of necessity requires the introduction of many parameters, which makes agreement almost inevitable. Paul et al. (1970), in fact, conclude that it is not possible to obtain a good agreement between experiment and theory by assuming that the only effect of deuteration is to change the tunnelling integral. Furthermore Nelmes et al. (1978) have performed a structure determination under pressure which suggests that the difference between the minima in the H potential is not pressure dependent. If this result is confirmed it invalidates the simple tunnelling-model explanation of the pressure dependent results. In conclusion Nelmes et al. (1972) show that the structures of KH₂PO₄ and KD₂PO₄ differ so it is hardly to be expected that the model will be appropriate if only the tunnelling integral is assumed to depend on deuteration.

This leads us to the question of whether the tunnelling model is a good description of the KDP materials. The motion of the H atoms is certainly correlated with the motion of all the other atoms in the structure. This coupling alters the effective exchange coupling, §1.5.2.3 (Kobayaski 1968), but its effect on the tunnelling integral Ω is never discussed. Since the neighbours of an H atom move, the potential is locally not symmetric about the centre making the tunnelling to the other side more difficult. If, however, a cooperative tunnelling model is adopted the effective mass of all the atoms is clearly sufficiently large that tunnelling will be relatively unimportant compared with the hopping described by the Glauber model, §1.5.2.1. Certainly the results on KDP could be described by a soft mode with a large and very temperature dependent damping, and a frequency which was altered greatly on deuteration or by the application of pressure. Clearly further work is needed before we have a microscopic theory of these systems which lie between the displacive and order–disorder extremes.

### 1.5.3. Electron–phonon models

#### I.5.3.1. The formalism

It is frequently convenient to divide the interatomic force between two ions into two parts; a direct ion–ion interaction and an interaction mediated by the electrons, although the distinction between the ions and the other electrons is dependent upon the particular problem and assumptions. The calculation of the frequencies of the normal modes, or of the energies in the spin representation, is then a very complex subject as shown by the reviews in Horton and Maradudin (1974). In this section we attempt only to outline the essential points of the development with particular reference to the effects which may lead to structural phase transitions.

The potential seen by an electron in the crystal at the point, r, may be expanded as a power series in the normal-mode coordinates

\[ W(r) = W^0(r) + \sum_{q_j} W(q_j, r) \Phi(q_j) + \ldots \]  
(1.5.22)
Structural phase transitions

The change in the potential at \( r \) due to a normal mode \( (q_j) \), then causes a change in the electron distribution at the point \( r' \) which results in a change in the energy of the normal mode. If we assume that the symmetry is such that mode \( q_j \) couples only to itself, then the electron-phonon contribution to its self-energy is

\[
\Sigma^E (q_j) = -\int W(q_j, r) W(-q_j, r') \chi^E(r, r') \, dr \, dr'. \tag{1.5.23}
\]

where \( \chi^E(r, r') \) is the electron density response function. The frequency of the normal mode is given by

\[
\omega(q_j)^2 = \omega^B(q_j)^2 + \Sigma^E(q_j), \tag{1.5.24}
\]

where \( \omega^B(q_j) \) is the contribution to the frequency arising from the direct ion–ion interaction, and also from the second-order terms in the expansion of \( W(r) \) in powers of \( Q(q_j) \).

It is often convenient to rewrite eqn. (1.5.23) in terms of Fourier components by making use of translational invariance when

\[
\Sigma^E(q_j) = -\sum_{\tau, \tau'} W(q + \tau, j) W(-q - \tau', j) \chi^E(-q - \tau, q + \tau'). \tag{1.5.25}
\]

where

\[
W(q + \tau, j) = \int W(q_j, r) \exp(-i(q + \tau) \cdot r) \, dr. \tag{1.5.26}
\]

It is of interest to compare this result with the developments of §§ 1.4.1.6 and 1.5.2.3. In the latter case \( \omega(q_j)^2 \) is the inverse susceptibility of the phonon normal mode with which the spins are interacting; eqn. (1.5.20) for \( J \) is then of the same structure as eqn. (1.5.25). The extra complication of the sum over \( \tau \) and \( \tau' \) arises because the electron distribution is defined for all \( r \), whereas the phonon displacements or spin variables are defined only at the lattice points.

