

STUDIES OF A DILUTE HEISENBERG ANTIFERROMAGNET
AND THE FERROELECTRIC TRANSITION IN CsH_2AsO_4

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Sentence first - verdict afterwards

Lewis Carroll

Alice in Wonderland.

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I declare that this thesis is my own work and that where experiments were performed in collaboration with co-workers a significant contribution was made by the author.

Gerald M Meyer.

ABSTRACT

An alternative method of analysing coupled oscillator fits of Raman spectra is presented. It is compared with conventional methods of obtaining the temperature dependence of the ferroelectric mode in KDP type ferroelectrics.

As continuous structural phase transitions are approached, an increase in both the Debye-Waller factor and the nuclear quadrupole coupling coefficient is predicted. The predicted form for uniaxial ferroelectrics is shown to differ from that at other transitions because of its macroscopic electric field. It is shown to be consistent with the temperature dependence of the quadrupole resonance in CsDA. The form at other transitions allows the critical exponent, γ , to be obtained.

Previously reported structure in DCsDA is shown to result from multiple Bragg scattering in which two ferroelectric domains are involved. Variations in the hydrogen-deuterium concentration are believed to cause the 60K smearing of the transition. Measurements of the Σ_2 acoustic mode are consistent with the elastic constant C_{66} being small. Measurements of the temperature dependence of the shear angle show that the transition in CsDA is first order.

The neutron scattering from the magnetic excitations in the substitutionally disordered antiferromagnet $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$ have been measured at 6K. The results show structure in the line shape which is similar to that predicted by some of the calculations based on the coherent potential approximation and to that predicted in recent computer simulations.

Some of the critical exponents pertaining to the antiferromagnetic transition in the dilute disordered system, $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$, have been obtained by measuring the wavevector and temperature dependence of the neutron scattering. These are compared with the exponents found in the pure system, MnF_2 , and also with some of the recent predictions of the renormalisation group.

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CHAPTER 1

NEUTRON SCATTERING

1. 1 INTRODUCTION.

The theory for the scattering of slow neutrons was developed by Weinstock¹ and by Halpern and Johnson² many years before experiments were possible. Van Hove showed that in the first Born approximation, the nuclear scattering cross section³ and magnetic scattering cross section⁴ could always be expressed in terms of a suitably generalised pair distribution function, depending on a space vector $\underline{r}$ and a time interval t .

With the design of a spectrometer using a single crystal monochromator by Zinn⁵, it became possible to perform structural studies on crystals. However, it was not until the advent of the triple axis spectrometer, designed by Brockhouse during the - late Fifties⁶, that it was possible to perform experiments in which the energy transfer of an inelastic process could be reliably measured. (Brockhouse and Stewart⁷ had measured energy transfers as early as 1955 using a less sophisticated instrument). Over the same period there was the development of instruments which used a measurement of the time of flight⁸ of neutrons to obtain the energy transfer.

Another powerful method in the hands of Solid State Physicists is X-ray scattering or diffraction. Experiments using X-rays have been performed since the early part of this century when Bragg⁹ first determined a crystal structure. X-ray Bragg scattering is generally the method used to find the structure of crystals. The technique has the advantage that only small crystals are needed ($\sim 0.2\text{mm}$). It may be impossible to obtain larger samples for neutron work. A structural determination can be made in a relatively short time using either photographic or counter methods. The main disadvantage for structural work is that the scattering of X-rays depends on the square of the electron distribution within the atom, so it becomes difficult to refine the positions of the lighter elements.

Although X-rays can scatter inelastically, there can be no energy resolution of this scattering. However, 'thermal diffuse scattering' can be used to look at low energy branches such as 'soft modes'. The temperature dependence of the scattering can be measured close to the transition temperature and an estimate of the background can be obtained at high temperatures.

In contrast to X-rays, the scattering of neutrons is mainly of nuclear origin - except in magnetic materials, where there is also a strong interaction with unpaired electrons. The scattering length for neutrons increases throughout the periodic table, but with resonances some light elements have quite large scattering lengths. Neutron diffraction then becomes complimentary to X-ray diffraction and it is used to position the lighter elements in the unit cell. It is of course much more expensive to use neutron scattering from single crystals, rather than X-ray scattering. The rate of data collection can be improved by scattering the neutrons from a powder sample. This technique cannot be employed with X-rays since the line shape is not readily parameterised, as is the case for neutrons.

A program developed by Rietveld¹⁰ is used to analyse the line shape of the powder profile and from this it can produce a structural refinement

A more recent program by Pawley et al.¹¹ proves to be more convenient when a large degree of constraint, such as in molecular crystals, is required.

Co-incidental with the development of techniques for inelastic neutron scattering was the development of an optical M.A.S.E.R.¹², or what is now called a laser, which became a useful tool for inelastic light scattering experiments. During the last 10 to 15 years there has been a great improvement in the resolution of spectrometers used in neutron scattering

and light scattering experiments, and in the same period there has been an improvement in the neutron and photon fluxes. The operation of instruments in both fields has become largely automated, so that scans can be fed in via a computer, which also processes the results to a form where they are ready for analysis.

Light scattering is extensively used to study the optic phonon branches. In general the resolution of the spectrometer is such that measurements of the natural widths of phonons or magnons can be made. The photon count rate is extremely high so that to all intents and purposes statistical fluctuations need not be considered, and the complete spectrum can be measured in a matter of days. The drawback of the method is that certain branches are not optically active, and so go undetected in a Raman scattering experiment. Furthermore one is restricted to making measurements close to the zone centre for which $q \sim 0$ (only in comparison to the size of the Brillouin zone).

With neutrons, it is possible to measure the frequencies of phonons and magnons throughout many zones enabling, in principle, the measurement of all the excitations. In practice, there may be some difficulty with some materials, either because of the number of branches or because of a high incoherent scattering or absorption cross section. One is also limited to materials which can be grown as single crystals to a volume $\sim 1\text{cm}^3$ - although if all the conditions are favourable, a smaller crystal might suffice.

There are a number of texts in which the equations for the scattering of thermal neutrons are derived (eg. Marshall and Lovesey¹³, Egelstaff¹⁴). In the next few sections we shall briefly show the origin of the nuclear and magnetic scattering cross sections, before going on to a discussion of experimental neutron scattering using a triple axis spectrometer. We will indicate the types of problem likely to arise in experiments.

1.2 THEORY OF NEUTRON SCATTERING.

A plane wave with wavevector $\underline{k}_1$ strikes a target and is scattered to a plane wave with wavevector $\underline{k}_2$. If both the initial and final states are eigenstates of a Hamiltonian, H , and the scattering is caused by a perturbation $\hat{V}$, then the transition probability per unit time between the initial state $|i\rangle$ and the final state $|f\rangle$ is given by Fermi's Golden Rule.

$$W_{\underline{k}_1 \rightarrow \underline{k}_2} = \frac{2\pi}{\hbar} |\langle f | \hat{V} | i \rangle|^2 \rho(E_f) \delta(E_i - E_f) \quad (1)$$

In a neutron scattering experiment we measure the scattered intensity in a solid angle $d\Omega$ and for a range of energies from $E_2 \rightarrow E_2 + dE$ as a fraction of the incident flux. When the wavefunctions are normalised within a box of side L , the incident flux is $\hbar k_1 / m_n L^3$, and the density of final states is

$$\rho(E_f) = \left(\frac{L}{2\pi\hbar} \right)^3 m_n \hbar k_2 d\Omega \quad (2)$$

A partial differential cross section for a scattering process in which the incident neutron state $|\underline{k}_1\rangle$ changes to $|\underline{k}_2\rangle$ and the state of the target changes from $|m\rangle$ to $|n\rangle$ can then be written as

$$\left(\frac{d^2\sigma}{d\Omega dE} \right)_{\substack{\underline{k}_2, n \\ \underline{k}_1, m}} = \frac{k_2}{k_1} \left(\frac{m_N}{2\pi\hbar^2} \right)^2 |\langle \underline{k}_2, n | \hat{V} | \underline{k}_1, m \rangle|^2 \times \delta \left(\frac{\hbar^2 k_2^2}{2m_N} + E_n - \frac{\hbar^2 k_1^2}{2m_N} - E_m \right) \quad (3)$$

where we have removed the dependence on L by an appropriate renormalisation of the wavefunction which are now of the form

$$\psi_i = \exp(i \underline{k}_1 \cdot \underline{r}) \psi_m \sigma_1 \quad (4)$$

The first term represents the neutron plane wave, the second term specifies the initial state of the target through a complete set of quantum numbers denoted by m . We might also need to take account of the spin states of the neutron through σ_1 . A similar equation exists for ψ_f , the wave-

function of the final state of the system.

To obtain the total partial differential cross section for all possible scattering processes, equation 3 is summed over all final states of the target n and an average is taken over all the initial states, which occur with probabilities given by

$$P_m = \frac{1}{Z} \exp \left(\frac{-E_m}{k_B T} \right) \quad (5)$$

Including a summation over neutron polarisation states, we get for the total partial differential cross section in the first Born approximation.

$$\begin{aligned} \frac{d^2 \sigma}{d\Omega dE} &= \frac{k_2}{k_1} \left(\frac{m_N}{2\pi\hbar^2} \right)^2 \sum_{m\sigma_1} P_m P_{\sigma_1} \times \\ &\times \sum_{n\sigma_2} \left| \langle \underline{k}_2 \sigma_2^n | \hat{V} | \underline{k}_1 \sigma_1^m \rangle \right|^2 \delta(\hbar\omega + E_m - E_n) \end{aligned} \quad (6)$$

where we have used

$$\hbar\omega = \frac{\hbar^2 k_1^2}{2m_N} - \frac{\hbar^2 k_2^2}{2m_N} \quad (7)$$

for the energy transfer.

The change in states is brought about by the interaction potential $\hat{V}$ between the neutron and the scatterer. There are two basic interactions between the neutron and the scatterer. The first is nuclear in origin and is an interaction between the neutron and the nuclei in the sample. The second is an interaction of the neutron with the magnetic field produced by the electrons in the sample. We discuss these interactions in the next two sections.

1. 3 NUCLEAR SCATTERING.

Although the interaction between a neutron and a nucleus is very strong and the states become distorted in the nucleus, the scattering is still isotropic in the case where the neutron wavelength is large in comparison to the region of interaction. Fermi has shown that we can replace the strong nuclear interactions by a pseudopotential

$$\hat{V}(\underline{r}) = \sum_1 \frac{2\pi\hbar^2}{m_N} b_1 \delta(\underline{r} - \underline{r}(1)) \quad (8)$$

which is a delta function at the sites of the nuclei, giving the correct form of s-wave scattering. In a monatomic crystal $\underline{r}(1)$ is the position of the single atom in the 1th primitive unit cell. b_1 is dependent upon the isotope and spin of the nucleus.

Writing the initial and final states of the neutron as wavefunctions we get

$$\begin{aligned} \langle \underline{k}_2 | \hat{V} | \underline{k}_1 \rangle &= \frac{2\pi\hbar^2}{m_N} \sum_1 b_1 \int \exp(-i\underline{k}_2 \cdot \underline{r}) \delta(\underline{r} - \underline{r}(1)) \exp(i\underline{k}_1 \cdot \underline{r}) d\underline{r} \\ &= \frac{2\pi\hbar^2}{m_N} \sum_1 b_1 \exp(i\underline{Q} \cdot \underline{r}(1)) \end{aligned} \quad (9)$$

where we have used

$$\underline{Q} = \underline{k}_1 - \underline{k}_2 \quad (10)$$

for the wavevector transfer. There is a variation in b_1 through the distribution of isotopes and nuclear spins. If we are using unpolarised neutrons, it proves useful to average out this variation in b_1 , at the same time removing the dependence on the spin state of the neutron. The scattering can then be divided into two parts.

$$\sum_{ll'} b_l b_{l'} = \left(\sum_l b_l \right)^2 + \left(\sum_{ll'} b_l b_{l'} - \left(\sum_l b_l \right)^2 \right) \quad (11)$$

We can define a coherent scattering length which arises from the interference of waves scattered from different atoms

$$b^{\text{coh}} = \frac{1}{N} \sum_l b_l \quad (12)$$

and an incoherent scattering term which arises from the scattering from single atoms, averaged over all the sites

$$b^{\text{inc}} = \left(\frac{1}{N} \sum_l (b_l^2 - (b^{\text{coh}})^2) \right)^{\frac{1}{2}} \quad (13)$$

This allows us to split up the differential cross section into two terms

$$\begin{aligned} \left(\frac{d^2 \sigma}{d\Omega dE} \right)^{\text{tot}} &= \left(\frac{d^2 \sigma}{d\Omega dE} \right)^{\text{coh}} + \left(\frac{d^2 \sigma}{d\Omega dE} \right)^{\text{inc}} \\ &= \frac{k_2}{k_1} (b^{\text{coh}})^2 S^{\text{coh}}(Q, \omega) \\ &\quad + \frac{k_2}{k_1} (b^{\text{inc}})^2 S^{\text{inc}}(Q, \omega) \end{aligned} \quad (14)$$

and for a monatomic system the scattering functions are of the form

$$S^{\text{coh}}(Q, \omega) = \sum_{nm} p_m \left| \langle n | \sum_l \exp(iQ \cdot \underline{r}(l)) | m \rangle \right|^2 (E_m - E_n + \hbar\omega) \quad (15)$$

and

$$S^{\text{inc}}(Q, \omega) = \sum_{nm} p_m \left| \langle n | \exp(iQ \cdot \underline{r}(l)) | m \rangle \right|^2 (E_m - E_n + \hbar\omega) \quad (16)$$

These equations can be readily generalised to multi-atom systems.

$S^{\text{inc}}(\underline{Q}, \omega)$ can be split up into elastic and inelastic parts. Incoherent one - phonon scattering has no explicit momentum conservation, so in principle one should be able to obtain the phonon density of states. In practice the experimental corrections, even in strong incoherent scatterers, are considerable and the results are of doubtful merit. Apart from this, there is no other use for incoherent scattering. It proves to be a nuisance in most experiments. We will take the theory of incoherent neutron scattering no further.

$S^{\text{coh}}(\underline{Q}, \omega)$ is usually known as the van Hove correlation function. It is of interest to note that instead of depending on the 6 variables required to specify $\underline{k}_1$ and $\underline{k}_2$ it only depends on 4 variables - the three components of the wavevector transfer $\underline{Q} = \underline{k}_1 - \underline{k}_2$ and the single component of the energy transfer, $\hbar\omega$.

A derivation of $S(\underline{Q}, \omega)$ (dropping the superscript coh from now on) does not depend on the scattering of a particular 'particle' (ie neutron). It can be shown that the scattering of X-rays is adequately described by

$$\left(\frac{d^2\sigma}{d\Omega dE}\right)^{\text{X-ray}} = \left(\frac{\omega_2}{\omega_1}\right)^3 \left(\frac{e^2}{mc^2}\right)^2 \frac{1}{2} (1 + \cos 2\theta) |F(\underline{Q})|^2 S(\underline{Q}, \omega) \quad (17)$$

ω_1 and ω_2 are the frequencies of the X-rays before and after scattering and to a good approximation $\omega_1 = \omega_2$. $F(\underline{Q})$ is the form factor for the scattering of X-rays and is the Fourier transform of the electron density function of the ion. The cross section is usually measured in terms of $(e^2/mc^2)^2$.

Raman scattering may also be written in terms of $S(\underline{Q}, \omega)$, but this requires making approximations which are not found to be valid for the general scattering of light.

Van Hove ³ has shown that the scattering function is essentially the Fourier transform over $\underline{r}$ and t of the pair distribution function.

$$G(\underline{r}, t) = \int \langle \rho(\underline{r}^1, t^1) \rho(\underline{r} + \underline{r}^1, t + t^1) \rangle d^3 \underline{r}^1 \quad (18)$$

$G(\underline{r}, t)$ expresses the probability that if an atom is at the site $\underline{r}^1$ at time t^1 , there will also be an atom a distance $\underline{r}$ away at a time t later.

We have made no mention of the form of the excitations in the crystal.

If the excitation is a phonon, the atoms in the crystal at the rigid lattice sites $\underline{R}(l)$ will be displaced by an amount $\underline{u}(l)$ in some periodic manner throughout the crystal. Replacing $\underline{r}(l)$ in the scattering formula, equation 15, by $\underline{r}(l) = \underline{R}(l) + \underline{u}(l)$ (19)

allows us to make what is known as the phonon expansion.

$$\sum_l e^{\pm i \underline{Q} \cdot \underline{r}(l)} = \sum_l e^{\pm i \underline{Q} \cdot \underline{R}(l)} \left[1 \pm i \underline{Q} \cdot \underline{u}(l) - \frac{(\underline{Q} \cdot \underline{u}(l))^2}{2!} + \dots + \frac{(\pm i)^s}{s!} (\underline{Q} \cdot \underline{u}(l))^s + \dots \right] \quad (20)$$

In the harmonic approximation the crystal displacements $\underline{u}(l)$ can be expressed in terms of the phonon frequencies ¹⁵ through

$$\underline{u}(l) = \sum_{\underline{qj}} \left(\frac{\hbar}{2MN\omega(\underline{qj})} \right)^{\frac{1}{2}} \underline{e}(\underline{qj}) \exp(i \underline{q} \cdot \underline{R}(l)) (a(\underline{qj}) + a^*(-\underline{qj})) \quad (21)$$

where M is the mass of the atom, there are N unit cells, $\underline{e}(\underline{qj})$ are the eigenvectors of the mode and a and a^* are destruction and creation operators. We can then separate out the terms in equation 16 into those for which $a(\underline{qj})$ and $a^*(-\underline{qj})$ couple to give a changed state and those that don't. The former gives rise to single and multi-phonon scattering and the latter reduces to the well known Debye-Waller factor.

