MAGNETIC EXCITATIONS IN $\text{MnF}_2/\text{ZnF}_2$ ALLOYS

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To my wife, Jenny, for her forbearance and not the least for her part in my financial support, I offer my thanks.
The major part of this thesis is a study of magnetic excitations in mixtures of manganese fluoride and zinc fluoride using the technique of the inelastic scattering of thermal neutrons. Experiments were performed at liquid-helium temperatures on three single crystals having nominal molar concentrations of zinc of 0.20, 0.32 and 0.65. For the former two concentrations a well-defined excitation, corresponding to the spin-wave that occurs in pure manganese fluoride, is observed. Qualitatively the result of the addition of the zinc is the broadening and shifting to lower frequency of the excitation peak. The crystal having the nominal zinc concentration of 0.65 was found to have a concentration gradient such that approximately half the crystal was disordered at 4.2K. By shielding the crystal, results were obtained for the ordered and disordered parts separately, as well as for the whole crystal. In all cases the excitation was overdamped. The data for all three crystals were characterised by fitting a classical-oscillator response function to the inelastic component. The variation with wave vector of the frequency and width parameters obtained displayed the same general features in all cases. The results for the ordered and disordered parts of the largest-concentration sample were markedly similar. The results for the observed cross-section were compared with theoretical calculations based on the
coherent potential approximation for disordered systems. The agreement is quite good for wave vectors close to the zone boundary but deteriorates as the wave vector is decreased.

The final chapter of this thesis is a theoretical study of the nature of the scattering from ferroelectric crystals in the vicinity of the phase transition when the momentum and frequency transfer are small. An improved method of correcting the perturbation expansion for the phonon self energy in this regime is presented. The approximate solution of the resulting equation for the renormalised interaction vertex is shown to yield two extra contributions to the self energy; the appearance of these terms is determined by the symmetry of the crystal. It is suggested that these terms are responsible for the quasielastic scattering that has recently been observed in some materials.
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1.1 Introduction

The major part of this thesis is a study of the magnetic excitations in single crystals of mixtures of manganese fluoride (MnF$_2$) and zinc fluoride (ZnF$_2$) using the experimental technique of the inelastic scattering of thermal neutrons. Application of Hund's Rules to the five 3d electrons of the doubly-ionised manganese ion Mn$^{++}$ yields a state for which the spin and angular momentum quantum numbers are given by $S = \frac{5}{2}$ and $L = 0$. Thus the ion possesses a non-zero magnetic moment. The rutile structure salt MnF$_2$ orders antiferromagnetically at temperatures below 67K. The body-centred tetragonal magnetic structure is uniaxial with the spin direction along the C-axis as a result of anisotropy effects which are predominantly dipolar in origin. The thermally-excited collective excitations, corresponding to the deviation of the spins from the aligned ground state, manifest themselves in a large number of physical quantities to varying degrees and may be observed directly in some scattering experiments. By far the best probe is the neutron. As the neutron has a finite magnetic moment corresponding to a spin quantum number $\frac{1}{2}$, as well as the nuclear interaction with the ions, there will be a magnetic interaction with the unpaired electrons. The mass of a neutron is such that, having energies typical of magnetic excitations, it will also have comparable
wave-vectors. And as reactors produce neutrons with energies in the range of interest, the scattered intensity of the neutrons may be measured for a wide range of energy and momentum transfers. Neutron scattering experiments have been carried out on a large number of magnetic insulators of which $\text{MnF}_2$ is one of the simplest. The dispersion curves of the magnetic excitation (or magnon or spin-wave as it is variously referred to in the literature) have been determined using neutron scattering by Okazaki et al (1964) and more extensively by Nikotin et al (1969). In both experiments, performed at a temperature $T = 4.2\text{K}$, a well-defined excitation belonging to a single branch was observed.

Zinc fluoride also has the rutile structure, but, as $\text{Zn}^{++}$ has zero magnetic moment, the substance is not magnetic. Due to the chemical similarity of manganese and zinc, mixtures of $\text{MnF}_2$ and $\text{ZnF}_2$ form a solid solution at all concentrations and it is possible to grow large single crystals of these mixtures suitable for neutron-scattering experiments. This is an example of a magnetic substitutional defect. In this case the defect is non-magnetic.

A study has been made of the system $\text{Mn}_{1-C}\text{Zn}_C\text{F}_2$, where $C$ is the molar concentration of zinc, for three crystals with nominal values of $C=0.20, 0.32$ and $0.65$.

The part of this thesis pertaining to this study consists of four chapters. In the remainder of this
chapter the theory of magnetic excitations in MnF$_2$ and the derivation of the neutron-scattering cross-section of these excitations are reviewed. Also a comparative discussion of the effect of defects on the excitations in various types of systems and a description of the methods of observing them are given. Finally the results of scattering experiments on the MnF$_2$/ZnF$_2$ system are reviewed.

In chapter 2 the principles of triple-axis spectrometry are reviewed. The relevant aspects of the experimental method are presented including the effects of instrumental resolution. The results of the determination of the Neel temperatures of the crystals, and hence their concentrations, are given.

In chapter 3, the results of the neutron-scattering experiments are presented. An attempt to characterise the results in a systematic fashion is made by the least-squares fitting of simple response functions to the observed peaks. A Lorentzian and the response function appropriate to a classical oscillator are used. A Gaussian is fitted to the elastic contributions. Thus the results are conveniently presented in terms of the parameters of these functions.

In chapter 4 the results are compared with the calculations for a theory based on the coherent potential approximation.
1.2 Magnetic Excitations in Manganese Fluoride

The magnetic structure of MnF$_2$ has been established by Erickson (1953) using neutron diffraction. The body-centred tetragonal unit cell, shown in figure 1, contains two manganese atoms. The direction of alignment of the spins is along the C-axis: the spins at the cell corners being antiparallel to the spin at the centre. This configuration, referred to as the Neel state, is not the exact ground state. It represents, however, a sufficiently good approximation for the purpose of this work. It can be seen that the magnetic unit cell corresponds to the chemical unit cell. As Mn$^{4+}$ has zero orbital moment, crystal field and spin-orbit effects are negligible. It has been found that the anisotropy responsible for the uniaxial ordering is due overwhelmingly to the magnetic dipolar interaction of the spin. Also, in discussing the magnetic excitations it is sufficient to represent the dipolar interaction by an effective field along the C-axis. The comparison of this approximation and an exact calculation of the dipolar terms has been made by Nikotin et al (1969).

The Heisenberg hamiltonian is used to describe the localised spins in this system and is given by

$$H = \frac{1}{2} \sum_{i,j} \left[ J_{ij} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + \frac{1}{2} \sum_{i,j} \left( S_i^+ Z_i S_j^Z + S_i^- Z_i S_j^Z \right) \right].$$

(1.1)

The exchange integral describing the interaction between the spins on the sites i and j is $J_{ij}$ and the Ising term
FIGURE 1.1
Unit cell of MnF$_2$
includes the dipolar effective field $H_A$, so that
\[ I_{ij} = J_{ij} H_A / S. \]
The spin raising and lowering operators, given by the usual definitions in terms of the Cartesian components of the spin operator, have been introduced.
For MnF$_2$ the spin operator used in this hamiltonian is that of the actual manganese ion.

The most convenient method for calculating the scattering properties of a system described by such a hamiltonian is that of two-time Green's functions developed by Zubarev (1960). The retarded Green's function that is of particular use is defined by
\[ G_{ij}(\omega) = \langle S_i^+ ; S_j^- \rangle. \] (1.2)
The details of this function are given in appendix 1.
From the point of view of notational convenience it is better to use the function defined by
\[ P_{ij}(\omega) = G_{ij}(\omega) / 2 <S_i^Z>. \] (1.4)

The equation of motion for the Green's function is linearised using the Tyablikov decoupling procedure (see Tyablikov 1967) which is the replacement of the z-components of the spin operators by their thermal averages. The resulting equation for $P$, in an obvious matrix notation, is then
\[ P^{-1} = \omega I + D \] (1.5)
where
\[ D_{ij} = J_{ij} <S_j^Z> - \delta_{ij} \sum_k I_{ik} <S_k^Z>. \] (1.6)
We replace the site index \( i \) by the pair of indices \( (\frac{1}{k}) \)
where \( 1 \) indicates the unit cell and \( k \) the sublattice
and introducing the spatial Fourier transforms of the
quantities in equations (1.5) and (1.6) according to

\[
J_{kk'}(q) = \sum_{1} J(\frac{1}{kk'}) \exp i q \cdot (R(\frac{1}{k}) - R(\frac{1}{k'}))
\]  

(1.7)

where \( R(\frac{1}{k}) \) is the position of the \( (\frac{1}{k}) \) magnetic ion,
we have

\[
D_{kk'}(q) = J_{kk'}(q) <S^Z_{kk'}, -S^Z_{kk'}> = \sum_{kk''} I_{kk''}(0) <S^Z_{kk''}>,
\]  

(1.8)

Now for the two-sublattice antiferromagnetic MnF\(_2\), the
matrices in equation (1.5) for \( P \) are two-dimensional so
that the right-hand side is easily inverted to obtain
an expression for \( P \). We label the up-spin sublattice
\( k = a \) and the down-spin sublattice \( k = b \). Now, as a result
of the equivalence of the positive and negative
\( z \)-directions in MnF\(_2\)

\[
D_{aa} = -D_{bb} = A
\]  

(1.9)

and

\[
D_{ba} = -D_{ab} = B.
\]

And then

\[
P(q, \omega) = \frac{1}{\omega^2 - \omega^2(q)} (\begin{array}{cc}
\omega - A & B \\
-B & \omega + A
\end{array})
\]

(1.10)

where

\[
\omega^2(q) = A^2 - B^2.
\]

(1.11)

As the poles of the Green's function give the excitation
spectrum of the system we see that \( \omega(q) \) is the spin-wave
frequency. In fact we have two degenerate excitations.
The degeneracy results from the above mentioned equivalence of the z-directions and would obviously be removed by the application of an external magnetic field.

We consider the case where a spin couples to its nearest and next-nearest neighbours only. Referring to the unit cell shown in figure 1, the nearest neighbours of the central spin are at \((0,0,C)\) with respect to it. The spins are on the same sublattice and the interaction is ferromagnetic so that

\[ J_{aa}(q) = -z_1 J_1 \gamma_1(q), \]

where \(z_1\) is the number of nearest neighbours and the geometric factor is given by

\[ \gamma_1(q) = 1 - 2 \sin^2 \pi \xi. \]

We have used the reduced notation for the magnon wave vector: \((\xi, \eta, \zeta)\) so that

\[ q = 2\pi \left( \frac{\xi}{a_x}, \frac{\eta}{a_y}, \frac{\zeta}{c} \right) \]

The exchange parameter, \(J_1\) characterising the strength of the interaction is a positive quantity.

The next-nearest neighbours are at the unit-cell corners and couple antiferromagnetically, so that

\[ J_{ab}(q) = z_2 J_2 \gamma_2(q) \]

where

\[ \gamma_2(q) = \cos \pi \xi \cdot \cos \pi \eta \cdot \cos \pi \zeta. \]

And then

\[ A = S z_1 J_1 (1 - \gamma_1(q)) + S z_2 J_2 + H_A, \quad (1.12) \]
and \[ B = S z_2 J_2 \gamma_2(q) \] \hspace{1cm} (1.13)

In the preceding analysis the expectation values of the z-components of the spin operators have been replaced by their Neel state values. That is \(<S^z_a>_a = S = - <S^z_b>\). This approximation and the Tyablikov decoupling are equivalent to the so-called spin-wave approximation that is usually discussed in terms of approximate boson operators (see Kittel 1963). It is found that a good fit to neutron-scattering-determined dispersion curves (Nikotin et al 1969) is obtained with the following values of the parameters (in THz):

\[
\begin{align*}
J_1 & = 0.032 \\
J_2 & = 0.0744 \\
H_A & = 0.0222.
\end{align*}
\] \hspace{1cm} (1.14)

Inclusion of third nearest neighbours gives an exchange constant with the value 0.0018 so its neglect is justified.

The Green's function that we set out to calculate at the beginning of this section is now given by

\[
G(q,\omega) = \frac{S}{\omega(q)} \left( \frac{1}{\omega(q)-\omega} + \frac{1}{\omega(q)+\omega} \right) \left( \begin{array}{cc} A-\omega & B \\ B & A+\omega \end{array} \right)
\] \hspace{1cm} (1.15)

where \(\omega(q)\), A and B are given by equations (1.11), (1.12) and (1.13) respectively.

We list some values of the magnon frequency at some important points in the Brillouin zone which will be of some use in later chapters. At the zone centre

\[
\omega_0 = (2 S z_2 J_2 H_A + H_A^2)^{1/2}
\]
1.3 Observation of Magnetic Excitations

As the technique of neutron scattering is of particular interest in this thesis, we shall consider the formalism in some detail.

The magnetic moment of the neutron interacts with the magnetic field of the unpaired electrons. As the energy of the interaction is small compared with the kinetic energy of the neutron, the scattering rate, and hence the scattering cross-section, may be calculated in the first Born approximation. The differential scattering cross-section of unpolarised neutrons from magnetic ions has been given by van Hove (1954) and is

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \left[\frac{8}{2\pi}\right] \sum_{ij} f_i(Q)f_j(Q)e^{-iQ(R_i-R_j)} \sum_{\alpha\beta} \frac{Q_{\alpha\beta}}{Q^2} \epsilon_{\alpha\beta} \langle S_i^\alpha(0) S_j^\beta(t) \rangle.
\]

Here \(Q = k - k'\) is the momentum transfer from the neutron to the crystal and \(\omega\) is the corresponding energy transfer;
$r_0$ is the electron radius and $g$ the neutron $g$-factor. The magnetic form factor, $f_i(Q)$, for the $i$th ion is normalised to unity for zero momentum transfer. The Debye-Waller factor is omitted as the experiment is performed at only one temperature and for a relatively small range of scattering vectors: the factor is effectively a constant close to unity. For $\text{MnF}_2$, in which the orbital moment is zero, the operators appearing in the expression are the actual Cartesian components of the spin operator of the $i$th ion.

For a predominantly exchange coupled system, the off-diagonal Cartesian components of the correlation function may be ignored. Introducing the spin raising and lowering operators, we have, for a system with the spins aligned along the $z$-direction, the following expression for the cross-section:

$$
\frac{d^2\sigma}{d\omega dQ} = (r_0 g)^2 \frac{k_i}{k_f} f_i(Q) f_j(Q) e^{-iQ(R_i - R_j)} \int_0^\infty dt e^{-i\omega t} x \left( \frac{Q^2}{Q_0^2} \right) \left< \bar{S}_i^z(0) S_j^z(t) + S_i^z(0) S_j^z(t) \right> + \left( 1 - \frac{Q^2}{Q_0^2} \right) \left< S_i^z(0) S_j^z(t) \right> .\tag{1.18}
$$

It is the latter term, the longitudinal term, that is responsible for the elastic magnetic Bragg scattering. Replacing the $z$-components of the spin operators by thermal averages gives, for the elastic cross-section,
Replacing the index $i$ by the full indices $(\ell \kappa)$, this becomes
\[
\frac{d\sigma}{d\Omega} = (r_0 g)^2 \sum_{ij} f_i(Q) f_j(Q) e^{-iQ \cdot (R_i - R_j)} <S^Z_i \cdot S^Z_j>. \tag{1.19}
\]

where $b = \Sigma f_\kappa(\tau) <S^Z_\kappa> e^{iQ \cdot R_\kappa}$

and we have used the identity
\[
|\Sigma e^{iQ \cdot R_\ell}|^2 = N \Sigma \frac{(2\pi)^3}{v} \delta(Q-\tau), \tag{1.20}
\]

where $\tau$ is a vector of the reciprocal lattice and $v$ is the volume of the unit cell. For the Neel state of MnF$_2$, it is easily shown that
\[
b = f(\tau) S(1 - e^{i\pi(h+k+l)})
\]

where $\tau = 2\pi \left( \frac{h}{a}, \frac{k}{a}, \frac{l}{c} \right)$

$h$, $k$ and $l$ being integers.

So that for $h+k+l = \text{odd}$, there will be a magnetic reflection, while for $h+k+l = \text{even}$ there will not. We refer to these reciprocal lattice points as being magnetic and non-magnetic respectively. However the factor of $(1-\frac{Q_2^2}{Q^2})$ in the cross-section ensures that there will be no reflection for the scattering vector parallel to the spin direction. It can be shown from a consideration of the nuclear scattering cross-section that the nuclear Bragg reflections will be absent for $h+k+l = \text{odd}$ with either $h$ or $k$ zero. So we see that there are reflections, such as $(100)$, that will be present in the ordered phase. 

\[\text{(magnetically)}\]
only. The property of the temperature dependence of this particular reflection is exploited to determine the ordering temperatures of the specimens.

There will be some inelastic scattering due to the longitudinal term. However this is of a quasi-elastic nature and will only be significant in the vicinity of the phase transition.

Returning to the transverse part of the cross-section, we can write the correlation functions in terms of functions which may be determined from the Green's function discussed in the previous section. It is convenient to interchange the indices $i$ and $j$ in the summation. We see that

\[ <S_j^+(0) S_i^-(t)> = G_{ji}^>(-t) \]
and \[ <S_j^-(0) S_i^+(t)> = G_{ji}^< (t). \]

After performing the temporal Fourier transforms, these quantities may be expressed in terms of the spectral density. We have

\[ G_{ji}^>(\omega) = n(\omega) \rho_{ji}(-\omega) \]
\[ = - (n+1) \rho_{ji}(-\omega) \]
and \[ G_{ji}^<(\omega) = (n+1) \rho_{ij}(\omega). \]

Defining the function

\[ F_{ij}(\omega) = \rho_{ij}(\omega) - \rho_{ji}(-\omega), \]
the transverse part of the cross-section which we assume to be the sole source of inelastic scattering, becomes
\[
\frac{d^2 \sigma}{d \Omega d\omega} = \frac{1}{2\pi} (r_0 g)^2 \frac{K'}{K} \frac{1}{4} \left( 1 + \frac{Q^2}{Q'^2} \right) S(Q, \omega) \tag{1.21}
\]

where we have introduced the scattering function

\[
S(Q, \omega) = (n+1) \sum_{ij} f_i(Q) f_j(Q) F_{ij}(\omega) \exp iQ \cdot (R_i - R_j). \tag{1.22}
\]

Using the full indices \( (\mathbf{k}) \), the sum becomes, on substituting the spatial Fourier transform of \( F_{ij}(\omega) \) and using the identity of equation (1.20),

\[
S(Q, \omega) = (n+1) |f(Q)|^2 \sum_{q} \eta_{\mathbf{kk}'}(\mathbf{r}) F_{\mathbf{kk}'}(q, \omega) \left( \frac{2\pi}{\nu} \right)^3 \delta(Q-q-\mathbf{r})
\]

where

\[
\eta_{\mathbf{kk}'}(\mathbf{r}) = \exp[-iQ \cdot (\mathbf{R}_k - \mathbf{R}_k')]
\]

For \( \text{MnF}_2 \),

\[
\eta_{aa} = \eta_{bb} = 1
\]

and

\[
\eta_{ab} = \eta_{ba} = \eta(\mathbf{r}) \begin{cases} -1 \text{ for magnetic} \\ \text{reciprocal lattice point} \\ +1 \text{ for non-magnetic} \\ \text{reciprocal lattice point} \end{cases}
\]

Now

\[
F_{\mathbf{kk}'}(q, \omega) = \rho_{\mathbf{kk}'}(q, \omega) - \rho_{\mathbf{k}'k}(q, -\omega)
\]

and then

\[
S(Q, \omega) = (n+1) |f(Q)|^2 \sum_{q} \eta_{\mathbf{kk}'}(\mathbf{r}) \left( \frac{2\pi}{\nu} \right)^3 \left\{ \rho_{\mathbf{kk}'}(q, \omega) \delta(Q-q-\mathbf{r}) - \rho_{\mathbf{k}'k}(q, -\omega) \delta(Q+q-\mathbf{r}) \right\}
\]

Using the result for the Green's function obtained in the last section, given by equation (1.15), the spectral density is then

\[
\rho(q, \omega) = \frac{S}{\omega(q)} \left\{ \delta(\omega-\omega(q)) - \delta(\omega+\omega(q)) \right\} \begin{pmatrix} A-\omega \\ -B \end{pmatrix} \begin{pmatrix} -B \\ A+\omega \end{pmatrix},
\]
so that

\[ \Sigma \eta_{KK'}(\tau) \rho_{KK'}(q, \omega) = \frac{2\pi}{\omega(q)} \{ \delta(\omega - \omega(q)) - \delta(\omega + \omega(q)) \}(\Delta - \eta(\tau)B). \]

Then, for neutron energy loss, i.e. spin-wave creation, the scattering function is

\[ S(Q, \omega) = |\tau(Q)|^2 \sum_{q} \frac{2\pi}{\omega(q)} (n_q + 1) \delta(\omega - \omega(q))(\Delta - \eta(\tau)B)(\frac{2\pi}{v})^3 \delta(Q - q - \tau). \]

The effect of the factor \( \Delta - \eta(\tau)B \) is to produce a greater intensity of scattering in the zones containing a magnetic reciprocal lattice point than those containing a non-magnetic point.

There are a variety of optical techniques available to probe excitations in antiferromagnetic insulators. Of these, Raman spectroscopy and infrared absorption have proven the most useful. In both methods the information that may be obtained is limited by the requirement that the momentum transfer be zero. However the resolution obtainable is superior to that of neutron scattering experiments. Raman scattering, in which the intensity of the scattered light is measured as a function of frequency transfer for a monochromatic incident beam, has been most successful in observing vibrational excitations (phonons) in crystals. Both zero wave vector (zone centre) phonons and two-phonon effects have been observed (see Cowley 1971 for review). The spectrum of MnF\(_2\) in the ordered phase has been obtained by Fleury et al (1967). They did not
observe the one-magnon peak but did observe a strong two-magnon excitation. As the density of states of MnF$_2$ is peaked in the region of the zone boundary (see Nikotin et al 1969) the position of the observed peak is at approximately twice the zone-boundary magnon frequency. The Raman spectrum of FeF$_2$, which possesses the same magnetic structure as MnF$_2$, has been obtained by Fleury and Loudon (1968) and in this case both one- and two-magnon peaks are observed; the latter having the greater intensity. These authors attribute the observation of the one-magnon peak to the large anisotropy of FeF$_2$. The interpretation of the two-magnon spectra is somewhat complicated by the necessity of the inclusion of magnon interactions in the theory even at low temperatures (Elliot and Thorpe 1969). Nevertheless, the calculation in the spin-wave approximation carried out by Fleury and Loudon (1968) does not differ all that greatly from the observed spectra.

In infrared absorption experiments the absorption is measured as a function of frequency. The resulting spectra are similar to those of Raman scattering. The two-magnon absorption in MnF$_2$ has been measured by Allen et al (1966).

1.4 Impurity Systems

A simple illustration of the concept of the collective excitation may be given by the model of a Bravais lattice
of spins that align ferromagnetically in the ground state. The obvious excited state for the system is for one spin to be deviated from its aligned direction. Such a state cannot be an eigenstate of the system as it violates translational symmetry. However a linear combination of such states taken with the deviation on all possible sites weighted by the appropriate phase factor is an eigenstate. Imposing periodic boundary conditions, this state may be labelled by a wave-vector. This state is the collective excitation. With a hamiltonian, such as the Heisenberg hamiltonian, described in section 1.2, the energy of the state can be calculated. This is just what has been done in section 1.2 for the more complex, but essentially similar, case of the antiferromagnet. The excitation is infinitely long-lived and is manifested by a delta-function line in the neutron-scattering cross-section at the energy of the excitation. At finite temperatures account must be taken of the possibility of more than one deviation from the aligned state. The idea of a spin-wave characterised by a wave-vector may be retained if the concept of a finite spin-wave life time resulting from interactions between the collective excitations is admitted. This leads to a finite width of the peak in the neutron-scattering cross-section. In fact, in MnF$_2$, Schulof et al (1971) have observed a well-defined peak in the cross-section for small wave vectors at temperatures right up to the transition.

The collective excitations of the motions of the ions
of a crystal lattice have also been much studied by the methods of neutron and photon scattering. In this case the assumption of a potential that depends quadratically on the ionic displacements - the harmonic approximation - yields infinitely long-lived excitations. The finite phonon width arises from the inclusion of higher order terms in the potential.

Conduction electrons in metals, as they are usually treated in the one-electron theory, have been shown by Bohm and Pines (1953) to be excitations of the actual valence electrons. In some respects the bands that emerge in the Bloch picture may be thought of as collective excitations of such a system. Unfortunately this system is not accessible experimentally in the way that the magnetic and vibrational systems are and information on the band structure of metals has to be obtained by indirect methods. Although these examples do not exhaust the list of collective excitations in solids they are the ones that have attracted the most theoretical and experimental attention.

We are interested in the effect that the introduction of substitutional impurities into these systems will have on their collective excitations. Although there are important differences between the systems we have mentioned, Izyumov (1965) has shown that by using the language of Green's functions they can be discussed on the same basis. The most obvious effect of the introduction of impurities is the removal of the periodicity of the crystal and thus
the excitations cannot be labelled with a wave-vector. However periodicity can be restored by replacing quantities calculated for a crystal with a particular distribution of impurities, by their configuration averages. That is an average over an ensemble of crystals having all possible random distributions of impurities. As has been pointed out by Leath (1970), this replacement will be valid if the energy shifts at a particular site, induced by a distribution of impurities a distance from the site that is small compared with the crystal size, are smaller than the resolution width of the experiment measuring these quantities.

For a general understanding of the effects of introducing impurities, we turn to the simplest system for which solutions have been obtained: vibrations of a cubic Bravais lattice in which a single ion has been replaced by one of differing mass without changing the force constants. This problem has been treated using Green's functions by Elliot and Taylor (1964 and 1967). The simplicity resides in the fact that the impurity matrix, in the equation for the Green's function in the site representation, has only one entry corresponding to the defect site. For a light defect the perturbation will be localised on the impurity and a non-propagating mode will be present above the band of host excitations. This mode appears in the phonon spectral density as a delta-function. Resonant modes will also be present in the band but they are masked by the density of states.
unless they are low in the band which will be true only for heavy impurities. Some modification of the theory is required to treat a finite number of impurities in the dilute limit to obtain the phonon self-energy to lowest order in the concentration. For light impurities a narrow impurity band appears straddling the local mode frequency. This has been observed with neutron scattering in copper with aluminium impurities by Nicklow et al (1968) along with shifts in frequency of the host excitations. For heavy impurities the theory predicts shifted and broadened host excitations and a resonant mode that may, under some conditions, be of the same intensity as the host mode. Using neutron scattering Svensson et al (1965 and 1967) have studied phonons in gold-doped copper but were unable to resolve the resonant mode. However calculated lineshapes, with instrumental resolution effects included, were in good agreement with observed neutron groups.

The situation in magnetic systems is not so simple. An impurity, chemically similar to the host, will have a spin and interaction with the surrounding ions that differ from the host. Even assuming interaction of the impurity only with the $z$ nearest neighbours the impurity matrix will be of dimension $(z+1) \times (z+1)$. The theory of neutron scattering in the dilute limit using the spin-wave approximation has been worked out for ferromagnets by Izyumov (1966) and for antiferromagnets by Lovesey (1968). The best understood magnetic insulators are the rutile
structure antiferromagnets \( \text{XF}_2 \) and the perovskite structure antiferromagnets \( \text{KXF}_3 \) where \( X \) is one of the magnetic transition metals - Co, Mn, Fe or Ni - and consequently there has been considerable theoretical and experimental work on dilute mixtures of these materials for low temperatures. The work has recently been reviewed by Cowley and Buyers (1972) and it would appear that the current theory adequately explains the observed effects. A good illustrative example is Ni in \( \text{KMnF}_3 \) which has been studied using neutron scattering by Holden et al (1971). The spin-wave spectrum of \( \text{KMnF}_3 \) is well described by a Heisenberg model with exchange interactions between a Mn\(^{++}\) ion and its six nearest neighbours plus a small anisotropy term (Pickart et al 1966). The Ni\(^{++}\) ion has an effective spin of 1 and its interaction with the neighbouring Mn\(^{++}\) ions is well approximated by the geometric mean of the exchange parameters of the pure crystals (Cowley and Buyers 1972). The values of these quantities represent appreciable departures from those of the host crystal, so we would expect the consequent effects to be relatively large. This is one advantage that the magnetic systems have over the vibrational systems as far as experimental observation is concerned. An impurity with a mass that is significantly different from that of the host ions will also differ chemically and in size and will thus produce local strains. And there is the concomitant technical problem of growing large single crystals, particularly with large defect concentrations.
The finite dimensionality of the defect matrix admits the possibility of several defect modes. In the case under consideration, group theory predicts four modes: one localised mainly on the defect, one localised mainly on the neighbours of the defect and two localised wholly on the neighbours. Theoretically (Holden et al. 1971), the latter three modes are expected to have similar frequencies and in fact are observed in the neutron scattering experiment, unresolved from each other, in a narrow band just above the band of the host excitations. The mode localised on the impurity is observed at a frequency well above the top of the host band.

The experimental inaccessibility of excitations makes it difficult to test theories of defects in electronic systems and averaged effects such as, for example, the concentration dependence of the absorption edge in Au-Ag alloys are calculated (Levin and Ehrenreich 1971). However such systems have provoked much theoretical interest as a result of the importance of their electrical transport properties.

1.5 The MnF$_2$/ZnF$_2$ System

The doubly ionised Zn$^{++}$ ion has ten 3d electrons and has zero magnetic moment. As one of the transition metals it is a candidate for an impurity in the magnetic systems mentioned in the previous section: in this case a non-magnetic impurity. One theoretical attraction of such an impurity system is that there are no unknown
model parameters. As there is no magnetic host-impurity interaction, the parameters of the pure system - spin, exchange constants and anisotropy - should be sufficient to affect a complete theoretical description of the system. Like MnF$_2$, ZnF$_2$ has the rutile structure with lattice parameters that are extremely similar to those of MnF$_2$ (Wyckoff 1963) and thus it is expected that the MnF$_2$/ZnF$_2$ system would form a solid solution at all concentrations. That this is the case is shown by x-ray diffraction experiments reported by Baker et al (1962) and Buchanan et al (1972) who observed lines corresponding to a gradual change in lattice parameters with concentration and none due to either material alone.

The most obvious effect on the magnetic properties of the MnF$_2$/ZnF$_2$ system is the reduction of the Neel temperature with increasing concentration of the non-magnetic constituent. By determining the temperature at which the fluorine nuclear resonance disappears, Baker et al (1961) have measured the Neel temperature for a number of concentrations. The Neel temperature was observed to decrease almost linearly with increasing zinc concentration and to be zero for $C \approx 0.75$.

The magnetic excitations in this system have been studied by both neutron scattering and optical techniques. In a neutron scattering experiment on a sample with $C=0.05$, Svensson et al (1969) observe excitations corresponding to those of the pure crystal but with increased width and decreased frequency. As the impurity...
is non-magnetic, no mode localised on the impurity is expected. As a function of wave vector, the impurity induced width is found to have a maximum corresponding to a spin-wave frequency of approximately 1.3THz. The authors give a simple interpretation of this effect on the basis of the Ising model. Considering only the stronger next-nearest-neighbour interactions, a manganese ion that is the next-nearest-neighbour of a zinc impurity will have its Ising frequency reduced by a factor \((z-1)/z = 7/8\). The calculated frequency of this resonant mode is in good agreement with the observed value. These authors also present results of a Green's function calculation for the shift and width that are in excellent agreement with what is observed.

The infrared and Raman scattering have been measured by Mitlehner et al (1971) and Buchanan et al (1972): the former for samples with \(C < 0.1\) and the latter over the whole concentration range. As the concentration is increased, the two-magnon Raman scattering peak is broadened and shifted to lower frequencies. The rate of increase of the width is initially quite rapid and then falls off. The latter authors give the spectrum for \(C = 0.67\) which is approaching the critical concentration. Although the overlap of the two-magnon peak with the Rayleigh line is considerable, it is still distinct. Phonon contributions to the infrared absorption, particularly for large \(C\), make it difficult to separate out the two-magnon peak. However it appears to have
the same form as the peak in Raman spectra.

Although neither set of authors have carried out detailed calculations, Buchanan et al have calculated the two-magnon Raman cross-section on the basis of the multiple-cluster Ising model and obtain agreement with their experimental results that is surprisingly good considering the crude nature of the model. Including only next-nearest neighbours they calculate the Ising energies for creation of pair excitations on clusters having all possible numbers of zinc atoms. With appropriate weighting, this procedure yields a histogram for the spectral shape of the cross-section.