Equation (1.5.24) shows that a structural phase transition will result if \( \Sigma^E \) becomes sufficiently negative, while eqn. (1.5.25) shows that this may occur if either the electron–phonon interaction, \( W \), is sufficiently large or the electronic susceptibility is sufficiently large. In particular eqn. (1.5.25) shows that whenever there is an instability of the electron gas, \( \chi^E \to \infty \), then unless the electron–phonon coupling happens to be zero, there will always be a structural phase transition which occurs at a temperature somewhat in excess of the temperature at which the electronic system alone is unstable (cf. the difference between the clamped and free transition temperatures in § 1.4.1.6). We are therefore concerned with the possible instabilities of the electronic system, which may take on a variety of different forms; for example, Jahn–Teller instabilities, charge density wave instabilities, spin density waves, Wigner crystallization and the Mott metal–insulator transition.

Before discussing some of these transitions in more detail, it is, however, useful to collect together some expressions (Sham 1974) for the electron–phonon interaction and the electronic susceptibility for systems with electron energy bands. If the electron–ion pseudo-potential is \( v_\kappa(r - r(lk)) \) then the electron–phonon interaction is given by

\[
W(q_j, r) = \sum_{l_k} \left( \frac{1}{NM_\kappa} \right)^{1/2} e(\kappa, q_j) \cdot \nabla_{R(lk)} v_\kappa(R(lk)) \exp(iq \cdot R(lk)). \tag{1.5.27}
\]
If the electrons do not interact with one another and are described by Bloch waves with a wave-vector \( \mathbf{k} \) and band index \( \lambda \) and have energy \( v(\mathbf{k}, \lambda) \), then the electronic susceptibility becomes

\[
\chi^0(\mathbf{q} + \mathbf{\tau}, -\mathbf{q} - \mathbf{\tau}) = -\sum_{\lambda'} \sum_{\mathbf{k}} \frac{n(\mathbf{k}, \lambda) - n(\mathbf{k} + \mathbf{q}, \lambda')}{v(\mathbf{k}, \lambda) - v(\mathbf{k} + \mathbf{q}, \lambda')} <\lambda|\exp(i(\mathbf{q} + \mathbf{\tau}) \cdot \mathbf{r})|\mathbf{k} + \mathbf{q}, \lambda'| \langle \mathbf{k} + \mathbf{q}, \lambda' | \exp(-i(\mathbf{q} + \mathbf{\tau}) \cdot \mathbf{r})|\lambda\rangle,
\]

where \( n(\mathbf{k}, \lambda) \) is the Fermi occupation number.

In practice electrons interact with one another through a potential whose Fourier transform we write as \( v^E(\mathbf{q}) \). Within the random-phase approximation the electronic susceptibility is then given by a matrix equation in \( \mathbf{\tau} \) and \( \mathbf{\tau}' \) which we can write schematically as

\[
\chi^E = \chi^0 - \chi^0 v^E \chi^E.
\]

The form of \( v^E(\mathbf{q}) \) is in general unknown: within the Hartree approximation \( v^E(\mathbf{q}) \) is given by the Fourier transform of the Coulomb interaction, but usually modifications are made to this form of \( v^E(\mathbf{q}) \) to incorporate the effects of exchange and correlation at least approximately.

### 1.5.3.2. Jahn–Teller systems

The simplest and most elegant examples of the cooperative Jahn–Teller effect occur in the rare earth zircons as reviewed in detail by Gehring and Gehring (1975). In these systems, DyVO₄, TmVO₄ and TbVO₄ for example, the 4f electrons on the rare earth ions are well localized and have a strong spin–orbit splitting. The lowest \( J \) multiplet is then split by the crystal field which, in the high-symmetry phase of these materials, is a tetrahedral field. In the simplest case, TmVO₄, the ground state of the Tm ion is a degenerate state whose degeneracy can be lifted by a distortion of the tetrahedral crystal field.

Since the 4f electrons are well localized this problem is particularly simple because we can calculate the electronic response, \( \chi^E \), for each rare earth ion independently when, using eqn. (1.5.23), we obtain

\[
\Sigma^E(\mathbf{q}, \mathbf{\tau}) = -|W(\mathbf{q}, \mathbf{\tau})|^2 \chi^E.
\]

In §1.5.2.1 we calculated the susceptibility of a two-level spin \( S = \frac{1}{2} \) system. We can use the results for TmVO₄ if we neglect the interactions between the different spins, when \( \chi^E = \frac{1}{2} \beta \), where we have labelled the two electronic levels by the spin variable. The phase transition then occurs at the temperature \( T_c \) given by the maximum value of \( |W(\mathbf{q}, \mathbf{\tau})|^2/(4\beta g_0 \omega(\mathbf{q}, \mathbf{\tau})^2) \), which also determines the wave-vector and branch index of the soft mode.