Using Blech's identity¹⁶ the Debye-Waller factor becomes

$$\begin{aligned} \exp(-\frac{1}{2}W) &= \exp(-i\mathbf{Q} \cdot \mathbf{u}(1)) = \exp(-\frac{1}{2} \langle (\mathbf{Q} \cdot \mathbf{u}(1))^2 \rangle) \\ &= \exp(-\frac{1}{2} \sum_{\mathbf{qj}} \frac{\hbar}{2M\omega(\mathbf{qj})} |\mathbf{Q} \cdot \mathbf{e}(\mathbf{qj})|^2 (2n(\mathbf{qj}) + 1)) \end{aligned} \quad (22)$$

where $n(\mathbf{qj}) = [1 - \exp(-\frac{\hbar\omega(\mathbf{qj})}{kT})]^{-1}$ is the Bose-Einstein population factor.

Using the expansion (equation 20), we can now obtain the zero phonon or Bragg scattering term - generalised to the multi-atom case and including the scattering length it is

$$S^0(\mathbf{Q}, \omega) = N |\mathbf{F}(\mathbf{Q})|^2 \delta(\hbar\omega) \delta(\mathbf{Q} - \underline{\gamma}) \quad (23)$$

where the elastic structure factor is given by

$$\mathbf{F}(\mathbf{Q}) = \sum_{\mathbf{K}} b_{\mathbf{K}}^{\text{coh}} \exp(-\frac{1}{2}W_{\mathbf{K}}) \exp(i\mathbf{Q} \cdot \mathbf{R}(\mathbf{K})) \quad (24)$$

The summation is over all atoms in a unit cell, with positions given by $\mathbf{R}(\mathbf{K})$. Bragg scattering is obtained at reciprocal lattice vectors, $\underline{\gamma}$, and when the energy transfer is zero. The intensity will vary from reflection to reflection as determined by the structure factor. Some reflections may be absent because the structure factor is zero through symmetry considerations.

Other terms in the expansion of equation 20, lead to single-phonon and multi-phonon scattering. Single phonon scattering is given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_2}{k_1} S^1(\mathbf{Q}, \omega) = \frac{k_2}{k_1} N^2 \sum_{\mathbf{qj}} |\mathbf{F}(\mathbf{qj}, \mathbf{Q})|^2 \delta(\mathbf{Q} - \mathbf{q} - \underline{\gamma}) \times$$

$$\times \begin{bmatrix} (n(\omega) + 1) \delta(\hbar\omega - \hbar\omega(qj)) \\ n(|\omega|) \delta(\hbar\omega + \hbar\omega(qj)) \end{bmatrix} \quad (25)$$

where the two terms respectively give creation and annihilation of a phonon. The inelastic structure factor is given by

$$F(qj, q) = \sum_K^{coh} b_K \exp(i \underline{q} \cdot \underline{R}_K) \exp(-i \underline{q} \cdot \underline{R}_K) \times \\ \times \left(\frac{\hbar}{2M_K N \omega(qj)} \right)^{\frac{1}{2}} \underline{q} \cdot \underline{e}(K, qj) \quad (26)$$

It can be seen that by an appropriate choice of the wavevector transfer $\underline{q}$ we are able to differentiate between longitudinal and transverse branches. In Figure 1a we show the scattering configuration for obtaining a longitudinal phonon ($\underline{q} \parallel \underline{e}(qj, K)$) and in Figure 1b we show the configuration for obtaining a transverse phonon ($\underline{q} \perp \underline{e}(qj, K)$).

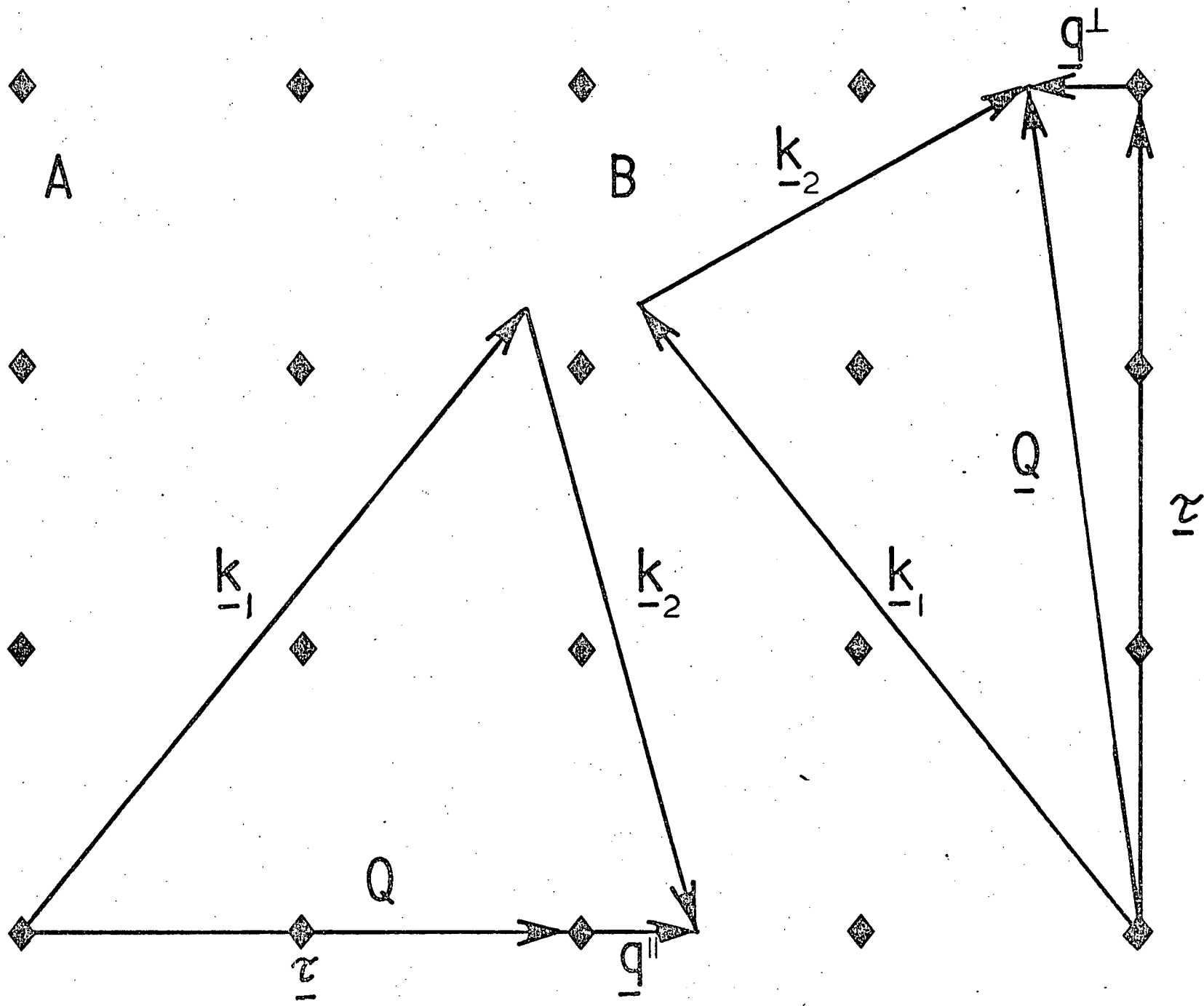
If the crystal is treated more realistically by including anharmonic effects, there will be an interchange of energy between the modes since they are no longer normal. This will result in an alteration to the frequencies of the modes and they will now possess width. If the anharmonic effects are small, we can treat the crystal in the quasi-harmonic approximation¹⁵. The scattering cross section for the creation of a phonon will then be given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{2Nk_2}{k_1} \hbar\omega (\bar{n}(\omega) + 1) \times \\ \times \sum_j |F(qj)|^2 \frac{2\tilde{\gamma}(qj)}{(\tilde{\omega}^2(qj) - \omega^2)^2 + 4\omega^2 \tilde{\gamma}^2(qj)} \quad (27)$$

This results in a peak of half-width $\tilde{\gamma}(qj)$ at the quasi-harmonic frequency $\tilde{\omega}(qj)$. The structure factor is then given by

FIGURE 1

The diagram shows the configuration required to get scattering from (A) a longitudinal phonon and (B) a transverse phonon. The latter shows the configuration in which a neutron group would appear focused when creating a transverse acoustic phonon. The neutron group for destruction of a phonon would appear defocused.



$$F(\underline{Q}) = \sum_K b_K M_K^{-1/2} \exp(-i\underline{W}_K) (Q \cdot \underline{e}(K, \underline{q})) \exp(i\underline{q} \cdot \underline{r}(K)) \quad (28)$$

1. 4 MAGNETIC SCATTERING.

Neutrons scatter magnetically from systems in which there are unpaired electrons. These electrons have localised wavefunctions about the ions in the crystal, or in some cases they may be itinerant in nature. In this section we shall only consider scattering from the former.

An element will possess a magnetic field if there is an unpaired electron in an internal shell. Examples of elements of this type which possess magnetic properties are those with incomplete 3d shells (eg Iron, Manganese, Nickel) or incomplete 4f shells (Gadolinium, Terbium, Dysprosium).

The partial differential cross section for magnetic scattering of neutrons, is given by equation 6. - however the interaction potential is no longer the Fermi pseudopotential. Instead the interaction is that between a neutron and a magnetic field.

$$\hat{V} = - \gamma \mu_N \hat{\underline{\sigma}} \cdot \underline{H} \quad (29)$$

Where $\gamma = -1.91$ is the neutron magnetic moment measured in terms of nuclear magnetons, μ_N . $\hat{\underline{\sigma}}$ is the set of Pauli spin matrices and $\underline{H}$ is the magnetic field due to the unpaired electrons at the ion site. In an analogous way to nuclear scattering, we can define a magnetic scattering length:

$$P = \frac{\gamma e^2}{m_e c^2} F(\underline{Q}) \underline{s}_N \cdot \{ \hat{\underline{Q}} \times (\underline{s} \times \hat{\underline{Q}}) \} \quad (30)$$

where e is the charge on an electron and m_e is its mass. $F(\underline{Q})$ is the

magnetic form factor, which is just the Fourier transform of the spatial distribution of unpaired electrons within an ion. The spin of the neutron is given by $\underline{S}_N$ and the term in curly brackets reduces to the component of the atomic spin which is perpendicular to the scattering vector, $\hat{\underline{Q}}$. It can then be shown¹³ that the differential cross section for an unpolarised beam of neutrons can be written as

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} &= \frac{1}{\hbar} \left(\frac{\gamma_e^2}{mc^2} \right)^2 \left(\frac{1}{2g} F(\underline{Q}) \right)^2 \frac{k_2}{k_1} \times \\ &\times \exp(-W(\underline{Q})) \sum_{\alpha\beta} \left\{ \left(\delta_{\alpha\beta} - \underline{Q}_\alpha \underline{Q}_\beta / Q^2 \right) \times \right. \\ &\times \left. \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \sum_1 \left\langle S_0^\alpha(0) S_1^\beta(t) \right\rangle \exp(i\underline{Q} \cdot \underline{r}(1)) \right\} \end{aligned} \quad (31)$$

We recognise the terms in the last line as being the Fourier transform in space and time of the spin pair correlation function. $\langle S_0^\alpha(0) S_1^\beta(t) \rangle$ is the probability of finding the β -component of the spin $\underline{S}_1(t)$ at position $\underline{r}(1)$ and time t , when the spin $\underline{S}_0(0)$, at the origin at time 0, had a particular α -component. The spin S may not be the pure spin but may be the total angular momentum or some other effective spin operator. In this case the terms $\frac{1}{2g} F(\underline{Q})$, where g is the Lande splitting factor for the ion, take up values appropriate to the form of coupling. The other term in the summation over α and β is a "weight factor" arising from the polarisation states in an unpolarised neutron beam. We might also note that there is a term for the Debye-Waller factor.

A number of expressions exist for the scattering cross sections. These depend on the type of magnetic structure in the crystal and are of varying complexity. For example we can take the Heisenberg Hamiltonian for a ferromagnetic system with an external field in the Z direction.

$$\hat{\mathcal{H}} = - \sum_{11^1} J(1-1^1) \underline{S}_1 \cdot \underline{S}_{1^1} - g \mu_B H \sum_1 \sum_{1^1}^Z S_1^Z \quad (32)$$

where $J(1-1^1)$ is the exchange parameter between spins at sites 1 and 1^1 . The introduction of non commuting raising and lowering operators

$$S_{\pm}^{\pm} = S^x \pm iS^y \quad (33)$$

for the spin angular momentum means we can write

$$\underline{S}_1 \cdot \underline{S}_{1^1} = S_1^Z S_{1^1}^Z + \frac{1}{2}(S_1^+ S_{1^1}^- + S_1^- S_{1^1}^+) \quad (34)$$

In a Bravais crystal, the equation of motion in the linear approximation ($S^Z \rightarrow S$) is then given by

$$i\hbar \dot{S}_1^+ = [S_1^+, \mathcal{H}] = g\mu_B H S_1^+ + 2S \sum_{1^1} J(1-1^1) (S_1^+ - S_{1^1}^+) \quad (35)$$

Inserting the transformation relations

$$S_1^+ = \frac{1}{N} \sum_{\underline{q}} \exp(i\underline{q} \cdot \underline{r}(1)) S_{\underline{q}}^+ \quad (36)$$

$$J(\underline{q}) = \sum_1 J(1) \exp(-i\underline{q} \cdot \underline{r}(1)) \quad (37)$$

$$S_{\underline{q}}^+(t) = \exp(-i\omega t) S_{\underline{q}}^+ \quad (38)$$

into equation 35 we obtain

$$\hbar \omega(\underline{q}) = g\mu_B H + 2S \{J(0) - J(\underline{q})\} \quad (39)$$

for the dispersion relation for linear spin waves in a Heisenberg ferromagnet. In the small $\underline{q}$ limit this can be written as

$$\hbar \omega(\underline{q}) \simeq g\mu_B H + Dq^2 \quad (40)$$

where D can be expressed in terms of the exchange parameters.

$$D = \frac{1}{3} S \sum_l |\underline{r}(l)|^2 J(l) \quad (41)$$

The Heisenberg model is most valid when the wavefunctions of the magnetic ion are an s state rather than a p or d state. If the external field is removed, the frequency $\omega(0)$ at the zone centre will be zero. Inclusion of anisotropic terms in the Hamiltonian, will produce what is known as an anisotropy gap; i.e. $\omega(0) \neq 0$. This produces an effect similar to an external magnetic field. Using equations 31 - 34, the transverse cross section for spin waves is given by

$$\begin{aligned} \left(\frac{d^2 \sigma}{d\Omega dE} \right)^{\pm} &= \left(\frac{\gamma_e^2}{m_e c^2} \right)^2 \left(\frac{1}{2} g F(Q) \right)^2 \frac{k_2}{k_1} (1 + (Q_z/Q)^2) \times \\ &\times \exp(-W(Q)) \frac{1}{2} S N \frac{(2\pi)^3}{V_0} \sum_{\underline{q}, \underline{\tau}} (n(\underline{q}) + \frac{1}{2} \pm \frac{1}{2}) \delta(\hbar\omega(\underline{q}) \mp \hbar\omega) \\ &\delta(\underline{Q} - \underline{q} - \underline{\tau}) \end{aligned} \quad (42)$$

It is of interest to note that in contrast to nuclear scattering, the intensity of the magnetic scattering has no explicit frequency dependence other than through the Bose-Einstein population factor. The + or - sign throughout indicates creation and annihilation of a magnon respectively. The intensity falls off quite rapidly in $\underline{Q}$ - space through the magnetic form factor $F(Q)$ which dominates over the more slowly varying Debye-Waller factor.

An antiferromagnet can be considered as two interpenetrating lattices given by vectors $\underline{m}$ (the "up" lattice) and $\underline{n}$ (the "down" lattice). The Heisenberg Hamiltonian is of the form

$$\hat{H} = 2J \sum_{\underline{m}, \underline{r}} \underline{S}_{\underline{m}} \cdot \underline{S}_{\underline{m} + \underline{r}} \quad (43)$$

where the summation $\underline{m}$ is over all sites in the "up" lattice and only nearest neighbour exchange to the sites on the "down" lattice is considered. We shall only be concerned with the excitations that occur as the spins deviate from their assumed ground state values - ie deviations from all spins up on one lattice and down on the other. It proves convenient to transform the spin operators associated with the ions on the $\underline{n}$ sublattice by a rotation of the axes of the sublattice by 180 degrees about the X-axis. In which case

$$\underline{S}_{\underline{n}} (x, y, z) \rightarrow \underline{T}_{\underline{n}} (x, \bar{y}, \bar{z}) \quad (44)$$

and the raising and lowering operators are given by

$$\underline{S}_{\underline{n}}^{\pm} = \underline{S}_{\underline{n}}^x \pm \underline{S}_{\underline{n}}^y = \underline{T}_{\underline{n}}^{\mp} \quad (45)$$

We define the Fourier transforms

$$\underline{S}_{\underline{m}}^{\pm} = \frac{1}{N} \sum_{\underline{q}} \exp(\pm i \underline{q} \cdot \underline{m}) \underline{S}_{\underline{q}}^{\pm} \quad (46)$$

and

$$\underline{T}_{\underline{n}}^{\pm} = \frac{1}{N} \sum_{\underline{q}} \exp(\mp i \underline{q} \cdot \underline{n}) \underline{T}_{\underline{q}}^{\pm} \quad (47)$$

where $\underline{q}$ is restricted to the first Brillouin zone of one sublattice with N sites. Applying commutation rules, the linear equation of motion for a Heisenberg Hamiltonian with nearest neighbour interactions is

$$i\hbar \dot{\underline{S}}_{\underline{m}}^{\pm} = 2S \sum_{\underline{r}} J(\underline{r}) (\underline{S}_{\underline{m}}^{\pm} + \underline{T}_{\underline{m} + \underline{r}}^{\mp}) \quad (48)$$

and inserting equations 47 and 48 we obtain

$$i\hbar \dot{S}_q^+ = 2S (J(0)S_q^+ + J(q) T_q^-) \quad (49)$$

and similarly

$$i\hbar \dot{T}_q^- = -2S(J(0)T_q^- + J(q) S_q^+) \quad (50)$$

Solving equations 49 and 50 we obtain two degenerate solutions for the spin wave frequencies.

$$\hbar \omega(q) = 2S [J(0)^2 - J(q)^2]^{\frac{1}{2}} \quad (51)$$

The frequencies at low q are linearly dependant on q in comparison to the quadratic dependence found in ferromagnets. Equation 51 can be readily generalised¹³ to include uniaxial anisotropy and the application of an external magnetic field.