The resonant shell mode observed in the neutron scattering experiment has not been observed by either optical technique.
CHAPTER 2

THE EXPERIMENT

2.1 Introduction

The magnetic neutron scattering cross-section of three crystals of manganese zinc fluoride has been measured at liquid-helium temperature. The nominal molar concentration of zinc in the three crystals was 0.20, 0.32 and 0.65 respectively. The experiments were performed on two triple-axis crystal spectrometers: for the 0.20 and 0.65 crystals, the spectrometer at the C5 facility of the NRU reactor at the Chalk River Laboratories, Atomic Energy of Canada Limited was used, and for the 0.32 crystal, the spectrometer at the PLUTO reactor of the Atomic Energy Research Establishment, Harwell.

In this chapter the execution of the experiment is described. As the methods of triple-axis spectrometry are well documented in the literature and as, by any standards, the experiments to be described here are quite straightforward, details about technical aspects will not be given except where they contribute to differences between the experiments that are important in interpreting results. This latter point refers particularly to the effects of instrumental resolution. Also, as the author had nothing whatsoever to do with the design, construction or development of any equipment used and as the equipment was maintained by technicians, no technical description of the equipment such as cryostats, is given.
2.2 Triple-Axis Spectrometry

The measurement of the neutron scattering cross-section is, in practice, the determination of the intensity of the neutrons scattered from the specimen for particular values of energy and momentum transfer for a fixed incident intensity. The choice of these values is governed by the nature of the contributions to the cross-section that are of interest.

Both the production of a monoenergetic incident beam and the analysis of the scattered beam are brought about by the application of Bragg's law: for neutrons incident on a crystal with angle $\theta$, only those with a wave vector of magnitude given by

$$k = \frac{\pi}{d} \sin \theta$$

are reflected. Here $d$ is the spacing of the planes reflecting the neutrons. The scattering angle is $2\theta$. The energy distribution of neutrons produced by a reactor is approximately Maxwellian and if the beam is allowed to fall on a single crystal then neutrons of the energy required may be obtained by selecting the appropriate Bragg angle. Similarly the neutrons scattered from the specimen will possess some distribution of energies that can be analysed by Bragg scattering from a crystal. Thus, once the incident and scattered energies are determined, the momentum transfer is fixed by the scattering geometry.

Figure (2.1) is schematic diagram of triple-axis crystal spectrometer. The neutrons are incident on the monochromator crystal ($X_1$) from the left and are scattered
FIGURE 2.1

Schematic diagram of the triple-axis crystal spectrometer.
Fig. 2.1
through an angle $2\theta_N$ so that they are incident on the specimen crystal (S). Those neutrons scattered by the specimen through an angle $\varphi$ having the appropriate energy are reflected by the analyser crystal ($X_2$) through an angle $2\theta_A$ into a boron fluoride counter. Of the collimators (C), the two immediately before and after the specimen, which are usually of the Soller slit type, are the tightest and serve to define the direction of incident and scattered wave vectors. The low-efficiency monitor counter (M) immediately before the specimen provides a measure of the incident intensity. The scattered intensity is measured for a fixed number of monitor counts.

There are six angles that may be varied: the scattering angles at each of the three crystals and the orientations of the crystals to the respective scattering directions. However, the changes in the orientations of the monochromator and analyser crystals are always half that of the scattering angles so once the initial configuration is fixed the number of angles which need be specified is reduced by two.

For dispersion curves that are not too steep, the most convenient way of observing excitations is to vary the energy transfer, keeping the momentum transfer constant. This is the "constant-Q" mode (Broekhouse 1961). From the form of the cross-section derived in the previous chapter, it can be seen that there will be a peak in the histogram obtained at the frequency corresponding to that of the magnon having the wave vector determined by the choice of
scattering vector. Two simplifying possibilities are considered. In varying the energy transfer, both the incident and the scattered energy may be varied or one or other of the two may be kept constant. These latter two cases will be referred to as "constant-$k_0$" and "constant $k'$". In performing a constant-$k_0$ experiment, the monochromator angle is held constant while in a constant $k'$ experiment it is the analyser angle that is held constant. So having selected a value of the incident or scattered energy, in performing a constant-$Q$ experiment, only changes in three angles are specified.

2.3 The Equipment

Although there are many differences between the C5 and PLUTO spectrometer - in their design and construction and in their control and counting systems - in essence they are the same. The more modern machine, PLUTO, offered a greater range of angles, but apart from a greater ease of operation, had no real advantages over C5 for these experiments.

All experiments were carried out at liquid helium temperatures. The crystals were oriented so that the \{010\} axis was vertical and mounted in helium cryostats. Temperature measurement and control equipment was used such that the specimen temperatures were measurable to an accuracy of 1K with a stability of better than 1K.

From among the crystals that are suitable for use as monochromators and analysers, the choice for a particular
experiment is based on the plane spacing that will give convenient scattering angles for the energies of interest. The top of the spin-wave band in MnF$_2$ is at approximately 1.65 THz so the maximum energy transfer required is about 2.5 THz which is low in comparison with what is usually used in phonon experiments.

Both constant $k'$ and constant $k_0$ experiments have been carried out. For the constant $k'$ experiment the monochromator was Germanium with the scattering from the (111) planes (Ge(111)) and for the analyser pyrolytic graphite was used. This high reflectivity material is only ordered in the {001} direction and the lowest order (002) (PG(002)) reflection is used. There is the problem of second order reflection from the monochromator which will contribute neutrons of the desired energy and will thus contaminate the scattering at the required energy and momentum transfer. However as the (222) reflection is absent in Ge, this problem does not arise. The germanium crystal used had been squeezed to increase its mosaic spread and hence its reflectivity (Dolling and Niemann 1967). With PG(002) as analyser and a scattering angle at the analyser of $2\theta = 50^\circ$, the energy of the scattered neutrons is 2.46 THz.

The majority of the data on the C=0.32 specimen was collected in a constant-$k_0$ experiment. For both monochromator and analyser, PG(002) was used. To remove the contribution from the (004) reflection of the monochromator a broad mosaic pyrolytic graphite filter was used.
As has been shown by Minkiewicz and Shirane (1970), such a filter will appreciably attenuate the second order neutrons in a beam with energy in the range 13-15 meV. The filter was placed between the monitor and the specimen and was tuned, by varying its orientation, to give a maximum attenuation of the (004) reflection at that particular energy.

A summary of the experimental conditions is given in Table 2.1.

2.4 Instrumental Resolution Effects

In this section the relationship, between the theoretical concept of the differential scattering cross-section and what is actually measured, is discussed.

A spectrometer set up to receive neutrons with particular values of energy and momentum will, in practice, admit neutrons to the counter with values in a range about the nominal setting. This is due to the mosaic spreads of the monochromator and analyser crystals and the finite divergences of the collimators. The formalism for the discussion of these resolution effects was developed by Cooper and Nathans (1967). The intensity for the energy-wavevector transfer \( P = (Q, \omega) \) is given by

\[
I(P_0) = \int R(P_0, P) \sigma(P) \, dP
\]  

(2.1)

where \( R(P_0, P) \) is the resolution function, characteristic of the instrument, and \( \sigma(P) \) is the cross-section for scattering with energy-momentum \( P \). These authors show that if the transmission functions of the collimators and the analyser and monochromator crystals are Gaussian then
TABLE 2.1

Summary of the experimental conditions
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Spectrometer</th>
<th>Experiment Type</th>
<th>Monochromator</th>
<th>Analyser</th>
<th>Incident/Scattered Energy(THz)</th>
<th>Monochromator/Analyser Angle</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>Cs, Chalk River</td>
<td>constant $k'$</td>
<td>Ge(111)</td>
<td>PG(002)</td>
<td>2.461</td>
<td>50°</td>
<td></td>
</tr>
<tr>
<td>0.32</td>
<td>PLUTO Harwell</td>
<td>constant $k_0$</td>
<td>PG(002)</td>
<td>PG(002)</td>
<td>3.579</td>
<td>41°</td>
<td>PG filter before specimen</td>
</tr>
<tr>
<td></td>
<td></td>
<td>constant $k'$</td>
<td>Ge(111)</td>
<td>PG(002)</td>
<td>2.461</td>
<td>50°</td>
<td>Only a small amount of data collected</td>
</tr>
<tr>
<td>0.65</td>
<td>Cs, Chalk River</td>
<td>constant $k'$</td>
<td>Ge(111)</td>
<td>PG(002)</td>
<td>2.461</td>
<td>50°</td>
<td></td>
</tr>
</tbody>
</table>
the resolution function is also Gaussian and is given by

\[ R(P, P_0) = R_0(P_0) \exp \left( -\frac{1}{2} X : M(P_0) : X \right) \]  

(2.2)

where \( X = P - P_0 \).

Thus the surfaces of constant \( R \) are ellipsoids in \( P \)-space.

It is usual to refer to the surface for which the resolution function is one-half its maximum value as the resolution ellipsoid. We may also think of the scattering cross-section as a set of surfaces in \( P \)-space when the excitations are non-interacting which is referred to as the dispersion surface. One would only expect to get any appreciable contribution to the integral when the resolution ellipsoid intersects the dispersion surface. In an experiment, the intensity is measured as \( Q \) and \( \omega \) are varied and this can be visualised as the moving of the resolution ellipsoid through the dispersion surface. Cooper and Nathans (1967) have shown that the resolution ellipsoid is markedly aspherical so that the nature of the scan and hence the way the ellipsoid is moved through the dispersion surface will effect the width of the observed peak. By choosing the spectrometer parameters so that the long axis of the resolution ellipsoid is oriented in the tangent plane of the dispersion surface, and by choosing a path in \( P \)-space so that the ellipsoid moves through the surface with this axis as nearly as possible in the tangent plane, it is possible to minimise the observed width. This effect is known as focusing. As a knowledge of the resolution
function is required for the former type of focussing it is not usually attempted apart from some rather general considerations. As far as focussing of the latter type is concerned, considerations of interpretative simplicity require constant-Q scans unless the dispersion curves are unusually steep. However, as there is a choice of Brillouin zones in which to make the measurement and a choice of two theoretically equivalent wave-vector directions in each zone, it is usually found that for a particular wave vector there is a scattering vector that more nearly fulfils the conditions stated above. Advantage is taken of focussing in the experiments to be described below.

If the excitation under study possesses a finite width then in the comparison of a theory with experimental results account must be taken of the resolution broadening of the observed peak. In the experiments of this thesis the contribution of the resolution effects to the width of the peak are much smaller than the intrinsic width of the excitation. This reduces the importance of the resolution corrections and allows the adoption of a rather empirical approach.

Svensson et al (1969 and private communication) have performed experiments on pure MnF₂ under conditions identical to that used for the C=0.20 and C=0.65 experiments and, as the only contribution to the observed width is from resolution effects, it is possible to obtain information on the resolution function. The
peaks in the constant-Q scans are Gaussian which, as Chesser and Axe (1972) have demonstrated, is expected on the basis of the Cooper-Nathans expression (equation 2.2).

If changes in the resolution function, as the resolution ellipsoid is scanned through the dispersion surface, can be ignored then

$$R(P_0, P) = R(P_0 - P)$$

and the observed intensity is the convolution of the resolution function with the theoretical cross-section:

$$I(P_0) = \int R(P_0 - P) \sigma(P) dP$$  \hspace{1cm} (2.3)

It is assumed that the integration over $Q$ does not contribute significantly in a constant-Q scan, and the resolution function can thus be written as a normalised Gaussian of the frequency; that is

$$R(Q, \omega) = \left\{ \frac{1}{\pi W^2(Q)} \right\}^{1/2} \exp \left\{ - \frac{1}{2} \left( \omega W(Q) \right)^2 \right\}$$  \hspace{1cm} (2.4)

so that the peak in MnF$_2$ has a full width at half maximum given by

$$FWHM = 2(2\log 2)^{1/2} W(Q)$$  \hspace{1cm} (2.5)

The results of Svensson et al (1969) are shown in figure (3.4) of chapter 3.

For the specimens of MnF$_2$/ZnF$_2$, which have intrinsic peak widths, it is assumed that the measured intensity is given by
where the parameters \( W(Q) \) are those obtained from the pure \( \text{MnF}_2 \) experiment. This is an approximation due to the different form of the dispersion surface in the defect materials, however, as was noted above, the resolution contribution to the observed width is small in comparison with the intrinsic width, so that the approximation is expected to be valid.

Even if the collimators and the monochromator and analyser crystals were ideal there are still corrections to be taken into account when comparing experimental results with theory. These corrections are extensively discussed by Sears and Dolling (1972). We may write the differential scattering cross-section as

\[
\frac{d^2 \sigma}{dQd\omega} = \left( \frac{k'}{k_0} \right) S(Q, \omega)
\]  

(2.7)

In a constant-\( k' \) experiment, the analyser-counter system accepts only neutrons of one energy so that its efficiency is immaterial when the relative intensities are of interest. As the monitor counter is placed just before the specimen, the variation in efficiency of the monochromator with energy is also immaterial. The efficiency of the monitor counter, in the energy range of interest, is inversely proportional to the neutron velocity which removes the factor of \( 1/k_0 \) in the cross-section. So it can be seen that, in a constant-\( k' \) experiment, constant-\( Q \) scans provide almost a direct
measure of the scattering function. The situation is not as simple for constant-\(k_0\) experiments. In this case the cross-section is measured with respect to a variation in the analyser angle rather than with respect to the energy transfer, so that a correction factor is required.

The energy transfer \(\omega\) is the difference between the constant incident energy \(\varepsilon_0\) and the varying scattered energy \(\varepsilon:\)

\[
\omega = \varepsilon_0 - \varepsilon,
\]

i.e. \(d\omega = -d\varepsilon\).

Applying Bragg's law to the analyser crystal, we have

\[
\varepsilon \propto \sin^2 \theta A = \text{constant}
\]

so that \(d\omega = 2\varepsilon \cot \theta A \, d\theta A\).

And thus

\[
\frac{d^2\sigma}{d\omega d\theta A} = 2\varepsilon \cot \theta A \left(\frac{k'}{k_0}\right) S(Q, \omega)
\]

It is more usual to write this correction factor in terms of \(k'\). Keeping only the factors that vary, we have

\[
\frac{d^2\sigma}{d\omega d\theta A} \propto k'^4 \cos \theta A \, S(Q, \omega) \quad (2.8)
\]

This premultiplying factor will be referred to as the \(k'\)-correction. Chesser and Axe (1972) emphasise the importance of this factor in the determination of the integrated intensities of harmonic phonons.

There will be a variation of analyser reflectivity with energy in a constant-\(k_0\) experiment. However, as
the energy range is small, it is assumed to be constant.

From the preceding discussion it can be seen that constant-k' experiments are to be preferred. The unavailability of a high quality squeezed Ge crystal at Harwell, however, necessitated the use of PG as a monochromator and as the filter was mounted before the specimen, the experiment had to be performed with the incident energy held constant. Some ancilliary work was done for the C=0.32 sample with a rather inferior germanium monochromator, using constant scattered energy.

2.5 The Determination of the Neel temperatures and the Concentrations

The Neel temperatures of the crystals were determined by measuring the intensity of (100) Bragg reflection as a function of temperature. As was shown in chapter 1, there is no nuclear reflection corresponding to this reciprocal lattice point and also the magnetic reflection intensity is proportional to the sublattice magnetisation. So, as the temperature is increased in the ordered phase, the intensity of the (100) reflection will go to zero at the Neel temperature. The concentrations were determined by comparing the values of the Neel temperature so obtained with the results of Baker et al (1961) for the variation of the Neel temperature with concentration in MnF$_2$/ZnF$_2$ systems.

With the spectrometer set for elastic scattering and to the value of Q appropriate to the (100) reflection,
the peak intensity was measured for several temperatures. The results for the C=0.20 and the C=0.32 crystals, shown in figure (2.2), are as expected. A smooth curve has been drawn through the points and the temperature obtained from the extrapolation to zero intensity is taken to be the Neel temperature. The results of Baker et al (1961) are well described by a linear relationship between the Neel temperature and the concentration and from this we deduce the concentrations of the specimens. Results are shown in table (2.2).

It was found that not all of the C=0.65 specimen was ordered at T=4.2K. It was observed, by shielding the crystal with cadmium, that all the intensity in the (100) reflection was coming from the upper part of the crystal. This could be explained on the basis of a concentration gradient in the crystal. The peak intensity of the (100) reflection from the upper part of the crystal was measured as a function of temperature and the results are shown in figure (2.3). The shape of the curve is consistent with a concentration gradient. The range of Neel temperatures across the upper part of the specimen is seen to be 5-14K. Although the results of Baker et al (1961) are not accurate at large concentrations, it would appear that the range of concentrations in the upper part of the crystal is approximately 0.6-0.7.
Figure 2.2

Temperature dependence of the peak intensity of the (100) Bragg peak for the crystals of MnF$_2$/ZnF$_2$ with $c=0.32$ and 0.20.
**TABLE 2.2**

Results of the determination of the Neel temperature and concentration of the three crystals of $\text{MnF}_2/\text{ZnF}_2$. 
<table>
<thead>
<tr>
<th>Sample</th>
<th>Neel Temperature $T_N$ (K)</th>
<th>Molar Concentration of Zinc - C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>49.5 ± 1.0</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>0.32</td>
<td>39.0 ± 1.0</td>
<td>0.32 ± 0.02</td>
</tr>
<tr>
<td>0.65</td>
<td>5-14</td>
<td>0.6-0.7</td>
</tr>
</tbody>
</table>
FIGURE 2.3
Temperature dependence of the peak intensity of the (100) Bragg peak for the upper part of the c=0.65 MnF$_2$/ZnF$_2$ crystal.
2.6 The Experiment

The peak in the cross-section, due to the magnetic excitation, has been measured for various values of the wavevector in the two principal symmetry directions in the Brillouin zone: the \{100\} and the \{001\} directions. Although there is a choice of zones in which to measure the excitation, this choice is restricted by considerations of focusing, magnetic form factor and whether the zone is magnetic. As the form factor falls off rather quickly with \(Q\), it is desirable to keep \(Q\) as small as possible. From the discussion of the cross-section in chapter 1, it can be seen that the intensity of scattering is greater in the magnetic zones.

All the experiments were performed with the (010) axis vertical, and the available zones satisfying the above conditions that were used are those containing the reciprocal lattice points (100) and (001). Throughout, the spectrometer was used in the \(M\)-configuration: scattering to the left at the monochromator, to the right at the sample and to the left at the analyser. This configuration is shown in figure (2.1). Resolution considerations show that optimum focusing is obtained in the \(M\)-configuration for wave vectors in the \{100\} direction when the wave vector is in fact taken in the \{100\} direction from the (001) reciprocal lattice point, and for the \{001\} direction, when the wave vector is in the \{001\} direction from the point (100).
data were also collected for these wave vector directions in the (101) zone. Figure (2.4) is a map of the relevant part of the plane of the reciprocal lattice.

Constant-Q scans were made for the wave vector in the focussed direction at intervals of 0.05 in the reduced wave vector from 0 to zone boundary, 0.5. In the cases where the magnetic excitation was at low frequency the scan was taken through the elastic peak. This applied to all scans in the 0.32 and 0.65 specimens. The scans were continued a sufficient way from the peaks for the background count to be ascertained.

For the experiment carried out on the PLUTO spectrometer, the energy was incremented through the scan, whereas on the C5 spectrometer the monochromator angle $2\theta_M$ is incremented. This latter procedure produces a slightly non-linear energy scale, in which the energy interval decreases with increasing energy but has the advantage that the change in the interval follows the change in resolution function. For the PLUTO experiments the energy increment was $\omega = 0.048 \text{ THz}$, while for C5 the spacing of the values of the energy transfer varied from 0.023 THz at $\omega = -0.5 \text{ THz}$ to 0.093 THz at $\omega = 2.3 \text{ THz}$.

For each scan, the monitor count is chosen to give a sufficient number of counts in the excitation peak.
Map of the region of the \{010\} plane of reciprocal space for the MnF$_2$ lattice in which the major portion of the data were collected. A square represents a nuclear reflection and a full symbol represents a magnetic reflection. Most of the scans were made for scattering vectors having their tips on the dashed lines.
CHAPTER 3

THE RESULTS OF THE SCATTERING EXPERIMENTS

3.1 Introduction

In this chapter the results of the neutron-scattering experiments on the three crystals of MnF$_2$/ZnF$_2$ are described. To facilitate this description the results are characterised by the least-squares fitting of simple line-shape functions to the scans. We begin with a verbal description.

3.2 Description of the Results

\( c = 0.20 \):

Constant-Q scans were carried out for an energy range corresponding to the pure crystal band for wave vectors in the \( \{100\} \) and \( \{001\} \) directions in all three zones (see figure 2.4). A single well-defined excitation was observed for all scattering vectors apart from \( (101) \) where the nuclear Bragg reflection completely obscured the extremely weak excitation peak. Some examples of the observed peaks are shown in figure 3.1. From the dispersion of the excitation and its variation with frequency it is obvious that it is just the spin wave that occurs in pure MnF$_2$ but with increased width and decreased peak frequency. No other excitation, magnetic or lattice, was apparent.

That the peaks observed in the nuclear zone \( (101) \) are broader and weaker than those in the magnetic zone is a
FIGURE 3.1

Some examples of neutron groups for the c=0.20 sample of MnF$_2$/ZnF$_2$ showing the fitted Lorentzian and classical oscillator line-shapes with a Gaussian fitted to the elastic peak. The points with energies above the dashed line have not been included in the fit (see text)

(a) $Q = (-0.2, 1)$
(b) $Q = (-0.3, 1)$
(c) $Q = (-0.5, 1)$
(d) $Q = (1,0.1)$
(e) $Q = (1,3,0)$
(f) $Q = (1,0.5)$

Note: In this and subsequent figures the scattering vector is given in the reduced notation defined in the text. Also as this vector is confined to the (010) plane its y-component is always zero and will thus always be omitted.)
Fig. 3.1(a)
MNF2:ZN(20%)  \( Q = (-0.5, 1.0) \)

**Fig. 3.1(c)**

- **COUNTS**
- **ENERGY (THZ)**
- **classical oscillator**
- **Lorentzian**
MNF2.ZN(20\%) \quad \mathbf{Q} = (1.0, 0.1)

Fig. 3.1(d)
MNF2: ZN(20%) \( q = (1.3, 0.0) \)

Counts

Energy (THZ)

Fig. 3.1(f)

Classical oscillator

Lorentzian
reflection of both the broader resolution effects and the property of the cross-section, pointed out in chapter 1 for the pure case, that the intensity is less in the nuclear zones. This effect can be seen quite clearly by comparing the scans for \( Q = (-0.3, 0, 1) \) and \( Q = (1.3, 0, 0) \) shown in figure 3.1.

\[ c=0.32: \]

The results for this sample are similar to those for \( c=0.20 \). As would be expected the extent of the shifting and broadening of the peaks is greater. Some examples are shown in figure 3.2. These results cannot be compared directly with those for the 0.20 crystal as the resolution conditions are somewhat different. As well as performing the experiment with looser collimation, the constant-\( k_0 \) experiment produces a slightly distorted scan. This effect was discussed in the previous chapter. For the constant-\( k' \) scans the resolution is slightly better but not as good as for the \( c=0.20 \) experiment. A constant-\( k' \) scan and constant-\( k_0 \) scan, both obtained for the same scattering vector, \( Q = (-0.3, 0, 1) \), are shown in figure 3.2.

\[ c=0.65: \]

The results for this specimen fall into three groups: those for the whole crystal, those for the ordered upper part of the crystal and those for the disordered lower part. In all cases the excitation was overdamped. It is evident that some remnant of the dispersion of the magnon exists as the shoulder of the elastic peak becomes more pronounced as the wave vector is increased, but in no case
FIGURE 3.2

Some examples of scans for the c=0.32 sample of MnF$_2$/ZnF$_2$ showing the classical oscillator fitted to the inelastic peak and a Gaussian fitted to the elastic peak

(a) $Q = (-0.15, 1)$ constant-$k_0$ experiment
(b) $Q = (-0.3, 1)$ ditto
(c) $Q = (1, 0.5)$ ditto
(d) $Q = (-0.3, 1)$ constant-$k'$ experiment
Fig. 3.2(a)
Fig. 3.2(b)
MNF2: ZN(32%)  \[ \theta = (1.0, 0.5) \]

Fig. 3.2(c)
MNF2 Zn(32%) $Q = (-0.3, 1.0)$

Fig. 3.2(d)
is there a well-defined peak. Some examples are shown in figure 3.3. The most interesting aspect of these results is the similarity of the scans from the ordered and disordered parts of the crystal.

3.3 Characterisation of the Results

The usual way of characterising a phonon or magnon peak in a neutron-scattering experiment is to quote the position of the peak and its full width at half maximum (FWHM), but as the data obtained for all three crystals was of such high quality it was decided to fit the scans with some suitable lineshape function. Also, the overdamped results for the c=0.65 sample are not amenable to this simple approach so the only method available is the least-squares fitting of a function.

From a knowledge of the cross-section for the pure system it is assumed that the scattering function is of the form

$$S(Q,\omega) = A(Q) |f(Q)|^2 kT B(\omega/kT)(1+Q^2/Q^2)F(Q,\omega)$$

(3.1)

where $B(x) = x/(1 - e^{-x})$, and $A(Q)$ is the intensity scaling parameter. All the other symbols have their usual meanings. The line-shape function is $F(Q,\omega)$.

An obvious choice of response function is that for a classical oscillator as this function is capable of describing both the well-defined peak and the overdamped situation. The classical oscillator line-shape function
FIGURE 3.3

Some examples of scans for the \( c=0.65 \) sample of \( \text{MnF}_2/\text{ZnF}_2 \) showing the fitting of the classical oscillator plus Gaussian

(a) \( Q = (0,0.5) \) whole crystal
(b) \( Q = (0,0.5) \) lower (disordered) part of crystal
(c) \( Q = (0,0.6) \) upper (ordered) part of crystal
(d) \( Q = (1,0.2) \) ditto
(e) \( Q = (-0.5,1) \) ditto
MNF2:ZN(65\%) \quad Q = (0.0,0.5)

Fig. 3.3(a)
MNF2: ZN (65%)  \( \theta = (0.0, 0.5) \)

Fig. 3.3(b)
Fig. 3.3(c)
MNF2:ZN(65%) \hspace{1cm} Q = (1.0, 0.2)

Fig. 3.3(d)
MNF2: ZN(65%)  $Q = (-0.5, 1.0)$

Fig. 3.3(e)
where $\omega_0$ and $r$ are the frequency and width parameters.

Another function which has been used to characterise one-magnon neutron-scattering peaks is the Lorentzian (see for example Schulof et al 1971) which has the lineshape function

$$F(Q,\omega) = \frac{r}{(\omega - \omega_0)^2 + \omega^2 r^2} \qquad (3.2)$$

$$\text{where } \omega_0 \text{ and } r \text{ are the frequency and width parameters.}$$

$$F(Q,\omega) = \frac{r}{2\pi} \left\{ \frac{1}{(\omega - \omega_0)^2 + r^2/4} + \frac{1}{(\omega + \omega_0)^2 + r^2/4} \right\} \qquad (3.3)$$

There are physical arguments both for and against the choice of these functions. The functions are both unphysical in the sense of their failure to satisfy sum rules but as we are only interested in their behaviour at and near the peak and not at high frequencies this shortcoming may be ignored. Our reasons for the choice are pragmatic: these functions are simple and are extremely widely used to describe magnon and phonon peaks.

The Lorentzian cannot describe the overdamped spectra so it is of no use for the $\gamma=0.65$ sample but where there is a well-defined peak it has the advantage over the classical oscillator in that the interpretation of the parameters is more straightforward: provided the two components of the function do not overlap significantly the parameters of the Lorentzian, $\omega_0$ and $r$ are the actual peak position and FWHM. This may not be true if the peak is extremely broad and the variation of the detailed-

(to page 56)
From the discussion of the resolution function in chapter 2, it is expected that the lineshape of the elastic scattering will be Gaussian. Consequently in the fitting to scans that go through the elastic peak a function of the form
\[ E(Q, \omega) = C(Q) \exp \left( -\omega^2 / a^2 W^2(Q) \right) \]  
(3.6)
is used to account for this component. The quantity C is the intensity scaling parameter and W is the FWHM of the peak if
\[ a = 1 / 2 \left( \log 2 \right)^{1/2}. \]
Thus the function used for the fitting is
\[ I(Q, \omega) = S(Q, \omega) + E(Q, \omega). \]

It should be remarked that the parameters obtained from the fitting of these functions contain the effects of instrumental resolution, so that corrections must be made if they are to be made characteristic of the specimen only. The possibility and the necessity for doing this are discussed in section 3.7.

In each scan there is a background count that is predominantly due to fast neutrons. This count is assumed to be constant across the scan and a value, chosen by inspecting the intensity at the ends of the scans away from the peaks, is assigned to each scan and added to the fitting function \( I(Q, \omega) \). For the constant-\( k_o \) scans \( I(Q, \omega) \) is multiplied by the \( k' \)-correction factor before the background is added.
The non-linear least-squares fitting was carried out using a routine written by the computing department of AECL, Chalk River. The weighting of the points was that appropriate to Poisson statistics and the quoted errors for the parameters are the statistical errors; in this case the error is one standard deviation which is $2/3$ confidence levels.

3.4 Results of the Characterisation for the c=0.20 Crystal.

It was found that the scans were reasonably well fitted by both the classical oscillator and the Lorentzian except for those having wave vectors close to the zone boundary. In these cases the high-frequency sides of the peaks fell away extremely sharply. Since it was the upper part of the peak for which characterisation was really required, all points above a certain cut-off energy were excluded from the fit. For the wave vector in the \{100\} direction the value chosen was 1.6THz and for the \{001\} direction, 1.8THz. It is believed that this sharp fall away was the effect of the density of states, which for the pure crystal peaks sharply close to the top of the band and falls to zero at the top. According to Svensson et al (1969) the top of the band in the \{100\} direction is 1.506THz and in the \{001\} direction, 1.651THz. Some examples of the fitted lineshapes are shown in figure 3.1. From these examples it can be seen that the Lorentzian provided the better fit for small wave vectors while the classical oscillator was preferable near the

(to page 57)
balance factor across the peak becomes appreciable. The parameters for the classical oscillator are not precisely the peak position and FWHM: the greater the width the greater discrepancy between $\omega_0$ and the peak position. This means that the value of $\omega_0$ obtained will depend on the instrumental resolution conditions, but, as will be seen, this effect is quite small.

In the treatment of phonons, the classical oscillator is generally held to be the better approximation as the behaviour of the self energy is reproduced slightly better. Use of the Lorentzian is equivalent to the replacing of the self energy by a constant whereas expanding the self energy to lowest order in the frequency, giving a linear term, yields the classical oscillator response function. Although the dependence of the Green's function on the self energy for magnetic excitations is not so straightforward, it is hoped that the argument is to some extent applicable in the magnetic case.

In the limit where $\omega_0$ is much less than $\tau$, the classical oscillator function goes over to the Debye function which is given by

$$P(Q,\omega) = \frac{\tau}{1 + \omega^2 \tau^2}$$

(3.4)

where $\tau$ is a relaxation time. The relationship between this parameter and those of the classical oscillator in the extreme overdamped limit is

$$\tau = \frac{\tau}{\omega_0^2}$$

(3.5)
zone boundary. In all cases the Lorentzian fell below the classical oscillator on the low-frequency side of the peak and provided the better fit in this region, whereas it is the classical oscillator that falls below the Lorentzian on the high-frequency side of the peak and provides the superior fit in this region. On balance it was felt that overall the classical oscillator was preferable to the Lorentzian and so it is for the former that the values of the model parameters are presented in detail. The width and frequency parameters from the Lorentzian for the two wave vector directions in the focussed positions are shown in figure 3.14. The corresponding parameters from the fitting of the classical oscillator function for the same set of scans are shown in figure 3.5. Scans were also performed for the same wave vector but different scattering vectors (see figure 2.4) and the frequency and width parameters are plotted in figure 3.6. In figure 3.7 the results for the intensity parameter $A$ are presented. The values obtained have been scaled to a common monitor. The apparent oscillation of $A$ in one region is not significant. The lower points have been obtained by fits to scans that do not pass through the elastic peak while the upper points are obtained from ones that do. This behaviour highlights a failing of the least-squares fitting method: the calculated errors in the parameters can be quite small even though the fit to the data is not particularly good. From the figure, the reduction in intensity in the non-magnetic zone (101)
FIGURE 3.4

The frequency and width parameters, obtained from the fitting of a Lorentzian line-shape function to the scans for the c=0.20 sample of MnF₂/ZnF₂ in the focussed positions, compared with the position and FWHM of the peaks in pure MnF₂ obtained by Svensson et al (1969).

(a) The frequency parameters (open circles) and the MnF₂ peak position (full circles). The induced frequency shift is shown in the lower part of the figure.