In the rare earth zircons the degeneracy of the electronic ground state is split by a shear of the surrounding tetrahedron, and the structure is such that the most energetically favourable mode is the acoustic shear mode determined by the elastic constant \( C_{11} - C_{12} \). In other instances the soft mode is more complicated as for the Jahn–Teller distortion of the Cu ions in \( K_2 \text{PbCu(NO}_2)_6 \) for which the unstable mode has an incommensurate wave-vector \( q = (0.425, 0.425, 0) \) \( 2\pi/a \) (Yamada 1977).

Jahn–Teller phase transitions may also occur even if the electronic ground state of the high-temperature phase is not degenerate. Consider a two-level system with a
splitting Ω, while the distortion of crystal field causes transitions between these states. This is then an isomorphous problem with the tunnelling model discussed in §1.5.2.2, and the electronic susceptibility can be obtained from eqn. (I.5.12) with \( J = 0 \). The high-temperature phase is stable only while
\[
\Omega \coth \beta \Omega < \frac{W(q_j)^2}{4\omega^2(q_j)^2},
\]
which shows that there is a critical value of the splitting beyond which there is no ordering. This type of behaviour occurs in DyVO₄ and TbVO₄ although the crystal field structure is more complex than the doublet discussed above (Gehring and Gehring 1975). In magnetism this behaviour is known as an induced moment system (Grover 1965). This approach has been remarkably successful in explaining the properties of the rare earth zircons. Although it is not possible to calculate the electron–phonon interactions \( W(q_j) \) from first principles, a very successful theory has been developed with relatively few adjustable parameters and this theory gives a good account of a very large quantity of experimental data, as reviewed by Gehring and Gehring (1975).

More complications arise in the theory of the rare earth pnictides because they are metals or semi-metals: the conduction electrons give rise to an interaction between the different rare earth ions. Qualitatively the theory can then be developed as above but using the full interacting susceptibilities of §§ 1.5.2.1 and 1.5.2.2 for the electronic susceptibility instead of the non-interacting susceptibilities used above, but it is then almost impossible to make calculations.

Finally this theory may be invalid for the 3d transition metal ions because in these systems there is a very strong coupling between the electronic levels and the surrounding ionic environment so that keeping only the leading terms in the expansion (I.5.22) is invalid. It is then possible to proceed by treating the interaction between an ion and its local environment using cluster methods, and coupling up the clusters using a mean field theory, as described by Thomas (1977). Of course difficulties then occur when the cluster around one 3d ion contains ions which are also part of the cluster surrounding another rare earth ion.

### 1.5.3.3. Charge density waves

In this section we discuss the structural phase transitions associated with charge density waves in metallic systems, as elegantly reviewed in more detail by Friedel (1977). The electronic susceptibility is dependent upon (eqn. (I.5.28))
\[
I(q) = \frac{\sum_{k\lambda} n(k\lambda) - n(k + q\lambda')}{v(k\lambda) - v(k + q\lambda')}. \tag{I.5.30}
\]
This expression and hence \( \chi^0 \) will become large if the electron energy denominators are small. In metallic systems this occurs particularly when the states \((k + q\lambda')\) and \((k\lambda)\) are both at the Fermi level. Now, for any direction of \( q \), there will be a limiting value of \( q = K_F \) such that for \( q > K_F \) both \((k + q\lambda')\) and \((k\lambda)\) may be at the Fermi surface but not for \( q < K_F \) or vice versa. We therefore expect a special contribution to \( I(q) \) when \( q \) is close to these wave-vectors. There are three cases of importance.

(a) If the two Fermi surfaces have a tangent plane but different curvatures, as found in a [3d] free-electron system, the \( I(q) \) becomes
\[
I(q) = K_1 + K_2 p \log |p|. \tag{I.5.31}
\]
where $K_1$ and $K_2$ are constants while $q \parallel K_F$ and $p = |q - K_F|$. This shows that $I(q)$ has an infinite derivative (Kohn 1959) when $q = K_F$, and hence $I(q)$ cannot be a maximum for these wave-vectors. In this instance a charge density wave will not occur with $q_c = K_F$.