The cross section for the creation and annihilation of a magnon in an antiferromagnet becomes

$$\begin{aligned} \left(\frac{d^2 \sigma}{d\Omega dE} \right)^{\pm} &= \left(\frac{\gamma_e^2}{m_e c^2} \right)^2 \left(\frac{1}{2} g F(q) \right)^2 \frac{k_2}{k_1} (1 + (Q_z/Q)^2) \times \\ &\times \exp(-W(Q)) \frac{1}{2} S N \frac{(2\pi)^3}{v} \sum_{q, \gamma} (n(q) + \frac{1}{2} \pm \frac{1}{2}) (\hbar \omega(q) \mp \hbar \omega) \times \\ &\times \delta(Q - q - \gamma) \{ u^2(q) + v^2(q) + 2u(q)v(q) \cos \underline{r} \cdot \underline{\gamma} \} \end{aligned} \quad (52)$$

We see that the scattering cross section for an antiferromagnet differs from that of a ferromagnet by the last term. This amounts to a phase factor. For a nearest neighbour Heisenberg antiferromagnet without anisotropy, the terms are given by

$$u^2(q) = (1 + SJ(0)) \quad (53)$$

$$v^2(q) = -(1 - SJ(0)) \quad (54)$$

and

$$u(q) v(q) = 2SJ(q) \quad (55)$$

This phase factor leads to a variation of the scattered intensity at different points in the zone in addition to the variation caused by the form factor. The intensity is at a minimum near the nuclear Bragg points and is at a maximum near superlattice reflections.

1. 5 EXPERIMENTAL NEUTRON SCATTERING

Instruments for neutron scattering are situated close to a fission reactor. The heavy decay products are rapidly stopped within the reactor core or shortly afterwards, but a high flux of γ rays and neutrons with energies up to several MeV escape. Beam ports are arranged about the reactor core so that there is no line-of-sight path for the γ rays, so they are reduced. The beam ports are directed towards the moderator which surrounds the core. This will be some light material such as H_2O , D_2O or graphite. The neutrons come into thermal equilibrium with this material. The neutron flux can be approximated by a Maxwell distribution and the number of neutrons, irrespective of direction, is given by

$$N(k)dk = n \frac{2\pi^4 \beta}{m_N^2} k^3 \exp\left(\frac{-\beta \hbar^2 k^2}{2m_N}\right) dk \quad (56)$$

There are additional neutrons at higher energies which have not been completely moderated. The maximum neutron flux occurs at about 50meV for a moderator working at about $T = 1/k_B \beta \sim 350^\circ K$. For some experiments it is an advantage to work with low energy neutrons, so a

further moderator is used. For example at Risø, a pressurised H₂ "cold source" operating at 28°K is employed. This shifts the Maxwell distribution to lower energies and it is found to have its maximum at about 15 meV¹⁷. However, the real gains come when it is required to use neutron energies around 5 meV when a 10-fold increase in the flux is obtained when using a hydrogen source instead of the standard source.

1. 6 TRIPLE AXIS SPECTROMETER.

In an experimental reactor various instruments can be placed at the beam ports. Some of these are used for structural studies (eg. four - circle diffractometer, powder diffractometer), whilst others can be used to study dynamic effects (eg triple axis spectrometer, time of flight spectrometer and in restricted cases, two axis spectrometer). In this section we describe the instruments which have been used in obtaining information for this thesis. All the experiments were performed at the DR3 reactor of the Danish Energy Commission at Risø. The instruments used were TAS 1 and TAS 6 which are attached to the cold source and TAS 3 and TAS 4 which are conventional triple axis spectrometers. On occasion, TAS 3 and TAS 6 were operated in a double axis mode. TAS 5 was also used. This instrument is restricted to double axis operation.

In Figure 2 we show a schematic diagram of a triple axis spectrometer. After the moderated neutrons leave the reactor, they are constrained in a slightly divergent beam by using a soller collimator, Cl. The collimator consists of an open ended box, typically 0.3 - 1m long with the other dimensions 5 - 10cm. The box has a system of slots whereby a number of cadmium plates can be held parallel and equidistant to each other. The horizontal angular divergence of the beam (F.W.H.M.) is approximately spacing between plates / length of plates (typically 20 - 80 min). How good this approximation is depends on how straight the

plates are and on whether they are truly equidistant. The vertical divergence is approximately the height of the box divided by its length. There are a sufficient number of slots in the box so a variety of horizontal divergences can be obtained. Constraint of vertical divergences, if needed, is usually achieved by masking the ends of the box with cadmium. Collimators C2, C3 and C4 are basically the same as C1, but they may have slightly different dimensions from each other.

The beam strikes the monochromator M, which might be a crystal of graphite, germanium or zinc, and is Bragg reflected through an angle P. This selects neutrons of wavevector $\underline{k}_1$ with an uncertainty $d\underline{k}_1$. A one to two system ensures that once the monochromator is set on a reflecting position, with the beam passing through collimator C2, then a beam passes through C2 for all settings of the angle P. Collimator C2 helps to reduce the spread in the wavevector of the "monochromatic" beam.

The beam intensity is monitored by a low efficiency He^3 counter, F, before passing on to the sample. The sample can be rotated and set at various angles, R. Q selects the angle through which the scattering takes place with collimator C3 defining the direction of the outgoing $\underline{k}$ -vector. The magnitude of $\underline{k}_2$ is selected by Bragg scattering from the analyser into the forth collimator. Finally a high efficiency B^{10}F_3 counter detects the neutrons.

In Figure 2b it can be seen that the two scattering conditions (equations 7 and 10) can be satisfied by an appropriate choice of the angles P, Q, R and S. It is also apparent that there is no unique solution. This is of great help if spurious processes are suspected when scattering under a different configuration, will in general produce a different result if certain types of spurious process occur.

In a double axis spectrometer one does away with the analyser crystal and fourth collimator. The detector would be in the position of the analyser in the Figure. It is a simple matter to run a triple axis spectrometer in a double axis mode. The analyser is removed and the computer controlling the spectrometer is given zero for the value of the reciprocal lattice vector of the non existent analyser. The angle S will then remain at zero degrees. It can then be seen that only the direction of the output vector $\underline{k}$ is specified and scattering for $-\infty < \hbar\omega < \frac{\hbar^2 k_1^2}{2m}$ is picked up. From equations 7 and 10 it can be seen that for any particular frequency ω a particular $\underline{Q}$ is obtained and varying ω will produce different values of $\underline{Q}$.

Each of the spectrometers at Risø is controlled by a PDP8 computer which is given such information as crystal vectors and zero angles. In general we want to perform a scan in $(\underline{q}, \omega)$ space. One makes the choice between doing a constant energy transfer scan (ω fixed) or a constant wavevector transfer scan ($\underline{Q}$ fixed). These are illustrated in Figure 3.

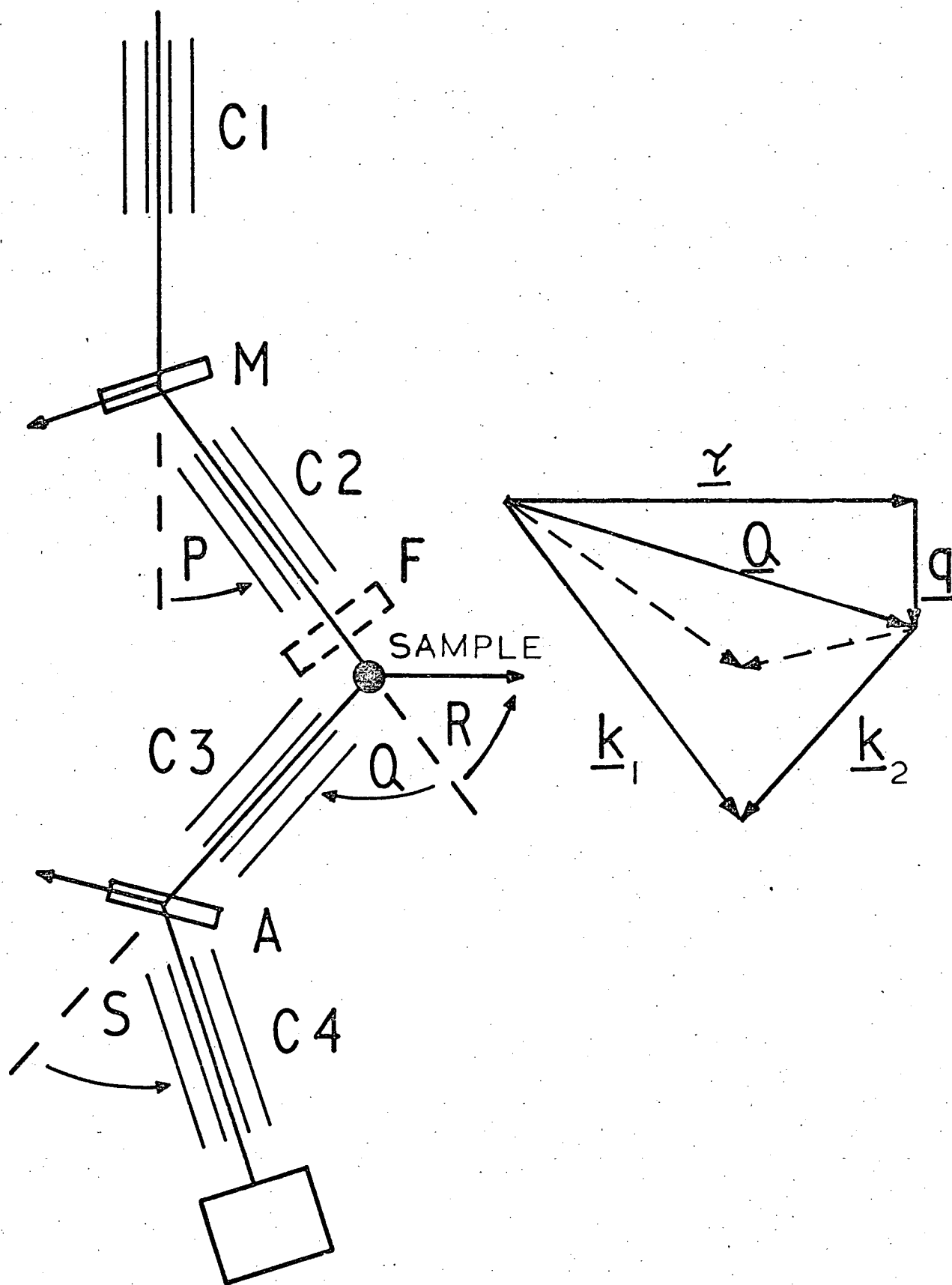
As was stated earlier, there are more adjustable parameters than we need. Either the angle P or the angle S is fixed at some convenient value. If the former is the case the spectrometer is being run on an analyser scan; the latter would be a monochromator scan. An analyser scan is illustrated on the fourth diagram in Figure 3.

The PDP8 can also control such things as temperature and magnetic field and just treats these as further 'angles' which can be set. A scan is set up by sitting at various points in $(\underline{q}, \omega)$ space. A new point can be moved to after counting for a set period or alternatively after a certain number of monitor counts has been obtained. The number of neutrons reaching the detector and any other information which is required is printed out on a teletype with a paper tape puncher. A more recent development is the recording of the output directly onto magnetic cassettes.

FIGURE 2

This shows a schematic diagram of a triple axis spectrometer. A scattering configuration like that shown by the continuous line drawing on the right of the diagram is set up using the angles P , Q , R and S . The same $S(Q, \omega)$ can be obtained in a different configuration (broken line) using a different set of angles P' , Q' , R' and S' . Collimation of the neutron beam is provided by the soller slits $C1 - C4$. The ingoing and outgoing neutron wavevectors are selected by Bragg scattering from a monochromator M and an analyser A . A counter F monitors the incident flux and the scattered neutrons are counted by a detector .

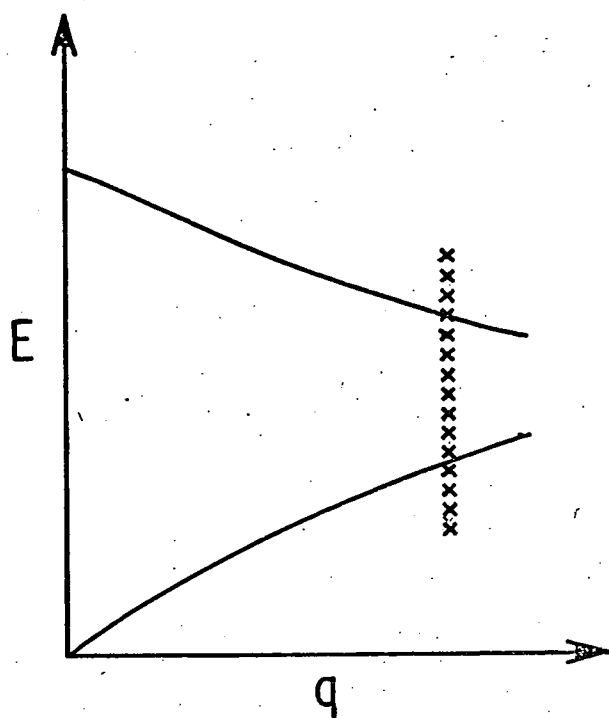
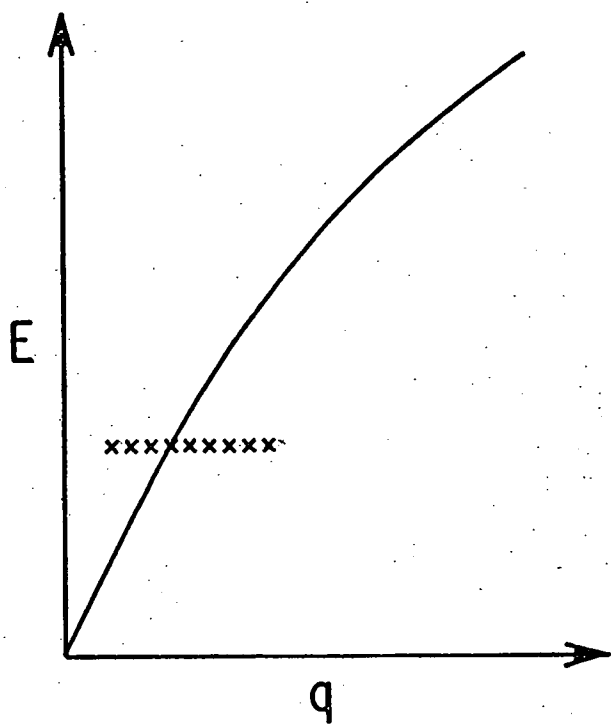
REACTOR



DETECTOR

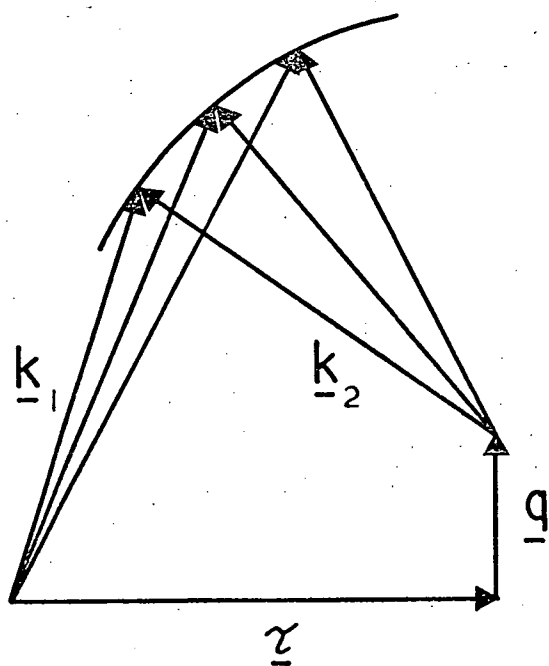
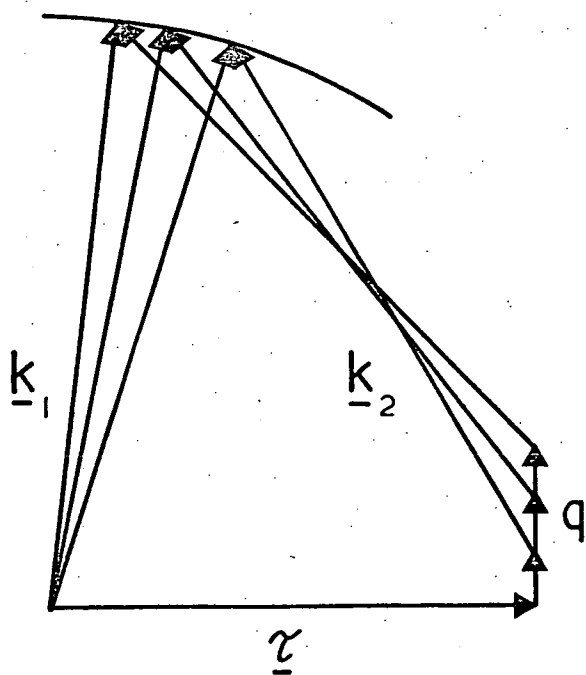
FIGURE 3

This illustrates a constant energy transfer scan and a constant wavevector transfer scan on a dispersion relation. The lower diagrams illustrate the scattering configurations used to obtain the upper diagrams.