(b) The width parameter (open circles) and the FWHM of the MnF₂ peaks (closed circles). The intrinsic width obtained by the deconvolution procedure is shown in the lower part of the figure.
FIGURE 3.5
Frequency and width parameters obtained by the fitting of a classical oscillator line-shape to the scans for the $c=0.20$ sample of $\text{MnF}_2/\text{ZnF}_2$ in the focussed positions.
FIGURE 3.6

The frequency and width parameters obtained from the fitting of the classical-oscillator line-shape to scans, other than those made in the focused positions, for the c=0.20 sample of MnF$_2$/ZnF$_2$. 
FIGURE 3.7
The spin-wave scaling parameter (A) obtained from the fitting of the classical-oscillator line-shape to the data for the c=0.20 sample of MnF$_2$/ZnF$_2$.

FIGURE 3.8
The FWHM (W) and scaling parameter (C) obtained from fitting a Gaussian to the elastic peak in the same procedure.
REDUCED WAVE VECTOR
REDUCED WAVE VECTOR

A (arb. units)

W (THz)

C (arb. units)

\((-q_x, 1)\)  
\((0, 1-q_z)\)

\(c = 0.20\)
discussed above, can be seen quite clearly.

In all cases the elastic peak was well fitted by a Gaussian and the parameters - W, the FWHM and C, the intensity - are presented in figure 3.8.

3.5 Results of the Characterisation for the c=0.32 Crystal

The Lorentzian was found not to give a reasonable fit under any circumstances, while the quality of the fit for the classical oscillator was generally much better than for the c=0.20 sample. The success of the latter function is attributable to two possible factors. Firstly, the peaks are at lower energy and thus further away from the top of the pure-crystal band than in the c=0.20 sample and hence the effect of the sharp peaking of the density of states is not so pronounced. Secondly, the resolution is broader, tending to smooth out the density-of-states effect. Also the peaks are intrinsically broader which allows a greater variation of the self energy and thus the assumption of a constant self energy which is inherent in the Lorentzian is less likely to be applicable.

In carrying out the fitting procedure it was found that the elastic peaks were not centred at precisely zero energy. Repeating the fitting allowing the position of the Gaussian to vary showed that the peaks were displaced by amounts around 0.05THz. This displacement is probably due to the irregularly-shaped crystal lying somewhat off-centre in the neutron beam. As this quantity could be determined extremely accurately in the fitting, the
energy scale was adjusted in each scan to position the elastic peak at zero energy.

Some examples of the fits are shown in figure 3.2. The constant-\(k'\) and constant-\(k_0\) scans for \(Q = (-0.3,0,1)\) are given and the sharper peaks in the former, resulting from the better resolution, can be seen quite clearly.

The constant-\(k_0\) experiment width and frequency parameters for the two symmetry directions in the foçussed position are plotted in figure 3.9. Qualitatively, the variation of the parameters with wave vector is extremely similar to the corresponding results for the \(c=0.20\) crystal (figure 3.5). These two parameters for the remaining constant-\(k_0\) scans are plotted in figure 3.10. The spin-wave intensity parameter \(A\) and the parameters of the Gaussian fit to the elastic peaks for the constant-\(k_0\) scans are given in figure 3.11. Again the qualitative behaviour of \(A\) is extremely similar to that for the \(c=0.20\) sample (figure 3.7). In this case, however, the oscillators are absent; all the scans were taken through the elastic peak. But, more importantly, the classical oscillator gives a much better fit at this concentration.

The fitting parameters for the limited amount of data collected in the constant-\(k'\) experiment are plotted in figure 3.12.
FIGURE 3.9

The frequency and width parameters obtained from the fitting of the classical-oscillator line-shape to the focussed-position scans for the $c=0.32$ sample of MnF$_2$/ZnF$_2$. These data were collected in a constant-$k_0$ experiment.
FIGURE 3.10

The frequency and width parameters obtained from the fitting of the classical-oscillator line-shape to scans for the c=0.32 sample of MnF$_2$/ZnF$_2$ measured in the constant-$k_0$ experiment.
REDUCED WAVE VECTOR

FREQUENCY (TH₂)

(1 + kₓ, 0)
(0, 1 - k₂)

WIDTH (TH₂)

(1 - kₓ, 1)
(1, 1 - k₂)

kₓ   k₂
0   0
-.5  -.5

C = 0.032
FIGURE 3.11

The spin-wave scaling parameter (A) and the elastic peak FWHM (W) and scaling parameter (C) obtained from the fitting of a classical oscillator plus Gaussian to the constant-\(k_0\) scans for the \(c=0.32\) sample of MnF\(_2\)/ZnF\(_2\).
FIGURE 3.12

The parameters obtained from the fitting of a classical oscillator plus Gaussian to the scans for the constant-$k'$ experiment on the $c=0.32$ sample of MnF$_2$/ZnF$_2$. 
3.6 Results of the Characterisation for the $c=0.65$ Crystal.

Some examples of the fitting of the classical oscillator function to scans for this sample are shown in figure 3.3. For the $c=0.20$ and 0.32 samples the number of counts in the peaks was always sufficiently large for the fractional statistical error to be small. In this case, where the excitation intensity is weak, this is no longer so; consequently the scatter of points about the fitted line.

In fitting these scans it was found that there was a correlation between the parameters $\omega_0$ and $r$ of the form

$$r \propto \omega_0^2$$

which, in the light of equations (3.4) and (3.5), is just what would be expected for a highly overdamped classical oscillator. It was found, however, that in no case did the Debye function, given by equation (3.4), give a good fit.

The parameters obtained from the fitting of the classical oscillator for the whole crystal are plotted in figure 3.13; for the upper (ordered) part of the crystal in figure 3.14 and for the lower part in figure 3.15.

To improve the statistical error, some scans for the upper part of the crystal were repeated and they are indicated by the open circles. The errors are not shown for these points as they are much the same as for the corresponding points.
FIGURE 3.13

The parameters obtained from the fitting of a classical-oscillator plus Gaussian to the scans for the whole of the c=0.65 crystal of MnF$_2$/ZnF$_2$. 
REDUCED WAVE VECTOR

\[ A \text{ (arb. units)} \]

\[ W \text{ (THz)} \]

\[ C \text{ (arb. units)} \]

\[ q_x \]

\[ q_z \]
FIGURE 3.14
The parameters obtained from the fitting of a classical-oscillator plus Gaussian to the scans for the upper (ordered) part of the c=0.65 crystal of MnF$_2$/ZnF$_2$. 
FIGURE 3.15

The parameters obtained from the fitting of a classical oscillator plus Gaussian to the scans for the lower (disordered) part of the c=0.65 crystal of MnF$_2$/ZnF$_2$. 
REDUCED WAVE VECTOR

- FREQUENCY (THz)
- WIDTH (THz)

(0.1-k_z) (1.k_z)

A (arb. units)

W (THz)

C (arb. units)

C = 0.65 (DISORDERED)
3.7 Resolution Corrections for the $c=0.20$ Results.

The widths of the spin-wave peaks for the $c=0.20$ crystal obtained by the least-squares fitting of the Lorentzian function have been corrected for instrumental resolution effects.

As has been pointed out in section 2.4, the observed intensity is the convolution of the theoretical cross-section with the resolution function which is assumed to be Gaussian. The FWHM of this Gaussian is known for each scattering vector from the measurements, under conditions identical to those of the $c=0.20$ experiment, by Svensson et al (1969 and private communication) of the widths of the spin waves in pure MnF$_2$, which have zero intrinsic width and hence give the width of the resolution function in that region of $(Q,\omega)$ space. (This procedure is further discussed in section 4.4).

The method used was to numerically convolute a unit Gaussian with a Lorentzian for a range of widths and determine the FWHM's of the resulting peaks. And since only the intrinsic and measured widths relative to the resolution width are important, this allows the intrinsic width to be determined by interpolating the values so obtained. The results are plotted in figure 3.4(b).

As the frequency parameter in the Lorentzian function may be interpreted as the peak position, the results of Svensson et al (1969) for the peak positions in pure MnF$_2$ have been used to generate the induced shifts from these parameters. The results are plotted in figure 3.4(a).
One of the most interesting effects observed in the experiment performed by Svensson et al. (1969) on the $c=0.05$ crystal is the pronounced peak in the induced width at a wave vector part way between the zone centre and boundary, and interpreted by them as a resonant mode. There is also the equally pronounced minimum in the reduced shift of the peak position. Neither of these effects are evident in the results shown for the $c=0.20$ crystal in figure 3.4.

3.8 Comments

The classical oscillator line-shape function has been shown to give a good fit to the scans in all three crystals apart from the one qualification in the $c=0.20$ case. Although the frequency parameter is expected to vary for peaks of the same wave vector having a different scattering vector due to the varying width that results from the variation in the resolution conditions with scattering vector, it is found for the $c=0.20$ and 0.32 crystals, however, that this effect is small even in the comparison of the constant-$k_0$ and constant-$k'$ results in the latter crystal.

The dispersion curves for the frequency parameter for the two smaller-concentration crystals resemble the pure crystal curves quite closely as to shape. It should be noted that the frequencies for small wave vector are not accurate. This is the effect of instrumental resolution.
In section 2.11., it was assumed that the dispersion surface be planar over the region that the resolution ellipsoid cut it. Obviously this is not the case in the vicinity of the deep minimum in the dispersion surface at the zone centre. The effect is to give an observed frequency that is slightly higher than the actual frequency. As this only affects frequencies at wave vectors with magnitudes up to 0.05, no attempt at correcting this has been made.

There is also a strong similarity in the variation of the width parameter with wave vector between the c=0.20 and 0.32 crystals. The width increases monotonically apart from the point $q = (0,0,0.45)$ for both concentrations. That this point should be as it is in both samples is interesting but the effect is not sufficiently large, in comparison with the errors, to be significant.

The similarity between the results for the upper (ordered) part and the lower part of the c=0.65 crystal that can be seen by simply inspecting the scans is further reinforced by the frequency and width parameters. The criterion for ordering we have used is a non-zero value of the order parameter: the intensity of the (100) Bragg peak which is the square of the sub-lattice magnetisation. Obviously the intensity of the scattered neutrons is not zero above the transition due to the many other contributing processes but there is observed for the c=0.20 and 0.32 crystals an unequivocally-sharp fall off in intensity over a narrow temperature range that allows a Neel temperature to be ascribed to the sample. For
the c=0.65 sample the reduction in intensity takes place over a broad temperature range which is interpreted as being due to a concentration gradient. As the scattered intensity from the upper part of the crystal is comparable to that from the lower, the concentration gradient straddles the critical concentration. The results for the upper and lower parts of the crystal represent concentration-averaged behaviour of the system just below and just above the transition. The critical concentration of the MnF₂/ZnF₂ system is of interest, both experimentally and theoretically, as an example of a dilute magnetic system. The only experimental determination of this quantity of which this author is aware is by Baker et al (1961) which has already been discussed above. They report a value of 0.75 which agrees with the percolation theory result (see Shante and Kirkpatrick 1971) for the critical concentration of a b.c.c. lattice of 0.757. (This may be compared with the results of the s.c. and f.c.c. lattices of 0.693 and 0.805).

Generally the behaviour of the frequency and width for the c=0.65 sample follows the pattern of the other two concentrations: both quantities increasing with wave vector. This behaviour lends considerable weight to simple interpretation of this contribution to the inelastic scattering as overdamped spin waves.
CHAPTER 4

COMPARISON OF THE RESULTS WITH THEORY

4.1 Introduction

In this chapter the experimental results are compared with calculations based on the coherent potential approximation (CPA) for excitations in disordered systems; introduced initially by Soven (1967) in his theory of electrons in disordered alloys. This theory, as is described below, was adapted to spin waves in disordered antiferromagnets by Buyers, Pepper and Elliot (1972) (referred to below as BPE) and applied to (Mn,Co)$_2$F$_2$ and K(Mn,Co)$_3$F$_3$ systems. The theory used in this chapter is essentially similar to theirs although somewhat different approximations have been made in detail. Similar calculations have now been reported by Buyers, Pepper and Elliot (1973).

The equation for the spin-wave Green's function was derived in chapter 1 and is given by equation (1.5). In the presence of impurities, the interaction matrix $D$ may be separated

$$D = D - V$$

(4.1)

so that $D$ now corresponds to the interaction matrix of the pure crystal and $V$ contains the impurity terms. If $G$ is the Green's function of the impurity system it follows from equations (4.1) and (1.5) that

$$G = P + PVG$$

(4.2)
As $V$ and hence $G$ lack the translational symmetry of the pure crystal, solutions to this equation cannot be simply obtained in the form of Fourier transforms. As has been shown for vibrational systems by Elliot and Taylor (1964), for ferromagnets by Izyumov (1966) and for antiferromagnets by Lovesey (1968), if there is only one defect and it affects only a small number of surrounding sites, the matrix $V$ consists of a single block of manageable proportions and the problem may be solved exactly. For dilute systems, Elliot and Taylor (1967), by assuming that $V$ consists of non-overlapping blocks each corresponding to a particular defect, show that in this case solutions can also be obtained.

The theory is most naturally formulated in terms of the self energy which is formally introduced by the equation

$$<G> = P + P \Sigma <G>,$$  \hspace{1cm} (4.3)

where the angular brackets denote the configuration average. Since the averaging has restored the translational symmetry, the equation can be solved by Fourier transforming. Elliot and Taylor (1967) in fact reduce their problem to this form.

Svensson et al (1969), in their calculation of the neutron-scattering cross-section for the $c=0.05$ MnF$_2$/ZnF$_2$ system, have used an approach which is essentially the same as Elliot and Taylors. And, as was discussed in chapter 1, obtained very good agreement.
with experiment.

Obviously there is no possible extension of these approaches to systems with large defect concentrations. It would appear that a self-consistent method would offer the best prospect. Before describing such a method, we introduce an extremely simple model that, apart from being of some use in concentrated defect systems in its own right, provides an approximation that makes the self-consistent procedure workable.

4.2 The Cluster Model

The cluster model is reviewed by Cowley and Buyers (1972) and their notation is followed for the application to MnF$_2$/ZnF$_2$. This model uses the Ising approximation: that is the transverse part of the Hamiltonian, given by equation (1.1), is ignored and thus the model is only applicable at the $\{100\}$ zone boundary. Also only the second-nearest-neighbour exchange, which is the strongest, is considered and the dipolar anisotropy, which is relatively unimportant at the zone boundary, is ignored. For the pure system the interaction matrix becomes, as a result of equation (1.8), quite simply

$$D_{ij} = \omega_i \delta_{ij} p_i$$

where the Ising frequency is defined by

$$\omega_i = z IS$$

and $p_i$ is $\pm 1$ according as to whether $i$ is on the a or
b sublattice. The resulting cross-section is easily seen to be of the form of two delta functions at plus and minus the Ising frequency corresponding to neutron energy loss and gain. With $I = J_2$ and taking the value given in chapter 1, the Ising frequency is $1.488 \text{ THz}$ which may be compared with the result of $\omega_{(200)} = 1.506 \pm 0.013 \text{ THz}$ determined by Svensson et al (1969).

For the sake of generality we consider a system in which the defect is magnetic. The host species, A, having spin and Ising parameter $S_A$ and $I_{AA}$ and the defect species B; $I_{BB}$ and $S_B$. The host-defect interaction being $I_{AB}$. For the magnetic-ion sites with $z$ nearest neighbours there are $2z+1$ different impurity clusters: an A surrounded with from 1 to $z$ B's and a B surrounded with from 0 to $z$ A's. For a site with $r$ B's on the nearest neighbours, the contribution to the impurity potential will be

$$V_A(r) = \sum p_i \delta_{ij}$$

where

$$V_A(r) = r (S_B I_{AB} - S_A I_{AA})$$

if the ion is an A, and

$$V_B(r) = \sum p_i \delta_{ij}$$

where

$$V_B(r) = r S_B I_{BB} + (z-r)S_A I_{AB} - z S_A I_{AA}$$
if the ion is a B. These clusters will then have
Ising frequencies

$$\omega_A(r) = \omega_I + V_A(r)$$

$$= z I_{AA} S_A = r (I_{AB} S_B - I_{AA} S_A). \quad (4.8)$$

and

$$\omega_B(r) = \omega_I + V_B(r)$$

$$= r I_{BB} S_B + (z-r) S_A I_{AB}. \quad (4.9)$$

The intensity of the delta function in the cross-section at a particular cluster frequency is given by the concentration of that cluster weighted by the appropriate scattering length. Thus, for A say, the intensity is

$$b_A^2 c_A P(r)$$

where $P(r)$ is the probability of a site having $r$ B's on the neighbouring sites and is given by

$$P(r) = (1-c)^{z-r} c^r. \frac{z!/(z-r)!}{r!}. \quad (4.10)$$

where we have taken $c = c_B = 1-c_A$ and $b_A$ is the scattering length of the ion of type A. Thus the spectrum will consist of $2z+2$ delta functions - considering only neutron energy loss - through which a smooth curve may be drawn to approximate the cross-section.

For MnF$_2$/ZnF$_2$, the impurity being non-magnetic, the cluster frequencies will be given by

$$\omega(r) = (z-r) I S \quad (4.11)$$

where $I = J_2$ in this approximation. There will be no
contributions from the clusters centred on an impurity. Using the values of $J_2$ and $S$ appropriate to pure MnF$_2$, the frequencies and intensities may be calculated. However it is possible to produce a continuous function that smoothly interpolates the histogram produced. By simply replacing the factorials in equation (4.10) by Gamma functions the continuous function given by

$$S(\omega) \propto \frac{1}{1-e^{-\beta \omega}} c(1-c)^{\omega/IS} \frac{\Gamma(z+1)}{\Gamma(\omega/IS+1)\Gamma(z-\omega/IS+1)}$$

is obtained.

The results for the three concentrations are shown in figure (4.1) with the experimental results for the {100} zone boundary scans. The theoretical intensity has been scaled to give the best fit in each case and the elastic scattering has been fitted with a Gaussian as described in the previous chapter. Resolution corrections, the details of which have been given in a later section, have been made. As can be seen, the agreement in each case is quite good.

The use of a cluster model by Buchanan et al (1972) to describe the two-magnon peak in the Raman spectra of MnF$_2$/ZnF$_2$ systems has been mentioned in section (1.5). In this case the cluster is two nearest-neighbour magnetic ions surrounded by their own nearest neighbours. The Ising frequency is the energy required to produce spin deviations on both ions. Their calculation proceeds in much the same way as for the one-magnon excitation.
FIGURE 4.1

Comparison of the cluster-model cross-section with the [100] zone-boundary scans in the focussed positions for the three samples of MnF$_2$/ZnF$_2$. A Gaussian has been fitted to the elastic peak:

(a) $c=0.20$

(b) $c=0.32$ constant-$k'$ experiment

(c) $c=0.65$ upper (ordered) part of crystal
MNF2: ZN(20%) \ O = (-0.5, 1.0)

Fig. 4.1(a)
MNF2: Zn(65%)  \( Q = (-0.5, 1.0) \)

COUNTS

1000

750

500

250

0

-0.50

0.00

0.50

1.00

1.50

ENERGY (THZ)

Fig. 4.1(c)
The Coherent Potential Approximation

A self-consistent method has been developed for the model of a single electron band in the tight-binding representation by Soven (1967) for which the defect potential is the sum of the contributions from the individual atomic sites. This latter point represents a considerable simplification. Soven suggested that the actual crystal be replaced by an effective medium that is determined by the requirement that on average the scattering from a single site be zero. The single-site T-matrix for the scattering from a site $i$ in the effective medium with potential $\tilde{V}_i$ relative to the medium is shown by Soven to be

$$\tilde{t}_i = \tilde{V}_i + \tilde{V}_i g \tilde{t}_i$$

(4.13)

where $g$ is the electron Green's function for the effective medium. The requirement for no further scattering is just

$$\langle \tilde{t}_i \rangle = 0$$

(4.14)

which is

$$\sum_{\lambda} c_{\lambda} \tilde{t} = 0$$

(4.15)

where $c_{\lambda}$ is the concentration of scattering centres of type $\lambda$. The potential describing the effective medium is called the coherent potential and it is determined by the last equation.

The way in which the coherent potential arises in the most general case may be seen as follows. The
The equation (4.2) for the exact Green's function can be written as

$$G^{-1} = P^{-1} - V \quad (4.16)$$

$$= P^{-1} - W - (V - W) \quad (4.17)$$

where $W$ is the, as yet unspecified, coherent potential. Thus

$$G^{-1} = g^{-1} - V \quad (4.18)$$

where

$$\tilde{V} = V - W \quad (4.19)$$

is the impurity potential relative to the effective medium, and

$$g = P + PWg \quad (4.20)$$

is the Green's function for the effective medium. Now from equation (4.8)

$$G = g + g \tilde{V} G \quad (4.21)$$

$$= g + g T g \quad (4.22)$$

where the latter equation defines the full crystal $T$-matrix of the effective medium. The requirement for no further scattering on the average is

$$\langle G \rangle = g \quad (4.23)$$

or equivalently

$$\langle T \rangle = 0 \quad (4.24)$$

In the single-site approximation this reduces to the result given by equation (4.14). Comparison of equations (4.20) and (4.3) shows that
the coherent potential is just the self energy.

Leath (1968), using the diagrammatic analysis of Langer (1961), has obtained a result equivalent to the CPA for a mass-disordered vibrational system. He shows that within the single-site approximation this is the best self-consistent procedure.

In applying the CPA to an antiferromagnet there are some further considerations that must be made. As the defect potential at a given site in this system will depend not only in the type of ion at the site but also on the nature of the nearest neighbours, it will not be of the simple form assumed above. This may be overcome by identifying clusters of the type discussed in section 2 as the scattering entities and ignoring the correlation between them. There are 2z+2 types of clusters; including that of the pure crystal for which the defect potential is zero.

In the single-site approximation the self energy is diagonal in the site representation so that the spatial Fourier transform is independent of wave vector. As there are two magnetic ions in the unit cell, there will be two independent components of the self energy. But as a result of time-reversal invariance

\[ \sigma_{aa}(q,\omega) = -\sigma_{bb}(q,-\omega) \] (4.25)

and consequently the two components of the self energy are related so that
\[ \Sigma(q, \omega) = \left( \Sigma(\omega) \right)_0 - \Sigma(-\omega). \quad (4.26) \]

Only the Ising terms are assumed to contribute to the defect potential and these are just the terms discussed in section (4.2) and given by equations (4.5) and (4.7).

The Green's function that appears in the denominator of the single-site T-matrix is just the diagonal component of \( g \);

\[ g_0(\omega) = \frac{1}{N} \sum_q g_{aa}(q, \omega). \quad (4.27) \]

Since the defect potential of the pure cluster is zero, the configuration average of the T-matrix may be manipulated so that

\[ \Sigma(\omega) = \sum_\lambda c_\lambda x^\lambda \quad (4.28) \]

where this sum, and all subsequent sums over \( \lambda \), are sums over all the types of defects, i.e. all \( 2z+1 \) clusters.

As for the simple cluster model, in the MnF_2/ZnF_2 system only the \( z \) clusters surrounding a manganese ion are counted. The quantity defined by

\[ x^\lambda = V_\lambda / \left( 1 - (V_\lambda - E) g_0 \right) \quad (4.29) \]

has the property

\[ x^\lambda_a(\omega) = x^\lambda_b(-\omega) \quad (4.30) \]

which follows from equation (4.25).

Equations (4.26-4.28), along with the relationship

\[ g^{-1}(q, \omega) = p^{-1}(q, \omega) - \Sigma(q, \omega), \quad (4.31) \]
where $P$ is as given by the equation (1.10), constitute
the set of equations that must be solved self-consistently
to obtain the self energy and hence the Green's function.

As the off-diagonal components of the self energy
are zero there will be no renormalisation of the transverse
terms so some attempt must be made to accomplish this.
In particular the Goldstone theorem requires that for an
isotropic system the excitation frequency for zero wave
vector be zero. So it can be seen that in this sense
the approximations made yield an unphysical result. As
always the excitation spectrum of the system is given by
the poles of the Green's function; in this case by the
zeros of the determinant of equation (4.31). So the
transverse terms must be corrected in such a way that
they effect the cancellation of the longitudinal terms in
the determinant at zero wave vector and frequency and
thus satisfy the Goldstone theorem. To this end BPE
replace $B^2(q)$ by

$$
\left\{ B(0) + \Sigma(-\omega) \right\} \left\{ B(0) + \Sigma(\omega) \right\} \frac{B^2(q)}{B^2(0)}
$$

which will have the desired effect and will not be an
unreasonable form for the transverse part over the whole
of $(q, \omega)$ space. They further suggest that this method
of correction will be applicable to anisotropic systems.

The method used in this thesis to correct the
transverse part follows a suggestion by Cowley (private
communication) which is to treat $B$ in the average crystal
approximation. The average value of $B$ is obtained by
constraining the pole of the Green's function at zero frequency and wave vector, which is just the anisotropy gap, to take on a value that represents some appropriate average. For the present system it is assumed that

$$\omega_0 = \omega_0^{\text{pure}} \cdot (1-c)^{3/2}.$$ 

The justification of this choice may be seen by the inspection of equation (1.16) which shows the square of the zone-centre frequency in pure MnF$_2$ to be proportional to the product of the spin and the anisotropy field. Upon assuming that the spin scales as the concentration of manganese and that the anisotropy field depends on the square of the spin this relation is obtained. This would seem a reasonable variation of the zero-wave-vector frequency with concentration as this quantity would be expected to be characteristic of the long-range behaviour of the crystal. There is some experimental evidence to support the choice of the concentration dependence of the anisotropy gap. Foner (1964) has measured the antiferromagnet resonance frequencies of two samples of MnF$_2$/ZnF$_2$ with $c=0.10$ and 0.56 and these results are in reasonable agreement with values obtained from the value for pure MnF$_2$ (Bloor and Martin 1961) if this form of the dependence is assumed. Consequently in this treatment $B^2(q)$ is replaced by $f B^2(q)$ where $f$ is given by

$$\{ A(0) + E(0) \}^2 - f B^2(0) = \omega_0^2.$$ 

The calculation of the cross-section is facilitated
by the use of the conditional Green's functions introduced by Elliot and Taylor (1967) and further developed by Aiyer et al (1969); BPE give detailed considerations for the multi-defect case. In the present system, however, the defects are non-magnetic and only the host-host Green's function is required and this is given by

\[ G_{\text{HH}}^{\text{KK}}(q, \omega) = \bar{X}_K(\omega) \bar{g}_{\text{kk}}(q, \omega) \bar{X}_K(\omega) + \delta_{\text{kk}}, \bar{X}_K(\omega) \{ 1 - \bar{X}_K(\omega) \} \]

\[ g_{\text{kk}}(q=0, \omega). \]

It is found that the majority of the structure of the cross-section comes from the first term of this expression. The contribution from the second term is relatively small and slowly varying with frequency and may be regarded as incoherent scattering from randomly distributed manganese ions. As for the pure-crystal cross-section discussed in chapter 1, the components of \( G \) combine in different ways for the scattering vector in magnetic and non-magnetic zones; giving the greater intensity in the former.

The computation of the cross-section was carried out using a program written jointly with R.A. Cowley. The starting value of the self energy had the real part equal to the average impurity potential and the imaginary part equal to 0.1 THz. The convergence was extremely rapid requiring only four iterations to achieve four-figure accuracy for the MnF\(_2\)/ZnF\(_2\) system.
4.4 Instrumental Resolution Corrections

The basis of the instrumental resolution corrections has been discussed in section (2.4). For the experiments in which the scattered energy was held constant, the only correction is the frequency convolution of the theoretical cross-section with the resolution function which was shown to be well-approximated by a Gaussian. For the $c=0.20$ specimen the FWHM of the resolution Gaussian used in performing the convolution with the theoretical cross-section for a particular scattering vector is that for the observed width of the excitation in the pure system. For the other two concentrations the resolution width chosen was the FWHM of the elastic peak of the particular scan.

Two methods were used in performing the convolutions. The first was the direct numerical evaluation of the integral. The method used required the theoretical cross-section, which is tabulated at intervals of 0.025 THz, to be a continuous function. This was accomplished by interpolating between the seven nearest points to the frequency specified giving an accuracy of better than 1 except for the small wave-vector peaks which are extremely narrow. The second method was based on the property that the Fourier transform of the convolution of two functions is the product of the Fourier transforms of the functions. This use may be made of routines that exploit extremely efficient fast-Fourier-transform algorithms. The program used is due to Ure and Flinn (1971). This method proved to be some seventeen times faster than the first. Although there is a slight loss of accuracy, this is not significant.
FIGURE 4.2
An example of the effect of the convolution of the theoretical cross-section with the resolution Gaussian.
Fig. 4.2

MNF$_2$:ZN(32\%)  \( Q = (-0.35, 1.0) \)
EFFECT OF CONVOLUTION

INTENSITY

12.000

9.000

6.000

3.000

0.000

ENERGY (THZ)

0.00  0.50  1.00  1.50  2.00
As the resolution width is generally much less than the width of the theoretical peak, the principal effect is not the broadening but the removal of fine structure. As can be seen from the example shown in figure (4.2) all detailed structure that occurs on a frequency scale smaller than the resolution width is smoothed out.

For the constant-\(k_0\) experiments, the \(k'\)-correction was applied to the cross-section after the convolution was carried out. The factor is given by equation (2.8).

4.5 Comparison of Theory and Experiment

The results of the calculations show the cross-section to be of the form of a single peak with some structure, the amount of structure increasing with increasing concentration of zinc. Most of this structure, however, is removed by the convolution with the resolution function. Qualitatively the theory is in good agreement with the results of the \(c=0.20\) and \(0.32\) crystals: the peak position increasing monotonically with wave vector and the width increasing with wave vector for small wave vectors but showing little change close to the zone boundary. Although it would be possible to make a quantitative comparison of peak positions and widths this only gives limited information so that only direct comparison of theoretical lineshapes and neutron groups are made.

\(c=0.20\):

The comparison of theory and experiment is shown in figure 4.3. As before the intensity has been scaled to
FIGURE 4.3

Comparison of the CPA theory with the neutron groups for the c=0.20 crystal of MnF$_2$/ZnF$_2$ at various wave vectors. A Gaussian has been fitted to the elastic peak

(a) $Q = (-0.1, 1)$

(b) $Q = (-0.25, 1)$

(c) $Q = (-0.5, 1)$

(d) $Q = (1, 0.15)$

(e) $Q = (1, 0.35)$
MNF$_2$:ZN(20%) \quad Q = (-0.1, 1.0)

Fig. 4.3(a)
Fig. 4.3(b)
MNF2:Zn(20%)  \( Q = (-0.5, 1.0) \)

**Fig. 4.3(c)**
MNF$_2$:Zn(20\%) \quad \theta = (1.0, 0.15)

**Fig. 4.3(d)**
MNF2:ZN(20%) \quad Q = (1.0, 0.35)

Fig. 4.3(e)
give the best fit. For large wave vectors the agreement is quite good, particularly on the high-frequency side of the peak. On the low-frequency side, the theory is seen to decrease too quickly. For small wave vector the agreement is still reasonable as to shape but the theory peaks at higher frequency; the discrepancy increasing with decreasing wave vector. This discrepancy is most probably due to the inadequacy of the method used to correct the transverse terms since the theory is bound to be more sensitive to this correction at small wave vectors.

\( c=0.32 \):

The comparison with the constant-\( k' \) experiment is shown in figure 4.4 and with the constant-\( k_0 \) experiment in figure 4.5. As for the \( c=0.20 \) crystal, the agreement is better for large wave vector but here the discrepancy between experiment and theory, which again peaks at too high a frequency, is far more pronounced.

\( c=0.65 \):

The comparison of theory and the results for the upper (ordered) part of the crystal is shown in figure 4.6. The theory shows a well-defined peak for large wave vectors that is not apparent from the experimental points. As the results of this experiment are obtained at a temperature just below the transition, it is obvious that the spin-wave approximation is not applicable. It may well be that the overdamped nature of the scattering is that appropriate to an antiferromagnet
Comparison of the CPA theory with the neutron groups for the $c=0.32$ crystal of $\text{MnF}_2/\text{ZnF}_2$ obtained in the constant-$k'$ experiment, at various wave vectors. A Gaussian has been fitted to the elastic peak

(a) $Q = (-0.2, 1)$

(b) $Q = (-0.4, 1)$
Fig. 4.4(a)

COUNTS

ENERGY (THZ)

MNF2, ZN(32%)  \( q = (-0.2, 1.0) \)
MNF2:ZN(32%)  \( \mathbf{Q} = (-0.4, 1.0) \)

**Fig. 4.4(b)**
Comparison of the CPA theory with neutron groups for the c=0.32 crystal of MnF$_2$/ZnF$_2$, obtained in the constant-$k_0$ experiment, at various wave vectors. A Gaussian has been fitted to the elastic peaks

(a) $Q = (1,0.2)$
(b) $Q = (-0.5,1)$
(c) $Q = (1,0.35)$
Fig. 4.5(a)

MNF2:ZN(32%) $\mathbf{Q} = (1.0, 0.2)$
Fig. 4.5(b)
MNF2:Zn(32%) \quad \mathbf{q} = (1.0, 0.35)

![Graph](image)

Fig. 4.5(c)
FIGURE 4.6

Comparison of the CPA theory with neutron groups for the upper (ordered) part of the c=0.65 crystal of MnF$_2$/ZnF$_2$ at various wave vectors. A Gaussian has been fitted to the elastic peak

(a) $Q = (-0.4, 1)$

(b) $Q = (1, 0.3)$
just below the critical concentration. Also the concentration gradient will lead to a combination of components with different peak positions which will tend to reduce the definition of any peak that could possibly occur. This latter possibility is supported by the observation by Buchanan et al (1972) of a well-defined two-magnon Raman-scattering peak in a c=0.67 sample at a temperature of 5 K. At least it can be said that no gross inconsistency between theory and experiment is apparent.