(b) If the two Fermi surfaces have a common tangent and one common curvature then

$$I(q) = K_1 + K_2/(K_3 + p^{1/2}). \quad (I.5.32)$$

This is the form of the expression obtained for a $[2d]$ free-electron system and shows that there may be a maximum in $I(q)$ when $q = K_F$. This suggests that there may be a charge density wave instability with $q_c = K_F$.

(c) If the Fermi surfaces have a common tangent and two common curvatures, then

$$I(q) = K_1 + K_2 \log |p|, \quad (I.5.33)$$

which is the divergent expression characteristic of a $[1d]$ electron system (Peierls 1955, Froehlich 1954). This suggests, neglecting electron–electron interactions, that a structural phase transition will always occur in this case, and the behaviour is known as an example of perfectly nesting Fermi surfaces.

These concepts originated with the work of Jones (1934) on the crystal structure of alloys. In our cases (b) and (c), the lattice distortion, if it occurs, opens up a gap in the electron energy spectra at the Fermi level. Consequently there are new Brillouin zone boundaries and a lowering of the total electron energy in the distorted phase.

Before discussing the application of these concepts in practice, it is necessary to mention the role of the electron–electron interactions. For simplicity we consider the case of nearly free electrons, when $\chi^E(q + \tau, -q - \tau)$ becomes diagonal in the wave-vector, and furthermore we neglect the effect of Umklapp processes. We can then write eqn. (I.5.25) as

$$\Sigma^E(q,j) = -|W(q,j)|^2 \frac{I(q)}{1 + v^E(q)/I(q)},$$

which then leads to a condition for the stability of a normal mode from eqn. (I.5.24) as (Chan and Heine 1973)

$$\frac{|W(q,j)|^2}{\omega^B(q,j)^2} - v^E(q) < \frac{1}{I(q)} \quad (I.5.34)$$

where $v^E(q)$ is the Fourier transform of the electron–electron interaction and in the Hartree approximation is positive and given by $e^2/\epsilon_0 g^2$. Equation (I.5.34) has the unexpected property that in the absence of electron–phonon interaction, there would be no charge density instabilities of an electronic system because $I(q)$ is necessarily positive (Friedel 1977). It shows furthermore that charge density wave instabilities occur even in $[1d]$ systems only if $|W(q,j)|^2/\omega^B(q,j)^2$ is sufficiently large. A completely convincing theory of a structural phase transition can be carried out only if there is a careful calculation of the electron–phonon interaction $W(q,j)$, the susceptibility $I(q)$ and the electron–electron interactions $v^E(q)$.

In practice this programme has not been carried out to completion for any system. Many of the calculations have concentrated on calculating the core of the non-interacting electronic susceptibility, $I(q)$, by using simple models and more
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recently by using the results of detailed band structure calculations. In the case of the [1d] conductors such as KCP(K₂Pt(CN)₄Br₅·3H₂O) (Comès et al. 1973 a) and TTF-TCNQ (Comès et al. 1973 b) the distorted structure has a wave-vector \( \mathbf{K}_F \) along the chain direction which is exactly consistent with the expected value of \( \mathbf{K}_F \) from the known electron density. Consequently there is no doubt that the distorted structure results from the peak in the electronic susceptibility for \( q = \mathbf{K}_F \) predicted by eqn. (I.5.33). Electron–electron interactions play a role however not only for the interactions along the chains, but also in giving rise to forces between the chains (Barisic 1971) without which there would not be a transition to a [3d] ordered structure. Clearly until the theory of the interacting [1d] electron gas is more perfectly understood we cannot hope to have a completely satisfactory theory of these materials.

The layered transition metal dichalcogenides have distorted phases described by incommensurate wave-vectors. These were initially assumed to arise from cylindrical parts of the Fermi surface associated with the layered structure, giving rise to a corresponding peak in \( I(q) \). This model, however, fails to explain why different examples of the series have very similar periodicity for the charge density waves: NbSe₂ and TaSe₂ both have incommensurate phases with \( q_s = (1 - \delta) \alpha^* / 3 \) with \( \delta \approx 0.02 \). Furthermore calculations by Myron et al. (1977) of \( I(q) \) using a self-consistent muffin tin potential for TaSe₂ show only a very weak peak for \( q \approx q_s \), and similar calculations for TaS₂ give a peak at larger wave-vectors than \( q_s \) (fig. 1.51). Clearly the nature of the electron–phonon interaction, and of the electron–electron interactions in these materials is of crucial importance.