CONSTANT E

CONSTANT Q



1. 7 EXPERIMENTAL RESOLUTION

Because of the finite collimations and the mosaic spread of the monochromator and analyser in a triple axis spectrometer, there is a variation in the values of $\underline{k}_1$ and $\underline{k}_2$ about their average values $\underline{k}_{10}$ and $\underline{k}_{20}$. It is usually also the case that the crystal being studied consists of mosaic blocks leading to a spread in the $\underline{\gamma}$ vectors about their mean positions. It is mathematically convenient to regard this contribution as being part of the instrumental effect. Having a finite instrumental resolution means that there is a probability of detecting a process with scattering vector $\underline{q}$ and energy transfer E which differ from the average values of $\underline{q}_0$ and E_0 . If it is assumed that the collimators have a gaussian transfer function, we can define a function

$$R(\underline{q} - \underline{q}_0, E - E_0) = R_0 \exp \left[- \sum_k^3 \sum_l^3 M_{kl} Y_k Y_l \right] \exp \left[-M_{44} Y_4^2 \right] \quad (57)$$

known as the resolution function, which is proportional to the transfer function of the instrument. Cooper and Nathans¹⁸ were able to derive the constants M_{kl} in terms of the collimations, mosaic spreads, scattering angles and scattering vectors. In which case $Y_1 = q_x - q_{0x}$ is parallel to the scattering vector $\underline{q}$, $Y_2 = q_y - q_{0y}$ is perpendicular to $\underline{q}$, but still in the scattering plane, Y_4 is the component out of the scattering plane and $Y_3 = E - E_0$. Now when the spectrometer is set at $\underline{q}_0$ and E_0 we observe intensity which is the convolution of the cross section for the scattering process $\sigma(\underline{q}, E)$ with the experimental resolution function $R(\underline{q} - \underline{q}_0, E - E_0)$

$$I(\underline{q}_0, E_0) = \iint R(\underline{q} - \underline{q}_0, E - E_0) \sigma(\underline{q}, E) d\underline{q} dE \quad (58)$$

By scanning through a Bragg reflection for which $\sigma(q, E) \sim \delta(q) \delta(E)$ we can map out the resolution function. It is convenient to plot contour lines for the half peak intensity as a function of E and wavevector q . The half peak intensity produces a surface which is an ellipsoid in four dimensions. There is a correlation between the wavevector resolution perpendicular to the scattering vector and the energy resolution - there is little correlation with other directions of q . We can use this correlation on transverse scans to obtain focusing of the phonon creation neutron group at $(\gamma, q, 0)$ - defocusing of the neutron group will occur at $(\gamma, -q, 0)$. Other methods have been developed to calculate the effect of the resolution on intensities and widths. Dietrich¹⁹ used a Monte-Carlo simulation to calculate the resolution. Møller and Neilsen²⁰ use a method to calculate the intensities which is an analytic function of k_1 and k_2 rather than of q and E as was used by Cooper and Nathans¹⁸. Their convolution is a 6 - dimensional integral.

$$I(k_{01}, k_{02}) \propto \iint P_M(k_1 - k_{01}) \sigma(k_1 \rightarrow k_2) P_A(k_2 - k_{02}) dk_1 dk_2 \quad (59)$$

where $P_M(k_1 - k_{01})$ is the probability of the monochromator system producing a neutron of wavevector k_1 rather than with the average value k_{01} and $P_A(k_2 - k_{02})$ is the probability of the analyser system scattering a neutron with wavevector k_2 rather than with the average value k_{02} . $\sigma(k_1 \rightarrow k_2)$ is the cross section for the scattering process $k_1 \rightarrow k_2$.

Normally one measures the resolution function at a Bragg point and adjusts the parameters in the method used for the calculation to get a better fit. A 5% or 10% adjustment in the F.W.H.M. values of some of the collimations and mosaic widths is usually required to produce agreement with the measured resolution function.

1. 8 DISTURBING PEAKS.

Scattering picked up in a spectrometer at a general point in (q, ω) space does not always arise from a one phonon or one magnon process. First of all we consider two processes which can arise in elastic scattering (ie $\omega = 0$). These are illustrated in Figure 4.

Multiple Bragg scattering arises when two reflections simultaneously lie on the Ewald sphere. The diagram shows the situation for two points in the scattering plane, but points out of the plane can also accidentally fall on the Ewald sphere. As well as the single scattering process

$$\underline{\gamma} = \underline{k}_1 - \underline{k}_2 \quad (60)$$

a double scattering process

$$\underline{k}_1 - \underline{k}_3 \text{ followed by } \underline{k}_3 - \underline{k}_2 \quad (61)$$

takes place. Depending on the structure factors for scattering from (31), $(\bar{1}2)$ and $(\bar{4}1)$, the intensity observed at (31) can be either increased or decreased by the multiple scattering. Altering the wavelength of the neutrons or rotating the crystal about the scattering vector, $\underline{\gamma}$, will in general move unwanted reflections from the Ewald sphere. In the chapter on (D) Cs DA we look at a more complicated form of multiple scattering arising from the presence of several reciprocal lattices.

The second diagram in Figure 4 shows a scattering diagram for second order neutrons. As well as the normal scattering equation in the monochromator and analyser, Bragg scattering of the form

$$(2\gamma) = 2(2k) \sin \Theta \quad (62)$$

can take place. So as well as selecting neutrons of energy E, they will select neutrons with energy 4E and possibly even 9E. The proportion of higher order neutrons depends on the energy and increases

rapidly as the energy is reduced. Several methods have been developed to reduce the number of higher order neutrons. One method is to use a crystal which has a reflection γ but 2γ is absent through symmetry reasons. The Germanium (111) reflection has frequently been used because of this property. There is still the possibility of scattering third order neutrons.

Another method which has been successfully applied is to use a filter. This is placed after the sample, if monochromator scans are being used and before the sample if analyser scans are being used. Two materials commonly used for filters are a 5cm thickness of pyrolytic graphite and a cooled Beryllium filter. The former only works at a selected number of wavelengths, whereas the latter is fairly transparent below about 5 meV and has a number of step functions before effectively removing all neutrons above 6.8 meV. These filters operate on the principle of Bragg scattering the unwanted higher order neutrons out of the beam. Higher order contaminant will show up as increased intensity at a reflection or the appearance of Bragg like scattering at, for example, the zone boundary.

Unwanted scattering can occur at more general points in the zone. Incoherent scattering is frequently a nuisance. It is particularly troublesome for substances containing hydrogen. Deuterating such samples overcomes the problem by reducing the spin incoherent scattering. One normally associates incoherent scattering with zero energy transfer, but it can be observed at other energy transfers when a higher order reflection takes place in the monochromator and/or analyser.

Bragg scattering can also be picked up at inelastic settings due to the shape of the resolution function. This occurs when the extension of the major axis of the resolution ellipsoid passes through $g = 0$, $E = 0$ and a peak in the scattered intensity will be observed. This type of

FIGURE 4

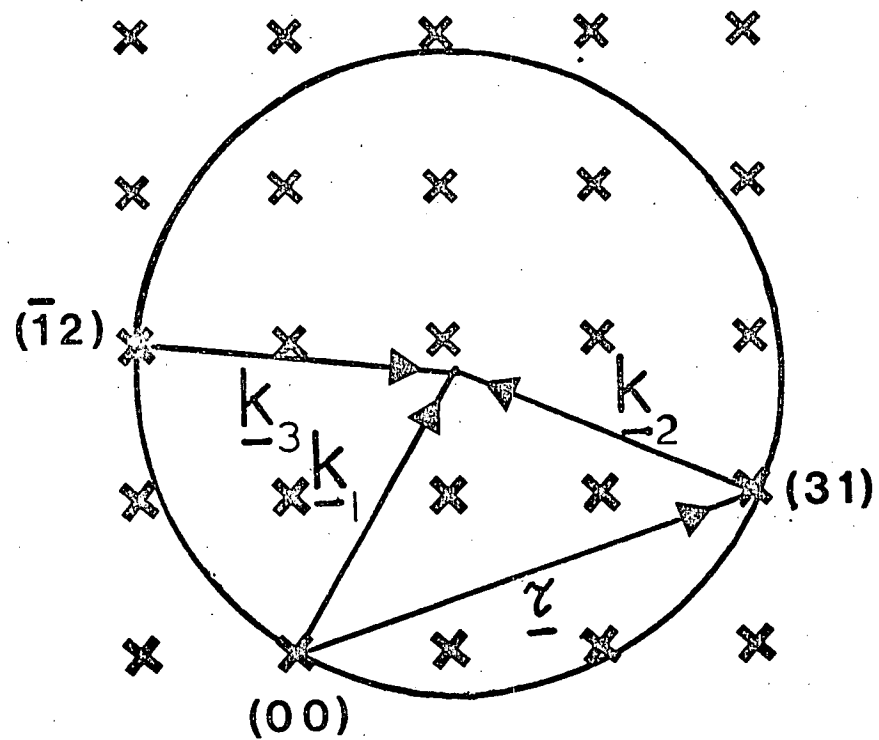
(A) This illustrates how multiple Bragg scattering can occur when two reflections simultaneously fall on the Ewald sphere.

$$\underline{\gamma} = (\underline{k}_1 - \underline{k}_3) + (\underline{k}_3 - \underline{k}_2) \equiv \underline{k}_1 - \underline{k}_2$$

(b) When a spectrometer is set to scatter at a reciprocal lattice vector, $\underline{\gamma}$, there can be additional contributions from processes of the form

$$2 \underline{k}_1 - 2 \underline{k}_2 = 2 \underline{\gamma}$$

A



B

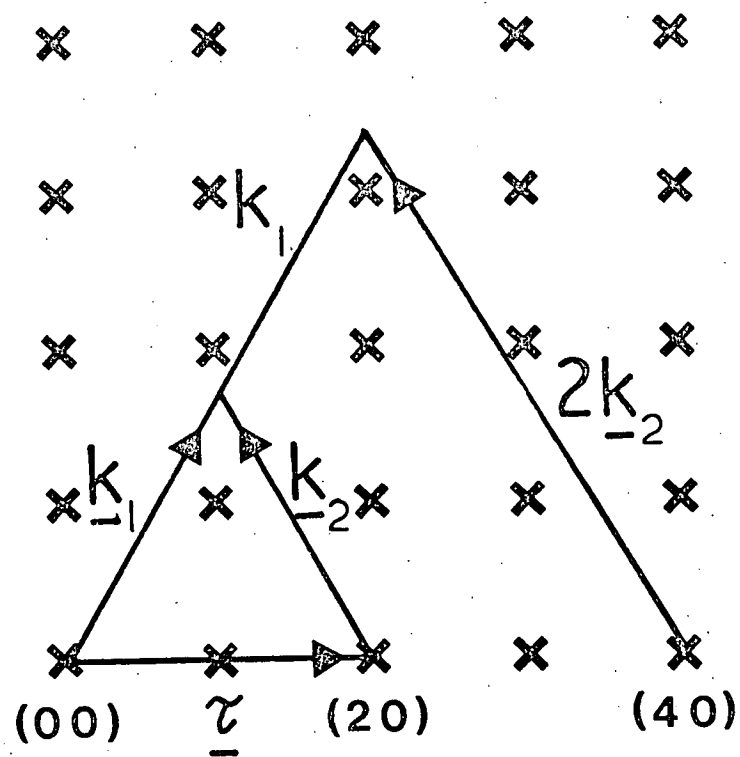


FIGURE 5

(A) This illustrates the recording of an unwanted phonon process. The spectrometer is set to give

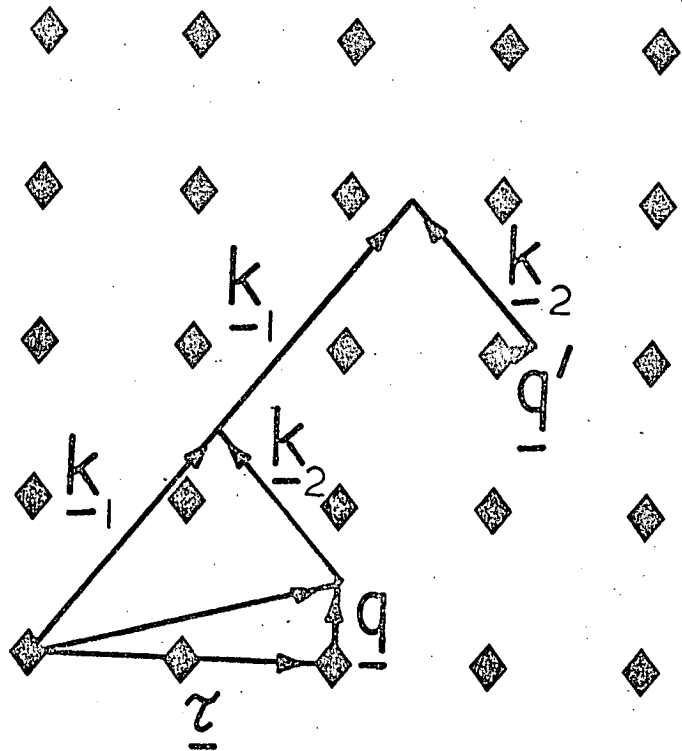
$$\underline{k}_1 - \underline{k}_2 = \underline{Q} = \underline{\gamma} + \underline{q}$$

but owing to higher order contaminant in the incoming beam it also picks up scattering at a different energy transfer and wavevector transfer through

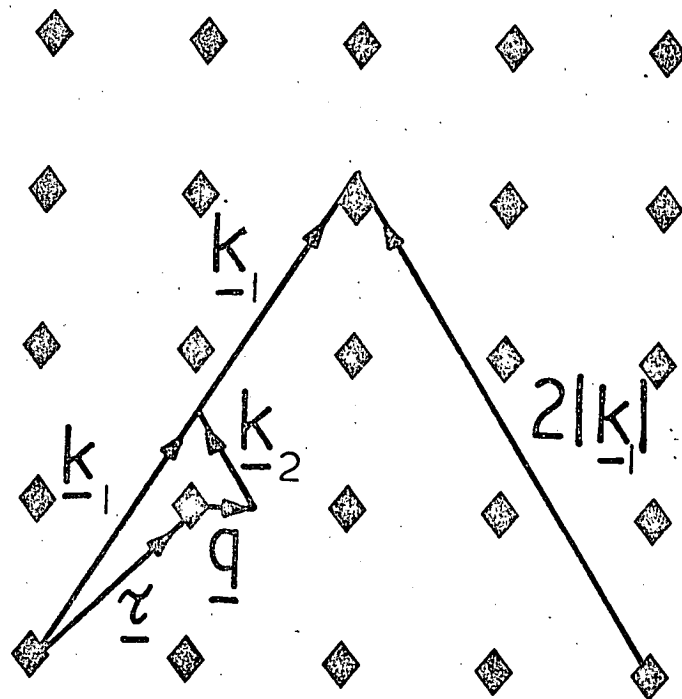
$$2 \underline{k}_1 - \underline{k}_2 = \underline{Q}' = \underline{\gamma}' + \underline{q}'$$

(B) This illustrates a spurious process involving Bragg scattering in the monochromator and sample with incoherent scattering in the analyser.

A



B



scattering will produce what appears to be a linear "dispersion curve" dying away further out in the zone.

A phonon at a different wavevector and energy transfer can be picked up if there is higher order scattering in the monochromator or analyser. An example of the former is shown in Figure 5a. In Figure 5b we show how it is possible to get Bragg reflection in the crystal at inelastic settings. This situation can arise when there is Bragg scattering in the monochromator and incoherent elastic scattering in the analyser (or vice versa). Although our example shows the Bragg scattering taking place with second order neutrons, first order neutron scattering can also produce this effect.

Also a nuisance are the background neutrons in the reactor hall which find their way to the detector. This might amount to 1 neutron/min and makes it harder to measure the phonons; particularly if they are weak. In addition to this, there will be scattering from the sample container producing Debye-Scherrer cones which show up as a powder like profile. Cadmium is normally used to mask off as much of the container as possible to reduce this scattering.

1. 9 CHOOSING A SCAN

The Bose-Einstein population factor becomes important when $\hbar\omega \gtrsim k_B T$, so it is always an advantage to create a phonon or magnon rather than to destroy one.

Normally one does constant wavevector scans, since in most situations these produce the sharpest neutron groups. The situation is different if the dispersion relation has a steep slope and then constant energy scans are usually chosen. It is easier to interpret data taken from a constant wavevector scan. One has a further choice between fixing the ingoing or outgoing neutron wavevector. Monochromator scans are

most convenient for analysing, since the efficiency of the monitor is proportional to the neutron wavevector $\underline{k}_1$. This can be cancelled out with the $1/\underline{k}_1$ dependence in the scattering formula so a direct measure of $S(\underline{Q}, \omega)$ is obtained. In contrast, in an analyser scan $\underline{k}_2$ is allowed to vary and one measures

$$\frac{d^2\sigma}{d\Omega d\Theta} \propto \frac{(k_2)^3}{k_1} \cot(\Theta_a) S(\underline{Q}, \omega) \quad (63)$$

The results must therefore be corrected for the $k_2^3 \cot(\Theta_a)$ term, where Θ_a is the scattering angle of the analyser.

Phonon scattering is greater (on average) at large $\underline{Q}$ because of the term proportional to Q^2 in the scattering formula. At sufficiently large values of $\underline{Q}$ the Debye-Waller factor begins to cancel out this factor. In contrast, in magnetic scattering the form factor falls away rapidly with $\underline{Q}$ so the neutron scattering is greatest in the vicinity of magnetic Bragg points with small reciprocal lattice vectors.

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CHAPTER 11

THE COUPLED OSCILLATOR MODEL IN KDP TYPE FERROELECTRICS.

II.1 INTRODUCTION

The theory of displacive ferroelectrics, developed by Cochran¹ and Anderson², explained the temperature dependence of the dielectric properties in terms of a particular normal mode of vibration. As the temperature of the ferroelectric phase transition is approached, the frequency of this mode decreases with a temperature dependence of the form

$$\omega^2 = A(T - T_c) \quad (1)$$

At the transition, the crystal becomes unstable and distorts to the ferroelectric crystal structure. Below the transition temperature, the electric moment arises from the collective motions of the atoms and ions.