4.6 Conclusion

The one-magnon contribution to the coherent cross-section for the inelastic scattering of thermal neutrons from three crystals of MnF$_2$/ZnF$_2$ has been measured at a temperature of 4.2 K for a range of scattering vectors corresponding to wave vectors in the two principal symmetry directions in several Brillouin zones. For the crystals with a concentration of zinc c=0.20 and c=0.32, a single well-defined excitation is observed for all wave vectors. These results taken with those for pure MnF$_2$ and the c=0.05 crystal (Svensson et al 1969) show that the qualitative effect of the addition of the non-magnetic zinc is the broadening and shifting to lower energy of the excitation peak.

The third crystal was found to have a concentration gradient such that only the upper part of the crystal, which had an average concentration of 0.65, was ordered
at 4.2 K. Data were collected for the whole crystal and for the upper and lower parts separately. In all cases the excitation was overdamped. In an attempt to characterise the data, the classical oscillator response function was fitted to the observed spectra for all concentrations. The fit proved to be satisfactory in all cases except for wave vectors close to the zone boundary in the c=0.20 crystal where the peaks cut off rather sharply at the top of the band. By excluding from the fit the points above a certain energy, it was possible to achieve a reasonable fit to the upper part of the peaks. Consequently it has proved possible to characterise all the results in terms of the important parameters of the model: the peak position and width. Although the parameters extracted for the c=0.65 sample vary with wave vector in a manner similar to that found in the other samples, their physical interpretation is far from clear. The proximity of the transition temperature and the presence of the concentration gradient also serve to obscure their significance.

What makes these experiments interesting is their use as a test of recently developed self-consistent theories of concentrated alloys based on the coherent potential approximation. The advantage of the MnF$_2$/ZnF$_2$ system as an example of a magnetic defect system is that it allows a comparison of theory and experiment without the need for a least-squares adjustment of any model parameters. And it has been shown that the theory based on the single-site approximation, in which only the Ising
terms are assumed to contribute to the impurity potential, is in qualitative agreement for the c=0.20 and 0.32 crystals at not too small wave vectors. Undoubtedly the deterioration of the agreement between theory and experiment as the wave vector is decreased is due to the crudity of the rather ad hoc method used to correct the transverse terms in lieu of the failure of the single-site approximation to accomplish this. Overall improvement of the theory would be brought about by the improvement of this method. The good agreement at (100) zone boundary is not significant as the almost equally good agreement of the simple cluster model shows that this is not a particularly stringent test.

It is unfortunate that the c=0.65 crystal was not of better quality as the testing of the theories for concentrated samples is of considerable interest. Also the theoretical peaks show structure that is not resolvable in the present experiments. As this structure is more pronounced for the higher zinc concentrations, it might well be observable with only slightly improved experimental resolution.

Undoubtedly further experiments are called for; not only for MnF₂/ZnF₂ systems but also for concentrated examples of the systems that have been studied in the dilute limit. Although for magnetic defects the host-defect exchange constant is not known independently, in many cases it can be deduced from the observed local mode frequency in the corresponding dilute system. To
fully test the theory, comparison must be made with as wide a variety of systems as possible.

That the self energy is diagonal in the single-site approximation and hence fails to include the effects of the transverse terms is a major fault but it does have the virtue of computational simplicity. The self energy, in a theory that takes into account pairs, would be a function of wave vector and thus the two independent components of the self energy would have to be evaluated at each wave vector required.
SCATTERING PROPERTIES OF FERROELECTRICS

5.1 Introduction

In this chapter some theoretical work on the scattering properties of ferroelectric crystals will be described. A large part of this work has been published in the form of two papers: Coombs and Cowley (1973) and Cowley and Coombs (1973) which hereafter will be referred to as I and II. As these papers appear bound in this thesis as appendices, the work described in them will only be repeated in this chapter in so far as is necessary to present a coherent account.

The ferroelectric state is usually defined in terms of the static dielectric properties of the crystal: the existence of a spontaneous electric moment that is reversible by the application of an electric field. This chapter is concerned with the dynamic properties of certain types of ferroelectrics at temperatures in the vicinity of the phase transition to the non-ferroelectric, i.e. paraelectric state. Although we are interested in dynamic behaviour close to the phase transition, we will not consider critical effects in the sense that this term is usually understood (Stanley 1971). Also, the area of interest includes materials that undergo related structural phase transitions between states that are not ferroelectric.

The experimental techniques, that have proved most profitable in the study of the dynamical behaviour of such
systems, are light scattering (Raman effect) and the inelastic scattering of thermal neutrons. The latter method allows the measurement of scattered intensity as a function of both energy and momentum transfer, whereas the former is restricted to effectively zero momentum transfer. The light-scattering cross-section may be shown to be related to the polarization correlation function and that for neutrons, to the atomic density correlation function. As will be discussed below, under certain conditions these correlation functions can be calculated on the basis of a single unified theory using Green's functions. A third technique that has been of some use is infra-red spectroscopy, which may be used to determine the dielectric susceptibility of a crystal.

The success of a suggestion by Cochran (1960), that the behaviour of a ferroelectric at the phase transition was due to the approach to zero of the frequency of a normal mode of vibration, is probably responsible in a large part for the fact that ferroelectricity is widely discussed in the language of conventional lattice-dynamical theory. It is, in particular, the structural phase transitions in SrTiO$_3$ and related perovskite-structure crystals that have provided the most convincing justification of the soft-mode hypothesis. As predicted by Cochran, it is the mode frequency at the centre of the Brillouin zone that goes to zero in a transition to a ferroelectric phase, such as in BaTiO$_3$. In SrTiO$_3$ the frequency of a normal mode vanishes at a zone corner when
the crystal is cooled through a non-ferroelectric structural phase transition. These temperature dependent modes have been observed directly in BaTiO$_3$ by Harada et al. (1971) using neutron scattering, and in SrTiO$_3$ using Raman scattering by Scott et al. (1968), and using neutron scattering by Shirane and Yamada (1969).

There have been several attempts to treat the soft-mode behaviour of perovskites within the context of lattice dynamics. In the standard approach, the interionic potential is expanded as a Taylor series in the ionic displacements and is assumed to converge sufficiently rapidly for the series to be truncated after a small number of terms. Inclusion of only the quadratic term - the harmonic approximation - yielding excitations that are exact eigenstates of the Hamiltonian: phonons. Finite phonon lifetimes and phonon energy renormalisation result when the anharmonic terms are taken into account. The importance of these terms at the phase transition has been pointed out by Cowley (1965), who suggests that it is the reduction of the anharmonic contribution to the soft-mode frequency with decreasing temperature that is responsible for the instability. Recently, Pytte and Feder (1969) have attempted to treat the soft-mode in SrTiO$_3$ at the 105 K phase transition using lattice dynamics. They use a simplified effective Hamiltonian in which the quartic anharmonic terms are assumed to be more important than the cubic. Using a molecular field approximation, they show that there is a mode with observed temperature dependence,
however, the gross simplifications that, by necessity, they are required to make reduces the weight of their conclusions.

In several of the perovskites, of which BaTiO$_3$ is the classic example, the soft-mode ceases to be well-defined as the transition is neared. As the response of the soft-mode is well-described by that of a classical oscillator, the mode is said to be overdamped. In such cases, it may not be clear that the phonon remains a valid concept, but as the change from underdamped to overdamped behaviour is described by the classical oscillator lineshape, the concept of phonon is still felt to retain its meaning.

Another much-studied class of ferroelectric crystals is KH$_2$PO$_4$ (KDP) and its isomorphs. Using light scattering, Kaminov and Damen (1968) have measured a strongly temperature-dependent overdamped mode in KDP. By fitting a classical-oscillator lineshape to their spectra, they have extracted a characteristic frequency that decreases with decreasing temperature and extrapolates to zero at the transition temperature. The applicability of the weakly-anharmonic model of lattice dynamics to KDP is not clear, as the protons, which are of undoubted importance in the dynamics of the transition, are believed to move in highly anharmonic potential wells. The more extensive Raman scattering work of Ryan et al (1972) on KDP and isomorphs has shown that consideration must be given to the anharmonic coupling of the soft mode to another mode of
the crystal in determining the temperature dependences of the soft mode frequency and width.

There is a large class of ferroelectric materials which undergo order-disorder transitions in which, it is believed, no soft mode is involved. An example is NaNO$_2$. Neutron scattering experiments by Sakurai et al (1970) have not revealed any mode with soft mode type temperature dependence. The ionic motions involved in the transition, in this case the reorienting of the nitrite groups, are so slow that any anelasticity is not resolvable from the observed elastic peak.

In this chapter all calculations are based on the weakly-anharmonic crystal model, in which only cubic anharmonic terms are included. Although in some cases, quartic terms may lead to effects of equal magnitude, their exclusion does not alter the essential physics of the problem and, in some situations, they do not contribute to dissipative effects to the same order as cubic terms.

For reasons to be discussed, the effects described in this chapter only occur in crystals of the piezoelectric classes. This, of course, includes all crystals in the ferroelectric phase. In the paraelectric phase, it excludes the perovskites but includes KDP-type materials. Despite the comments made above, it is hoped that the work described is of some relevance to the latter type of crystals.

This chapter is concerned primarily with the nature of the scattering in the region where the momentum transfer and the energy transfer are small. The scattering vector
Q, which is equal to the momentum transfer in our units, is said to be small when the condition \( Q/q_{\text{max}} \ll 1 \) holds; where \( q_{\text{max}} \) is the maximum wave vector in the Brillouin zone of the crystal. If \( \tau \) is some characteristic or average lifetime of the normal modes, then the frequency (energy) \( \omega \) is small for \( \omega \tau \ll 1 \). As has been recognised by Cowley (1967), in this, the collision-dominated regime, consideration must be taken of the fact that in a period of the probe the system has sufficient time to establish local thermodynamic equilibrium. Using neutron scattering, Svensson and Buyers (1968) have measured the temperature dependence of the elastic constants of KBr. The phonon frequencies measured are considerably greater than their width and thus the results are obtained in the collisionless regime. Their results differ significantly from those obtained by ultrasonic techniques, which are made in the collision-dominated regime. The concept of a local thermodynamic variable is useful in describing effects in the collision-dominated regime. Fluctuations in the local thermodynamic equilibrium are due to fluctuations in the local temperature and local phonon drift velocity. It would be expected that the scattering would be sensitive to these fluctuations and to the manner in which they decay. As we shall see, the latter type do not contribute. Also the scattering reflects the deviations from local thermodynamic equilibrium.

The analysis of this chapter is based on a diagrammatic representation of a perturbation expansion. And, as will
be shown, the important contributions to the scattering in the collision-dominated regime arise from diagrams containing pairs of lines describing phonons belonging to the same branch and differing in energy and momentum by amounts equalling the energy and momentum transfer of the scattering experiment. The problem is to isolate this class of diagram and calculate its contribution in some appropriate approximation. The connection between this analysis and the local thermodynamic description is made use of.

We shall be interested in the response of the transverse optic mode of vibration, which can be studied by all the techniques mentioned above, subject to the relevant selection rules. In section 2 the hamiltonian is given and the appropriate response functions defined. The conditions under which the light- and neutron-scattering cross-sections and the dielectric susceptibility may be expressed in terms of the one-phonon Green's function will be described. In section 3 the additional contributions to the self energy of the transverse optic phonon, that arise in the collision-dominated regime, will be calculated and the self energy will be shown to be related to a renormalised phonon-interaction vertex function. In section 4 the integral equation for the vertex function will be set up and shown to reduce to the Peierls phonon Boltzmann equation under certain approximations. Using the formalism of Gruyer and Krumhansl (1966), approximate solutions of the equation are obtained in terms of
Griffins (1965) dynamic thermal response coefficient.
In section 5 the effects of crystal symmetry on the appearance of these terms is discussed and it is shown that, under certain conditions, there is the possibility of the coupling of the transverse optic mode to a propagating temperature mode (second sound) in pyroelectric crystals. In section 6 the relevance of this work to several recent experiments is discussed.
5.2 Formalism

We write the Hamiltonian of the crystal as

$$H = H_0 + H_A$$

where the harmonic part is given by

$$H_0 = \sum_{q} \omega(q) \left( a^+(q)a(q) + \frac{1}{2} \right)$$

Here $\omega(q)$ is the frequency of the phonon with wave vector $q$ belonging to branch $j$; $a^+(q)$ and $a(q)$ are the creation and destruction operators for this phonon. We shall use a reduced notation in which $a_1$ implies $a(q_1 j_1)$ and $a^+_1$, $a(-q_1 j_1)$. The anharmonic part of the Hamiltonian is

$$H_A = \sum_{123} V(123) A_1 A_2 A_3$$

where $A_1 = a_1 + a^+_1$.

The coefficient $V(123)$ is related to spatial Fourier transform of the third derivation of the interionic potential. Details are given by Born and Huang (1954) and Cowley (1963). We shall only consider this contribution to the anharmonic Hamiltonian, neglecting higher order terms.

The response of the system is described in terms of the retarded one-phonon Green's function, which, following appendix 1, is given by

$$g_1(\omega) = \langle A_1 ; A_1^- \rangle$$

Although the Green's function is diagonal in wave vector, it is not in the branch index. We ignore these off-diagonal components without a great loss of generality.
of the argument. They are of importance in some cases which will be discussed below.

In the harmonic approximation, the Green's function may be calculated exactly and is given by

\[ g^0 \left( \omega \right) = G^0 \left( \omega + i \epsilon \right) \]

where

\[ G^0 \left( \omega \right) = \frac{2 \omega_1}{\omega_1^2 - \omega^2} \]

The corresponding spectral density and correlation function are then

\[ \rho^0 \left( \omega \right) = \delta \left( \omega - \omega_1 \right) - \delta \left( \omega + \omega_1 \right) \]

and

\[ C^0 \left( \omega \right) = (n_1 + 1) \delta \left( \omega - \omega_1 \right) + n_1 \delta \left( \omega + \omega_1 \right) \]

where \( n_1 = n(\omega_1) \).

The importance of the retarded Green's function is in the relationship it bears to the neutron and photon scattering cross-sections and to the dielectric susceptibility. The one-phonon coherent scattering cross-section for neutrons from a particular normal mode is simply related to the correlation function \( C \left( \omega \right) \) defined from equations (A5.10) and (A5.6). A similar expression for the one-phonon Raman scattering cross-section obtained when the polarization operator is expanded in terms of the phonon coordinates (Cowley 1971) and the linear terms retained. The linear response of a dielectric crystal to an applied electric field has been shown by Cowley (1963), using the formalism of Kubo (1957), to be given by the dielectric susceptibility
\[ \chi_{c\bf p}(\omega) = \frac{1}{N_v} \langle M_{\alpha} ; M_\beta \rangle \]  

where \( M_\alpha \) is the \( \alpha \) Cartesian component of the dipole moment operator and \( N_v \) is the volume of the crystal. Again, retaining the linear terms of the phonon coordinates gives just the retarded Green's function for the TO mode.

Although there are methods available for calculating approximate forms of the retarded Green's function in the presence of anharmonicity, we prefer to calculate a related function: the thermodynamic Green's function defined by

\[ D_1(u) = <PA_1(u)A_1(0)> \]

where \( A_1(u) = e^{uH} A_1 e^{-uH} \).

The operator \( P \) orders the operator with the greater argument to the left. This Green's function is calculated by perturbation theory using a diagrammatic representation of the terms by the method developed for phonons by Maradudin and Fein (1962) and Cowley (1963).

The periodicity of \( D_1(u) \) allows it to be expanded as a series;

\[ D_1(u) = \sum_{n=-\infty}^{\infty} D_1(i\omega_n) e^{i\omega_n u} \]

where \( \omega_n = \frac{2\pi n}{\beta} \) and \( n \) is an integer.

The coefficients are given by

\[ D_1(i\omega_n) = \frac{1}{2\beta} \int_{-\beta}^{\beta} D_1(u) e^{-i\omega_n u} du \]
It is possible to think of these coefficients as a function defined on an infinite set of points spaced equally along the imaginary axis in a complex frequency plane. Henceforth, this function will be referred to as the thermodynamic Green's function. This identification is further enforced by the relation that follows from the definitions of the relevant functions, namely

$$D_1(i\omega_n) = \frac{\rho(x)}{\beta} \int_{-\infty}^{\infty} \frac{1}{x+i\omega_n} \, dx \quad (5.3)$$

Comparison with equation A1.9 shows that it is possible to obtain the retarded Green's function from the thermodynamic Green's function if the appropriate analytic continuation can be made. The conditions under which it can be made have been derived by Baym and Mermin (1961) and are certainly satisfied in the cases considered here.

So we have that

$$g_1(\omega) = \beta D_1(i\omega_n) ; i\omega_n \rightarrow \omega + i\epsilon$$

The thermodynamic Green's function may be calculated in the harmonic approximation directly from its definition giving

$$D^0_1(i\omega_n) = \frac{2\omega_1}{\beta} \cdot \frac{1}{\omega_1^2 + \omega_n^2} \quad (5.4)$$

which may be compared with equation 11.

The relationship between the Green's function and the phonon self energy, has been given diagrammatically by Maradudin and Fein (1961) and is shown in figure 5.1. Symbolically the relationship is

$$D = D^0 + D^p D.$$
Equation for the Green's function (double line) in terms of the self energy and the harmonic Green's function (single line).

(a) Lowest order contribution to the self energy
(b) Lowest order contribution to the two-phonon Green's function.

The self energy in terms of the renormalised vertex function.

(a) Equation for the vertex function showing the dependence on the irreducible T-matrix
(b) Some lower order contributions to the irreducible T-matrix.

The diagram producing the lowest order contribution to the pyroelectric coefficient for the strain-free case.
From this it can be seen how the off-diagonal components of the Green's function arise. The harmonic Green's function is intrinsically diagonal, but the self energy is not necessarily so. In this case a matrix equation must be solved to obtain D. However, assuming the self energy to be diagonal, and using equation 5.4 for D°, the result is

\[
D_1(i\omega_n) = \frac{(2\omega_1/\beta)/(\omega_1^2 + \omega_n^2 - \frac{2\omega_1}{\beta} \Pi_1(i\omega_n))}{(5.5)}
\]

In making the analytic continuation of the self energy, it is usual to define its real and imaginary points by

\[
-\frac{1}{\beta} \Pi_1(\omega + i\varepsilon) = \Delta_1(\omega) - i\Gamma_1(\omega)
\] (5.6)

It has been shown that the real part is an even function of frequency and the imaginary part an odd function. It is usual to include the shift \(\Delta_1(\omega)\) with \(\omega_1\), ignoring its frequency dependence, to give a renormalised phonon frequency. The form of the retarded Green's function is then

\[
g_1(\omega) = \frac{2\omega_1}{(\omega_1^2 - \omega^2 - i 2\omega_1 \Gamma_1(\omega))}
\] (5.7)

An approximation to the width function, \(\Gamma_1(\omega)\), which has been much used in characterising the results of experiments, probably because of its simplicity, is its replacement by the first term in its Taylor series expansion, giving

\[
g_1(\omega) = \frac{2\omega_1}{(\omega_1^2 - \omega^2 - i\gamma \omega)}
\] (5.8)

where \(\gamma\) is a real positive constant. This is just the
response function of a classical damped oscillator.

For thermal phonons the lowest-order contribution to the imaginary part of the self energy is given by the diagram of figure 2a. This term has been calculated by Maradudin and Fein (1962). Generalising their result, the self energy may, in this approximation, be expressed in terms of the two-phonon Green's function, $K_{12}(i\omega_n)$, given by the diagram of figure 2b. The self energy is then given by

$$\Pi_1(i\omega_n) = 18\beta^2 [V(i123)]^2 K_{23}(i\omega_n), \quad (5.9)$$

and the expression for the two-phonon Green's function is

$$K_{12}(i\omega_n) = \frac{1}{n_1} D_1(i\omega_n) D_2(i\omega_n - i\omega_n).$$

Substitution for the Green's function's in terms of their spectral densities, using equation (5.3), and performance of the sum over $n_1$ yields

$$K_{12}(i\omega_n) = \frac{1}{\beta} \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \rho_{1}(x_1) \rho_{2}(x_2) \frac{c(x_1) + c(x_2)}{x_1^2 + x_2^2 + i\omega_n}, \quad (5.10)$$

where

$$c(x) = n(x) + \frac{1}{2}$$

$$= - c(-x)$$

The result of Maradudin and Fein is recovered by using the harmonic spectral densities. This result may be analytically continued to obtain the retarded two-phonon Green's function, which is then
\[ K_{12}(\omega) = (n_1 + n_2 + 1) \left( \frac{1}{\omega_1 + \omega_2 + \omega} + \frac{1}{\omega_1 + \omega_2 - \omega} \right) + (n_2 - n_1) \left( \frac{1}{\omega_1 - \omega_2 + \omega} + \frac{1}{\omega_1 - \omega_2 - \omega} \right). \] (5.11)
5.3 Small $Q$ and $\omega$ limit

A consideration of the scattering properties of a condensed system, when the momentum and energy transfer are small, using many-body theory was first carried out by Nozieres and Luttinger (1962). They gave a formal microscopic justification of the Landau theory of Fermi liquids. Both their formalism and approach are similar to that of this chapter, although the fermion hamiltonian leads to a four-point vertex compared to the three-point interaction introduced in the previous section. They emphasised the need for specifying the order for the limits of zero momentum and energy. Following these authors and Landau (1959), we refer to the limit of $Q$ going to zero followed by $\omega$ going to zero as the $\omega$-limit and the reverse situation as the $Q$-limit. In lattice dynamical systems the $Q$-limit represents isothermal conditions and the $\omega$-limit, adiabatic conditions. In these limits, the retarded Green's function for the TO phonon is just the static susceptibility. As the adiabatic and isothermal susceptibilities only differ in pyroelectric crystals (Nye 1955), it is expected that the order of the limits would be immaterial in crystals of higher symmetry.

There has been considerable work on phonon systems in the hydrodynamic regime; particularly by Kwok and Martin (1966), Sham (1967), Niklasson and Sjolander (1968), and Klein and Wehner (1968). Of these authors, all but Sham use non-equilibrium variational techniques to calculate the Green's function. Kwok and Martin demonstrate the
appearance of a second sound mode on the same footing as the usual first sound mode, using a simplified Hamiltonian that describes only longitudinal acoustic modes. Sham uses diagrammatic perturbation theory, without recourse to non-equilibrium statistical mechanics, to derive a similar result. Klein and Wehner and Niklasson and Sjolander generalise these ideas. Part of the development of the theory in this chapter is a generalisation of Sham's work. Although we are particularly interested in the coupling of a probe to the dielectric fluctuations - the TO phonon - in the vicinity of the phase transition.

Nozières and Luttinger (1962) introduce the convenient notion of an irreducible scattering diagram: one which never has in its internal propagator lines, a pair belonging to the same phonon branch that differ by \((Q, \omega)\) due to momentum and energy conservation. This allows the decomposition of any diagram into two types of parts thus isolating, in the reducible parts, the complex analytic behaviour that arises as \(Q\) and \(\omega\) approach zero. As the two-phonon Green's function (see figure 2b) is obviously the simplest example of such a diagram, we shall use it to introduce some of the ideas that are needed in calculating the self energy and other diagrams.

Examination of the latter two terms in equation (5.11) for this quantity shows that in the case of the two phonons belonging to the same branch, the limit of \(Q = q_1 + q_2\) and \(\omega\) going to zero, a singularity occurs. Introducing the difference wave vector \(q_1 = (q_1 - q_2)/2\), we have
For $Q$ small, expanding the phonon frequencies gives

$$\omega_1 = \omega_i + \frac{1}{2} Q \cdot V_i$$

where $$V_i = \left( \frac{\omega(qj_i)}{q} \right)_{q=q_1}$$

Also expanding the Bose-Einstein occupation factors to first order in $Q$,

$$n_i = n_i - \frac{1}{2} \beta Q \cdot V_i n_i(n_i+1), \quad (5.12)$$

the leading contribution to the two-phonon Green's function are given by

$$K_i(Q,\omega) = \frac{2n_i+1}{\omega_1} + \beta Q \cdot V_i n_i(n_i+1) \left( \frac{1}{Q \cdot V_i + \omega} + \frac{1}{Q \cdot V_i - \omega} \right). \quad (5.13)$$

It should be noted that this result is not independent of the type of limit. This is due to the ignoring of the anharmonic part of the Hamiltonian. Strictly, the self-energy insertions in the phonon lines should be included but it is sufficient to replace the harmonic Green's functions by their thermal counterparts. This could be accomplished by using the spectral densities derived from the thermal Green's function given by equation (5.7). In fact use of the approximate form, equation (5.8), enables the integrals to be performed, however we will use a somewhat different approach that makes the small $(Q,\omega)$ approximation before integrating: an approach that will
be of use in further considerations. Going back to equation (5.10), the summation over it may be replaced by integrations around the branch cuts of the integrand; a method that is reviewed by Abrikov, Gorkov and Dzyaloshinskii (1965). The result is analytically continued to give the retarded two-phonon Green’s function.

\[ K_{12}(\omega) = \frac{1}{2\pi i} \int dx \ c(x) \left\{ \Delta g_1(x)g_2(\omega-x) + \Delta g_2(x)g_1(\omega+x) \right\}. \]

Exploitation of the analytic properties of the Green’s function allows this result to be manipulated into the form

\[ K_{12}(\omega) = \frac{1}{2\pi i} \int dx \ (c(x) - c(x-\omega)) \ g_1(x) \ g_2(\omega-x). \]

In a similar manner to Sham (1967), the small \((\omega_1, \omega)\) approximation for the Green’s function product is made, using the thermal phonon form given by equation (5.7).

With the notation as before this is

\[ g_1(x)g_2(\omega-x) = g_1^0(x)g_2^0(-x) + 2\pi i \ \frac{\omega}{\omega - \omega_1} \ \frac{\beta}{1+i2\omega_1} \ \frac{1}{\Gamma_1(x)} \ \rho_1(x). \]

Substitution of this expression, expansion of the factor \(c(x-\omega)\) for small \(\omega\),

\[ c(x-\omega) = c(x) + \beta_0 \ n(x) \ \{n(x) + 1\}, \]

and taking the spectral density in the harmonic approximation, gives the result

\[ K_1(Q_\omega, \omega) = \frac{2n_1+1}{\omega_1} + 2\beta n_1(n_1+1) - \beta_0 n_1(n_1+1) \left( \frac{1}{\omega - Q_\omega} \right) \left( \frac{1}{\omega + Q_\omega + i2\Gamma_1} \right) \]

\[ - \left( \frac{1}{\omega + Q_\omega + i2\Gamma_1} \right), \]

where \(\Gamma_1 = \Gamma_1(\omega_1)\).
The first two terms come from the zeroth-order contribution to the Green's function product. Care must be taken in performing the integral over this contribution as the poles of the Green's functions coalesce. The preferred method is to go back to the sum over $n_1$ in evaluating this term.

This result for the retarded two-phonon Green's function is the same as that obtained by Klein and Wehner (1969).

In calculating the self energy, account can be taken of all possible diagrams by replacing one of the vertices by a renormalised vertex as shown in figure 3. The relationship of the self energy to this vertex function is then given by the equation

$$\Pi(Q,j,i\omega_n) = 6\beta \sum_{12} V^{(Q-q_1-q_2)} \sum_{n_1} D_1(i\omega_n) D_2(i\omega_n - i\omega_{n_1}) \times$$

$$x \Lambda \left( -Q j_1 j_2 ; i\omega_{n_1}, i\omega_n - i\omega_{n_1} \right) \quad (5.17)$$

which serves to define the function $\Lambda$. The zeroth order approximation is $\Lambda^0 = 3\beta V$.

In what follows it will be convenient to suppress the dependence of the various functions on $Q,j$ as this does not enter into the immediate argument. The equation then becomes

$$\Pi(i\omega_n) = 6\beta \sum_{12} V^{12} \sum_{n_1} \left[ D_1(i\omega_n) D_2(i\omega_n - i\omega_{n_1}) \Lambda_{12}(i\omega_n, i\omega_n - i\omega_{n_1}) \right] \quad (5.18)$$

The sum over $n_1$ may be manipulated in the same way as that for the two-phonon Green's function. This is based on the assumption that $\Lambda$ is analytic in the region of interest; the justification of which is discussed by Klein and
Webner (1968). As it is the contribution to the self energy, for which \( j_1 = j_2 \), that is of particular interest, attention is confined to this particular term. The other contributions may be calculated ignoring vertex corrections.

Making the small \((q, \omega)\) approximation and using equation (5.14) for the Green’s function product, with the spectral density in the harmonic approximation, the contribution to the self energy becomes

\[
\Pi(\omega) = i \frac{18\beta^2}{\omega} \sum_i V_i n_i(n_i+1) (X_i + X^-_i) \tag{5.19}
\]

The term involving \( g^0_i(x) g^0_i(-x) \), which leads to the first two terms in the two-phonon Green’s function (equation 5.16), has been ignored as they are assumed to be small. The functions

\[
X_i = Y_i(\omega_i) \tag{5.20}
\]

and

\[
Y_i(x) = \frac{1}{3\beta \omega_1} \frac{\Lambda_i(x, \omega-x)}{\omega x - \omega_1 X^2 + i\omega_1 \gamma_1(x)}, \tag{5.21}
\]

have been introduced along with the notation

\[
V_i = V(Q - q_i - Q/2, q_i - Q/2) = V_i^j \tag{5.22}
\]

and similarly for \( \Lambda_i \). The quantity \( \Lambda_i(x, \omega-x) \) is the analytic continuation of the function \( \Lambda_i(i\omega_{n_i}, i\omega_n - i\omega_{n_i}) \) with

\[
i\omega_{n_i} \rightarrow x + i\varepsilon
\]

and

\[
i\omega_n - i\omega_{n_i} \rightarrow \omega - x + i\varepsilon.
\]

The function \( Y \) has the important property that

\[
Y_i(x) = -Y_i(-x) \tag{5.23}
\]
which follows from the properties of $\Lambda_1(x, \omega-x)$, discussed by Klein and Wehner (1968). (This function is $F_{\lambda_1^{\lambda_2}} (\omega/2 + \omega' + in, \omega/2 - \omega' + in$ in their notation). Thus the functions defined by

$$Y_1^+(x) = \frac{1}{2} (Y_1(x) + Y_1(-x))$$

(5.24)

go to $Y_1^+(x)$ under the operation $i+i$. Then

$$\Pi(\omega) = i 36 \beta^2 \omega \sum_i V_{1i} n_i (n_i + 1) X_1^+.$$  
(5.25)

It thus remains to determine the function $X_1^+$ in some suitable approximation.
5.4 Equation for the Vertex Part.