In the A15 compounds, Nb₃Sn and V₃Si, the situation is also confused. The first model proposed to explain the transition was put forward by Labbe and Friedel (1966). Essentially their model describes the shear as arising from an inequivalence of the electron energy bands in the different directions of the distorted crystal. There is then a redistribution of the electrons and a consequent lowering of the energy. This effect is included in the calculation of \( I(q) \) in eqn. (I.5.33), but is only large enough to give an instability if the density of states at the Fermi surface is large. Labbe and Friedel obtained a large enough density of states by postulating [1d]-like bands arising from the chains of metal atoms in the A15 structure. The symmetry of the A15 structure also causes a degeneracy of the electron energy bands at the [100] zone boundary. If the crystal distorts, this degeneracy is lifted and Gorkov (1973) suggested that if the Fermi surface was nearly [1d] and very close to the [100] zone boundary this splitting would account for the transition. Unfortunately Mattheiss’s calculations (1965, 1975) of the band structure failed to substantiate these simplified models of the band structure and in more recent theories, such as those of Bhatt (1977), it is difficult to obtain a simple physical picture.

Calculations on other systems have been less ambitious.

I.5.3.4. Other charge density waves

Besides the charge density waves associated with the Fermi surface effects described above, there are a number of structural phase transitions associated with other types of electronic instability. In this section, we only briefly indicate some of these transitions.

The first example is the charge ordering which takes place in Fe₃O₄. In the high-temperature phase the iron ions have two sites; a tetrahedral site which is occupied
by an Fe$^{3+}$ ion and two octahedral sites occupied by Fe$^{2+}$ and Fe$^{3+}$ ions. In the high-
temperature phase the distribution of Fe$^{2+}$ and Fe$^{3+}$ ions is random but below the
Verwey transition at 123 K the Fe$^{2+}$ and Fe$^{3+}$ ions take up an ordered arrangement
(Verwey and Haayman 1941, Hamilton 1958). In both phases the electrons are
localized but the hopping conductivity is drastically reduced at the phase transition.
Since this phase transition is clearly associated with the charge distribution, there is
a corresponding structural distortion. Both of these effects have been determined
using neutron diffraction techniques as reviewed by Shirane (1977).

This transition is qualitatively not very different from a metal-insulator
transition (Mott and Zinamon 1970). Basically in a system with one electron/atom,
the correlation energy favours a situation in which each electron is situated on a
different atom in an antiferromagnetic configuration. If the overlap with the
neighbouring ions is sufficiently small there will be a gap between this insulating
state and one in which the electrons can propagate through the crystal. This possible
change in the electron wavefunctions causes a change in the electron density and
hence may give rise to a structural phase transition.

Another example of where a change in the electronic properties gives rise to a
structural phase transition is in the fluctuating valence systems, such as SmS,
Sm/YS or Ce/Th alloys. In these systems (Varma 1976) the atomic 4f levels are close in energy to the 5d–6s bands and as composition, temperature or pressure are varied, the electrons may take up either the localized 4f states or the band states. In SmS alloyed with YS, for example, at 19% of YS there is a first-order transition from a semiconducting phase with localized 4f electrons to a metallic phase of mixed 4f and 5d–6s states (Tao and Holtberg 1975). This transition is associated with a 12% decrease in volume. As discussed in §I.4.1.5, a bulk modulus instability has no critical fluctuations and is necessarily of first order due to cubic terms in the free energy. These conclusions are in excellent accord with the available experimental results for the acoustic modes in the Sm/YS system by Penney et al. (1976).

Finally we discuss magnetic transitions. If electron–phonon interactions are neglected then eqn. (I.5.34) suggests that electronic systems will only show phase transitions if ϵE(q)<0. This is indeed the case for magnetic transitions because exchange interactions are attractive, and eqn. (I.5.34) with W(qj)=0 is the well-known Stoner (1946) criterion for itinerant electron magnetism. The coupling to the phonons requires, however, more discussion. In the absence of spin–orbit interaction W(qj)=0 and there is no linear coupling between the spin density and the phonon modes. The phonon modes play the role of secondary order parameters. Inclusion of the spin–orbit coupling allows a non-zero interaction, but this is frequently very much weaker than the corresponding coupling to charge density waves.