Some ferroelectrics are of the order-disorder type in which the transition is accompanied by an ordering of the constituents among various equilibrium positions. A pseudospin model describes the alternative positions, and the constituents can tunnel between them. An effective Hamiltonian can be set up to describe the motions³. This also leads to a temperature dependence of a similar form, with the ferroelectric mode frequency becoming zero at the clamped Curie temperature.

In KDP (KH_2PO_4) and its isomorphs the pseudospin states are related to the two equilibrium positions of a proton in a hydrogen bond^{5,6}. Many experiments have been performed in an attempt to find the temperature dependence of the ferroelectric mode, and in particular, the temperature at which its frequency extrapolates to zero.

More recently, it has been suggested by Coombs and Cowley⁷, that in the piezoelectric ferroelectrics such as KDP, there is a contribution to the ferroelectric mode self energy at low frequencies, arising

from the coupling of the mode with phonon density fluctuations. The low frequency dielectric constant then diverges at the Curie temperature, but the frequency of the ferroelectric mode, as measured in a high frequency Raman scattering experiment, becomes zero at some temperature $T_0 > T_c$.

Raman scattering experiments have been performed by Ryan et al.^{8,9} on KDP, KDA (KH_2AsO_4), CsDA (CsH_2AsO_4), and ADP ($\text{NH}_4\text{H}_2\text{PO}_4$); by Lowndes et al.¹⁰ and Tornberg et al.¹¹ on KDA, RbDA (RbH_2AsO_4), CsDA, DKDA (KD_2AsO_4), DRbDA (RbD_2AsO_4) and DCsDA (CsD_2AsO_4); by Kaminow and Damen¹² on KDP; by Lagakos and Cummins on KDP¹³ and CsDA¹⁴. The analysis of their data is complicated because the ferroelectric mode couples to an optic mode, necessitating a non linear least squares fit to the Raman spectra using a two coupled oscillator model. There are then too many adjustable parameters in this model, so it is not possible to get a unique description of the data.

Lowndes et al.¹⁰ point out that the range of the spectrum over which a fit is made is particularly critical for the deuterated isomorphs. They fitted the hydrogenated isomorphs out to 230 cm^{-1} but because of the presence of additional modes in the range 150 cm^{-1} to 300 cm^{-1} were unable to fit the deuterated isomorphs above 140 cm^{-1} . DCsDA was particularly troublesome in this respect. This may be related to the concentration of deuterium varying throughout the sample, as described in Chapter IV.

The analysis is further hampered by the fact that the soft mode is overdamped, so that reliable values of the frequency can not be obtained because of the large correlation between ω^2 and the damping, γ , so instead values of ω^2/γ are usually used to find T_0 .

Barker and Hopfield¹⁵ point out that the choice of real coupling

between oscillators ($\Gamma = 0$) or imaginary coupling ($\Delta = 0$), is arbitrary since, for any set of coupled oscillators, a unitary transformation can always be found, which diagonalises either the force constant tensor, or the damping tensor. When the analysis has been made in the real coupling representation, it was found that the soft mode frequency extrapolated to zero at a temperature T_0 , much lower than the clamped Curie temperature. 8,9,16,17,18.

Lagakos and Cummins¹³ and Young and Elliott¹⁹ point out, however, that the analysis has to be performed in the imaginary coupling representation before it provides meaningful evidence for the effects suggested by Cowley and Coombs²⁰ and Elliott and Young²¹.

Because of the high degree of correlation between some of the parameters, their values are very sensitive to small differences in the experimental data and there is some variation in the reported values.

It was with this in mind that the data was re-analysed, with a view to minimising this problem. The invariants of the coupled oscillator matrix are employed in a combination from which the temperature dependence of the ferroelectric mode frequency is readily extracted.

An advantage of using this form for comparison is that the results should be independent of whether real or imaginary coupling is used in the fitting. However, Tornberg et al¹¹ point out that the parameters obtained directly from an imaginary coupling fit, differ slightly from those obtained indirectly from a real coupling fit, using the Barker Hopfield transformation.

A further objective was to present all the available results in the same way, so that differences between the different materials are easily appreciated.

11. 2 THE TWO OSCILLATOR MODEL.

The coupled soft mode-optic mode equation for the clamped crystal can be written ²² as

$$\begin{bmatrix} G_1^{-1} & \Delta^2 - i\omega\Gamma \\ \Delta^2 - i\omega\Gamma & G_2^{-1} \end{bmatrix} \begin{bmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (2)$$

$$\text{where } G_1 = [\omega_1^2 - \omega^2 - i\omega\gamma_1]^{-1} \quad (3)$$

$$\text{and } G_2 = [\omega_2^2 - \omega^2 - i\omega\gamma_2]^{-1} \quad (4)$$

are the Greens functions of the respective modes when uncoupled.

The Raman spectrum is given by

$$I(\omega) = K \left[\frac{n(\omega) + 1}{n(|\omega|)} \right] \text{Im} \sum_{i,j} P_i P_j G_{ij}(\omega) \quad (5)$$

where $[n(\omega) + 1]$ and $[n(|\omega|)]$ give the Stokes and anti-Stokes spectrum respectively; $n(\omega)$ is the Bose-Einstein population factor; P_1, P_2 determine the scattering of each mode and K is a constant depending on the experimental conditions and is required only when absolute cross sections are to be measured; ω_1, ω_2 , are the frequencies of the modes and γ_1, γ_2 is their damping. Δ^2 and Γ describe the coupling between the modes.

The susceptibility is given by

$$\chi(\omega) = \sum_{i,j} P_i P_j G_{ij} = \frac{P_1^2 G_1 + P_2^2 G_2 - 2P_1 P_2 (\Delta^2 - i\omega\Gamma) G_1 G_2}{1 - (\Delta^2 - i\omega\Gamma)^2 G_1 G_2} \quad (6)$$

If these were classical oscillators, the parameters $\omega_1, \gamma_1, \omega_2, \gamma_2, \Delta$ and Γ would all be constant for a given temperature. When general anharmonic theory is used, they are dependent on the probing frequency, ω . At low frequencies, since all the parameters are even in ω , it might be expected that they are reasonably approximated by constants.

11. 3 FREQUENCY DEPENDENT SELF ENERGY.

Cowley and Coombs^{7,20} have suggested that the frequency dependence of the soft mode response function may be important in piezoelectric ferroelectrics. They argue that the soft mode can couple to phonon density fluctuations through third order anharmonicity. Their results were obtained within the framework of the weakly anharmonic crystal, and are therefore inappropriate for materials in which atoms or molecules undergo order-disorder transitions. Elliott and Young^{19,21} show that a similar effect can occur in the spin formalism, arising from terms of the form $\sigma^Z c_1^+ c_2$, which introduces a temperature and frequency dependent spin coupling. The results, however, are perhaps more dependent upon symmetry considerations than the details of the model.

The frequency dependent self energy gives rise to the soft mode frequency, as measured in a high frequency Raman scattering experiment, extrapolating to zero not at T_c , but at some lower temperature, and in addition, to quasi-elastic scattering on either side of the transition temperature.

Support for this model is provided by Lagakos and Cummins¹³, who report a quasi-elastic component whose intensity increases dramatically near the 122°K ferroelectric phase transition of KDP in a Brillouin scattering experiment. However, they were unable to resolve the width of this component, so that other processes cannot be ruled out as an explanation of their observations.

The self energy of the soft mode alters the response function of equation 3 to

$$G_1(\omega) = \left[\omega_\infty^2 - \omega^2 - i\omega\gamma_1 - \frac{\delta^2}{(1 - i\omega\tau)} \right]^{-1} \quad (7)$$

where τ is the average relaxation time of a phonon, probably 10^{-10} to 10^{-11} sec.

Raman scattering experiments can only be performed at frequencies far above $1/\gamma$. The high frequency response ($\omega \gamma \gg 1$), as measured in a Raman scattering experiment, is therefore given by the classically clamped harmonic oscillator with parameters ω_∞^2 and γ_1 .

The static response, however, is

$$G(0) = [\omega_\infty^2 - \delta^2]^{-1} = [\omega_0^2]^{-1} \quad (8)$$

The lifetimes of acoustic phonons are assumed to have a temperature dependence given by $\delta^2 = \alpha T$, and the soft mode frequency measured by Raman experiments is

$$\omega_\infty^2 = K(T - T_0) \quad (9)$$

so

$$\omega_0^2 = \omega_\infty^2 - \delta^2 = K(T - T_0) - \alpha T = (K - \alpha)[T - T_C^x] \quad (10)$$

so that

$$T_0 = [(K - \alpha)/K] T_C^x \quad (11)$$

where T_C^x is the clamped Curie temperature.

So far, detailed calculations have only been made for SrTiO_3 ²³. Although α has not been calculated for the KDP type ferroelectrics, it has been estimated from anharmonicity theory that it may be comparable in magnitude to K , in which case T_0 should be observed to be different from T_C^x . Young and Elliott, however, estimate α to be much smaller from pseudospin theory¹⁹.

11. 4 CHOICE OF MODES.

The Raman spectrum can be calculated for a system of two coupled modes, in terms of the seven parameters ω_1 , ω_2 , γ_1 , γ_2 , Δ , Γ and P_1/P_2 . Barker and Hopfield¹⁵ point out that there is an infinite choice of solutions that differ by a unitary transformation. At various times, different choices have been made to select one of

these by putting $P_1 = 0$, $\Gamma = 0$ or $\Delta = 0$, and these choices have then been used as the basis of the least squares fit of the Raman spectrum. Either of the last two choices enables an equally good fit to be obtained, but the first choice $P_1 = 0$ may not.

The eigenvectors produced by using the other two methods differ greatly. Katiyar et al.¹⁷ found that $\Gamma = 0$ produced the simplest temperature variation of the parameters and most researchers have followed their approximation.

From equation 6, the susceptibility diverges when $G_1 G_2 \Delta^4 = 1$ which is at a higher temperature than when either $G_1(0)$ or $G_2(0)$ diverges. $G_1(0)$ and $G_2(0)$ as given by equations 4 and 7 diverge when ω_1^2 and ω_2^2 respectively tend to zero. Lagakos and Cummins¹³ and Young and Elliott¹⁹ point out that this will always lead to a temperature difference between T_c and the temperature at which either ω_1^2 or ω_2^2 extrapolates to zero.

On the other hand when $\Delta = 0$, it is seen from equation 6 that $\chi(0)$ diverges when either $G_1(0)$ or $G_2(0)$ has diverged, implying that either ω_1 or ω_2 is zero.

11. 5 OVERDAMPED MODE.

The values of ω_1 , ω_2 , γ_1 , γ_2 and Γ are deduced from the Raman spectrum on the assumption that they are not too frequency dependent over the range of the spectrum being scanned, so can be taken as constants in the non-linear least squares fit program.

The question arises as to which is the best method of presenting these values, so as to obtain the best value of T_0 consistent with the data. Ideally a graph of ω_1^2 as a function of temperature, to give a best straight line, would be appropriate. This analysis, however, is unsatisfactory, because the parameters in the least squares fit are highly correlated when the modes are overdamped. A more satisfactory

parameter is $\Theta = \omega_1^2 / \gamma_1$, which varies as $(T - T_0)/T$. Then $T\Theta$ is expected to vary linearly with temperature, extrapolating to zero at a temperature equal to or less than that of the clamped Curie temperature.

The difficulty in determining the parameters is well shown by the recent work of Lowndes et al.¹⁰ who performed the fit, initially with $\Gamma = 0$, then transformed the parameters to the representation with $\Delta = 0$, and found they could be further refined.

Lagakos and Cummins found that Θ varied linearly with temperature in CsDA, rather than $T\Theta$ varying linearly with temperature, as had been found in earlier experiments^{10,17}.

11. 6 THE MATRIX INVARIANTS.

Difficulties arise because of the effects of the coupled eigenvectors and the overdamped modes, so that there is a considerable range of values which can produce a similar fit to the spectrum. The question arises as to whether there is an alternative, and possibly better method of obtaining T_0 , which is less sensitive to the data, and also independent of the eigenvector choice.

One might expect that in varying any of the parameters in a way which will still give a reasonable fit to the Raman spectrum, the invariants under a unitary transformation, the trace and determinant of the Greens function matrix defining the coupled modes, would remain constant. These invariants are

$$\omega_1^2 \omega_2^2 - \Delta^4 = \alpha_1 \quad (12)$$

$$\omega_1^2 + \omega_2^2 = \alpha_2 \quad (13)$$

$$\gamma_1 \gamma_2 - \Gamma^2 = \beta_1 \quad (14)$$

$$\gamma_1 + \gamma_2 = \beta_2 \quad (15)$$

The information about T_0 cannot be extracted from α_2 , unless some means can be found of accurately calculating ω_2^2 and subtracting

it from α_2 . On the other hand α_1 is expected to decrease to zero at T_0 , irrespective of the choice of eigenvectors. β_1 is very sensitive to the details of the model, because frequently, $\gamma_1 \gamma_2$ is comparable in magnitude to Γ^2 . β_2 is more usually independent of the model.

The parameters α_1 and β_2 are coupled because the modes are overdamped, therefore a suitable choice to determine the temperature dependence of the soft mode might be α_1/β_2 . This is expected to vary as $(T - T_0)/T$.

11. 7 ANALYSIS

The parameters

$$\lambda = \frac{\omega_1^2 T}{\gamma_1} \quad (16)$$

and

$$\mu = \frac{\alpha_1 T}{\beta_2} = \frac{(\omega_1^2 \omega_2^2 - \Delta^4) T}{(\gamma_1 + \gamma_2)} \quad (17)$$

have been calculated as a function of temperature for all the available data 8,10,11,13,16. When the data came from different sources,

these were combined, and a straight line fitted to the points, enabling a comparison of the methods to be made. The deviation of the points about a straight line is sometimes better for μ than for λ , and sometimes the reverse.

A virtue of using the μ method is that the Barker-Hopfield transformation does not affect the invariants, so the parameters can be obtained from either the $\Delta = 0$ or the $\Gamma = 0$ modes, or indeed, from any of the other infinite number of eigenvector choices.

The parameter ω_1^2 as a function of temperature was also fitted by a straight line. With the exception of KDP, this does not appear to provide a very good estimate of T_0 , so figures showing ω_1^2 plotted against temperature have been omitted.

The λ and μ data are plotted as a function of temperature for KDP, KDA, CsDA and RbDA in Figures 1-4 respectively. Figure 5 shows the λ and μ data for ADP and DKDA and Figure 6 shows the λ and μ data for DRbDA and DCsDA. The open circles on the graphs for the deuterated isomorphs have not been fitted by a straight line for the reasons given in the section on the deuterated materials.

On comparing the values of T_0 obtained by the three methods, and tabulated in Table 1, $T_0(\omega_1^2)$ is found to be unsatisfactory in many cases. $T_0(\mu)$ always comes out lower than $T_0(\lambda)$; usually by an amount about equal to the sum of the errors in each of the values. This is surprising since T_0 is where $\omega_1^2 \rightarrow 0$ (or alternatively $\gamma_1 \rightarrow \infty$), and this has the same effect on both expressions. It, however, illustrates the difficulty of reliably extracting T_0 from data.

11. 8 THE HYDROGENATED ISOMORPHS

In KDP, both methods give T_0 in the region 110 - 130 °K. The λ and μ data of Lagakos and Cummins¹³ show signs of an upward curvature. If this is taken into account, the difference between $T_0(\lambda)$ and $T_0(\mu)$ for their data might disappear, and both would occur at lower temperatures, nearer T_c^x . Ryan's data is less accurate, so similar conclusions cannot be drawn from it.

Lagakos and Cummins¹³ find that their results are more linear when they plot ω_1^2 as a function of temperature. This is surprising, since the damping is quite large ($\gamma_1 \simeq 3 - 5 \omega_1$). They only publish their results for KDP up to 206 °K, but say in a footnote that when temperatures up to 300 °K are included, there is a marked deviation from the simple temperature dependence found below about 240 °K. Within experimental error, T_0 does not appear to be different from T_c^x (= 117 °K)²⁴.

In KDA the λ and μ data both extrapolate to zero below the transition temperature. The λ data leads to a value of T_0 not all that different from the value which T_c^x might be expected to take. On the other hand, $T_0(\mu)$ and T_c^x are possibly different, but not significantly so.

T_0 lies 15 to 35 degrees below the transition temperature in CsDA, depending on whether $T_0(\lambda)$ or $T_0(\mu)$ is chosen. It is worth noting that Ryan's data⁸ produces values of $T_0(\lambda)$ for both ω_1 and ω_2 . In earlier work¹⁸ the mode which gives $T_0(\lambda) = 66^\circ\text{K}$ was chosen, because this mode shows the heavier damping. The other mode has been chosen here, since its values lie closer to those found by Tornberg et al.¹¹.

Pollina and Garland²⁵ show that the difference between the free and clamped Curie temperatures is much larger in CsDA than in KDP. The difference, $T_c - T_c^x = 20$ degrees, is explained by the unusually low shear elastic constant found in CsDA compared to that found in KDP²⁶. From this, Lagakos and Cummins¹⁴ conclude that there is no evidence for a relaxing self energy term affecting the ferroelectric soft mode in CsDA. Nevertheless there remains a 15 degree difference between $T_0(\mu)$ and T_c^x .

Although $T_0(\lambda)$ and $T_0(\mu)$ are different for RbDA, their experimental errors both cover T_c , and hence T_c^x , which is probably a few degrees lower.