If the irreducible T-matrix is introduced, the equation for the vertex part may be represented by the diagrams shown in figure 5.4a. Some of the lower order contributions are shown in figure 5.4b. In this way, the pairs of lines that produce the predominant contributions to the vertex part for small \((Q, \omega)\) are isolated. Thus it is largely immaterial how T is treated and so it may be replaced by its zeroth order value as given by the first term in its diagrammatic series. This is just the ladder approximation that has been used by Sham (1967). As is shown below, it is sufficient to treat the approximate expression for T in the harmonic approximation. The equation for the vertex part is then just

\[
\Lambda_{12}(i\omega_n, i\omega_n - i\omega_n) = \Lambda_0^{12} + 36 \sum_{345} V(135) V(245) \times \\
\times \sum_{n_2} \beta^2 D_3(i\omega_{n_2}) D_4(i\omega_n - i\omega_{n_2}) D_5(i\omega_{n_1} - i\omega_{n_2}) \Lambda_4(i\omega_{n_2}, i\omega_n - i\omega_{n_2}).
\]

As before, it is possible to convert the sum over \(n_2\) to an integral around the branch cuts of the summand. There are three terms: one from each Green's function in the summand. The analytic continuation is made by the replacement

\[
i\omega_n \to \omega + i\epsilon
\]

\[
i\omega_{n_1} \to \omega + i\epsilon
\]

The integral arising from the branch cut of \(D_5\) is
After expanding the occupation factor $o(x-\omega)$ for small $\omega$, as in equation (5.15), the first two terms are to give
\[
\int dx \int dy \left\{ c(x) + \frac{\beta \omega}{2} n(x) (n(x)+1) \rho \delta(y) - \frac{\beta \omega}{2\pi i} n(x) (n(x)+1) \text{Reg}_\omega(y) \delta(x+y-\omega') g_3^*(x)g_4^*(\omega-x) \right\}
\]

This particular term consists of two real and one imaginary contributions. The imaginary term is neglected as it does not contribute to the dissipative part of the vertex part and the second real part is assumed to be small in comparison with the first. The equation for the vertex part is now
\[
\Lambda^{12}_{12}(\omega',\omega-\omega') = \Lambda^{0}_{12} + 36 \Lambda^{(135)} \Lambda^{(245)} x
\]

At this point the small $(Q,\omega)$ approximation for the Green's function product is made. With $q_1 = q_2 = Q = q_3 + q_4$, defining $q_1 = (q_1 - q_2)/2$ and $q_j = (q_3 - q_4)/2$, and with the relabelling $k^* = k$ and change of variable $x_1 = \omega$, the equation becomes
\[
\Lambda^{1}_{1}(x_1,\omega-x_1) = \Lambda^{0}_{1} + 36 \sum_{jk} V(1jk)^2 x
\]

The $Q$-dependence of the interaction coefficients has been
ignored and the function $Y_j(x_j)$, defined by equation (5.21), introduced. It makes the notation a little more transparent if the relabelling $i,j,k \rightarrow 1,2,3$ is made. Using the invariance of $V(123)$ under the interchange of 2 and 3, the RHS may be manipulated into a more symmetric form. With this and the substitution of $Y$ for $A$ on the LHS, the equation becomes

$$(\omega x_1/\omega_1 - Q_y \nu_1) Y_1(x_1) + 1 \{ x_1 \} Y_1(x_1) = i V_1 +$$

$$+ 36\pi i V(123) |V(123)|^2 \int dx_2 dx_3 \{ c(x_2) + c(x_3) \} \rho_2(x_2) \rho_3(x_3)$$

$$Y_2(x_2) + Y_3(x_3) \delta(x_2 + x_3 - x_1).$$

(5.28)

The width function may be substituted using its defining equation (5.6) and equations (5.9) and (5.10). Making the changes $x_1 - x_1, 1 \rightarrow i, after some algebra the following equation is obtained

$$(x_1 \omega/\omega_1 - Q_y \nu_1) Y_1(x_1) = i V_1 - 36\pi i \{ n(x_1) \} (n(x_1)+1) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x_2 x_3 \rho_2(x_2) \rho_3(x_3) n(x_1) n(x_2) n(x_3) \{ Y_1(x_1) + Y_2(x_2)$$

$$+ Y_3(x_3) \} \delta(x_1 + x_2 + x_3).$$

(5.29)

This result is similar to that given by equation 10.6 of Niklasson and Sjolander (1968). The equation for $X_1 = Y_1(x_1 = \omega_1)$ is required. Taking the spectral densities in the harmonic approximation allows the integrals to be performed and the resulting equation is just the Peierls phonon Boltzmann equation (Peierls 1955) as obtained by similar methods by Sham (1967), Niklasson and Sjolander (1968) and Klein and Wehner (1968). The equation is

$$i(Q_y \nu_1 - \omega) X_1 = V_1 + \{ n_1(n_1+1) \} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} x_2 x_3 \rho_2(x_2) \rho_3(x_3) n(x_1) n(x_2) n(x_3) \{ Y_1(x_1) + Y_2(x_2)$$

$$+ Y_3(x_3) \} \delta(x_1 + x_2 + x_3).$$

(5.30)
\[
\sum_{2}^{12} X_{2} = \sum_{2}^{12} X_{1} + \frac{1}{2} |V(123)|^2 (n_{1}^{+1}) n_{2} n_{3} (X_{3}^{+} X_{2} - X_{1}) \delta (\omega_{3}^{+} - \omega_{2}^{+} - \omega_{1}^{+}) \\
+ |V(123)|^2 (n_{1}^{+1}) (n_{2}^{+1}) n_{3} (X_{3}^{+} X_{2} - X_{1}) \delta (\omega_{3}^{+} - \omega_{2}^{+} - \omega_{1}^{+})
\]

(5.31)

With the definitions

\[
D_{12} = i (Q_{1} - \omega) \delta_{12}
\]

\[
Z_{1} = \sqrt{n_{1} (n_{1}^{+1})} \cdot X_{1}
\]

\[
f_{1} = \sqrt{n_{1} (n_{1}^{+1})} \cdot V_{1}
\]

\[
C_{12} = \frac{P_{12}}{\sqrt{n_{1} (n_{1}^{+1}) n_{2} (n_{2}^{+1})}}
\]

the equation may be written in the operator form

\[
(D-C) |Z> = |f>
\]

(5.32)

It should be emphasised that all quantities in this equation are functions of \(Q\) and \(\omega\). Here \(D\) corresponds to the drift operator, \(C\) to the collision operator, and the inhomogeneous term \(|f>\) represents the coupling to the phonon, the self energy of which is being calculated.

The formalism of Guyer and Krumhansl (1966) is used to obtain solutions to this equation. They obtain formal solutions to the Boltzmann equation by exploiting the physical properties of the collision operator. This operator may be separated into a normal part \((N)\) which conserves momentum and the resistive part \((R)\) that does not. Two eigenvectors of \(N\) are known: the equilibrium distribution \(|0>\) which has zero eigenvalue with both \(N\) and \(R\), and the convective distribution \(|1>\) which has zero eigenvalue with \(N\). The solution is obtained by expanding \(|Z>\) in terms of the eigenvectors of \(N\), which
form a complete orthonormal set that is assumed to span the space of the solutions of the Boltzmann equation. The expansion is

\[ |Z\rangle = a_0 |0\rangle + a_1 |1\rangle + |2\rangle \quad (5.33) \]

The vector \( |2\rangle \) represents a linear combination of the remaining (unknown) eigenvectors of \( N \). The coefficients \( a_0 \) and \( a_1 \) are to be determined. The labelling of the vectors should not be confused with the suffices of the elements of the operators in wave-vector space. Both \( a_1 \) and \( |1\rangle \) are vectors in the space of \( Q \).

Niklasson (1970) has obtained formal solutions to this equation using a generalisation of Guyer and Krumhansl's method. He has shown that the first term in the expansion describes fluctuations in the local temperature, the second term describes the local phonon-drift velocity and the third term represents deviations from local thermodynamic equilibrium. Whereas, the vector \( |0\rangle \) is even under the reversal of the signs of the wavevectors in its indices, \( |1\rangle \) is odd. As a result of the equation (5.25) for the self energy only the even contributions to the vector \( |Z\rangle \) are required, so that there is no contribution from the local phonon-drift term.

Guyer (1966) has obtained approximate solutions to the inhomogeneous Boltzmann equation. Although his inhomogeneous term represents coupling to an acoustic phonon obtained from macroscopic considerations, his approach is sufficiently general to be of use in this
Expanding the inhomogeneous terms in the eigenvectors of $N$,

$$|f> = \sum_i b_i |i>$$  \hspace{1cm} (5.34)

and taking the appropriate matrix elements of the equation, the following equations are obtained:

$$a_{00} D_{00} + a_{11} D_{01} = b_0$$
$$a_0 D_{10} + a_1 r^{-1} = b_1$$  \hspace{1cm} (5.35)

where $r^{-1} = |><(D-R) - (D-R)(D-R-N)^{-1}(D-R)>$. Now $b_1 = 0$ as $f>$ is even and $|1>$ odd and from similar considerations $D_{00} = -i\omega$. These two equations may be solved to give

$$a_0 = -\frac{b_0}{i\omega} \tilde{z}$$

where $z^{-1} = 1 + \frac{r}{i\omega} D_{01} D_{10}$  \hspace{1cm} (5.36)

The function $\tilde{z}(Q,\omega)$ is the dynamic thermal response coefficient of Griffin (1965). This function is discussed in the next section.

Using the symmetry of the $V$ coefficients, equation (5.25) for the self energy may be written as

$$\Pi(\omega) = 136 \beta^2 <f|Z>$$  \hspace{1cm} (5.37)

In his treatment of the phonon self energy, Sham (1967) has only included the first term in the expansion of $Z$ and ignored the contribution from deviations from local thermodynamic equilibrium. As will be shown, this term is of some importance. Although we have no direct
knowledge of the vector $\mid \varphi \rangle$, it is possible to use the known properties of the operators and eigenvalues to obtain an expression that is amenable to approximation. From equation (5.33) and using the properties of the operators, we obtain

$$\mid \varphi \rangle = (D-N-R)^{-1} \mid f \rangle - a_0 (D-N-R)^{-1} D \mid 0 \rangle$$

$$- a_1 (D-N-R)^{-1} (D-R) \mid 1 \rangle,$$

and thus

$$\mid 2 \rangle = a_0 \left( 1 - (D-N-R)^{-1} D \right) \mid 0 \rangle$$

$$+ a_1 \left( 1 - (D-N-R)^{-1} (D-R) \right) \mid 1 \rangle$$

$$+ (D-N-R)^{-1} \mid f \rangle$$

(5.38)

Niklasson (1970) has obtained a formal version of this equation using projection operators. Although our approach, and the approximations that will be made, are crude by the standards of his work, they are sufficient for our purposes. Taking the inner product, ignoring the contribution from $\mid 1 \rangle$, yields the expression for the self energy:

$$\Pi(\omega) = -36\beta^2 \Re \{ W \omega \} + i \Re \{ \omega \} M$$

(5.39)

where $M = \langle f \mid (D-N-R)^{-1} \mid f \rangle$  

(5.40)

and $W = \langle f \mid (1-(D-N-R)^{-1} D) \mid 0 \rangle$,  

(5.41)

and the results $b_0 = \langle f \mid 0 \rangle$

$$= W(Q=0,\omega=0)$$

$$= W_0$$

have been used.
It can be seen that the contribution to the self energy from fluctuations in the local temperature is related to the dynamic thermal response coefficient through the matrix element $W$. Griffin (1965 and 1968) introduced this function in a discussion of Brillouin scattering from a crystal in the hydrodynamic regime and showed that its poles give the dispersion relation for a propagating temperature mode (second sound). Also Guyer (1966) has shown that the acoustic attenuation coefficient of a crystal is proportional to the imaginary part of this quantity. (In $\frac{E}{\omega}$ is referred to as the thermodynamic propagator $D$). Obviously the behaviour of $E$ is determined by the complicated matrix element $T^{-1}$. The different approximations that may be obtained in various situations are discussed extensively by Guyer and Krumhansl (1966 a and b). Under the condition $\omega \tau_N << 1 << \omega \tau_R$, where the relaxation times characterise the normal and resistive scattering rates, these authors show that

$$T^{-1} = -i\omega + \gamma$$

where $\gamma$ will be some combination of the relaxation times. And taking $D_{01} = i\lambda Q$ where $\lambda$ is some crystal dependent parameter, we can write

$$E = 1 + \frac{\lambda^2 Q^2}{\omega^2 + i\omega\gamma - 2\omega^2}, \quad (5.4.2)$$

so that a well-defined second-sound mode will appear if $\gamma$ is sufficiently small. If the resistive processes dominate, $T$ is a constant and the temperature fluctuations decay diffusively. From this expression for the dynamic
thermal response coefficient, it can be seen that it has different values in the $Q$- and $\omega$-limits. In the $Q$-limit $E^Q=0$, while in the $\omega$-limit $E^\omega=1$.

To evaluate the matrix element $W$, a knowledge is required of the form of the eigenvector $|0\rangle$. Krumhansl (1965) has shown that this vector has elements of the form $\mu_0 \sqrt{a_n(n_n+1)}$, where $\mu$ is a normalisation constant, which, for an isotropic dispersionless medium, is given by $\mu^2 = C_v/k$, where $C_v$ is the specific heat of the system at constant volume. To approximate the collision operator, it is simply replaced by a relaxation time. This same approximation has been used in I, although it is introduced in a somewhat different manner. In the light of these comments, the expression for $W$ becomes

$$W = \mu_0 \beta \sum I_v n_1(n_n+1) \omega_1 \left(1 - \frac{\omega - \frac{Q_v}{\omega} V_1}{\omega - Q_v V_1 + 1/\tau_1}\right), \quad (5.43)$$

where we have put $N+R = -1/\tau_1$. The matrix element $M$ may be evaluated in the same approximation, and the resulting contribution to the self energy is then

$$\Pi = -36\beta^2 \sum I_v |V_1|^2 n_1(n_n+1) \frac{\omega}{\omega - Q_v V_1 + 1/\tau_1}. \quad (5.44)$$

If corrections to the phonon vertex are ignored, although the coupling to the dynamic thermal response coefficient does not appear, there is a contribution to the self energy similar to that above but with $\tau_1$, the relaxation time for deviations from local thermodynamic equilibrium, replaced by the ordinary lifetime for
thermal phonons. This can be seen by replacing the vertex part by its zeroth order approximation in equations (5.19) and (5.21).

In this section it has been demonstrated that for small \((q, \omega)\) the contributions to the self energy arising from fluctuations in the local temperature and deviations from local thermodynamic equilibrium are significant. And that under certain conditions, the former fluctuations will decay via a propagating mode that leads to a resonance in the self energy.
5.5 Dielectric Properties and Symmetry Effects

Although it is virtually impossible to calculate the matrix elements, considered in the previous section, for any realistic models, it is possible to make some considerations based on the symmetry of the anharmonic coefficient in the situation where the momentum transfer is zero. As light scattering measurements are performed for $Q = 0$ the discussion in this section will be restricted to the one-phonon dielectric susceptibility; assuming only one TO phonon contributing. It is possible to relate $W_0$ to the static susceptibilities measured under isothermal and adiabatic conditions. Considering the ratio

$$ R = \frac{\chi^S_{\alpha\beta}}{\chi^T_{\alpha\beta}} - 1 \quad (5.45) $$

where $\chi^S_{\alpha\beta}$ and $\chi^T_{\alpha\beta}$ are the susceptibilities, it can be seen from equations (5.2) and (5.5) that this ratio may be written in terms of the self energy in the $\omega$- and $Q$- limits, giving

$$ R = \frac{2\omega_1}{\beta} \frac{\Pi^Q - \Pi^\omega}{\omega_1^2 - 2\omega_1 \Pi^Q} \quad (5.46) $$

The difference in the limiting values of the self energy arise solely from the corresponding difference for the dynamic thermal response coefficient with the result that

$$ R = \frac{72\beta}{\omega_1} W_0^2 $$
This is analogous to the result derived by Sham (1967) for the coupling to an acoustic phonon in which case the coupling coefficient is proportional to the Landau-Placzek ratio: the fractional difference in the specific heats at constant pressure and constant volume. This result for the ratio must be consistent with the thermodynamic result for the difference between the static susceptibilities, at least to the same order of perturbation theory that we have considered. The thermodynamic relation (Nye 1955) is

\[ S = T \frac{x_{\alpha\beta}}{x_{\alpha\beta}} = -\frac{T}{VC} p_{\alpha} p_{\beta} \]

for the strain-free configuration. The pyroelectric coefficient \( p_{\alpha} \) is just the temperature derivative of the static polarization \( p_{\alpha} \) which in turn is related to the thermal average of the phonon operator by the expression

\[ p_{\alpha} = \frac{1}{V} M_{\alpha} \langle 0 | A(0) \rangle \]

The lowest order diagram for \( \langle A(0) \rangle \) is shown in figure 5.5 and the resulting expression is

\[ \langle A(0) \rangle = -\left(\frac{6}{\omega_0}\right) \sum_i V(0 \overline{1})(2n+1), \]

so that

\[ p_{\alpha} = \frac{1}{V} M_{\alpha} 12(\kappa p^2/\omega_0) \sum_i V_1 \omega_1 n_1 (n+1) \]

\[ = 12 \sqrt{V\omega_0} \left( \frac{\beta}{V \omega_0} \right) M_{\alpha} W_0 \]

Taking \( x_{\alpha\beta} \approx M_{\alpha} M_{\beta} (2/\omega_0)/V \), it can be seen that the expression for \( R \) is equivalent to the thermodynamic relation. Thus the coupling coefficient is proportional
to the pyroelectric coefficient and the TO phonon couples to fluctuations in the local temperature only in pyroelectric crystals.

Of the thirty two crystal classes, twenty one are piezoelectric and of these, ten possess a unique polar axis and hence admit the possibility of pyroelectricity (Nye 1955). It has been shown in I that the anharmonic coefficient $V(0\Omega) = V^{q_1-q_1}_{j_1j_1}$, for $j$ an infrared active $j_{j_1j_1}$ TO mode, is identically zero for non-piezoelectric crystals as a consequence of symmetry. And further, the sum that appears in $W_0$ is non-zero only for the polar classes.

So in summary, it can be said that dielectric fluctuations couple to fluctuations in the local temperature only in the crystals of the polar classes and to fluctuations representing deviations from local thermodynamic equilibrium in crystals of the piezoelectric classes.
5.6 Experimental Evidence

Due to the finite instrumental resolution in scattering experiments, the low-frequency effects are inevitably obscured by the elastic scattering. However some recent observations of the scattering from the materials that undergo structural phase transitions have revealed strongly temperature dependent contributions to the elastic scattering in the neighbourhood of the transition that cannot be explained on the basis of the simple classical oscillator plus soft mode theory: SrTiO$_3$ above the transition by Riste et al (1971), SrTiO$_3$ and KMnF$_3$ above the transition by Shapiro et al (1972), Nb$_3$Sn above the transition by Shirane and Axe (1971) - all using neutron scattering. And using light scattering: CsH$_2$AsO$_4$ above the transition by Cowley et al (1971) and 5PbO. 3 GeO$_3$ below the transition by Hisano and Ryan (1972a and b).

Although the theory developed in this chapter does not predict extra contributions to the self energy of SrTiO$_3$ in the cubic phase, it is believed that these effects arise from essentially the same processes: the thermodynamic and non-thermodynamic fluctuations in the local phonon density. Silberglitt (1972) has shown that renormalisation of the lowest order diagram arising from quartic anharmonic effects will lead to a contribution to the elastic scattering. As a detailed comparison of theory and experiment is made in II, it will not be repeated here.

An interesting case is Nb$_3$Sn which undergoes a
cubic to tetragonal phase transition where it is a transverse acoustic mode that softens at the zone centre. As is pointed out in II, the symmetry of the soft mode is such that the situation is analogous to that of a TO mode in a transition from a non-polar piezoelectric phase to a ferroelectric phase.

Raman scattering, with its superiority of accuracy over neutron scattering, probably holds out the greatest hope for the acquisition of more detailed information of these effects. Techniques are also being developed to attenuate the elastic component in the scattered beam (Hisano and Ryan 1972b). The calculation of the effects for any realistic crystal model is virtually impossible, so that progress will only be made by parameterising the various expressions and fitting them to experimental spectra to obtain values of the parameters; as has been done with the classical oscillator. Such an approach demands detailed experimental results.
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Appendix 1. Summary of some results on Green's functions.

In this appendix are summarised some results of the theory of Green's functions that are used in this thesis. The approach is essentially that of Zubarev (1960).

The correlation function of two Heisenberg picture operators is defined by

\[ G^>(t) = \langle A(t) B(0) \rangle \tag{A1.1} \]

The thermal average is over a canonical ensemble at temperature \( T \). The Hamiltonian of the system is assumed to have no explicit time dependence, so that only relative times are important. In such a case the Heisenberg equation of motion for \( A \) can be integrated formally to give

\[ A(t) = \exp(iHt) A \exp(-iHt) \tag{A1.2} \]

Introducing the related correlation function

\[ G^<(t) = \langle B(0) A(t) \rangle \tag{A1.3} \]

it can be shown from equation A1.2 and the form of the thermal average that

\[ G^>(t) = G^<(t+i\beta) \tag{A1.4} \]

The function of central importance is the retarded Green's function which is defined by

\[ g(t) = -i \Theta(-t) \langle [A(t),B(0)] \rangle \tag{A1.5} \]

\[ = i \Theta(-t) \rho(t) \tag{A1.6} \]

where the square brackets indicate the commutator is to be taken and the function \( \Theta \) is zero for negative
argument and unity otherwise.

The temporal Fourier transform of the Green's function is given by

\[ g(\omega) = \int_{-\infty}^{\infty} g(t) e^{-i\omega t} \, dt = \langle A ; B \rangle \]

and it can be shown that

\[ g(\omega) = G(\omega + i\epsilon); \quad \epsilon \rightarrow 0^+ \]

where

\[ G(\omega) = \int_{-\infty}^{\infty} \frac{\rho(E)}{E - \omega} \, dE \]

The function \( \rho(E) \) is the spectral density and is just the Fourier transform of \( \rho(t) \) defined above. The Fourier transform of the correlation function \( G^< \) is related to this quantity by

\[ G^<(\omega) = \rho(\omega) / (1 - e^{-\beta\omega}) \]

\[ = \{ n(\omega) + 1 \} \rho(\omega) \]

where \( n(\omega) = 1 / (e^{\beta\omega} - 1) \),

and \( \beta = 1/kT \), \( k \) being Boltzmann's constant. These relationships follow from equations (A1.5), (A1.6) and (A1.4).

From equations (A1.8) and (A1.9) it follows that the spectral density is proportional to the discontinuity of \( G(\omega) \) at the real axis. We have
\[ \rho(\omega) = \frac{1}{2\pi i} \left\{ \mathcal{G}(\omega + i\epsilon) - \mathcal{G}(\omega - i\epsilon) \right\} \quad A1.12 \]

\[ = \frac{1}{2\pi i} \left\{ \mathcal{G}(\omega) - g^*(\omega) \right\} \quad A1.13 \]

\[ = \zeta(\omega) / 2\pi i \quad A1.14 \]

\[ = \text{Im } g(\omega) / \pi \quad A1.15 \]

where \( \zeta(\omega) \) is the discontinuity.

One method of calculating \( g(\omega) \) is to obtain the equation of motion. Differentiating the defining expression for \( g(t) \), using the Heisenberg equation of motion for \( A \), and then carrying out the Fourier transform yields

\[ \omega g(\omega) = \omega \langle A \langle B \rangle = \langle A, B \rangle - \langle \{ A, H \}; B \rangle \rangle \quad A1.16 \]

The second term on the RHS will generally be a complex combination of operators and the equation of motion for it may be obtained in terms of even higher order functions. At some level an approximation must be introduced.
APPENDIX 2.

PUBLISHED PAPERS

Some of the work of this thesis has been published in the papers listed below. These papers are to be found bound at the end of this thesis. They are


THE DIELECTRIC RESPONSE OF CRYSTALS

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Abstract. — By properly considering the coupling of the ferroelectric fluctuations to the low frequency fluctuations in the phonon density of a piezoelectric crystal, a new contribution to the phonon self-energy is obtained. It is suggested that this terms accounts for the anomalous temperature dependence of the relaxation time of the ferroelectric mode that has been observed in recent light scattering experiments. The resulting change in the scattering function is also considered.

In considering the low frequency dielectric response of a crystal, care must be taken in the treatment of the fluctuations in the phonon density to which the light couples through the transverse optic phonon. If the time scale of the fluctuations is long compared with some average phonon lifetime then the probability of phonon decay in the intermediate virtual states must be taken into account. We shall show that these considerations lead to a new contribution to the phonon self-energy of a piezoelectric crystal. The contribution is absent in crystals of higher symmetry as the relevant coupling coefficient is identically zero. In ferroelectric materials, it is obvious that this contribution will be important due to the large increase in the amplitude of the ferroelectric fluctuations as the phase transition is approached.

Kubo [1] has shown that the first order response function of a system is just the one-particle retarded Green's function. For the weakly anharmonic lattice dynamical model of a dielectric crystal, we may write the response function of the mode with wave vector \( q \) belonging to branch \( j \) as

\[
G'(q, \omega) = \omega^2(q) - \omega^2 + i \gamma(q) \omega.
\]

Here \( \omega(q) \) is the harmonic phonon frequency of this mode and \( \pi(q, \omega) \) is the self-energy of the mode due to the anharmonic terms in the Hamiltonian of the crystal. If we consider only the cubic anharmonic term then the lowest order perturbation theory contribution to the self-energy may, as was first demonstrated by Maradudin and Fein [2], be represented by the diagram shown in figure 1. The self-energy is a complex function of frequency: the real part making a small correction to the phonon frequency which we absorb into \( \omega(q) \) to give the shifted frequency \( \tilde{\omega}(q) \). It is the imaginary part of this function that is of interest. For the high frequency response it is sufficient to treat the internal lines of the diagram in the harmonic approximation and the imaginary part so obtained may be approximately represented by the first term in its Taylor series expansion which we write as

\[
G^{-1}(q, \omega) = \tilde{\omega}^2(q) - \omega^2 + 2 \gamma(q) \omega.
\]

which is the well-known result for a classical damped oscillator. It has been shown by Yamada, Shirane and Linz [3] that this form gives a reasonable description of the response of the soft transverse optic mode in non-piezoelectric BaTiO\(_3\). Cowley et al. [4] have demonstrated that this form is not adequate for the description of the light scattering from the piezoelectric materials CsH\(_2\)AsO\(_4\)(CsDA) and KH\(_2\)AsO\(_4\)(KDA) which undergo ferroelectric transitions. To correctly treat the coupling of the dielectric fluctuations to the low frequency fluctuations in the phonon density, we must revaluate the diagram of figure 1; replacing the harmonic phonon lines by thermal phonon lines for which we use the form of eq. 2. In the low frequency limit the predominant contribution of the phonon self-energy occurs when the two phonons represented by the internal lines of the diagrams are of the same branch. This was first pointed out by Sham [5]. The anharmonic coefficient which gives the
coupling of the $q = 0$ transverse optic phonon to those two phonons may be written as
\[ V_{ij}(\mathbf{q}) = \frac{\omega(q)}{\Delta} \left( \begin{array}{cc} q_1 & q_1 \\ j_1 & j_1 \end{array} \right) \]
and it is this coefficient that is identically zero for non-piezoelectric crystals.

Using techniques similar to those developed by Sham [5] and Klein and Wehner [6], the resulting contribution to the self-energy may be evaluated. There are two cases of interest. In the first case of piezoelectric but not pyroelectric crystal, the transverse optic mode couples to phonon density fluctuations which represent only deviations from the local thermodynamic equilibrium. In the second case of pyroelectric crystals, the transverse optic modes couple, in addition, to the fluctuations in the local thermodynamic equilibrium. In the former case the self-energy becomes
\[ \frac{\alpha T}{1 + i\omega \tau} \]
where $\alpha$ is a positive constant and $\tau$ is strictly a decay time for the deviation from local thermodynamic equilibrium but may be taken as some average phonon lifetime. We have made the high temperature expansion of phonon occupation factors with the result that the term is linearly dependent on the temperature $T$. The remainder of the self-energy has the same form as that discussed above. The response function for the ferroelectric mode is then
\[ G^{-1}(\omega) = \frac{1}{\omega_0^2 - \omega^2 + i\omega\gamma} - \frac{\alpha T}{1 + i\omega \tau} \]
whereas at high frequencies the response of the crystal was determined by the soft mode
\[ \omega_0^2 = k(T - T_0) \]
where $k$ and $T_0$ are constants, the response is now determined by
\[ \omega_0^2 - \omega T. \]

This follows if we note that the dielectric susceptibility is just proportional to this response function and if we assume that the static susceptibility has the usual experimentally determined form
\[ \gamma_0^{-1} \omega T - T_0 \]
where $T_0$ is the ferroelectric transition temperature. We see that
\[ T_0 = \left( \frac{k - \alpha}{k} \right) T_e \]
which implies that $T_e > T_0$.

It is this difference between the high and low frequency response that has been observed in the Raman scattering measurements on CsDA and KDA [1].

The imaginary part of the response function which determines the scattering properties of the crystal. The nature of the scattering described by the function we have derived depends sensitively on the parameters of the model. In some cases there are two peaks in the scattering which coalesce into one if either the temperature is raised or the strength of the anharmonicity parameter is increased. Unfortunately detailed experimental measurements are not available in the region $\omega \tau \sim 1$, and so we are not able to compare the results of these calculations with experiment in detail.

For relatively large values of the anharmonicity parameter $\alpha$ and temperatures not too close to the transition the low frequency part of the scattering function may be approximately written as
\[ \text{Im} \left[ \frac{G(\omega)}{G(0)} \right] = a(T) \cdot \frac{\omega \tau^*}{1 + (\omega \tau^*)^2} \]
where
\[ \tau^* = \frac{T_e}{T_0} \left( \frac{T - T_0}{T - T_e} \right) \tau \]
and
\[ a(T) = \frac{T(T - T_0)}{T_e(T - T_0)} \]

This just the Debye relaxation form with a relaxation time that diverges as the transition is approached. This form of the response, including the effects of different relaxation times, has been discussed in connection with a number of compounds by Yoshimitsu and Matsubara [7].

In pyroelectric crystals the form of the self-energy becomes more complicated but has qualitatively a similar structure. We expect that at small $\omega$ there will be an anomalous contribution to the self-energy which will give rise to additional response at low frequencies. The new features which occur in pyroelectric crystals are that the form of the response is singular as $q$ and $\omega \rightarrow 0$ and that the transverse optic mode may also couple to a second sound mode. We intend to publish a more detailed account of these results in the near future.

References

an additional contribution at low frequencies which arises from fluctuations in the phonon distribution caused by the ferroelectric mode. Although the anharmonic oscillator model is almost certainly not an adequate model for these hydrogen bonded materials, the effects discussed here depend primarily on symmetry so that the same concepts should be equally applicable in an analysis of the response of other models.

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1st June 1971


Mobility of an impurity in a Fermi liquid: analogy with a phase transition

Abstract. The equations of Josephson and Lekner describing the mobility of an impurity in a Fermi liquid admit three solutions for the mobility over a certain temperature range.

A model for the mobility of ionic impurities in a Fermi liquid has been proposed by Josephson and Lekner (1969). They calculate the force on an ion when it moves with a constant drift velocity through a gas of quasiparticles. The recoil of the ion, due to the scattering of the quasiparticles, is given by the scattering function $S(q, \omega)$, which Josephson and Lekner calculate in a Gaussian approximation.

The mobility, according to Josephson and Lekner, is given by the following set of equations. (We use units of unit volume and $h = 1$.)

$$\mu(0)^{-1} = \frac{1}{12} \int_0^{2\pi} dq q^3 \sigma(q) \int_{-\infty}^{\infty} dt \exp \left\{ -\frac{q^2 \gamma(t)}{2} \right\} / \cosh^2 \left( \frac{\pi t}{2\beta} \right)$$

(1)
perturbation theory, figure 2(a) is inadequate and it is necessary to obtain the selfenergy from the selfenergy diagram, figure 2(b), containing the renormalized vertex given by the equation of figure 2(c). In the case of materials which are not piezoelectric the matrix elements for scattering

\[ V^{(0, q_1 - p_1)}_{(j, j_1 - j_1)} \]

are identically zero. In nonpiezoelectric materials the damped harmonic oscillator expression, equation (1), is therefore expected to be adequate as found experimentally.

For materials which are piezoelectric these matrix elements are finite and we expect there to be an anomaly in the selfenergy of the soft mode at low frequencies. We have calculated the form of the response given by the selfenergy of figures 2(b) and 2(c), by use of the techniques developed by Sham (1967) and by Klein and Wehner (1969) for the analogous problem in ultrasonics. The theory as applied to ferroelectrics differs from that for ultrasonics in that the effects may be larger and also that the fluctuations in the phonon distribution couple to neither the temperature nor the heat current fluctuations. The details of the calculations will be reported elsewhere but the final result for the response function of a ferroelectric mode is

\[ G(\omega) = \left( \omega_0^2 - \omega^2 + i\omega \omega_0 - \frac{\alpha T}{1 + i\omega} \right)^{-1} \]

where \( \alpha \) is a positive constant and \( \tau \) is the lifetime of the modulations introduced into the phonon distribution by the fluctuations in the ferroelectric mode. At high frequencies, \( \omega \tau \gg 1 \), the response function is identical with that of a damped harmonic oscillator with

\[ \omega_0^2 = K(T - T_0). \]

At low frequencies the response is however determined by \( \omega_0^2 - \alpha T \) which is proportional to \( T - T_c \) with

\[ T_0 = \frac{(K - \alpha)T_c}{K}, \]

The difference between the high frequency response, \( \omega \tau \gg 1 \), and the low frequency response \( \omega \tau \ll 1 \), arises because at low frequencies the fluctuations in the phonon distribution function caused by the ferroelectric mode have time to decay within each period of the wave, whereas at high frequencies there is not sufficient time for this to occur.

The ratio of \( T_0/T_c \) determines the ratio of the anomalous contribution to the selfenergy to that of the regular term, \( \alpha/K \). This ratio is about 0.8 in KDA and 0.5 in CsDA, both results being very similar in magnitude to those found in calculations of the ultrasonic properties of KBr (Cowley 1967). The lifetimes of the fluctuations, \( \tau \), may be estimated by a comparison of the frequencies in Kaminow’s experiment (1965) and those involved in ours. This suggests that \( \tau \approx 10^{-10} - 10^{-11} \) s which agrees quite reasonably with typical phonon lifetimes.