1.5.3.5. Dynamic effects and temperature-dependent effects

In §I.5.3.1 the expression for the electronic response was evaluated assuming that a static field was set up by the normal modes. In principle, it is comparatively easy to generalize this by expressing the results in terms of the dynamic electronic susceptibility, which is given by the same expression as eqn. (I.5.28) but with the denominator replaced by v(k2)−v(k+q2′)+ω. This suggests that the dynamic response will only be significantly different from the static response if the frequencies ω of the normal modes are comparable with the difference in energy of the two electron states. In most instances nearly all the electronic energy denominators are comparable with the Fermi energy and consequently much larger than hω except for a very few electronic transitions between electron states close to the Fermi surface. In these cases there will be very little damping of the normal modes by the electronic excitations, and very little difference between the static and dynamic susceptibilities. There are two instances where this may not be the case. Firstly in [1d] conductors, KCP and TTF-TCNQ, the density of states at the Fermi surface is large and phonon damping may result as possibly illustrated in fig. 1.40. Secondly in the insulating Jahn–Teller systems discussed in §I.5.3.2, the energies of the electronic excitations are relatively small and well defined (Gehring and Gehring 1975) so that coupled mode spectra are observed similar to the behaviour discussed in §I.4.1.6.

Finally we discuss the temperature dependence of the phonon frequencies due to the electronic susceptibility. In many theories such as those of the A15 materials and of the transition-metal dichalcogenides, attempts have been made to explain the temperature dependence of the normal modes as arising from the change in the Fermi factors in χE(q) (eqn. (I.5.28)). This would appear to be unreasonable except in [1d] conductors and insulating Jahn–Teller systems because the Fermi temperature is much higher than the transition temperature. It is surely more reasonable to explain the temperature dependence as arising from the anharmonicity described in §I.5.1 and to make use of the electronic terms only to explain the unstable zero temperature 'harmonic' frequencies of the normal modes.
This combined approach has now been shown to be the appropriate one in describing the temperature and dopant concentration dependence of the soft mode and phase transition in doped SnTe. Pure SnTe has the NaCl crystal structure at high temperature but below about 120 K has a phase transition to a ferroelectric rhombohedral phase (Kobayashi et al. 1976, Pawley et al. 1966). This phase transition temperature is decreased as the carrier concentration is increased and reaches 0 K for a concentration of $8 \times 10^{26}$ m$^{-3}$. The soft mode has been studied below $T_c$ for several samples by Sugai et al. (1977b), fig. I.52. The first theory of the concentration dependence by Kristoffel and Konsin (1968) attempted to explain the results entirely in terms of the temperature dependence of the electronic response of the free carriers, but more recently Sugai et al. (1977a) found it necessary to include anharmonicity as well. This is basically because the Raman spectra, fig. I.52, show that the frequency of the TO mode has much the same temperature dependence, irrespective of the concentration, and arises from the anharmonicity, while the frequency at zero temperature is carrier dependent. Finally we comment that phonon interactions were also found to be of crucial importance in explaining the observed temperature dependence in KCP (Sham and Patten 1976).

![Fig. I.52](image)

The temperature dependence of the TO frequency squared in doped SnTe. (After Sugai et al. 1977a.)

**I.5.4. Conclusions**

The basic conclusions of this section have to be that the microscopic theory of structural phase transitions is in an unsatisfactory state. In part this reflects the very success of the Landau/soft mode theory which in terms of a few arbitrary parameters is able to correlate a very large amount of experimental data. It is then far too easy to invent a ‘microscopic model’ with a similar number of parameters which not surprisingly also correlates a large amount of experimental data. A microscopic model is only justified if either it predicts the parameters of a Landau theory $T_c, a, (q_j)$, etc., without introducing new parameters, or else also predicts the results of a large quantity of other microscopic data such as phonon-dispersion relations or optical reflectivity of a metal.
On these strict tests we have made very little progress. Except for the [$1d$] metals and, less convincingly, some order–disorder systems we can barely predict the wave-vector $q$, with any confidence let alone the transition temperature, $T_c$. We hope that this review, by cataloguing our inadequacies, will stimulate further work to develop more satisfactory microscopic theories, in the hope not just of improving our understanding, but also that we may make better use of the important technological properties of materials associated with structural transitions.

REFERENCES


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