The λ values of ADP possibly fall on an upwardly curved line. This would bring $T_0(\lambda)$ to a lower value, nearer to that of $T_0(\mu)$. Although T_0 is about 80 degrees lower than the transition temperature, this is not evidence for a relaxing self energy term, since ADP is antiferroelectric, so the transition is dependent on the freezing of a zone boundary phonon at T_c . A comparison would have to be made

TABLE 1

This shows the values of T_0 obtained by the three methods. The transition temperature and sources are also indicated. If the data produces more than one value of ω_1^2 or λ then the value which gives the least temperature dependent value of λ is given in brackets.

$$\lambda = \frac{\omega_1^2 T}{\gamma_1}$$

$$\mu = \frac{(\omega_1^2 \omega_2^2 - \Delta^4) T}{(\gamma_1 + \gamma_2)}$$

TABLE 1

MATERIAL	$T_o(\omega_1^2)$	$T_o(\lambda)$	$T_o(\mu)$	T_c	REFERENCES
KDP	83 ± 6 117 ± 1.5 98 ± 5	115 ± 6 128 ± 3 128 ± 4	108 ± 6 126 ± 3 122 ± 4	123	8 13 8, 13
KDA	— -43 ± 23 — —	97 ± 5 90 ± 9 86 ± 7 92 ± 6	79 ± 3 63 ± 4 62 ± 5 71 ± 7	96	8 16 10 8, 10
RbDA	53 ± 55 46 ± 57	119 ± 10 115 ± 8	101 ± 8 97 ± 9	110	16 10
CsDA	— — — —	135 ± 18 (66 ± 5) 107 ± 16 (-99 ± 12) 126 ± 3 (-70 ± 13) 130 ± 9 (0 ± 87)	107 ± 11 73 ± 33 112 ± 12 109 ± 7	143	8 16 10 8, 10
ADP	—	99 ± 20	60 ± 12	148	8
DKDA	223 ± 10 160 ± 23	224 ± 9 173 ± 6	223 ± 9 169 ± 7	160	16 10
DRbDA	— 169 ± 13	-136 ± 37 169 ± 10	— 165 ± 12	170	16 10
DCsDA and	(-20 ± 69) 198 ± 8 (89 ± 55)	71 ± 56 192 ± 5	63 ± 48 192 ± 4	203	16 10

FIGURE 1.

The two graphs show respectively the λ and μ data as a function of temperature for KDP.

Data: open circles - Ryan et al.^{8,9}
closed circles - Lagakos et al.¹³

$$T_c = 123^\circ\text{K}.$$

KDP

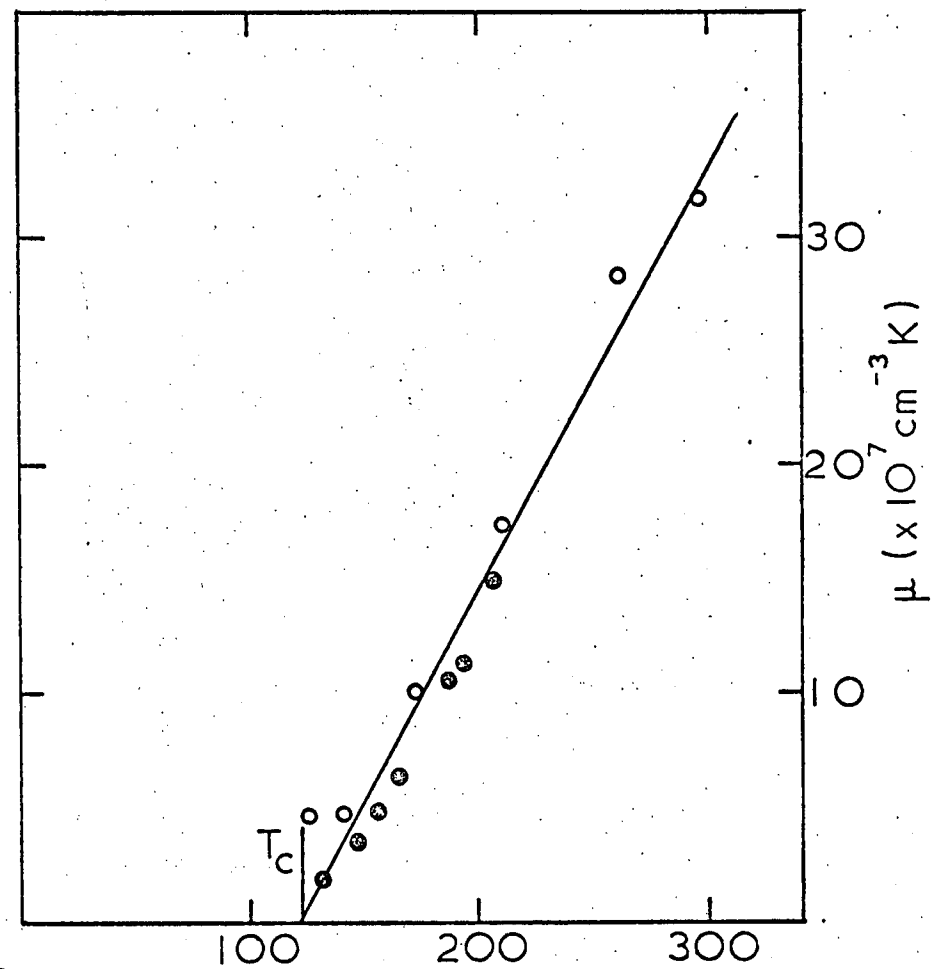
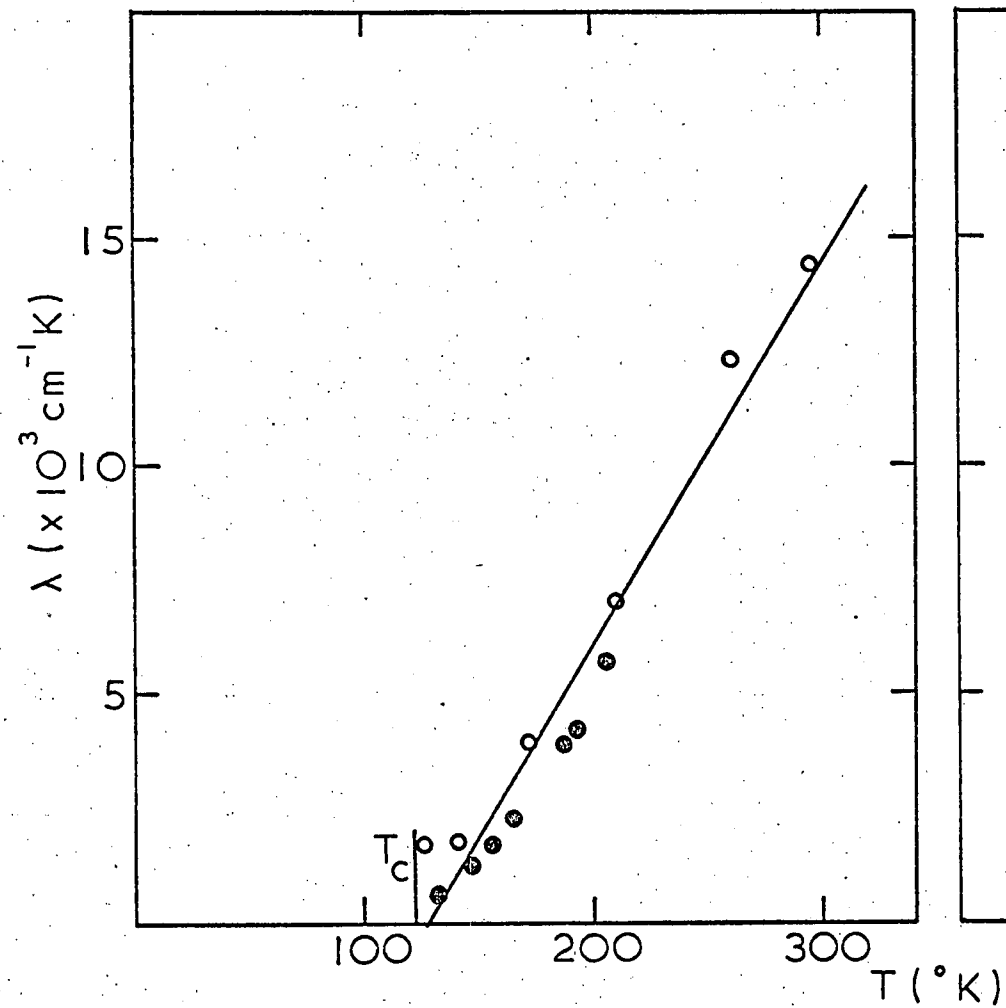


FIGURE 2.

The two graphs show respectively the λ and μ data as a function of temperature for KDA.

Data: open circles - Ryan et al.^{8,9}

closed circles - Leung et al.¹⁶, Lowndes et al.¹⁰ or Tornberg et al.¹¹

$T_c = 96^\circ\text{K.}$

K D A

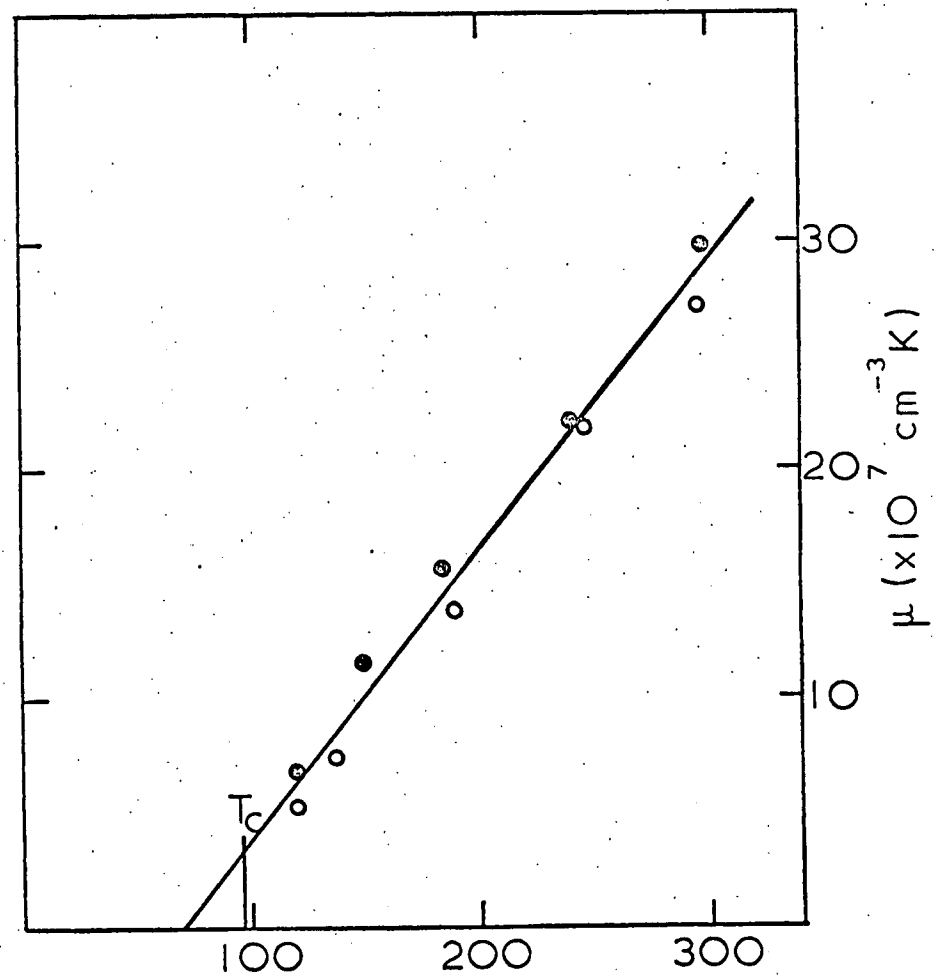
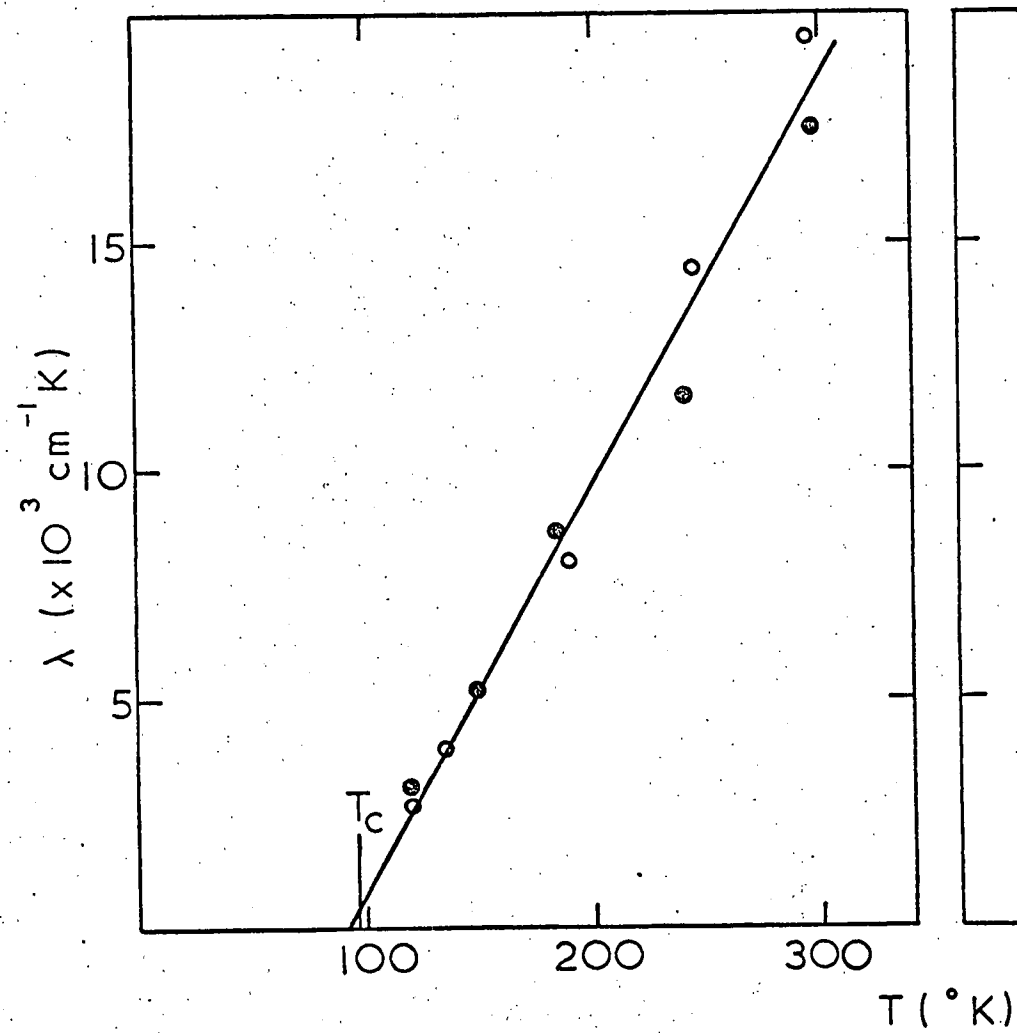


FIGURE 3.

The two graphs show respectively the λ and μ data as a function of temperature for RbDA.