The theory should also be applicable to the two similar materials KDP (KH2PO4) and DKDP (KD2PO4). In KDP the Raman spectra shows an overdamped mode whose width decreases as \( T_c \) is approached. Kaminow and Damen (1968) give \( T_0 = 0.98T_c \) showing that \( \alpha \) must be small in KDP. In DKDP the situation is still unclear. Hill and Ichiki (1963) have measured the dielectric properties while White et al. (1970) have observed the Raman spectra. Both sets of authors agree that the results cannot be fitted by a simple damped oscillator model but further work is needed to test our model. The lifetime, \( \tau \), for DKDP must certainly be considerably longer than that for KDA.

In conclusion we have shown that the damped single harmonic oscillator does not give an adequate description of the soft mode in piezoelectric ferroelectrics. The selfenergy has
with the other parameters. Since we might expect $\Gamma \propto (T - T_0)/T$ we show in figure 1 $\Gamma T$ plotted against $T$. The results give a reasonably straight line but the intercept with the temperature axis, $T_0$, is not the transition temperature, $T_T$, but considerably below. For CsD$_2$, $T_0 = (0.48 \pm 0.05)T_c$ and for KDA, $T_0 = (0.81 \pm 0.04)T_c$.

These results cannot arise because of the difference between the clamped and free Curie temperatures. In this class of materials this difference is only 1 or 2 K. Likewise the difference between $T_0$ and $T_T$ is not because the transitions are first order instead of second order. In both materials the transitions are believed to be very close to second order as shown particularly well by Kaminow (1965) for KDA. He finds that the dielectric constant at 9 GHz follows a Curie law temperature dependence with $T_c = T_T \pm 2$ K. We are unfortunately unaware of dielectric measurements on CsD$_2$ but Blinc et al. (1970) quote $T_c = T_T$ for CsD$_2$. Furthermore it is possibly of interest that they observe the temperature dependence of the inverse quadrupole coupling coefficient of $^{75}$As and find that it obeys a temperature dependence given by $(T - T_0)/T$ with $T_0 = 0.43T_c$. The simple soft mode theory gives a temperature dependence of $(T - T_c)/T$.

We conclude from our results that the damped simple harmonic oscillator model is not an adequate description of the soft mode in these materials. We believe that the origin of the difficulty lies in the anomaly in the response of the soft mode at low frequencies as discussed qualitatively before (Cowley 1970).

In the anharmonic theory of lattice dynamics the damping of the modes arises in lowest order from the decay of the phonon into pairs of other modes. The selfenergy diagram is shown in figure 2(a). In ferroelectric materials we are interested in the behaviour of the

![Figure 2. The selfenergy diagram applicable for the width of modes in low order perturbation theory (a). The selfenergy diagram modified to be correct as $q \to 0$ and $\omega \to 0$ (b). The equation for the renormalized vertex of (b) is shown in part (c).](image-url)
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Dielectric response in piezoelectric crystals

Abstract. Raman scattering measurements in KDA and CsDA are used to show that the soft mode in a piezoelectric ferroelectric may not be described as a classical damped oscillator. The discrepancy arises because of a contribution to the selfenergy of the mode at low frequencies which arises from the coupling of the mode with fluctuations in the phonon density.

The temperature dependence of the dielectric constant of a ferroelectric material is known to be associated with the temperature dependence of a long wavelength normal mode of vibration (Cochran 1960, and Anderson 1960). The relationship

\[ \omega_0^2 \propto \frac{1}{\varepsilon} \]

has been especially well verified for the near ferroelectrics SrTiO3 and KTaO3 by Fleury and Worlock (1968) using Raman scattering techniques. In other materials it has been found that the damping of the ‘soft’ mode is of importance, when the response of the soft mode to an applied frequency, \( \omega \), may be written as for a classical damped harmonic oscillator

\[ G(\omega) = \frac{1}{(\omega_0^2 - \omega^2 + i\gamma \omega)^{-1}}. \] (1)

This relationship has been shown to give a satisfactory description of the soft mode in many ferroelectrics, for example, BaTiO3 (Yamada et al. 1969). This response function
may also be obtained from the theory of a weakly anharmonic crystal (Maradudin and Fein 1962) when

$$\omega_0^2 \propto (T - T_c)$$

and

$$\gamma \propto T.$$ 

We have measured the Raman spectra from single crystals of CsDA (CsH$_2$AsO$_4$) and KDA(KH$_2$AsO$_4$). The measurements were performed with an argon ion laser and a double grating spectrometer and the Be(X(YX)Y) spectra recorded at several temperatures above the ferroelectric transition temperatures $T_T$ of 143 K and 92 K respectively.

The results showed scattering characteristic of an overdamped mode which is associated with the ferroelectric properties and also scattering from other modes at higher frequencies. We have analysed these spectra to find the parameters of the overdamped mode $\omega_0$ and $\gamma$ as functions of temperature. Since in fact the lowest of the phonon modes gave a characteristic interference with the wing of the overdamped mode the analysis was performed with two interfering modes as will be reported in detail elsewhere (Katiyar et al. 1971). The results for the parameters of the overdamped mode, $\omega_0$ and $\gamma$ were highly correlated but, in common with other overdamped mode situations, the width $\Gamma = \omega_0^2/\gamma$ was little correlated.
Paraelectric, piezoelectric and pyroelectric crystals: I.
Dielectric properties

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Abstract. The dielectric properties of crystals are studied on the basis of the weakly anharmonic crystal model. Particular emphasis is placed on the low frequency behaviour of the dielectric susceptibility and on the possibility of a coupling between the dielectric properties and the fluctuations in the phonon density distribution. These fluctuations cannot be treated by low-order perturbation theory but can be discussed by solving the appropriate transport equation. The approximate solution to this equation is obtained following the techniques developed for ultrasonic attenuation. The results show that in nonpiezoelectric crystals there is no coupling to the phonon density fluctuations; the susceptibility is equivalent to that given by the classically damped harmonic oscillator. In piezoelectric but nonpyroelectric crystals there is a coupling to the fluctuations in the phonon density distribution away from local thermodynamic equilibrium. This leads to additional dielectric loss at frequencies, \( \omega \), less than \( 1/T \), where \( T \) is an average phonon lifetime. In pyroelectric crystals there is also an additional coupling to the fluctuations in the local thermodynamic equilibrium. This gives rise to the possibility of observing second sound through the dielectric response.

1. Introduction

The low frequency dielectric properties of crystals are determined by the motion of the ions within them. For many materials the dielectric properties may be understood with the aid of a lattice dynamical model in which the normal modes are weakly interacting with one another. Considerable success has been had with this model in understanding the far infrared reflectivity of simple materials, such as alkali halides (see Cowley 1968 and references therein).

The theory of ferroelectricity developed by Cochran (1960) explains the temperature dependence of the dielectric properties in terms of the temperature dependence of a particular normal mode of vibration. As the temperature of the ferroelectric phase transition is approached the frequency of this mode decreases, until at the phase transition the crystal is unstable, and distorts to the ferroelectric crystal structure. Measurements have now confirmed that this concept is appropriate to a large number of different materials as reviewed by Nettleton (1970). Although in the original theory the origin of the temperature dependence was not discussed, it is now generally accepted (Silverman and Joseph 1964, Cowley 1965), that at least in some perovskites the temperature
dependence arises from the anharmonic interactions between the normal modes of vibration.

Despite these undoubted successes of the weakly anharmonic model there are still some experimental results with which the predictions of the lowest order theory are not in accord. The theory leads to a dielectric response at low frequencies which is identical with that given by a classically damped simple harmonic oscillator. In contrast the dielectric properties of TGS and KD$_2$PO$_4$ were shown by Hill and Ichiki (1962, 1963) to be inconsistent with this model as reviewed and discussed in detail by Yoshimitsu and Matsubara (1968). Recently obtained Raman spectra of KDA and CsDA (Cowley et al. 1971 and Blinc et al. 1971, private communication) also cannot be interpreted on this model. These results, and the stimulation of the interest in critical effects at structural phase transitions resulting from the work of Müller and Berlinger (1971) and of Riste et al. (1971), on SrTiO$_3$, have prompted us to study the low frequency dielectric properties of crystals in more detail.

In these two papers we re-examine the theory of the dielectric properties for a weakly anharmonic crystal. Preliminary accounts of this work have been published (Cowley 1970 and Coombs and Cowley 1972). In the next section we introduce the formalism and show that the predictions of the theory are very dependent upon the symmetry of the crystal. In nonpiezoelectric crystals the lowest-order theory for the dielectric properties does indeed reduce at low frequencies to that given by the classically damped simple harmonic oscillator. In less symmetric crystals the result is not so simple. There is an additional contribution to the dielectric loss at low frequencies arising from the interaction between the dielectric properties and fluctuations in the number density of the phonons. This process is a transport process and so can only be described by infinite order perturbation theory, as described for the case of ultrasonic attenuation by Sham (1967), Klein and Wehner (1968, 1969) and Niklasson and Sjölander (1968).

In crystals which are not pyroelectric the dielectric fluctuations only give rise to phonon density changes which do not alter the local temperature but disturb the local distribution of phonon densities away from equilibrium. In pyroelectric crystals there is coupling both to deviations from local thermodynamic equilibrium and to changes in the thermodynamic parameters. In §3 these results for the one-phonon dielectric response are described in detail for the different crystal symmetries.

Section 4 is concerned with extending the theory to include the effects of the direct coupling between the electric field and pairs of phonons. It is shown that this coupling may give rise to large changes in the dielectric response. It is possible to study the dielectric fluctuations at nonzero wavevectors by neutron or Raman scattering techniques. The results of the preceding sections are extended in §5 to nonzero wavevectors, by including the effects of acoustic as well as optic modes. A wide range of different behaviour is then possible, including the possibility of observing second sound through its influence on the dielectric properties.

In the second paper, we study the temperature dependence of these results with particular reference to the form of the response in the neighbourhood of a structural phase transition. We show that the results are very dependent on the symmetries of the different phases.

These results are all obtained within the framework of the weakly anharmonic crystal. They are therefore inappropriate for materials in which atoms or molecules undergo order–disorder transitions. Despite this limitation we believe that many of the results are more dependent upon symmetry considerations than the details of the model, and so may be of somewhat wider applicability than the weakly anharmonic crystal model itself.
2. Theoretical development

2.1. Symmetry and techniques

The hamiltonian of an anharmonic crystal is the sum of a harmonic term

$$H_0 = \sum_{q_j}\hbar\omega(q_j)\{a(q_j)a^+(q_j) + \frac{1}{2}\}$$

and an anharmonic term

$$H_A = \sum_{1,2,3} V_{123} A_1 A_2 A_3 + \ldots$$

where $\omega(q_j)$ is the frequency of a normal mode of branch $j$ and wavevector $q$. The phonon coordinate, $A(q_j)$, is the sum of the phonon creation, $a^+(-q_j)$, and destruction, $a(q_j)$, operators, and in the anharmonic term we have made use of the abbreviations $A(q_{1,j_1}) \rightarrow A_1$ etc. The expansion coefficients may be expressed in terms of the interatomic forces, and the normal mode eigenvectors and frequencies (Maradudin and Fein 1962).

We shall be particularly concerned with the processes in which a dielectric fluctuation decays into a pair of phonons, as described by the coefficients

$$V^{0}_{j j_1 j_1}$$

where the mode $(0)j$ is one which is responsible for the dielectric fluctuations. These coefficients satisfy, by definition, the symmetry relation

$$V^{0}_{j j_1 j_1} = V^{0}_{-j -j_1 -j_1}$$

They must also transform under the symmetry operations of the crystal, which transform a particular wavevector $q$ into any one of the set of wavevectors $q_s$, known as the star of $q$. It then follows

$$\sum_{q \text{ within } q_s} V^{0}_{j j_1 j_1} \neq 0$$

only if the mode $(0)j$ transforms like the identity representation of the crystal point group. This is the condition for pyroelectricity if the mode $(0)j$ describes dielectric fluctuations, and shows that these coefficients are nonzero for at least some $j$ values in the crystal classes 1, 2, 3, 4, 6, m, mm2, 3m, 4mm and 6mm. If the summation over $q$ does give zero then either all the $V$ coefficients are zero or else they are related to one another by symmetry. If the crystal has a centre of symmetry then using the odd parity of the dielectric fluctuations gives

$$V^{0}_{j j_1 j_1} = -V^{0}_{-j -j_1 -j_1}$$

which in association with equation (2.1) shows the coefficients to be zero. A similar argument applies in the case of the point group 432.

The second case arises in piezoelectric but nonpyroelectric classes: 222, 4, 42m, 422, 32, 6, 6m2, 622, 432 and 23, which for brevity we shall denote as PBNP classes. The behaviour of the coefficients for certain $j$ values in these cases may be illustrated by an example from the class 4. If the wavevector $q$ is $(X, Y, Z)$ the set of $q_s$ consists of $(X, Y, Z), (-X, -Y, Z), (-Y, X, -Z), (Y, -X, -Z)$. The coefficients for the last two
wavevectors are equal in magnitude but opposite in sign from those for the first two wavevectors.

Many of the properties of the crystal may be expressed in terms of the one-phonon thermodynamic Green functions, \( G(q_i, i\omega_n) \), as described by Abrikosov et al (1963), Maradudin and Fein (1962) and Cowley (1963). These functions may be obtained by diagrammatic techniques and are defined at the points on the imaginary frequency axis given by \( i\omega_n = 12\pi n/\beta \hbar \) with \( n \) an integer, and \( \beta \) the reciprocal temperature, \( (k_B T)^{-1} \). The physical properties are obtained by analytically continuing these functions to the real frequency axis,

\[
i\omega_n \to \omega + i\epsilon, \quad \epsilon \to 0^+.
\]

In real systems there is usually more than one mode, \( j \), of a particular symmetry and the Green function is a matrix in the two \( j \) indices. Since this complication does not significantly alter our results we shall neglect the other modes.

Many-body perturbation theory (Abrikosov et al 1965) shows that the thermodynamic Green functions satisfy the Dyson equation

\[
\{\omega_1^2 + \omega_n^2 + \Pi_1(i\omega_n)\}G_1(i\omega_n) = 2\omega_1
\]

(2.2)

where the anharmonic self energy is \( \Pi_1(i\omega_n) \). Once the analytic continuation is performed to the real \( \omega \) axis, the self energy has both real and imaginary parts and is usually written in the form

\[
\Pi_1(\omega + i\epsilon) = 2\omega_1\{\Delta_1(\omega) - i\Gamma_1(\omega)\}.
\]

Although this result is exact it is for many purposes impossibly difficult to evaluate in detail. In later sections we shall need an approximate form for the Green function which includes the lifetime of the phonons, but which is also simple enough to evaluate directly. A suitable approximation for the Green function is given by

\[
(\bar{\omega}_1^2 - \omega^2 - 2i\omega\gamma_1)G_1(\omega) = 2\omega_1
\]

in which \( \Delta_1(\omega) \) has been taken as a constant and independent of \( \omega \) and included into \( \bar{\omega}_1 \) while \( \Gamma_1(\omega) \) is assumed proportional to \( \omega \). This approximation assumes that \( G_1(\omega) \) has two poles at

\[
x_1^\pm = -i\gamma_1 \pm (\bar{\omega}_1^2 - \gamma_1^2)^{1/2}
\]

and can be written in the form

\[
G_1(\omega) = R_1 \left( \frac{1}{\omega - x_1^+} - \frac{1}{\omega - x_1^-} \right)
\]

(2.3)

with

\[
R_1 = \omega_1(\bar{\omega}_1^2 - \gamma_1^2)^{-1/2}.
\]

2.2. The two-phonon Green function

Many of the features described later are dependent upon the two-phonon Green function, which is shown diagrammatically in figure 1, for the independent phonon approximation. This function is

\[
K(q_1, q_2, i\omega_n) = K_{12}(i\omega_n) = \sum_{i\omega_m} G_1(i\omega_m) G_2(i\omega_n - i\omega_m).
\]
The sum over $i\omega_m$ may be evaluated using the techniques of Abrikosov et al (1965). In terms of the approximate Green functions (2.3), the result is

$$K_{12}(i\omega_n) = \beta h R_1 R_2 \left( \frac{n(x_1^+ + n(x_2^+ + 1)}{x_1^+ + x_2^+ - i\omega_n} + \frac{n(x_1^- + n(x_2^- + 1)}{x_1^- + x_2^- - i\omega_n} \right)$$

$$- \left[ \frac{n(x_1^- + n(x_2^- + 1)}{x_2^- + x_1^- - i\omega_n} + \frac{n(x_1^- + n(x_2^- + 1)}{x_2^- + x_1^- - i\omega_n} \right]$$

where $n(x) = \{\exp(\beta hx) - 1\}^{-1}$. In discussing the dielectric properties we are particularly concerned with the behaviour of this expression as wavevector $Q = q_1 + q_2$ and frequency, $\omega$, become small. There are in this limit two types of terms: one is independent of $Q$ and $\omega$ but the other is dependent upon the way in which the limit is performed. Normally in the terms for which $j_1 \neq j_2$ the expression is independent of the limiting process but if $j_1 = j_2$ this is not the case.

If the anharmonic effects are small, $\gamma_1 \ll \omega_1$, $\gamma_2 \ll \omega_2$ then equation (2.4) can be evaluated in detail to give in the limit as $Q$ and $\omega \to 0$,

$$K_{12}(\omega + i\epsilon) = \beta h \left[ K_{12}^0 + K_{12}^0 \delta_{12} + K_1(Q, \omega) \delta_{12} \right]$$

with

$$K_{12}^0 = 2(1 - \delta_{12}) \left( \frac{n_1 + n_2 + 1}{\omega_1 + \omega_2} - \frac{n_2 - n_1}{\omega_2 - \omega_1} \right) + \delta_{12} \left( \frac{2n_1 + 1}{\omega_1} \right)$$

$$K_1(Q, \omega) = -\omega K_1^0 \left( \frac{1}{\omega - Q \cdot v_1 + 2i\gamma_1} + \frac{1}{\omega + Q \cdot v_1 + 2i\gamma_1} \right)$$

where $n_1 = n(\omega_1)$ is the normal phonon occupation number, while

$$Q \cdot v_1 = \omega(q, j_1) - \omega(q, j_1)$$

showing that $v_1$ is the gradient of the dispersion curve.

If the anharmonic effects are large for one particular mode $\gamma_1 \gg \omega_1$, the most important changes occur in the terms for which both 1 and 2 belong to this overdamped branch, and their contribution at high temperature is then given by

$$K_1^0 = 4\omega_1^2/\beta h\omega_1^2$$

and
where the relaxation time, $\tau_1 = 4\gamma_1/\omega_1^2$.

This result, equation (2.9), has precisely the same structure as that of equation (2.8), at high temperature, but with $Q, v$ zero. It may therefore be readily incorporated into our analysis without difficulty and will not be treated explicitly in later sections.

2.3. Vertex renormalization

In much of the later work we shall be concerned with the coupling between a single phonon or probe and a two-phonon state. Such an interaction is represented schematically in figure 2a, and will be written as $Y_{12}(Q, \omega)$, which describes the interaction in which the phonon or probe described by $(Q, \omega)$ interacts with the pair of phonons $(q_1, j_1)$ and $(q_2, j_2)$. In the case of the interaction with a single phonon, $Y_{12}(Q, \omega)$ is the coefficient $V_{012}$ in the anharmonic expansion. In an anharmonic crystal, there is an interaction between the phonons 1 and 2 so that the interaction consists not solely of the direct process, figure 2a, but also of the more complex processes shown schematically in figure 2b.

In general it is possible to write the sum of all the possible ways in which the phonon or probe can interact with a pair of phonons in terms of a renormalized interaction, $Y_{12}(Q, \omega)$. This renormalized interaction is given by an integral equation, which if we restrict ourselves to the lowest order anharmonic terms, is shown schematically in figure 2c. At first sight it might seem that using a renormalized interaction is including terms which appear only in higher orders of anharmonic theory. At low frequencies, however, the energy denominators also involve the anharmonicity so that, as shown by Sham (1967), it is essential to sum the whole infinite series of anharmonic terms, represented by $Y_{12}(Q, \omega)$, in order to obtain a result which is consistent to lowest order anharmonic theory.
We shall not write out the integral equation of figure 2c explicitly but refer to the original papers of Sham (1967), Niklasson and Sjolander (1968) and Klein and Wehner (1969). One of us has given an alternative derivation of their results using diagrammatic techniques (Coombs 1972, unpublished). The important terms in the analysis of this equation are those terms in the two-phonon Green function which are singular as $Q$ and $\omega \to 0$; namely when $j_1 = j_2$ as given by $K_1(Q, \omega)$. After considerable analysis the integral equation may be rewritten in a form which is similar to the Peierls' phonon Boltzmann equation, when $j_1 = j_2$. If we define a new variable, $X_1(Q, \omega)$, by

$$X_1(Q, \omega) = \frac{-iY_{12}(Q, \omega)}{\omega - Q \cdot v_1 + 2i\gamma_1}$$

then Klein and Wehner (1969) show that

$$(\omega - Q \cdot v_1)X_1(Q, \omega) = -iY_{12}(Q, \omega) - \frac{i}{n_1(n_1 + 1)} \sum C_{12}X_2(Q, \omega)$$

where $C_{12}$ represents the collision operator for the phonon Boltzmann equation.

Before describing an approximate solution to this equation it is of interest to discuss the origin of these complexities. The terms which are causing difficulty in the two-phonon Green function, $K_{12}(\omega)$, are those terms for which $j_1 = j_2$. These terms represent a process in which the phonon or probe creates a phonon $(q_1 j_1)$ and destroys a similar phonon with only slightly different wavevector. On remembering that $a^\dagger a$ gives the phonon density we see that the phonon 0 or probe is creating a fluctuation in the phonon density distribution, $n(q_1 j_1)$, of the mode $(q_1 j_1)$. This fluctuation varies with the applied $Q$ and $\omega$. The derivation of the results for the independent phonon approximation in §2.2 assumed that these phonon density fluctuations all decayed independently of one another. In real crystals these fluctuations may cause changes in the local thermodynamic equilibrium and these will certainly not decay independently but in a manner that is described by the cooperative laws of thermodynamics.

This behaviour manifests itself in the Boltzmann equation (2.11) because the collision operator conserves energy, and in the absence of Umklapp processes also conserves momentum.

The solution to equation (2.11) is obtained by use of the approximation developed by Guyer and Krumhansl (1966) and Niklasson (1970). The quantity $X_1(Q, \omega)$, which in our development plays the same rôle as the phonon density in Guyer and Krumhansl’s work, may be divided into two parts. One part of the change imposed by the perturbation contributes to the fluctuations in the local thermodynamic equilibrium, while the remainder gives rise to deviations in the phonon density from local thermodynamic equilibrium;

$$X_1(Q, \omega) = U_1(Q, \omega) + \tilde{X}_1(Q, \omega)$$

where $U_1$ represents the contribution to the thermodynamic fluctuations and $\tilde{X}_1$ the departures from local thermodynamic equilibrium. All of the problems we consider are symmetrical in $q_1$ and $-q_1$, so that $U_1(Q, \omega)$ depends solely on the local energy, or temperature.

Now since the $\tilde{X}_1(Q, \omega)$ depends on the departures from local thermodynamic equilibrium, it is reasonable to assume that they decay with some relaxation time back towards local thermodynamic equilibrium. The collision operator is therefore approximated by
\[
\frac{1}{n_1(n_1+1)} \sum C_{12} \tilde{X}_2(Q, \omega) = 1/\tau_1 \tilde{X}_1(Q, \omega).
\]

When this is substituted into equation (2.11) and on remembering that the collision operator conserves energy, the result is

\[
X_1(Q, \omega) = U_1(Q, \omega) \left(1 - \frac{\omega - Q \cdot v_1}{\omega - Q \cdot v_1 + i/\tau_1}\right) - \frac{iY_{12}(Q, \omega)}{\omega - Q \cdot v_1 + i/\tau_1}.
\]

The thermodynamic response is dominated by those phonon density distributions which are not influenced by all or part of the collision operator (Guyer and Krumhansl 1966). These distributions are best represented as vectors in \((q, \omega)\) space and represent conservation of energy and conservation of momentum in the \(x\) direction.

A typical component of each vector is

\[
\eta_0 = \mu_0 \beta \hbar \omega_1 \{n_1(n_1+1)\}^{1/2}
\]

\[
\eta_x = \mu_x \beta \hbar q_x \{n_1(n_1+1)\}^{1/2}
\]

where the \(\mu\) are normalization coefficients, \(\mu_x^2 = (k_B C_V)^{-1}\), with \(C_V\) the specific heat. The former eigenvector is totally unaffected by the collision operator, while the latter one is influenced by Umklapp scattering but not by normal scattering processes. The solution to the Boltzmann equation is then written as

\[
U(Q, \omega) = a_0 \eta_0 + \sum_x a_x \eta_x
\]

where the coefficients are given by

\[
\omega a_0 - \lambda Q \cdot a_1 = -iW_0
\]

\[
\omega a_1 - \lambda Q \cdot \eta_0 = -i\gamma(Q, \omega) a_1
\]

and

\[
W_0 = \sum_{\lambda} Y_{11}(Q, \omega) n_1(n_1+1) \mu_0 \beta \hbar \omega_1
\]

\[
\lambda Q = \langle \eta_x | - \omega + Q \cdot v_1 | \eta_0 \rangle
\]

and \(\gamma^{-1}(Q, \omega)\) is a wavevector and frequency dependent relaxation time. Expressions for this relaxation time are given by Guyer and Krumhansl (1966) in various different cases. One of the most interesting occurs when \(\omega \tau_N \gg 1 \gg \omega \tau_U\) with \(\tau_N\) and \(\tau_U\) the normal and Umklapp relaxation times. In these circumstances if \(\tilde{v}^2\) is the phonon velocity squared,

\[
\gamma(Q, \omega) \approx 1/\tau_N + \tau_U \tilde{v}^2 Q^2.
\]

Using these results we obtain quite generally

\[
a_0 = \frac{W_0 \{-i\omega + \gamma(Q, \omega)\}}{\omega^2 - \lambda^2 Q^2 + i\omega \gamma(Q, \omega)}
\]

and hence we may write

\[
U_1(Q, \omega) = -i\mu_0 \beta \hbar \omega_1 W_0 D
\]

where \(D\) is the thermodynamic propagator.
Paraelectric, piezoelectric and pyroelectric crystals: I

\[ D = \frac{\omega + i\gamma(Q, \omega)}{\omega^2 - \lambda^2 Q^2 + i\omega \gamma(Q, \omega)} \]  

(2.15)

or alternatively

\[ = \frac{1}{\omega} \left( 1 + \frac{\lambda^2 Q^2}{\omega^2 - \lambda^2 Q^2 + i\omega \gamma(Q, \omega)} \right) \]

These equations taken together with equations (2.12) and (2.13) give our required approximate solution for the renormalized interaction \( Y_{12}(Q, \omega) \), in the case where \( j_1 = j_2 \), namely,

\[
Y_{12}(Q, \omega) = \delta_{12}(\omega - Q \cdot v_1 + 2i\gamma_1) \left\{ \frac{Y_{12}(Q, \omega)}{\omega - Q \cdot v_1 + i/\tau_1} + \left( 1 - \frac{\omega - Q \cdot v_1}{\omega - Q \cdot v_1 + i/\tau_1} \right) \mu \beta \omega \hbar W_0 D \right\} + (1 - \delta_{12}) Y_{12}(Q, \omega). \]  

(2.16)

This result could be improved formally by use of the elegant approach adopted by Niklasson (1970), but even in our case the difficulties in performing any quantitative calculations are enormous. Our results do have the merit that at high frequencies, \( \omega \) and \( Q \cdot v_1 \gg 1/\tau \), they reduce to the well known collisionless limit, while at low frequencies they also reduce to give the correct thermodynamic behaviour. It is to be hoped that they are at least a reasonable approximation at intermediate frequencies.

2.4. Phonon self energy

In an anharmonic crystal the self energy of a phonon is the sum of the square of the harmonic frequency and an infinite set of anharmonic terms. The lowest order diagram which gives an imaginary part to the self energy is shown in figure 3a. In the indepen-

![Figure 3. (a) The lowest order cubic anharmonic diagram for the phonon self energy: (b) a diagram with interactions between the two phonons; (c) the summation of all of those processes in terms of the renormalized vertex.](image-url)
dent-phonon approximation its contribution to the self energy may be written in terms of the two-phonon Green function of § 2.2. The result for the self energy of a mode with wavevector $\mathbf{Q}$ and branch $j$, as $\mathbf{Q}$ and $\omega \to 0$, is given by

$$\Pi_0^2(\omega) = -\frac{36\omega_0}{\beta \hbar^3} \sum_{12} |V_{012}|^2 K_{12}(\omega)$$

where $K_{12}(\omega)$ is given by equation (2.5) and we have labelled the mode $(\mathbf{Q} j)$ as 0.

In the preceding section it was shown that the independent phonon approximation is not satisfactory when $\omega \to 0$. The complete set of diagrams, figure 3, is summed by replacing $V_{012}$ by the renormalized interaction $\bar{V}_{012}$. The self energy is then given by

$$\Pi_0^2(\omega) = -\frac{36\omega_0}{\beta \hbar^3} \sum_{12} V_{0-1-2} \bar{V}_{012} K_{12}(\omega).$$

The renormalized vertex can now be obtained from the discussion of the preceding section. In particular, we showed that the renormalization is only of importance for those terms which are singular as $\omega \to 0$. We may therefore write the other terms as

$$\Pi_0^{2\delta}(\omega) = -\frac{36\omega_0}{\hbar^2} \sum_{12} |V_{012}|^2 (K_{12}^{0} + K_{12}^{10}).$$

These terms do not involve phonon density fluctuations and are the usual result of standard perturbation theory. The singular terms are obtained by noting that

$$\bar{V}_{012} K_{1}(\mathbf{Q}, \omega) = i\omega K_{1}^{0} X_{1}(\omega)$$

where we have made use of the symmetry of our expressions in $\mathbf{q}$ and $-\mathbf{q}$. There are then two contributions to the self energy. The first arises from the first term of equation (2.16) and describes the fluctuations in phonon density away from local thermodynamic equilibrium and is given by

$$\Pi_0^{2\delta}(\omega) = \frac{36\omega_0}{\hbar^2} \sum_{1} |V_{01-1}|^2 \frac{K_{1}^{0}}{\omega - \mathbf{Q} \cdot \mathbf{v}_1 + i/\tau_1}. \quad (2.18)$$

The contribution to the self energy from the fluctuations in the local thermodynamic equilibrium is given by

$$\Pi_0^{2\delta}(\omega) = \frac{72\omega_0}{\hbar} \beta W(0, 0) W(\mathbf{Q}, \omega) D \quad (2.19)$$

where

$$W(\mathbf{Q}, \omega) = \sum_{1} V_{01-1} n_1(n_1 + 1) \mu_0 \beta \hbar \omega_1 \left(1 - \frac{\omega - \mathbf{Q} \cdot \mathbf{v}_1}{\omega - \mathbf{Q} \cdot \mathbf{v}_1 + i/\tau_1}\right)$$

and $D$ is given by equation (2.15).

There are these three separate contributions to the self energy at low frequencies. One term is largely independent of $\mathbf{Q}$ and $\omega$ and arises from normal phonon scattering. The second term arises from the phonon causing deviations in the phonon densities away from local thermodynamic equilibrium, while the third term arises from the phonon causing changes in the local temperature and heat current. Both of these last two contributions are dependent on $\mathbf{Q}$ and $\omega$. 
3. Dielectric properties of crystals

3.1. Nonpiezoelectric crystals

The part of the hamiltonian describing the interaction of an applied electric field \( E \) with a crystal having a dipole moment \( M \) is given by

\[
H_1 = - M \cdot E
\]

The linear dielectric response in this case may be characterized by the susceptibility which is expressible in terms of a retarded Green function (Kubo 1957):

\[
\chi_{\alpha\beta}(\omega) = \frac{1}{Nv} G^R(M_\alpha M_\beta, \omega)
\]

where \( Nv \) is the volume of the crystal and \( \omega \) the frequency of the applied electric field. The retarded Green function may be obtained from the analytic continuation of the thermodynamic Green function \( G(i\omega_n) \) to the real axis (Abrikosov et al. 1965):

\[
G^R(\omega) = G(i\omega_n)
\]

with

\[
\omega_n \rightarrow \omega + i\epsilon
\]

where

\[ \epsilon \rightarrow 0^+ . \]

The connection with our earlier development is then made by expanding the dipole moment operator in powers of the phonon coordinates,

\[
M(Q) = \sum_J M(j) A(Q_j) + \sum_{12} M_{12} A_1 A_2 + \ldots
\]

(3.2)

where the coefficients are numbers dependent on the effective ionic charges and normal mode eigenvectors, while \( Q \) is the wavevector of the applied electric field, and \( Q = q_1 + q_2 \). In this section we shall take \( Q = 0 \) and consider only the first term of equation (3.2), but in §5 and §4 respectively we shall lift these restrictions. On substituting the first term of equation (3.2) into equation (3.1) and neglecting the components of the one-phonon Green function that are not diagonal in the branch indices, the susceptibility becomes

\[
\chi_{\alpha\beta}(\omega) = \frac{1}{\hbar Nv} \sum_J M_\alpha(j) M_\beta(j) G(0j, \omega + i\epsilon) .
\]

(3.3)

This now gives the dielectric susceptibility in terms of the one-phonon Green function discussed in §2.

Similarly, the scattering cross section for light, x rays and neutrons may be written
in terms of Green functions. It is possible to express the scattering for a wavevector transfer, $K$, and frequency transfer, $\omega$, as

$$\sigma(K, \omega) = \{ n(\omega) + 1 \} \text{Im}[G^{R}(F(K)F^{*}(K), \omega)]\Delta(Q - K)$$

where $\Delta(Q - K)$ implies that $Q - K$ is a reciprocal lattice vector, while the function $F$ is dependent upon $K$, the normal mode eigenvectors; and the scattering lengths of the different atoms. In complete analogy with equation (3.2) $F(K)$ may be expanded in a power series in the phonon coordinates

$$F(K) = \sum_{j} F(Kj) A(Qj) + F_{12}(K)A_{1}A_{2} + \ldots \tag{3.4}$$

The one-phonon part of the cross section is then very similar to the one-phonon contribution to the imaginary part of the dielectric susceptibility, equation (3.3), provided that $Q = 0$.

The structure of both the dielectric and scattering properties of a normal mode responsible for the dielectric properties are governed by the one-phonon Green function. This was given in terms of the self energy by equation (2.2).

In nonpiezoelectric crystals it was shown in § 2.1 that the anharmonic coefficients $v^{(0)}_{ij}$ were zero. Consequently the only terms which contribute to the self energy in the limit as $\omega$ approaches zero are the first terms occurring in equation (2.17). These are not singular and hence it is reasonable in this limit to replace them by the low frequency expansion or equivalently the approximate forms of equation (2.3);

$$G_{0}(\omega) = \frac{2\omega_{0}}{\omega_{0}^{2} - \omega^{2} - 2i\omega\gamma_{0}} \tag{3.5}$$

The response is identical to that of the classically damped simple harmonic oscillator.

There is a single damping constant which is expected to be frequency independent in the low frequency limit, say for $\omega/2\pi < 1$ THz. If the damping is very large the response reduces to that of a Debye relaxation form

$$G_{0}(\omega) = \frac{2\omega_{0}}{\omega_{0}^{2}(1 - i\omega\tau_{0})} \tag{3.6}$$

where the relaxation time is given by

$$\tau_{0} = 2\gamma/\omega_{0}^{2} \tag{3.7}$$

In calculating either the dielectric or scattering properties, the factor $2\omega_{0}$ in the numerator of equations (3.5) and (3.6) are exactly cancelled by identical factors in the denominators of $M(0j)^{2}$ and $F(Kj)^{2}$.

3.2. Piezoelectric materials

In materials which are piezoelectric but nonpyroelectric the self energy of those dielectric fluctuations which are coupled to strains by the piezoelectricity consists of two terms, $\Pi_{0A}(\omega)$ and $\Pi_{0B}(\omega)$ of equations (2.17) and (2.18). The dielectric fluctuations do not couple to the temperature fluctuations because in these crystals the symmetry of the
V coefficients is such that the $W(Q, \omega)$ of equation (2.20) is zero. The Green function may be written for zero wavevector, $Q$, as

$$G_0(\omega) = 2\omega_0 \left\{ \frac{\tilde{\omega}_0^2 - \omega^2 - 2i\omega\gamma_0 - \sum L_1 \left( 1 - \frac{\omega}{\omega + i/\tau_1} \right)}{\omega_0^2 - \omega^2 - 2i\omega\gamma_0 - \frac{i\omega\tilde{\tau}L}{1 - i\omega\tilde{\tau}}} \right\}$$  \hspace{1cm} (3.8)

where

$$L_1 = \frac{1}{72\omega_0 |V_{01-1}|^2 n_1(n_1 + 1)\beta h^{-1}}.$$  \hspace{1cm} (3.9)

If we assume that the lifetime of all the other phonons, $\tau_1$, is the same, $\tilde{\tau}$, then the Green function becomes

$$G_0(\omega) = 2\omega_0 \left\{ \frac{\tilde{\omega}_0^2 - L - \omega^2 - 2i\omega\gamma_0 - \frac{i\omega\tilde{\tau}L}{1 - i\omega\tilde{\tau}}}{} \right\}$$  \hspace{1cm} (3.10)

where

$$L = \sum L_1.$$  

At high frequencies $\omega\tilde{\tau} \gg 1$, this expression reduces to the classically damped simple harmonic oscillator of equation (3.5), but at low frequencies there is an additional contribution to the self energy which decreases the real part of the self energy and increases the damping. Since $\tilde{\tau}$ is the average phonon lifetime this result shows that additional dielectric loss is expected in piezoelectric crystals at frequencies lower than about 0.1 THz.

The form of the low frequency peak may be obtained from equation (3.10) in more detail. If we assume that the whole of the low frequency damping arises from the last term, $L\tilde{\tau} \gg 2\gamma_0$, and that $\omega^2 \ll \tilde{\omega}_0^2$, then

$$\frac{\text{Im}\{G_0(\omega)\}}{G_0(0)} = \frac{\omega\tau^* L}{1 + (\omega\tau^*)^2} \left( \frac{1}{\tilde{\omega}_0^2} \right)$$  \hspace{1cm} (3.11)

which is the well known Debye relaxation term with

$$\tau^* = \frac{\tilde{\tau}\omega_0^2}{\tilde{\omega}_0^2 - L}.$$  \hspace{1cm} (3.12)

Equation (3.11) was obtained by assuming that all the relaxation times, $\tau_1$, are equal. In practice there will be a distribution of relaxation times leading to a distribution of times, $\tau^*$. We have been unsuccessful however, in obtaining an explicit connection between the distribution of $\tau_1$ and $\tau^*$. The dielectric response of a piezoelectric crystal leads to a distribution of relaxation times and not to the single relaxation time predicted for nonpiezoelectric materials. It is of interest to note that a distribution of relaxation times has been found necessary to account for the dielectric properties of TGS and DKDP (Hill and Ichiki 1962, 1963) and of many other materials as discussed by Yoshimitsu and Matsubara (1968).

### 3.3. Pyroelectric crystals

In pyroelectric crystals the dielectric response consists of a spontaneous polarization in addition to the dielectric susceptibility. The spontaneous polarization, $\mathbf{M}^s$, is obtained by taking the thermal average over the dipole moment operator, equation 3.2;
\[ M^s = \sum_j M(j)\langle A(0j)\rangle + \sum_1 M_{1-1}(2n_1 + 1). \] (3.13)

The leading term arises in a pyroelectric crystal because the atoms are not all at special positions within the unit cell. They are dependent upon parameters which may vary with temperature, and these changes are described by static displacements of \( Q = 0 \) optic modes, \( \langle A(0j)\rangle \), which consequently vary with temperature. The second term arises because the two-phonon dipole moment operator, \( M_{12} \), obeys the same symmetry properties as the three-phonon anharmonic interactions discussed in §2.1. In pyroelectric crystals the second term is consequently nonvanishing.

The one-phonon part of the dielectric susceptibility along the direction of the pyroelectricity is obtained from equation (3.3), but the self energy of the \( (0j) \) mode now consists of all three terms \( \Pi_{0}^{2A}, \Pi_{0}^{2B} \) and \( \Pi_{0}^{2C} \) of equations (2.17–2.19). When \( Q = 0 \), the dielectric susceptibility has precisely the same form as for piezoelectric crystals, equations (3.8), but with

\[ L_1 = \frac{72\omega_0^2}{\hbar} n_1(n_1 + 1) (|V_{01-1}|^2 - W_0\omega_1\mu_0V_{01-1}). \] (3.14)

The last term arises from the \( \Pi_{0}^{2C} \) term. This result shows that the dielectric response of pyroelectric crystals is expected to be very similar to that of PBNP crystals, although the magnitude of the effects is different. In §5 we show that at finite wavevectors new phenomena are introduced in the pyroelectric case.

If an experiment is performed isothermally the above results are incorrect. It is then necessary to take the limit not as \( Q \rightarrow 0 \) followed by \( \omega \rightarrow 0 \), but \( \omega \rightarrow 0 \) followed by \( Q \rightarrow 0 \). In this latter case the expression for \( L_1 \) does not include the last term of equation (3.14) and is identical with that obtained for PBNP crystals, equation (3.9).

4. Coupling between one- and two-phonon processes

4.1. Nonpiezoelectric crystals

In the previous section the dielectric properties were discussed by considering a coupling of the electric field to only a single phonon. As shown in equation (3.2), the electric field may couple not only to a single phonon but also to pairs and more phonons. In this section we describe the changes in the results of §3 which occur when we include the two-phonon term from equation (3.2). The coefficients \( M_{12} \) have the same symmetry properties as the anharmonic interactions, \( V_{012} \), discussed in §2. In nonpiezoelectric crystals the terms \( M_{1-1} \) are zero.

The normal two-phonon contribution to the dielectric susceptibility is shown schematically by figure 4, which in our notation is

\[ \frac{2}{Nh^2\beta} \sum_{12} M_{\alpha,12} M_{\beta,-1-2} K_{12}(\omega) \] (4.1)

where \( \tilde{M}_{12} \) is the renormalized two-phonon dielectric vertex in the same sense as \( \tilde{V}_{012} \) is the renormalized, \( V_{012} \), anharmonic interaction. In nonpiezoelectric crystals the renormalization may be neglected because the absence of the \( M_{1-1} \) terms gives a two-phonon contribution to the dielectric susceptibility of
\[ \frac{2}{N\hbar} \sum_{\ell \neq 0} M_{\gamma,12} M_{\gamma,-1,2} K_{12}^0. \]  

(4.2)

Since \( K_{12}^0 \) is well defined as \( \omega \to 0 \), this term gives rise to an imaginary part of the susceptibility proportional to \( \omega \).

The three diagrams in figure 4c, d, and e all represent interference effects. They may most readily be incorporated into the formalism as a renormalization of the one-phonon processes by replacing the \( M(j) \) of equation (3.3) with \( M'(j) \) where

\[ M'(j) = M(j) - \frac{6}{\hbar \beta} \sum_{\ell \neq 0} M_{12} V_{0,-1,2} K_{12}(\omega). \]  

(4.3)

In the case of nonpiezoelectric crystals, the renormalization of the anharmonic vertex may be neglected to give

\[ M'(j) = M(j) - \frac{6}{\hbar} \sum_{\ell \neq 0} M_{12} V_{0,-1,2} K_{12}^0. \]  

(4.4)

There are several effects which may result from these terms. The two-phonon contribution is temperature and frequency dependent. The effective one-phonon coupling is therefore temperature and frequency dependent, and furthermore has both real and imaginary parts. The imaginary part may give rise to the characteristic interference effects which may have been observed, both when two phonons interact with one another in BaTiO\(_3\) (Rousseau and Porto 1968) and also when a phonon interacts with the two-phonon background in AlPO\(_4\) (Scott 1968). These interference effects will modify the shape of the dielectric response calculated in the preceding section. In the case of nonpiezoelectrics the low frequency response is unlikely to be altered significantly.

4.2. **PBNP crystals**

In PBNP crystals the renormalized interactions incorporate the effects of the fluctuations
in the phonon density away from local thermodynamic equilibrium. The expression for the two-phonon contribution to the susceptibility in these materials is

$$\frac{2}{N\hbar} \sum_{\alpha \beta} M_{\alpha \beta} M_{\alpha \beta} \left\{ K_{\alpha \beta}^0 + \delta_{\alpha \beta} K_{\alpha \beta} \left( 1 - \frac{\omega}{\omega + i/\tau_1} \right) \right\}$$  \hspace{1cm} (4.5)

while the effective one-phonon interaction is

$$M'(\omega) = M(\omega) - \frac{6}{h} \sum_{\alpha \beta} M_{\alpha \beta} V_{\alpha \beta} \left\{ K_{\alpha \beta}^0 + \delta_{\alpha \beta} K_{\alpha \beta} \left( 1 - \frac{\omega}{\omega + 1/\tau_1} \right) \right\}.$$  \hspace{1cm} (4.6)

Both of these terms are frequency dependent at low frequencies, and may drastically alter the form of the susceptibility at low frequencies. It is difficult to predict the detailed behaviour without a knowledge of both the one- and two-phonon terms in the expansion of the dipole moment. This knowledge is not available even for simple crystals.

4.3. Pyroelectric crystals

In pyroelectric crystals the effect of the two-phonon dipole moment operator is very similar to that in piezoelectric crystals. The two-phonon contribution to the dielectric susceptibility is the same as that for piezoelectric crystals, equation (4.5), except for the presence of additional thermodynamic terms. When an adiabatic response is studied these latter terms give a contribution to equation (4.5)

$$- \frac{4}{N\nu} N_\alpha(0) N_\rho(\omega)$$  \hspace{1cm} (4.7)

where

$$N(\omega) = \sum_{\alpha} M_{\alpha} n_{\alpha}(n_{\alpha} + 1) \mu_{\alpha} \beta h \omega_1 \left( 1 - \frac{\omega}{\omega + i/\tau_1} \right).$$  \hspace{1cm} (4.8)

On the other hand, for an isothermal response this term is zero.

In a similar manner there is an additional term to be added to the effective one-phonon dipole moment in the case of an adiabatic experiment. This term is

$$12N(\omega)W_0.$$  \hspace{1cm} (4.9)

Both of these terms are very similar in form to those obtained for piezoelectric crystals and will similarly modify the behaviour at low frequencies.

As was noted above, all of these terms are absent if the dielectric properties are observed under isothermal conditions. The difference between the adiabatic and isothermal static dielectric constants is given by equations (3.3), (3.10), (3.14), (4.7) and (4.9) as

$$\chi_{\alpha \beta}^{ad}(0) - \chi_{\alpha \beta}^{is}(0) = - \frac{4}{N\nu} \left( \frac{6M_{\alpha}(0)W_0}{h\omega_0^2} - N_\alpha(0) \right) \times \left( \frac{6M_{\beta}(0)W_0}{h\omega_0^2} - N_\beta(0) \right)$$  \hspace{1cm} (4.10)

if the difference between adiabatic and isothermal self energies is small.

By introducing the coupling of the displacement $\langle A(0) \rangle$ to the temperature fluctuations and using equation (3.13) for the spontaneous polarization, $M^s$, this result may be shown to be identical, as indeed it must, with the thermodynamic result

$$\chi_{\alpha \beta}^{ad}(0) - \chi_{\alpha \beta}^{is}(0) = - \frac{T}{N\nu C_V} \frac{\partial M_\alpha^s}{\partial T} \frac{\partial M_\beta^s}{\partial T}.$$
This is a more general form of the result obtained by Wehner and Klein (1971) for the 
elastic constants. It is more general because the lower symmetry of pyroelectric crystals 
gives rise to both the one- and two-phonon terms in equation (4.10). These terms would 
also be necessary in discussing the elastic properties of crystals in which the atoms were 
not at special positions within the unit cell.

In conclusion we have shown that the dielectric properties of pyroelectric crystals 
are given by the same expression as for PBNP crystals, and also that the microscopic 
theory leads to the thermodynamic result for the difference between the adiabatic 
and isothermal dielectric properties.

5. Nonzero wavevector transfer

5.1. Scattering properties

Raman, x ray and neutron scattering may be used to study dielectric fluctuations and 
have the advantage over dielectric measurements that they are not restricted to zero 
wavevector. In order to discuss the behaviour of the dielectric properties in a manner 
appropriate to these measurements, we need to extend the theory to include the coupling 
which occurs in crystals between the dielectric fluctuations and the acoustic waves. 
The formalism for the behaviour at low frequency must take account of the coupling 
between four different types of modes: an optic mode, an acoustic mode, fluctuations 
in the local thermodynamic equilibrium and fluctuations in the phonon density away 
from this local equilibrium. Unfortunately it becomes very cumbersome to continue 
developing the theory as we have done above. It is more elegant to now rewrite a slightly 
restricted form of the theory in terms of a self energy matrix \( H_{\omega \lambda}(\omega) \) where the indices \( \mu \) and \( \lambda \) run over the optic mode \( o \), acoustic mode \( a \), thermodynamic mode \( T \) and the 
many-phonon density fluctuation \( i \). This self energy matrix is

\[
H(\omega) = \begin{pmatrix}
\bar{\omega}_o^2 + i \omega \gamma_o - \omega^2 & b & V_{oT} & V_{oi} \\
b & \bar{\omega}_a^2 + i \omega \gamma_a - \omega^2 & V_{aT} & V_{ai} \\
V_{oT} & V_{aT} & D_{2T} & 0 \\
V_{oi} & V_{ai} & 0 & D_{2i}
\end{pmatrix}
\]

(5.1)

where \( \bar{\omega}_o \) and \( \bar{\omega}_a \) are the optic and acoustic mode frequencies, while \( \gamma_o \) and \( \gamma_a \) determine 
the damping constants at low frequency from the self energy terms \( \Pi^{2\mu}(\omega) \). The coefficient \( b \) describes the interaction between the optic and acoustic modes,

\[
V_{oT} = 3 \{ 2 \omega W(0, 0) W(Q, \omega) / h \}^{1/2}
\]

the coupling between the optic mode and the thermodynamic fluctuations, and \( V_{aT} \) 
the analogous coupling with the acoustic mode. The coupling with the nonthermo-
dynamic fluctuations are given by \( V_{oi} = 3 V_{aT} (2 \omega_o / h^3) \}^{1/2} \). The thermodynamic response 
\( D_{21}^{-1} = 4 \beta \omega D \), while the two-phonon response \( D_{2i} \) is

\[
D_{2i}^{-1} = 2 K_i^0 \left( 1 - \frac{\omega}{\omega - Q \cdot v_i + i/\tau_i} \right)
\]

and the index \( i \) runs over all the modes.
The Green functions are given by the matrix equation

\[
\begin{pmatrix}
2\omega_c & 0 & 0 & 0 \\
0 & 2\omega_a & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\]

The scattering properties can now be obtained from the Green function by introducing a vector \( \vec{F} \) with components \( F_0, F_a, F_T \) and \( F_\mu \) representing the interaction of the probe with the optic, acoustic, thermodynamic and nonthermodynamic processes respectively. In terms of our earlier discussion of dielectric properties \( F_\mu = M_\mu(j) \), \( F_a \) is the analogous one-phonon coupling to the acoustic mode, \( F_T = \{N_4(\omega)N_4(0)\}^{1/2} \), and \( F_1 = M_{\alpha,\Gamma_1} \). The scattering properties are then given by

\[
\text{Im}\left\{\sum_{\mu} F_\mu F_\mu G_{\mu\mu}(\omega)\right\}\{n(\omega) + 1\}
\]

It may be shown that the results of this formalism reduce to those of the previous sections if \( \vec{Q} = 0 \).

The wavevector dependence of terms in the self energy (equation (5.1)) are dependent upon the particular situation. At finite wavevectors \( \vec{Q} \), the optic, acoustic and thermodynamic modes may be classified by the irreducible representations of the little group of the wavevector \( \vec{Q} \). The thermodynamic modes transform as the identity representation \( \Gamma_1 \), and the optic and acoustic modes transform as \( \Gamma_0 \) and \( \Gamma_\text{ac} \). If \( \Gamma_0 \neq \Gamma_\text{ac} \) then \( b \) is identically zero, whereas if \( \Gamma_0 \neq \Gamma_1 \) then \( V_{\text{ot}} \) is zero while if \( \Gamma_0 \neq \Gamma_1 \) then \( V_{\text{at}} \) is zero. The coefficients \( V_{\text{ot}} \) and \( V_{\text{at}} \) may always be nonzero. In table 1 we list the wavevector dependence of these coefficients, and also of the \( F \) for Raman scattering, when \( \Gamma_0 = \Gamma_a = \Gamma_1 \).

The expressions can be obtained for other symmetries by putting the appropriate terms to zero.

<table>
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<tr>
<th>( \omega_a )</th>
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<th>( D_{20} )</th>
<th>( b )</th>
<th>( V_{\text{ot}} )</th>
<th>( V_{\text{at}} )</th>
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</table>
The $F$ coefficients for x-ray and neutron scattering are dependent upon the particular experiment, but it is always possible to perform an experiment for some wavevector $K$, such that all the $F$ coefficients are nonzero when $Q = 0$.

These equations describe a wide variety of different behaviour. At large frequencies $\omega \tau \gg 1$ or large wavevectors $Q \cdot v \gg 1$, the propagation of both the dielectric waves and acoustic waves is a collisionless process whereas at small wavevectors it is a thermodynamic or collision-dominated process. Likewise, if the dielectric fluctuations are damped, it is necessary to distinguish between the response measured in the clamped crystal region $\omega \gg \omega_0$ or in the free crystal region $\omega \ll \omega_0$ as shown schematically in figure 5a. Likewise, the acoustic response will be different at frequencies below the dielectric response frequency $\omega_D$, where the elastic constant at constant electric field is obtained, to that observed above these frequencies where the elastic constant is obtained at constant electric polarization as shown in figure 5b. The characteristic frequency of the dielectric response $\omega_D$ is given for small damping, $\gamma \ll \omega_0$, by $\omega_0$ but for large damping by $\omega_0^2/\gamma$.

The changes in the behaviour of both the dielectric constant and the acoustic waves have been studied in the piezoelectric materials KDP and DKDP. In KDP the dielectric constant was observed in the clamped region by Raman scattering measurements (Kaminow and Damen 1968). Neutron scattering measurements (Paul et al 1970) at larger wavevectors in the free crystal region gave the free crystal Curie constant. Likewise ultrasonic measurements of the acoustic velocity in DKDP (Litov and Uehling 1968), at low frequencies in the constant electric field region, showed a marked decrease in velocity as the transition was approached. Neutron scattering measurements at higher frequencies $\omega \gg \omega_D$ showed no such anomalies (Paul et al 1970).

Although experiments have been performed to exhibit the difference between the collisionless and thermodynamic sound velocities in crystals (Svensson and Buyers 1968), we are unaware of any similar experiments on the dielectric properties. It would be interesting to investigate such effects.

Finally these results have all been obtained for a crystal of infinite size. Once the magnitude of the wavelength becomes comparable with the size of the specimen, the
form of our results requires modification and the results are dependent upon the particular boundary conditions of the crystal.

5.2. Second sound

The results obtained in § 5.1 describe not only the behaviour of the acoustic and dielectric fluctuations but also the behaviour of the temperature fluctuations. These are described by the term $D_{2T}$ in the self energy matrix equation (5.1), and by the term $D$ in equation (2.15). The numerator of $D_{2T}$ is

$$\omega^2 - \lambda^2 Q^2 + i\omega\gamma(Q, \omega)$$

where $\gamma(Q, \omega)$ describes the frequency and wavevector dependent damping of the second sound mode whose velocity is $\lambda$. In most cases the second sound mode is heavily overdamped and the temperature fluctuations only give rise to quasi-elastic scattering. In certain circumstances, which are very difficult to realise in practice, a propagating second sound mode may occur (Guyer and Krumhansl 1966). This has been, however, demonstrated recently in very pure NaF by heat pulse techniques (Jackson and Walker 1971). It is of interest to study these fluctuations in more detail as might be achieved by Raman or neutron scattering. The possibility of the observation of second sound by Raman scattering was initially pointed out by Griffin (1965), and has recently been carefully studied by Wehner and Klein (1972). Griffin considered the scattering to occur entirely through the acoustic mode. $F_a$ was the only nonzero coupling in our notation, and further the coupling to the dielectric fluctuations was omitted. Wehner and Klein likewise omitted the dielectric fluctuations but considered the effects of the coupling $F_a$ and $F_T$. They point out that the spectra are markedly dependent upon the ratio of $F_a$ and $F_T$, and that the interference terms may have a very large influence on the shape of the spectra. In particular the ratio of the intensity of the peak in the scattering from the second sound mode to that from the first sound mode is not necessarily given by the Landau–Placzek ratio.

When the dielectric fluctuations are also included, the intensity is further modified by the coupling of the light to the dielectric fluctuations, which then decay into a second sound mode. If the coupling with the light is entirely through the dielectric fluctuations, $F_a = F_T = 0$, then the intensity of the second sound mode is dependent upon the difference between the adiabatic and isothermal susceptibilities $(\chi_a^{ad} - \chi_a^{is})/\chi_a^{is}$, which is analogous to the Landau–Placzek result when the coupling is by way of the acoustic modes. In practice, however, there will almost certainly be a direct coupling of the light with the thermodynamic fluctuations which will influence the intensity and spectral shape appreciably.

In nonpiezoelectric crystals dielectric fluctuations do not couple to the temperature fluctuations at small wavevectors, so that in these cases the temperature fluctuations cannot be readily studied through the dielectric fluctuations. In piezoelectric crystals the coupling of the light to the temperature fluctuations through the dielectric fluctuations at most is linear in $Q$ and hence is similar to that given by the acoustic waves. In pyroelectric crystals the coupling is nonzero at $Q = 0$ which gives the possibility of a greatly enhanced scattering cross section for studying the temperature fluctuations and possibly second sound.

Finally we should emphasize that the scattering by the temperature fluctuations is always superposed on a background from the nonthermodynamic fluctuations. Since
the temperature fluctuations frequently give a more sharply peaked response than the nonthermodynamic effects, it should be possible to distinguish them.

6. Conclusions

In this paper we have examined the dielectric properties of crystals paying particular attention to the low frequency response. The main point of the paper is that it is essential to distinguish between three different cases. In nonpiezoelectric crystals there is no coupling between the dielectric response and fluctuations in the phonon density distribution. The one-phonon response is given by a classically damped harmonic oscillator.

In piezoelectric but nonpyroelectric crystals the dielectric properties may couple to the fluctuations in the phonon density away from local thermodynamic equilibrium. It is then necessary to distinguish between the thermodynamic, \( \omega \bar{\tau} \ll 1 \), and collisionless, \( \omega \bar{\tau} \gg 1 \), response where \( \bar{\tau} \) is an average thermal phonon lifetime \( \approx 10^{-11} \) s.

In pyroelectric crystals there is further dielectric loss due to the coupling of the dielectric response to fluctuations in the local thermodynamic equilibrium. It is necessary in the thermodynamic region to distinguish between the adiabatic and isothermal response.

We have shown that these distinctions influence not only the one-phonon contribution to the dielectric response but also the two-phonon contribution. The analysis has also been extended to nonzero \( Q \) to apply to scattering properties.

There is unfortunately very little experimental information with which to compare our results. We have shown that the weakly anharmonic model may lead to expressions for the dielectric loss which are similar to those discussed by Yoshimitsu and Matsubara (1968). It is, however, very difficult to evaluate many of our expressions because they involve anharmonic coupling parameters and phonon lifetimes throughout the Brillouin zone. These are largely unavailable for ferroelectric materials. It may also be questionable to apply a weakly anharmonic crystal model to materials such as DKDP, but since our results are largely dependent upon symmetry the results should be applicable at least qualitatively. We hope this paper stimulates study of dielectric properties at frequencies of \( 10^{10} - 10^{12} \) Hz.

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Paraelectric, piezoelectric and pyroelectric crystals: II
Phase transitions

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Abstract. The response of a crystal in the neighbourhood of a structural phase transition is discussed. It is shown that the behaviour of the scattering cross section is very dependent upon the symmetry of the two phases. The weakly anharmonic crystal model is used within the framework of the Landau theory of phase transitions to discuss nonpiezoelectric/ferroelectric, piezoelectric/ferroelectric and transitions involving an increase in the size of the unit cell both of the improper ferroelectric kind and otherwise. In every case it is shown that the theory gives rise to the possibility of quasi-elastic as well as inelastic scattering below \(T_c\), but above \(T_c\) quasi-elastic scattering is expected in the piezoelectric/ferroelectric and improper ferroelectric phase transitions. Extensions of the theory to include critical, or deviations from Landau type behaviour, are then discussed and the results compared with the mode-mode coupling theory of critical phenomena and with the work of others.

1. Introduction

Cochran (1960) has suggested that the mechanism of the transition, in which a crystal distorts to a ferroelectric phase on cooling, may be understood in many materials on the basis of a particular normal mode of vibration becoming unstable. The mode in question is the transverse optic mode at long wavelength and its frequency has a temperature dependence above the transition temperature \(T_c\) of the form

\[ \omega^2(0j) = A(T - T_c) \]

(1.1)

where \(A\) is a constant.

This concept has been extended to structural transitions between phases that are not ferroelectric. It has been found that in many of these cases it is a mode other than the transverse optic that becomes unstable and at points in the Brillouin zone other than the centre.

The frequency response of this temperature dependent mode could, in many materials, be described by a classical damped harmonic oscillator and it was frequently found that the mode was overdamped. However, this model has been shown to be inadequate for the explanation of recent experimental results in SrTiO\(_3\) (Riste et al 1971), KDA and CSDA (Cowley et al 1971) and Nb\(_3\) Sn (Shirane and Axe 1971).

In the preceding paper (I: Coombs and Cowley 1973) we describe the low frequency dielectric properties of crystals. The form of the response was found to depend greatly
upon the symmetry of the crystals. In nonpiezoelectric crystals the response was identical in form to that of a classically damped harmonic oscillator but in crystals of lower symmetry there was additional response at low frequencies; \( \omega \bar{\tau} \ll 1 \), where \( \bar{\tau} \) is the average lifetime of the phonons in the crystal. The mechanism of this loss was the creation of changes in the phonon density distribution during the fluctuations in the dielectric response. This loss can only occur therefore if the frequency is sufficiently low for the density distribution to have time to respond. The detailed nature of the loss was dependent upon the way in which these changes in the phonon density decayed.

In piezoelectric but nonpyroelectric crystals, the changes in the phonon density distribution were such that local thermodynamic quantities, temperature etc, were not disturbed and the changes decayed to restore local thermodynamic equilibrium. In pyroelectric crystals the changes also disturb the local thermodynamic quantities and these deviations decay according to the laws of thermodynamics.

In this paper we make use of these results to discuss the dielectric response and scattering cross section of a crystal at temperatures in the vicinity of its structural phase transition. Throughout most of the paper (§ 2 and § 3) the theory is described within the framework of the Landau model of phase transitions. (See Landau and Lifshitz 1958). In our case this means that the temperature dependence of a normal mode, which involves a summation over all the normal modes, will be calculated including only the explicit dependence of temperature. The temperature dependence of some of the normal modes in the sum will be neglected. This is a good approximation so long as only a few of the \( N \) normal modes in the crystal are strongly temperature dependent, and provided that the frequencies of these modes are not too small. In § 5 we remove this constraint in order to discuss critical or non-Landau phenomena.

In paper I the results were very dependent upon the presence or absence of certain terms in the expansion of the crystal potential energy. Near a phase transition it is convenient to perform the expansion about the high temperature, high symmetry phase. In I the anharmonic potential energy was expanded as

\[
H_A = \sum_{123} V_{123} A_1 A_2 A_3 + \sum_{1234} V_{1234} A_1 A_2 A_3 A_4 + \ldots
\]

The notation we shall use in this paper will be as far as possible the same as that used in I. The distortion to the low temperature phase is represented by a static displacement of one of the normal modes, given by \( \langle A_0 \rangle \), where, in the ferroelectric phase, the spontaneous dipole moment \( M_s \) is proportional to \( \langle A_0 \rangle \). In the simple Landau or Devonshire theory the temperature dependence of the static displacement is given by

\[
\langle A_0 \rangle = K(T_c - T)^{1/2} \quad T < T_c
\]

where \( K \) is a constant, although in practice the temperature dependence is frequently more complex. With the aid of this result we may expand the anharmonic potential of the distorted phase as

\[
H_A = \sum_{123} V_{123}^D A_1 A_2 A_3 + \sum_{1234} V_{1234}^D A_1 A_2 A_3 A_4
\]

(1.2)

where

\[
V_{123}^D = V_{123} + 4\langle A_0 \rangle V_{0123} + 20 \langle A_0 \rangle^2 V_{00123} + \ldots
\]

(1.3)

and a similar expression for \( V_{1234}^D \). This result is particularly important in the case where \( V_{123} \equiv 0 \), because then \( V_{123}^D \) is proportional to \( \langle A_0 \rangle \) or \( (T_c - T)^{1/2} \) in the lowest order approximation.
We are now in a position to apply these results to various different phase transitions. In §2 we apply them to ferroelectric phase transitions. We exhibit the difference between transitions from nonpiezoelectric to ferroelectric phases and from piezoelectric to ferroelectric phases. In §3 we apply these results to other structural phase transitions. In §4 we suggest a way of extending the theory to include critical effects.