Data: open circles - Ryan et al.^{8,9}

$$T_c = 110^\circ\text{K}.$$

RbDA

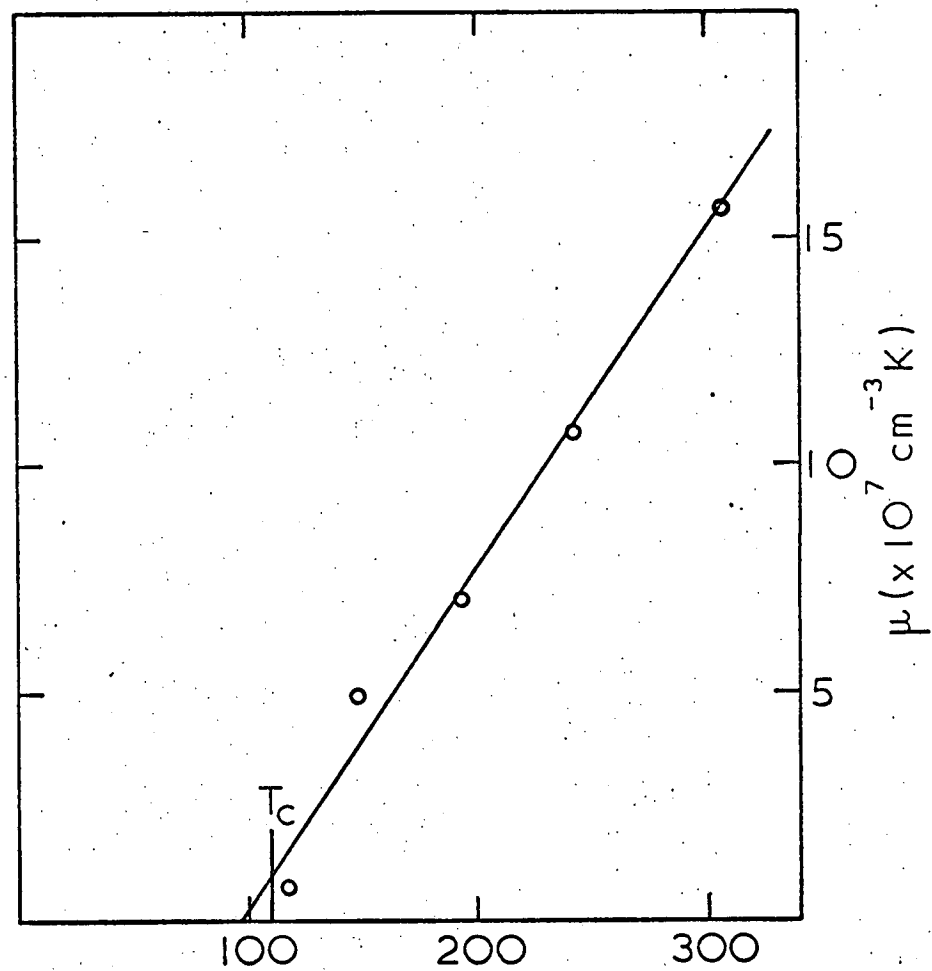
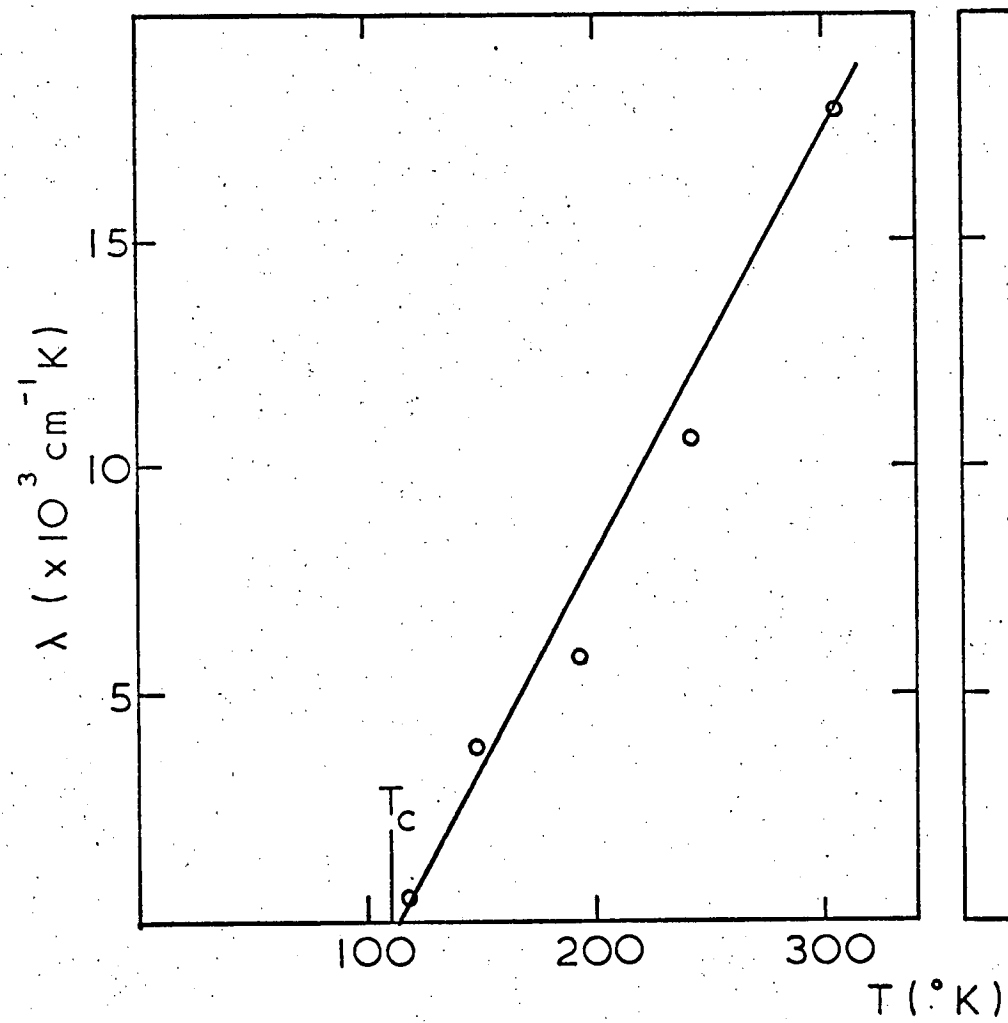


FIGURE 4.

The two graphs show the λ and μ data plotted as a function of temperature for CsDA.

Data: open circles - Ryan et al.^{8,9}

closed circles - Tornberg et al.¹⁰ or Lowndes et al.¹¹

$T_c = 143^\circ\text{K}.$

Cs D A

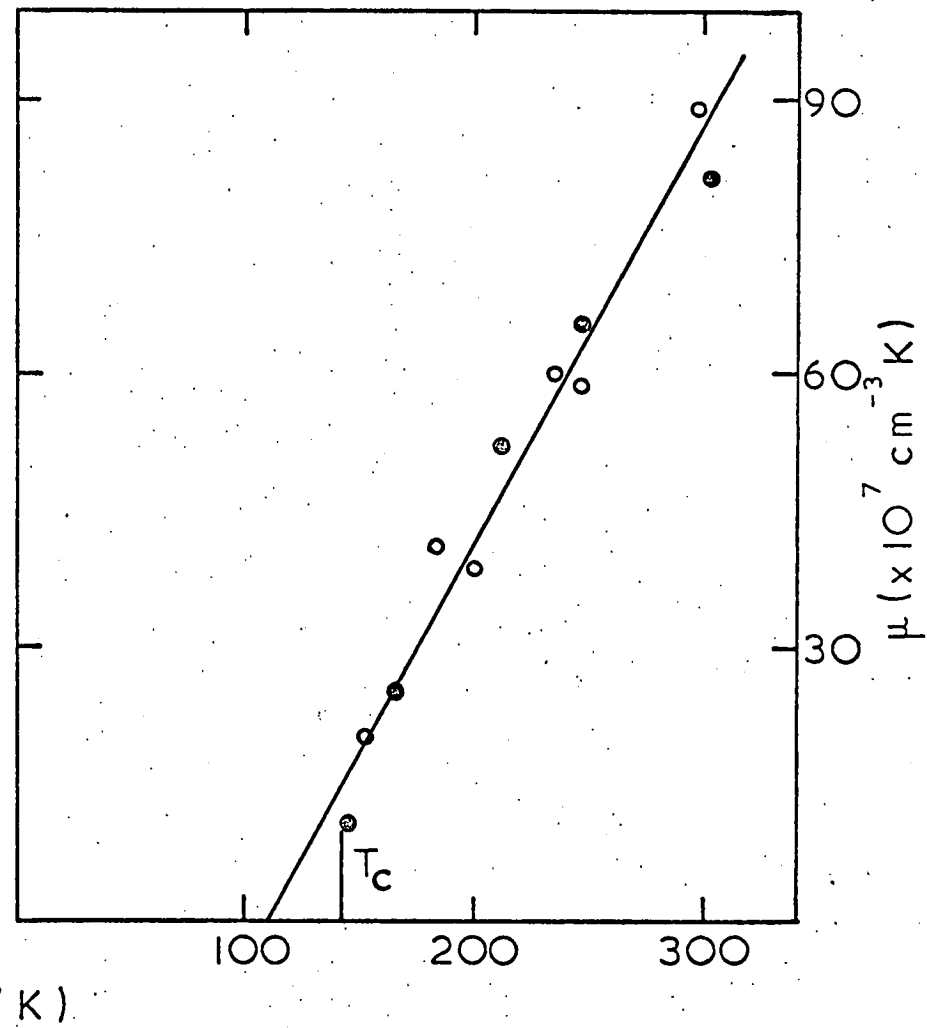
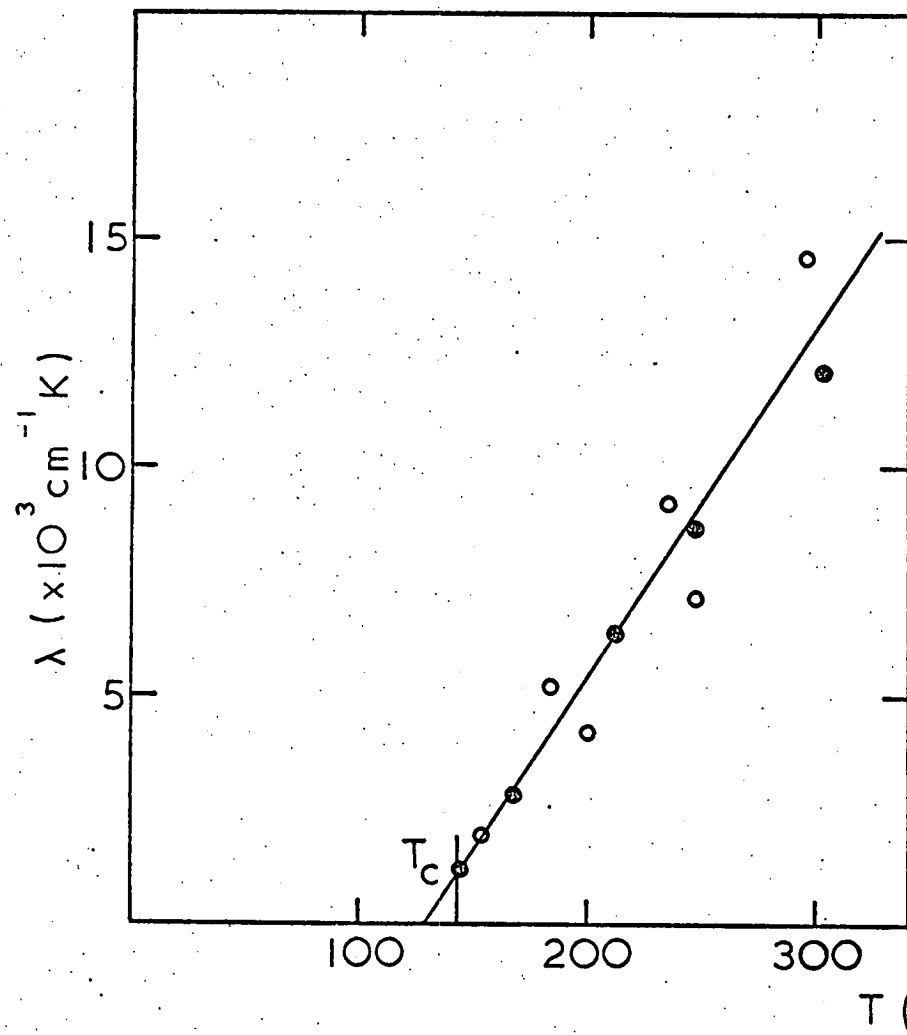


TABLE 2

Columns 1 and 3 show the values of λ and μ obtained by Lowndes et al.¹⁰ for the undeuterated samples directly after the transformation to the form with $\Delta = 0$ and columns 2 and 4 show the values obtained after further refinement of the data. Only the latter have been plotted in Figures 2,3 and 4.

TABLE 2.

Material	$\lambda = \frac{\omega_1^2 T}{\gamma_1} (\times 10^3 \text{ cm}^{-1} \text{ K})$		$\mu = \frac{(\omega_1^2 \omega_2^2 - \Delta^4) T}{(\gamma_1 + \gamma_2)} (\times 10^6 \text{ cm}^{-3} \text{ K})$		
	Γ_{trans}	Δ	Γ_{trans}	Δ	T(°K)
K D A	2.9	3.0	67	68	120
	5.2	5.2	114	116	149
	7.4	7.6	153	157	184
	11.5	11.6	220	220	240
	18.1	17.5	296	298	297
Rb D A	0.4	0.5	6	7	118
	3.7	3.9	48	50	148
	5.8	5.8	70	71	193
	10.8	10.6	109	106	242
	19.6	17.9	159	156	305
Cs D A	3.3	1.2	30	10	145
	2.4	2.8	23	25	168
	6.3	6.4	52	52	212
	8.8	8.6	67	65	247
	11.7	12.1	76	82	302
before		after	before		after
refinement			refinement		
(All parameters are in the form with $\Delta = 0$)					

with the temperature dependence of the static dielectric constant, but it is difficult to obtain a reliable value of the Curie temperature ⁹.

Lowndes et al.¹⁰ initially performed their fits with $\Gamma = 0$, then transformed the parameters to the representation with $\Delta = 0$, and found they could be further refined. In most cases this has no significant effect on the parameters λ and μ in the hydrogenated isomorphs KDA, RbDA and CsDA. Table 2 shows the values of the parameters obtained by the two methods.

11. 9 THE DEUTERATED ISOMORPHS

The data for the deuterated isomorphs all came from the same group of experiments ^{10,11,16}. Initially the Raman spectrum was fitted up to 230 cm^{-1} ¹⁶. Column 1 of Tables 3 and 4 lists respectively the parameters λ and μ obtained for these fits. No satisfactory values of the critical temperature are obtained from these values. Lowndes et al.¹⁰ point out that there is a poor fit to the Raman spectrum, because of additional phonon modes in the range 150 to 300 cm^{-1} , which are not present in the hydrogenated isomorphs. The Raman spectra were fitted ^{10,11} up to 140 cm^{-1} in the representation with $\Gamma = 0$. This produced a better overall fit. If the results are then transformed to the representation with $\Delta = 0$, the values for λ and μ in column 2 of Tables 3 and 4 are obtained. These are marked as open circles on graphs 5 and 6. Lowndes et al.¹⁰ found that these transformed parameters could be further refined, leading to the results for λ and μ obtained in column 3 of Tables 3 and 4. These are marked as closed circles on Figures 5 and 6. Only these points are fitted by the straight lines since the parameters have changed so much. The values of T_0 obtained are not significantly different from the transition temperatures in these materials. From

TABLE 3.

This shows the values of λ in the deuterated compounds obtained with fits up to 230cm^{-1} (column 1) and 140cm^{-1} (column 2). These are the parameters obtained directly after applying the Barker Hopfield transformation to obtain the parameters in the form with $\Delta = 0$. The third column shows the value of λ obtained on further refinement of the 140cm^{-1} fits. Column 4 shows the temperature.

TABLE 3.

$$\lambda = \frac{\omega_1^2 \tau}{\gamma_1} \quad (10^3 \text{ cm}^{-1} \text{ K})$$

MATERIAL	$\Gamma_{\text{trans}} (230\text{cm}^{-1})$	$\Gamma_{\text{trans}} (140\text{cm}^{-1})$	$\Delta (140\text{cm}^{-1})$	T
DKDA	2.5	0.1	1.7	219
	3.0	1.0	2.5	236
	3.7	0.8	3.6	254
	4.6	2.8	4.1	272
	5.6	4.6	4.5	291
DRbDA		9.3	0.5	186
	11.5			194
		9.7	1.4	219
	11.8			227
	10.4			245
		10.8	3.1	255
	11.2			263
		11.4	3.7	273
	14.2			299
DCsDA		6.2	0.3	210
	8.0			219
	9.0	8.6	0.5	227
	9.4			236
		9.0	1.0	265
	9.6			274
Continued.	10.4	9.7	1.2	283

continued

TABLE 3.

MATERIAL	$\Gamma_{\text{trans}}(230\text{cm}^{-1})$	$\Gamma_{\text{trans}}(140\text{cm}^{-1})$	$\Delta(140\text{cm}^{-1})$	T
DCsDA	10.5	11.8	1.6	292
	10.5			301
	10.6			310
	10.9			326

TABLE 4.

This shows the values of μ in the deuterated compounds obtained with fits up to 230 cm^{-1} (column 1) and 140cm^{-1} (column 2). These are the parameters obtained directly after transforming to the form with $\Delta = 0$. Further refinement of the data in column 2 provides the values of μ obtained in column 3. Column 4 shows the temperature.

TABLE 4.

$$\mu = \frac{(\omega_1^2 \omega_2^2 - \Delta^4) T}{(\gamma_1 + \gamma_2)} \quad (\times 10^6 \text{ cm}^{-3} \text{ K})$$

MATERIAL	$\Gamma_{\text{trans}}(230\text{cm}^{-1})$	$\Gamma_{\text{trans}}(140\text{cm}^{-1})$	$\Delta(140\text{cm}^{-1})$	T
DKDA	72	2	43	219
	87	25	62	236
	103	18	76	254
	128	69	98	272
	112	112	106	291
DRbDA		118	5	186
	135			194
		106	15	219
	129			227
	107			245
		107	32	255
	112			263
		111	37	273
DCsDA	129			299
		117	42	308
		36	2	210
	57			219
	62	50	4	227
	63			236
		55	7	265
	65			274
	69	58	9	283
	70			292
	66	65	12	301
	68			310
	70			326

FIGURE 5.

(a) This graph shows the λ and μ data as a function of temperature for the antiferroelectric, ADP.

Data: Ryan et al.⁸ -

closed circles, λ plotted

open circles, μ plotted

$T_c = 148^\circ\text{K}.$

(b) and (c) The two graphs show respectively the λ and μ data plotted as a function of temperature for DKDA.

Data: Tornberg et al.¹⁰ or Lowndes et al.¹¹

open circles: Data after transforming from the form $\Gamma = 0$ to the form $\Delta = 0$.

closed circles: Data after further refinement. The straight line is only fitted to this data.