2. Ferroelectric phase transitions

2.1. Nonpiezoelectric to ferroelectric

In paper I we showed that the dielectric susceptibility and scattering cross section were determined in the one-phonon approximation by the one-phonon Green function (equation (1.33) of I). In nonpiezoelectric crystals, or better whenever a particular dielectric susceptibility is not coupled to the strain by a piezoelectric constant, this was further shown to be equivalent to the response of a classically damped harmonic oscillator at low frequencies, equation (3.5) of I gives

\[ G_0(\omega) = \frac{2\omega_0}{(\omega_0^2 - \omega^2 - 2i\gamma_0)}. \]  

(2.1)

In materials which undergo a ferroelectric phase transition \( \omega_0^2 \) becomes small (equation (1.1)) and \( G_0(\omega) \) large. It is therefore reasonable to neglect the two-phonon terms discussed in §4 of I compared with the one-phonon terms. Equation (2.1) contains the harmonic frequency, \( \omega_0 \), which for ferroelectric materials is imaginary. No difficulty arises from this however, because the expressions for \( |M(i)|^2 \) and \( |F(K)|^2 \) contain the same \( \omega_0 \) in the denominator.

In a material which undergoes a ferroelectric transition \( \omega_0^2 \) is given by equation (1.1) and \( \gamma_0 = B_0 T \) at high temperatures with \( B_0 \) a constant. The susceptibility is then proportional to

\[ \{A(T - T_c) - \omega^2 - 2i\omega B_0 T\}^{-1}. \]  

(2.2)

Close to the phase transition, this reduces to a Debye relaxation form (equation (3.6) of I) with the relaxation time (equation (3.7) of I) given by

\[ \tau^* = \frac{2B_0 T}{A(T - T_c)} \]  

(2.3)

which diverges as \( T \to T_c \).

This form of the response has been found to give an excellent account of the dielectric and scattering properties in many crystals when the dielectric fluctuations are not coupled by piezoelectric constants. For example, the neutron scattering (Yamada et al 1969), infrared reflectivity (Barker 1966), and Raman scattering (Didomenico et al 1967) from \( \text{BaTiO}_3 \) have all been analysed with this expression.

Below the phase transition the crystal distorts to a ferroelectric (pyroelectric) phase in which the dielectric fluctuations couple to the phonon density fluctuations. The form of the one-phonon Green functions is now given by equation (3.8) of I with \( L_1 \) given by equation (3.14) of I. From this latter equation \( L_1 \) depends on the square of the interaction coefficients \( V_{01} \) which are proportional (equation 1.3) to \( \langle A_0 \rangle \), the distortion of the crystal from its paraelectric structure. Consequently the Landau theory predicts that \( L_1 \) is proportional to \( T(T_c - T) \) giving a response function

\[ G_0(\omega) = 2\omega_0 \left[ (T_c - T) \left\{ A' - B_1 T \left( 1 - \frac{\omega \tau}{\omega \tau + i} \right) \right\} - \omega^2 - 2i\omega B_0 T \right] \]  

(2.4)
where $B_0$ and $B_1$ are constants. The second term gives rise to the necessity of distinguishing between the response in the thermodynamic $\omega \tau \ll 1$ and collisionless regions, $\omega \tau \gg 1$ and may, if $B_1$ is sufficiently large, give rise to two peaks in the response, one at $\omega = 0$ and the other at a higher frequency. At high frequencies the response is that of a classically damped harmonic oscillator, given by equation (2.2), but at low frequencies the response may with suitable approximations be written in the form of a Debye relaxation, equation (3.11) of I. Using our present form for $L$ and $\tilde{\omega}_0$, the effective relaxation time is

$$\tau^* = \tau \left( \frac{A'}{A' - B_1 T} \right)$$

and the response is given by

$$\text{Im} \{G_0(\omega)\} = \frac{\omega \tau^*}{1 + (\omega \tau^*)^2} \left( \frac{B_1 T}{A'(A' - B_1 T)(T_c - T)} \right).$$

Since this expression was obtained with the approximations that $L\tilde{\tau} \gg 2\gamma_0$ and $\omega^2 \ll \tilde{\omega}_0^2$, it clearly fails close to the phase transition. It does, however, suggest that the relaxation time does not diverge as $T \to T_c$ but the intensity of the peak in $\text{Im} \{G_0(\omega)\}$ increases as $(T_c - T)^{-1}$. As $T \to T_c$, equation (2.4) states that the whole response narrows in frequency to give the critical slowing down. The temperature dependence of the peaks in the cross section, $(1/\omega) \text{Im} \{G_0(\omega)\}$, for this type of transition are shown schematically in figure 1 for the case where the mode is underdamped. To the authors’ knowledge, there is no direct evidence for the quasi-elastic peak below $T_c$ at this type of transition.

![Figure 1. Schematic diagram showing the possible temperature dependence of the peaks in the scattering cross section for $Q = 0$ for the Landau theory of phase transitions between nonpiezoelectric and ferroelectric phases.](image)

### 2.2. Piezoelectric to ferroelectric phase transition

The dielectric response of an optic mode in a piezoelectric crystal is given by equation (3.8) of I with $L_1$ given by equation (3.9) of I. The response at high frequencies $\omega \tilde{\tau} \gg 1$ is identical to that of a classically damped harmonic oscillator but at low frequencies the response is modified by the fluctuations in the phonon density distribution away from local thermodynamic equilibrium. At high temperatures, $L_1$ is proportional to temperature, so that if the static dielectric constant follows the well known Curie Law

$$\tilde{\omega}_0^2 = \sum L_1 = A(T - T_c)$$

this gives

$$\tilde{\omega}_0^2 = A(T - T_c) + \sum L_1 = A_1(T - T_{\lambda})$$
where \( A T_c = A_1 T_A \) and \( A_1 = A + \Sigma_1 L_1/T \).

Since \( L_1 \) is positive, \( A_1 > A \) and \( T_A < T_c \). The response function then reduces to

\[
G_0(\omega) = \frac{2\omega_0}{\left\{A(T - T_0) - \omega^2 - 2i\omega B_0 T + B_1 T \left(\frac{\omega\tau}{\omega\tau + 1}\right)\right\}}
\]

which at high frequencies \( \omega\tau \gg 1 \) gives

\[
G_0(\omega) = \frac{2\omega_0}{\left\{A_1(T - T_A) - 2i\omega B_0 T\right\}}.
\]

This is the same result as for the nonpiezoelectric case except that \( \omega_0^2 \) is zero not at the transition temperature \( T_c \), but at some lower temperature \( T_A \), whereas the static properties diverge when \( T = T_c \). This difference between the results for \( \omega\tau \gg 1 \) and \( \omega\tau \ll 1 \) has recently been demonstrated by Raman scattering measurements on CsDA and KDA (Cowley et al. 1971, Blinc et al. 1971, private communication). The results of fitting the high frequency Raman results to a classically damped oscillator yielded the relaxation time \( \tau^* = \omega_0^2/2\gamma_0 \). The conventional theory, equation (2.3), suggests this diverges as \( T/(T - T_c) \) whereas the equation (2.8) suggests \( T/(T - T_A) \). Clearly the results shown in figure 2 support the latter contention.

More detailed calculations of the spectra are shown in figures 3 and 4. In figure 3 we show the temperature dependence of the spectra for \( \gamma_0 \gg \omega_0 \). The mode is overdamped but there is a marked change in behaviour when \( \omega \) becomes less than \( 1/\tau \). In figure 4 we show similar results when \( \gamma_0 \ll \omega_0 \). There are two peaks in the spectra; the upper peak decreases in frequency with decreasing temperature, and would have zero frequency at \( T_A \), but in addition there is a low frequency peak which diverges as \( T \to T_c \). Using the approximate form for the low frequency peak given by equation (3.11) of I, the effective Debye relaxation time diverges,

\[
\tau^* = \frac{T_c(T - T_A)}{T_A(T - T_c)} \tilde{\tau}_0
\]

Figure 2. The temperature dependence of the reciprocal lifetime, \( 1/\tau \), of the dielectric fluctuations in CsDA (Cowley et al 1971) as determined by high frequency Raman scattering. A classically damped oscillator gives \( T \tau \propto (T - T_c) \), and the results show the failure of this description for a piezoelectric material.
Figure 3. The dielectric susceptibility of a piezoelectric material with an overdamped soft mode. $T_A/T_c$ was chosen to be 0.4, $\tau = 1$ THz, and $\gamma = 80$ THz and full curves are shown for various $(T - T_c)/T_c$. The broken line shows the susceptibility in the absence of coupling to the phonon density fluctuations.

Figure 4. The dielectric susceptibility of a piezoelectric material with an underdamped soft mode. The parameters are the same as for figure 3 except $\gamma$ which is now 0.5. Note the two peaks: the lower frequency one arises from the coupling to phonon density fluctuations.

as $T \to T_c$ and its behaviour becomes similar to that expected of a Debye relaxation form near a phase transition, namely

$$\text{Im} \{G_0(\omega)\} = \frac{B_1 T}{A(T - T_c)} \frac{1}{A'(T - T_A)} \frac{\omega \tau^*}{1 + (\omega \tau^*)^2}.$$  

Unfortunately there are neither detailed measurements of the shape of the whole spectra for these materials with which to compare our results, nor is it possible to perform anharmonic calculations for CsDA and KDA. The order of magnitude of discrepancy between $T_A$ and $T_c$ is reasonable if we consider that the whole of the temperature dependence of $\tilde{\sigma}_3^0$ results from anharmonicity. There is a similar distinction between the collisionless and thermodynamic regimes in discussing elastic constants, and for alkali halides it is known that the difference in the anharmonic self energy between these two regimes is about one half of the total anharmonic self energy (Cowley 1967). If it is also about one half in CsDA, this gives $T_c \approx 2T_A$ as found experimentally.  

When the crystal has distorted to the ferroelectric phase there is the additional possi-
bility of the dielectric fluctuations coupling to the changes in the local thermodynamic equilibrium. The response is still given by equation (3.8) of I but with $L_1$ given by equation (3.14) of I. Since however the additional term, the second term of equation (3.14) of I, varies as $T_c - T$, whereas the first term $|V_{01-1}|^2$ is nonzero both above and below the phase transition, it is reasonable to neglect the former term. The response is then similar in form to that in the paraelectric phase as shown by the temperature dependence of the peaks in $(1/\omega) \text{Im} \{G_0(\omega)\}$ in figure 5. There is a quasi-elastic peak both above and below $T_c$ with a relaxation time which diverges as $T \rightarrow T_c$. The high frequency regime gives rise, in the underdamped case, to an additional peak which is only weakly dependent upon temperature.

There is considerable experimental evidence now available to support these suggestions. In ferroelectric crystals which make a transition to a nonpiezoelectric phase, modes have been observed which decrease to zero as $T \rightarrow T_c$ in essentially the manner given by the theory. Examples are PbTiO$_3$ (Burns and Scott 1970, Shirane et al 1970) SbSI (Steigmeier et al 1971), NaClO$_3$ (Prasad Rao et al 1972) and Pb$_5$Ge$_3$O$_{11}$ (Hisano and Ryan 1972). Except in the case of SbSI, however, the quasi-elastic scattering below $T_c$ has not been observed directly. In SbSI the scattering has a very much larger frequency spread than would be expected from the theory developed here and so we must await further developments before assigning its origin. It would be interesting to study the quasi-elastic scattering below and close to the ferroelectric phase transition in more of these materials.

In crystals undergoing a ferroelectric to piezoelectric phase transition, the results shown in figure 2 show that above $T_c$ our picture is essentially correct for CsDA and KDA. In KDP there is a very much smaller, if any, difference between $T_A$ and $T_c$ (Kaminow and Damen 1968). Possibly this results from an accidentally small effect or possibly because the weakly anharmonic crystal model is not applicable to this material. Further study of the quasi-elastic scattering in this class of material both above and below $T_c$ would be very useful in testing our conclusions.

3. Transitions

3.1. Elastic transitions

The theory developed in the preceding sections may also be applied to nonferroelectric phase transitions. In Nb$_3$Sn and V$_3$Si a structural phase transition results from an
instability of the crystal against an acoustic mode of vibration with $Q$ along (110) and
the polarization vector along (1, 1, 0) (Keller and Hanak 1967, Rehwald 1968). Although
the origin of the temperature dependence of this mode is not well understood, we can
study it by using the same formalism as for ferroelectric phase transitions except that
$\omega_n^2 \propto T - T_c$ instead of $\omega_n^2$. This transverse mode does not transform like the identity
representation under the symmetry operations of the crystal; as indeed it cannot if it is
to cause a change in structure. It does not couple to the fluctuations in the local thermo-
dynamic equilibrium, but as shown by table 1 in I, it will give rise to fluctuations in the
phonon density away from local thermodynamic equilibrium. The situation is then
identical with that described for piezoelectric to ferroelectric phase transitions, except
that all frequencies are proportional to $Q$. We expect therefore that as $\omega_n^2$ decreases a
quasi-elastic component to the scattering will occur, the intensity of which will diverge
as the transition temperature is approached. These suggestions are in excellent accord
with the recent experiments of Shirane and Axe (1971) on $\text{Nb}_3\text{Sn}$ who have observed
this quasi-elastic component above the transition temperature.

3.2. Transitions to a multiple unit cell

Phase transitions also occur with an instability of the crystal against a normal mode with
a zone boundary wavevector. These lead to an increase in the size of the unit cell. It is
again necessary to distinguish between two different cases. If the unstable zone
boundary mode is labelled $(Q_j)$, then the cubic anharmonic coefficients $V^{0 \ Q - Q}_{j1 \ j \ j}$
coupling this mode with the zone-centre optic mode in the high temperature phase
may be zero or nonzero. An example of the former case is the 105 K phase transition in
$\text{SrTiO}_3$ and of the latter, the improper ferroelectrics, such as $\text{Gd}_2(\text{MoO}_4)_3$ (Levanyuk
and Sannikov 1969, Pytte 1970). In this section we shall discuss the former case and in
the next section the latter. The requirement for a nonzero $V^{0 \ Q - Q}_{j1 \ j \ j}$ coefficient is
less stringent than that discussed for ferroelectric transitions because in this case the
mode $(0j_1)$ may be of any of the irreducible representations for the normal modes at
$q = 0$.

If all the $V^{0 \ Q - Q}_{j1 \ j \ j}$ coefficients are zero, there is no coupling between the soft
mode and a zone centre mode. The response of the crystal is then identical with that of
a classically damped harmonic oscillator for the soft mode and the frequency has the
expected Landau exponents (Pytte and Feder 1969, Feder and Pytte 1970). Below the
phase transition the crystal structure is distorted, the mode transforms like the identity
representation, and so couples to the fluctuations in the phonon density. The response
function for the mode is given by equation (3.8) of I with $L_1$ given by equation (3.14) of
I. However, since the interaction coefficients $V^{Q \ q_1 - q_{11}}_{j \ j_1 \ j_1}$ are proportional to
$V^{Q - Q \ q_1 \ q_{11}}_{j \ j_1 \ j_1} \langle A(Qj) \rangle$, the form of response becomes identical with that proposed
for pyroelectric crystals in equation (2.4). The scattering cross section for this situation
is then similar to that of the nonpiezoelectric to ferroelectric phase transition, figure 1.
Above the transition temperature there is a single type of peak in the scattering cross
section, but below there may be two types of peak, one centred about $\omega = 0$ and the other at nonzero $\omega$.

3.3. Improper ferroelectrics

In materials in which there is a temperature dependent mode $Q_j$ and a nonzero coefficient $V_{j_1j_1j_1j_1}$ above the transition temperature the predictions of the theory are different. These materials have been called improper ferroelectrics by Pytte (1970) and Dvorak (1971). The reason for this is that a distortion of the crystal in the mode $Q_j$ below $T_c$, immediately gives rise to a displacement of the mode $(0j_1)$ and hence to spontaneous polarization. There is not, however, the anomaly in the dielectric susceptibility which is expected for a normal ferroelectric phase transition. The phenomenological theory has been presented by Pytte (1970) and Dvorak (1971), and gives a good amount of the measurements on this type of material by, for example, Cross et al (1968) and Axe et al (1971).

In this section we apply our approach to these transitions. Since the coefficients $V_{j_1j_1j_1j_1}$ are nonzero we expect a coupling of the mode $(0j_1)$ to the density fluctuations in the mode $Q_j$. Since these latter become very large close to the phase transition we might expect that they give rise to a large low frequency contribution to the self energy of the mode $(0j_1)$. If, as is reasonable close to the phase transition, we assume the mode $Q_j$ to be overdamped, the contribution to the self energy of the $(0j_1)$ mode is

$$-\sum_{1} \frac{c}{\omega_1^4} \left( \frac{1}{1 - i\omega\tau_1} \right)$$

where the suffix 1 refers to the soft mode $Q_j$ and those modes in its immediate neighbourhood of reciprocal space, while $\tau_1 = 4\gamma_1/\omega_1^2$ and $c$ is a constant. If the soft mode is isotropic in reciprocal space, its dispersion relation is given by $\omega_1^2 = A(T - T_c) + \alpha|q_1 - Q|^2$, and the self energy of the mode $(0j_1)$ at $\omega = 0$ is proportional to $-(T - T_c)^{-1}$. If this mode contributes to the dielectric properties, the static dielectric constant is now of the form

$$K = \frac{1}{1 - \Delta(T - T_c)^{-1}}$$

with $\Delta$ a positive constant. This diverges at $T_c + \Delta$, and the phase transition occurs because of an instability of the crystal against the mode $(0j_1)$ rather than as an instability against the mode $Q_j$. This contribution to the self energy of the mode $(0j_1)$ is restricted to very low frequencies $\omega\tau_1 \ll 1$, and $\tau_1$ diverges at $T - T_c$. Possibly part of the low frequency anomaly observed in the dielectric properties of Gd$_2$(MoO$_4$)$_3$ is of this origin, in addition to the usual assumed piezoelectric coupling. The effects discussed here are large only very close to $T_c$, and may therefore be entirely lost because the phase transitions, although close to second order, are in practice of first order.

The properties of improper ferroelectrics are somewhat analogous therefore to piezoelectric ferroelectrics. The soft mode does not reach zero frequency but in addition there is a low frequency response at the zone centre which diverges as the transition temperature is approached.

Below the phase transition the material is piezoelectric and so a low frequency
response is expected. This response will occur both through the \((0j_j)\) and the \((Qj_j)\) parts of the one-phonon response. In the former case it behaves analogously to the low frequency response in piezoelectric/ferroelectric crystals, and in the latter case analogously to the nonpiezoelectric/ferroelectric crystal. Although we have discussed these transitions as improper ferroelectric ones, the same behaviour occurs for any symmetry of the mode \((0j_j)\).

4. Critical phenomena

4.1. A selfconsistent self energy

The results in §2 and §3 were obtained by neglecting the temperature dependence of all the modes other than the one directly responsible for the phase transition. This is equivalent to the Landau theory of phase transitions, and inevitably leads, for ferroelectric transitions, to the static dielectric constant above \(T_c\) varying as \((T - T_c)^{-1}\), and the order parameter below \(T_c\) varying as \((T - T)_{\frac{1}{2}}\). In practice we must examine this approximation carefully especially in view of the discovery of critical effects at the 105 K structural phase transition in SrTiO\(_3\) by Müller and Berlinger (1971) and by Riste et al (1971). Müller and Berlinger have shown that below this phase transition the order parameter varies as \((T - T)_{0.33}\) while Riste et al have shown that the scattering cross section above \(T_c\) has a quasi-elastic component in addition to the inelastic peaks. Since in this phase transition \(Q\) is at the R zone boundary point and the third order anharmonic coefficients \(V_0^{0j_j} Q - Q\) are zero, a quasi-elastic component is not predicted by a Landau theory.

The theory developed above is invalid in the critical region because it is necessary to take explicit account of the temperature dependence of the modes in the neighbourhood of the unstable mode in reciprocal space. In the description of transitions from a nonpiezoelectric phase to a pyroelectric phase, §2.1, the low frequency response in the pyroelectric phase arose from a third order interaction produced from a fourth order anharmonic interaction \(V_{001-1}\) multiplied by the order parameter \(\langle A(0)\rangle\). Close to the phase transition the mode 0 not only has this static displacement but also is

![Figure 6](image)

Figure 6. The self energy diagram of importance in critical phenomena showing (a) the leading term, and (b) a higher order term with interactions between the pairs of similar phonons 2 and \(-2\). (c) a diagram representing the thermodynamic fluctuations as a broken line.
executing slow and large fluctuations. We therefore propose that it is important in this region to include the effects of these interactions not only through the static distortion but also through the fluctuations. Diagrammatically this is represented by the self energy diagrams of figure 6. Silberglitt (1972) has also come to the conclusion that these are the important diagrams to include in the critical region although he does not explicitly include the multiple scattering between the pair of phonons 1 and \(-1\).

The calculation of this term in the self energy is made easier if the spectral functions for the one-phonon and for the approximate two-phonon Green functions with the vertex renormalization are introduced. In general the spectral function \(\rho(x)\) is given by the relation

\[
\rho(x) = - \frac{1}{\pi} \text{Im} \{G(x)\}.
\]

(4.1)

In the case of the one-phonon Green function the spectral function is now obtained in terms of the total self energy through the equation (2.2) of I.

In the same way as was described in I for the self energy, these new terms factorize into two parts: one part results from the fluctuations in the local thermodynamic equilibrium and the other from the fluctuations away from that equilibrium. Treating the latter part first and neglecting all the irrelevant two-phonon terms for which the branch indices are unequal, the self energy of a mode 0 may be written as

\[
\Pi_0^{A}(\omega) = - \frac{576\omega_0}{h^2} \sum_{13} \left| V_{012} \right|^2 \int \int \frac{n(x) + n(y) + 1}{x + y - \omega} \rho_1(x) \rho_2(Q, y) \, dx \, dy \tag{4.2}
\]

where if mode 0 is the mode for which the self energy is required, mode 1 is a similar mode with a wavevector differing by a small wavevector, \(Q\), from that of mode 0 and \(\rho_1(x)\) is its spectral function, while

\[
\rho_2(Q, \omega) = - \frac{1}{\pi} \text{Im} \left\{ K_2^0 \left( 1 - \frac{\omega}{\omega - Q \cdot v_2 + iv_2} \right) \right\}.
\]

The second term results from the coupling to the thermodynamic fluctuations and is given by

\[
\Pi_0^{B}(\omega) = \frac{1152\omega_0}{h^2} \sum_{13} \int \int \frac{n(x) + n(y) + 1}{x + y - \omega} \rho_1(x) \rho_1(Q, y) \, dx \, dy \tag{4.3}
\]

where \(\rho_1(Q, y)\) is the thermodynamic spectral function for this particular problem namely

\[
\rho_1(Q, \omega) = - \frac{1}{\pi} \text{Im} \left\{ \beta \hbar \omega W_4(0, 0) W_4(Q, \omega) D \right\} \tag{4.4}
\]

where

\[
W_4(Q, \omega) = \sum_{2} V_{012} n_2(n_2 + 1) \mu_0 \beta \hbar \omega_2 \left( 1 - \frac{\omega - Q \cdot v_2}{\omega - Q \cdot v_2 + iv_2} \right)
\]

and \(D\) is also dependent on \(Q\) and \(\omega\) as given by equation 2.15 of I. These equations must be solved selfconsistently in two ways. Initially because \(\rho_1(x)\) can be obtained only from its self energy which is given by a similar equation to equation (4.2). This is certainly important. Secondly the summations over the two-phonon indices, 2, also include the temperature dependent modes and so should also be made selfconsistent. This latter selfconsistency is probably less important because the temperature dependent modes form only a small part of the total summation over 2. Although a solution to equations 4.2, 4.3 and 4.5 is very difficult, it is possible to understand qualitatively how a quasi-elastic peak might result. From our previous analysis, the two-phonon spectral function,
\( \rho_2(\mathcal{Q}, y) \), and the thermodynamic spectral function, \( \rho_1(\mathcal{Q}, y) \), are known to be peaked at small values of \( y \). It follows that if the one-phonon spectral function \( \rho_1(x) \) is also peaked near \( x = 0 \) then a peak will be generated in the imaginary part of \( \Pi_0^{3B} \) and \( \Pi_0^{3A} \) for small \( \omega \). This peak in the self energy will give rise, equation (4.1), to a peak in \( \rho_1(x) \) and hence the solution is selfconsistently correct. The criterion for selfconsistency is dependent upon the peak in the self energy being large enough to generate the assumed peak in \( \rho_1(x) \). The probability of this is enhanced if the peak occurs over a large range in wavevector \( \mathcal{Q} \), and if the anharmonic interactions are large. But it is always easier to satisfy the selfconsistency criterion if \( \omega_0^2 \), the frequency of the mode, becomes small. It is therefore most likely to occur close to a phase transition. Silberglitt (1972) comes to similar conclusions and shows, by making a number of approximations, that the numerical values for SrTiO\(_3\) are of the correct order of magnitude. In detail his theory does not take account of the thermodynamic effects, \( \pi_0^{3B}(\omega) \), although near to the phase transition these are likely to be very important because they give rise to a more pronounced peak in the spectral density at low frequency than is obtained from the nonthermodynamic processes. The importance of including the thermodynamic effects has also been stressed by Feder (1971). He emphasizes that the mode of propagation at low frequencies is different from that at high frequencies and suggests that this is responsible for the occurrence of a quasi-elastic peak in the scattering cross section close to a phase transition. He and Schneider (1972) use the terms adiabatic and isothermal where we would prefer to use collisionless and thermodynamic. Adiabatic and isothermal are, we think, better reserved for their well known thermodynamic connotations.

We have seen how the anharmonic theory may give rise to critical phenomena in the case of the zone boundary instability of SrTiO\(_3\). The application of the theory to ferroelectrics is much more complex because the theory requires a detailed knowledge of the spectral densities \( \rho_1(x) \) for all wavevectors, \( \mathcal{Q} \), in the neighbourhood of the soft mode. The response in this region was discussed in detail in §5 of I where we showed that the dielectric fluctuations interacted directly with the acoustic modes and the thermodynamic processes. The detailed calculation of diagrams such as those shown in figure 6 for ferroelectric transitions must include both this direct coupling as well as the selfconsistent coupling of importance in SrTiO\(_3\).

A further complexity arises from the effect of the macroscopic electric field on the dielectric fluctuations. Born and Huang (1954) show that the macroscopic electric field produces a singularity in the optic mode frequencies as \( \mathcal{Q} \to 0 \). Even if the frequency for the transverse modes becomes very small close to \( T_c \), the longitudinal modes will not have a small frequency. This drastically reduces the number of wavevectors, \( \mathcal{Q} \), in equations (4.2) and (4.3) for which \( \rho_1(x) \) has a large low frequency peak. It is therefore much harder for ferroelectric phase transitions to satisfy the selfconsistency criterion, and critical effects are expected to occur much closer to the phase transition temperature than in the nonferroelectric structural phase transitions. This appears to be in accord with recent experiments on TGS for which the critical region is found to occur only for \( |(T - T_c)/T_c| < 2 \times 10^{-5} \) (Deguchi and Nakamura 1972), whereas for the nonferroelectric transitions in SrTiO\(_3\) the critical region is \( |(T - T_c)/T_c| < 0.1 \) (Müller and Berlinger 1972).

4.2. Mode–mode coupling theory

Recently there has been considerable progress made in the study of the dynamical properties of systems in the neighbourhood of second order phase transitions. Several
different approaches have been adopted, for example by Kawasaki (1970), and the purpose of this section is to describe the similarity between their approaches and the developments described above. In their theories some particular modes are assumed to dominate the response near the phase transition, and these modes interact strongly with one another.

In the preceding section we discussed the self energy of a low frequency mode and suggested that the result was dominated by the interaction of the mode with the fluctuations in the phonon density. In the spirit of the mode–mode coupling approach we identified two modes; one was associated with the order parameter and the other with the phonon density fluctuations, and these were assumed to interact with one another to give the self energy diagram of figure 6.

The phonon density fluctuations are given by expressions which depend on a summation over all the phonons in the crystal, as described in §2 of I. Close to the phase transition the temperature dependence of these fluctuations will be dominated by those terms which depend on the low frequency phonons. The self energy diagram is shown in figure 7. These two sets of equations for the phonon self energies and the thermodynamic fluctuations must be solved selfconsistently. Both of these self energy diagrams are of the same form as those obtained by the mode–mode coupling approximation (see equations (4.26) and (4.27) of Kawasaki 1970). The main difference in the approach is in the coefficients of the expressions. In our case these are given by lower order anharmonic coefficients whereas in the mode–mode coupling theory they are obtained in terms of the static response functions of the system. This difference is very significant because the mode–mode coupling theories take the temperature dependence of these static functions from scaling theory, whereas the temperature dependence of our expressions is of necessity given by the appropriate Landau type of power law.

Schwabl (1972) has used the ideas of mode–mode coupling theory to discuss structural phase transitions with particular reference to SrTiO$_3$ at 105 K. He writes down equations for the phonon mode coupled to the total orthonormalized two-mode energy–rotation operator. We believe this to be the operator describing the phonon and thermodynamic fluctuations represented by the central part of figure 6c. The equations of motion lead to a response function which has the denominator

\[
\left( \bar{\omega}_0^2 - \omega^2 + i\omega \sigma - \frac{\omega b}{\omega + i\gamma} \right)
\]

where $b$, $\sigma$, and $\gamma$ are all constants and $\bar{\omega}_0^2$ is temperature dependent. Close to the phase transition this result is identical with that of equation (3.10) of I which we derived for the dielectric response of piezoelectric crystals. In his application, however, he assumes in the spirit of the mode–mode coupling that $\bar{\omega}_0^2$ varies as $(T - T_c)^{4/3}$, in contrast to our Landau assumption of $(T - T_c)$ in §2.2. He then finds that the theory gives good agreement with recent electron paramagnetic resonance experiments of von Waldrich et al (1972). Recently Schneider (1972) has criticized the form of equation (4.5) because it fails to satisfy the second and fourth moments of the self energy function. He suggests that $\sigma = 0$ and derives $b$ and $\gamma$ from these moments. This we feel is very unsatisfactory except very close to $T_c$. The moments are dominated by the high frequency part of the self energy function; the terms with $j_1$ and $j_2$ unequal in equation (2.4) of I, for the two-
phonon Green functions. These terms are irrelevant so far as the low frequency response is concerned. It is therefore very unsatisfactory to determine the form of the self energy at low frequency by a moment method except at $T_c$ where the low frequency part of the self energy is completely dominant.

The results of this section show that the mode–mode coupling theory of structural phase transitions deserves further study. The anharmonic theory is capable of providing a set of equations which must be solved selfconsistently, and which are very similar to those which have been used with success in other problems. It remains to try to compare these equations in detail with the equations of mode–mode coupling theory and also to solve them explicitly to test their predictions with experimental results.

5. Conclusions

The properties of structural transitions have been discussed using a Landau model in which only one particular normal mode is assumed to be temperature dependent. The model leads to the usual soft-mode picture above $T_c$ for materials which are not piezoelectric. In piezoelectric materials, however, the theory shows that the usual soft-mode picture may not be adequate. There may be a large response at low frequencies which becomes both more intense and narrower in frequency as the phase transition is approached. Below $T_c$ quasi-elastic scattering is expected to occur at all structural phase transitions. The occurrence of additional low frequency response does not, in piezoelectric and pyroelectric phases, show a failure of the Landau model. Below $T_c$ for ferroelectric and above $T_c$ in piezoelectric crystals low frequency response is expected even within a Landau model. Critical effects in the sense of deviations from a Landau model may give rise to additional quasi-elastic scattering at all phase transitions as suggested in §4.1. This effect arises only when the soft mode is treated selfconsistently and not within the Landau model.

Although many of the suggestions given by this approach have been confirmed by experimental results there is still a great need for more detailed information on the properties at low frequencies, $10^{10} < \omega < 10^{12}$ Hz, especially in the neighbourhood of phase transitions. It is to be hoped and expected that improved Raman and neutron scattering techniques will in the next few years be able to probe this important frequency region more successfully.

On the theoretical side there is considerable work to be attempted. The most obvious deficiency is the failure to provide a direct connection between the weakly anharmonic theory and the mode–mode coupling theory near the phase transitions. This paper has also not attempted to evaluate any numerical estimates to better than an order of magnitude. It is unfortunately very difficult to evaluate in detail many of the expressions obtained. In a large part this is because many of them contain the lifetime of all the phonons in the Brillouin zone. Furthermore, most ferroelectric materials have very much more complicated crystal structures than those for which detailed anharmonic calculations can be attempted. There is also the question of the validity of describing these complex systems, such as CsDA, by a weakly anharmonic model. Despite, however, all these complications in applying our results quantitatively, we are confident of their qualitative character. Many of the different features are dependent not so much on the details of our model but on the symmetry properties. They should therefore equally apply to more complex models. We look forward to additional experimental and theoretical work to elucidate in more detail the low frequency properties of crystals.
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