$T_c = 160^\circ\text{K}.$

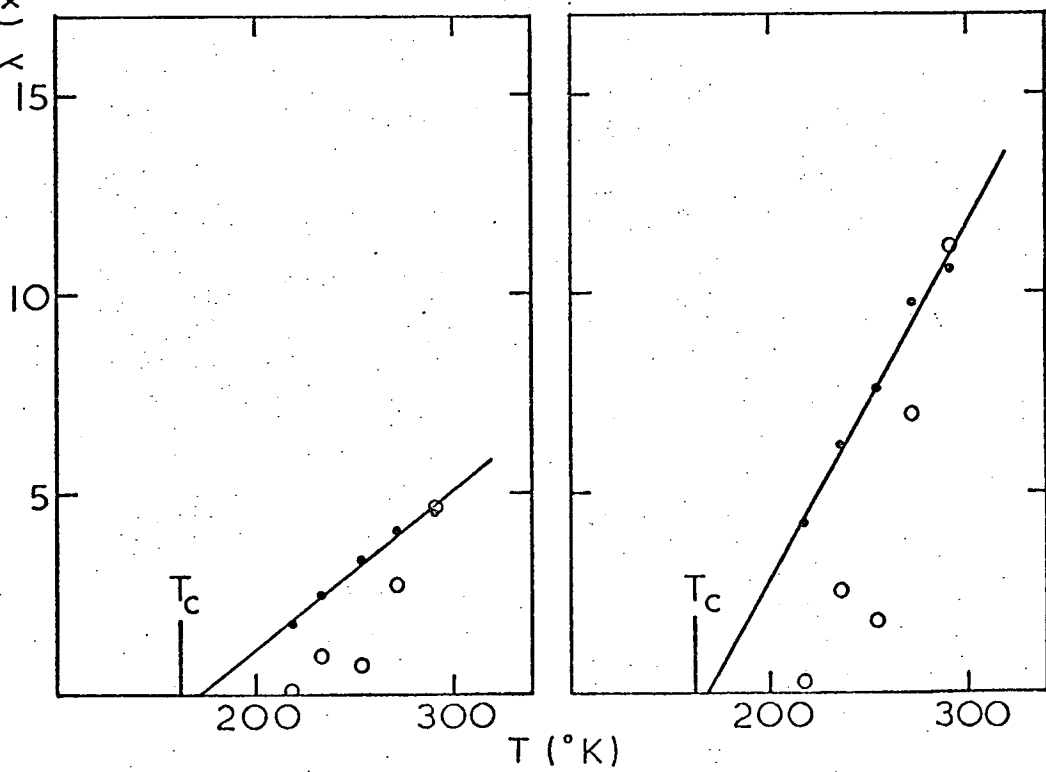
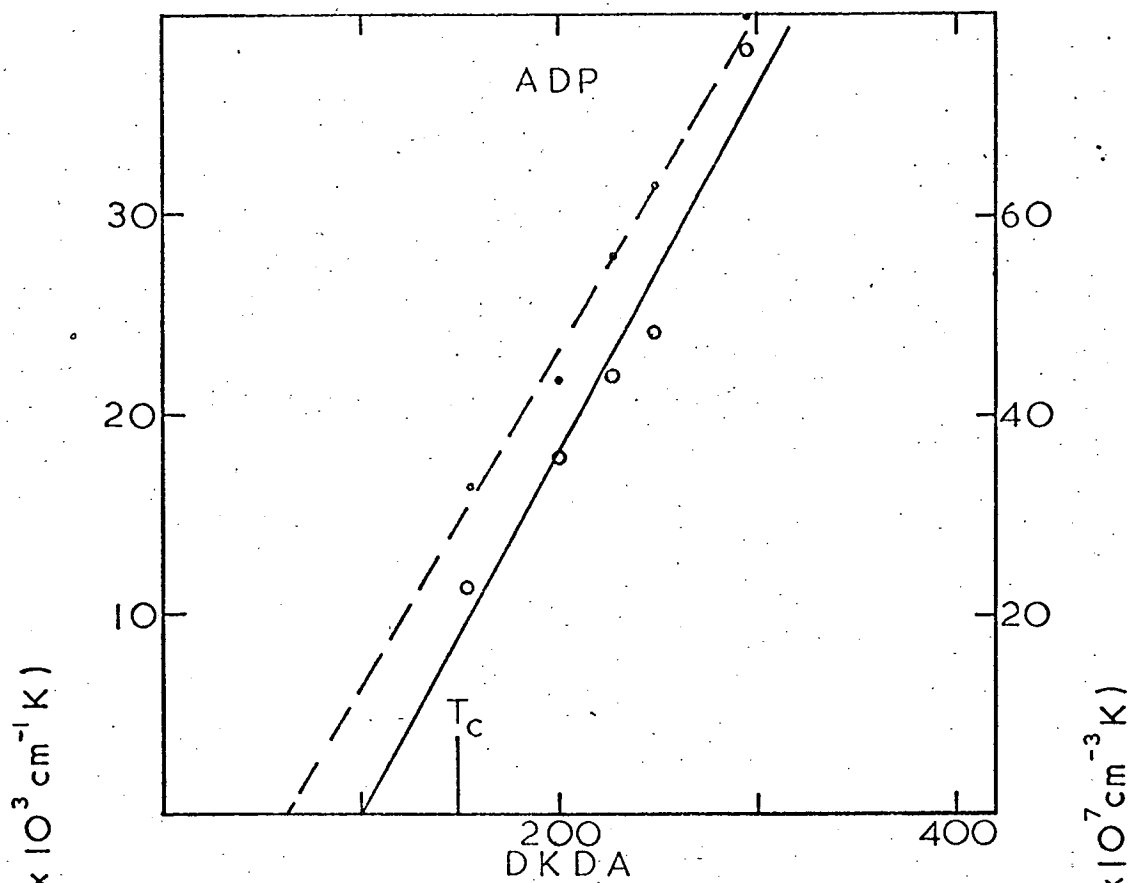


FIGURE 6.

(a) and (b). The two graphs show respectively the λ and μ data plotted as a function of temperature for DRbDA

$$T_c = 170^\circ\text{K.}$$

(c) and (d). The two graphs show respectively the λ and μ data plotted as a function of temperature for DCsDA.

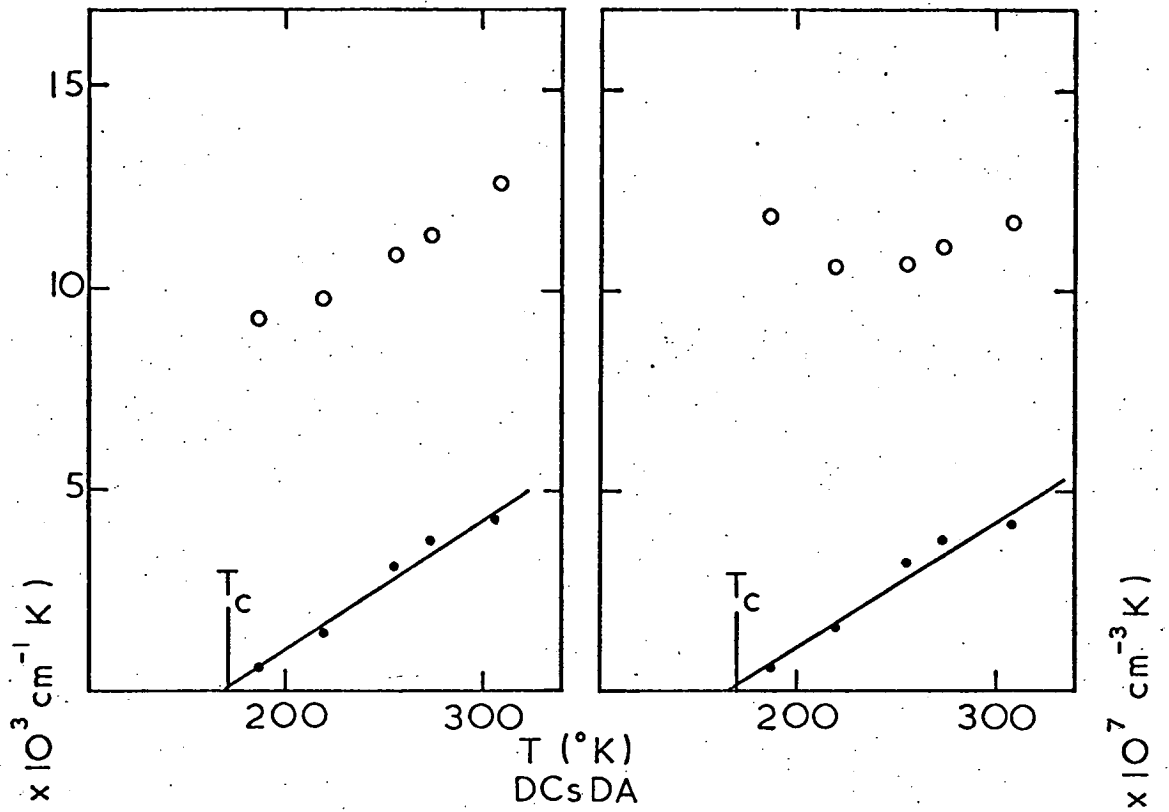
$$T_c = 203^\circ\text{K.}$$

Data: Tornberg et al.¹⁰ or Lowndes et al.¹¹

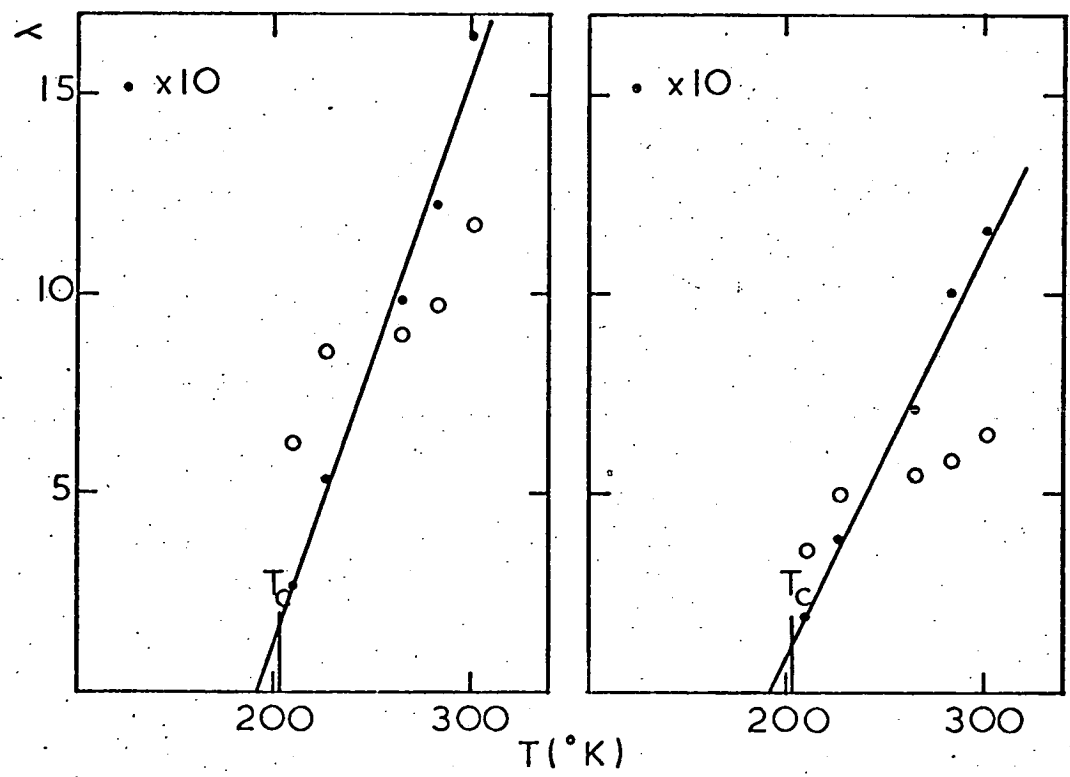
Open circles: Data after transforming from the form $\square$
= 0 to the form $\triangle = 0$.

Closed circles: Data after further refinement. The straight line is only fitted to this data.

DRbDA



DCsDA



the graphs, it is noticable that in contrast to the hydrogenated samples, the choice of modes with which the fit is made can produce a significant difference in the parameters, and they are no longer related by a simple transformation. If, as is suggested in Chapter IV, the deuterated isomorphs have peculiar growth properties which make it difficult to ensure a uniform distribution of hydrogen and deuterium throughout the crystal, then the measured temperature dependences of the ferroelectric modes in these crystals must be put in some doubt.

11.10 CONCLUSIONS

Data is gathered together on KDP, KDA, RbDA, CsDA, ADP, DKDA, DRbDA and DCsDA from different sources, and it is presented in a uniform form.

In determining the temperature variation of the ferroelectric mode, it is important to choose the correct basis vectors. These are the ones obtained from an analysis of the data in the form with $\Delta = 0$. There are then a number of ways in which the temperature variation of the modes can be found. The behaviour of ω_1^2 was in many ways found to be unsatisfactory. More satisfactory was that of $\omega_1^2 T / \gamma_1$ and $(\omega_1^2 \omega_2^2 - \Delta^4) / (\gamma_1^2 + \gamma_2^2)$ but in general these produced different results with the latter giving a lower temperature, T_0 .

Irrespective of the method used to obtain T_0 , some crystals show evidence for a difference between T_0 and T_c . Of the undeuterated crystals we can say that T_0 and T_c are different in CsDA, with the possibility of being different in KDA. Whether this is evidence for the self energy term considered by Cowley and Coombs²⁰ is put in some doubt by the recent measurements of the clamped Curie temperature of CsDA by Pollina and Garland²⁵ and the Raman scattering by Lagakos and Cummins¹⁴.

The results in the deuterated isomorphs must be put in some doubt in view of the widely differing parameters which can be obtained with the different fitting procedures. The results for DKDA (which we assign to Leung et al.¹⁶), illustrate that showing the parameters are well fitted by a straight line is not sufficient proof that the fits have been properly performed. In this example the three values of T_0 are in perfect agreement, but the results are 60 degrees above the transition temperature (see Table 1), which is clearly incorrect.

If the concentration variation in DCsDA (see Chapter V) is a general property of the deuterated arsenates, then the results of many of the experiments on these materials would need to be reconsidered.

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CHAPTER 111.

The Debye Waller Factor and Structural Phase Transitions.

111. 1 INTRODUCTION.

While there is much interest in the understanding of critical phenomena occurring at structural phase transitions, unfortunately many of the experiments in this field are difficult, time consuming and possible only when large single crystals are available. The Debye-Waller factor does not provide nearly such detailed information about the critical fluctuations as many other quantities, but it has the advantage that it can be measured readily by X-ray diffraction, neutron diffraction or Mossbauer spectroscopy and a closely related quantity can be measured by magnetic resonance techniques. In this chapter we discuss the effect on the Debye-Waller factor of the critical fluctuations occurring close to a structural phase transition, and suggest that some interesting information can be obtained by measuring it.

The behaviour of the Debye-Waller factor close to structural phase transitions has been discussed previously by several authors.¹⁻⁴ It is appropriate, however, to re-examine the topic partly because of the variety of results obtained by these authors, but also because of the recent advances made as a result of applying renormalisation group theory to these transitions⁵. In particular these results have emphasised that the critical fluctuations are dependent upon the degeneracy of the fluctuations and whether or not the transition is to a ferroelectric phase.

The Debye-Waller factor of an atom of type K in the ℓ th unit cell is given by

$$W_{\alpha\beta} = \langle U_{\alpha}(\ell K) U_{\beta}(\ell K) \rangle, \quad (1)$$

where $\underline{U}(\ell K)$ is the displacement vector of the atom. It is usually more convenient to rewrite the displacement in terms of the frequencies $\omega(\underline{qj})$ and eigenvectors $\underline{e}(K, \underline{qj})$ of the harmonic normal modes of vibration

when

$$W_{\alpha\beta} = \frac{\hbar}{2NM_K} \sum_{\underline{q}j} \frac{e_{\alpha}(K, \underline{q}j) e_{\beta}^*(K, \underline{q}j)}{\omega(\underline{q}j)} (2n(\underline{q}j) + 1), \quad (2)$$

$$\text{where } n(\underline{q}j) = \left[1 - \exp\left(-\frac{\hbar\omega(\underline{q}j)}{kT}\right) \right]^{-1}$$

is the Bose-Einstein occupation number of the normal mode of wavevector $\underline{q}$ and branch labelled by j . M_K is the mass of the K^{th} atom in the unit cell. The summation is over all the phonon branches, j , and all wavevectors, $\underline{q}$, in the first Brillouin zone - a total of N modes. In an anharmonic crystal the leading corrections to this expression are obtained by replacing the harmonic frequencies by the renormalised frequencies which include the effects of the anharmonicity⁶.

Structural phase transitions may frequently be treated as instabilities of the crystal against particular normal modes of vibration. It is convenient to divide $W_{\alpha\beta}$ into two terms; a part which is regular at the phase transition and a part which is singular and which arises from those terms in eqn. 1 for which the mode $(\underline{q}j)$ is a temperature dependent mode associated with the phase transition. These modes are then expected to have a low frequency compared with $k_B T / \hbar$ so that the Debye-Waller factor becomes

$$W_{\alpha\beta} = W_{\alpha\beta}^R + W_{\alpha\beta}^S, \quad (3)$$

where at high temperatures $W_{\alpha\beta}^R$ is proportional to temperature and

$$W_{\alpha\beta}^S = K_B T \sum_{\underline{q}j} \frac{C_{\alpha\beta}(\underline{q}j)}{\omega(\underline{q}j)^2} \quad (4)$$

The summation is only over the temperature dependent modes and the $C_{\alpha\beta}$ are temperature independent constants.

Although eqn. 4 was obtained within the framework of weakly anharmonic lattice dynamics, it is also applicable to order-disorder transitions if $\omega(\underline{q}j)^2$ is identified with the inverse of the static susceptibility for wavevector, $\underline{q}$.

The frequency of the nuclear quadrupole resonance is determined by the electric field gradient at the nucleus. The gradient may be expanded in terms of the normal mode displacements when their contribution to the gradient may be written² as

$$V_{\alpha\beta} = \frac{1}{N} \sum_{\mathbf{qj}} \frac{V_{\alpha\beta}(\mathbf{qj})}{\omega(\mathbf{qj})} (2n(\mathbf{qj}) + 1). \quad (5)$$

In a similar way to the Debye-Waller factor this may be separated into a regular and singular part close to T_c and the latter written as

$$V_{\alpha\beta}^S = \frac{2K_B T}{N\hbar} \sum_{\mathbf{qj}} \frac{V_{\alpha\beta}(\mathbf{qj})}{\omega(\mathbf{qj})^2} \quad (6)$$

In the remainder of this chapter we discuss the form of $w_{\alpha\beta}^S$ and $V_{\alpha\beta}^S$ at different phase transitions. The results are clearly dependent upon the form of $\omega(\mathbf{qj})^2$ allowed by the symmetry of the crystal so that different results are obtained for different types of structural phase transitions.

In section 6. we discuss the validity of our form of equation in the less than ideal situation of an experiment on a "real crystal" where some of the assumptions we have made may not always hold. In section 7. we introduce one of these "real crystal" effects - a coupling of the temperature dependent mode to the acoustic waves, through piezoelectric coupling.

111. 2 UNIAXIAL FERROELECTRICS.

Uniaxial ferroelectrics have a unique ferroelectric axis and consequently only one branch, j , which is anomalously temperature dependent. For small wavevectors the eigenvector of these modes may be taken as independent of wavevector, while the frequencies of the mode

are given by

$$\omega(\underline{q})^2 = \omega_0^2 + B^2 |\underline{q}|^2 + C^2 \frac{q_z^2}{|\underline{q}|^2}, \quad (7)$$

where z is the ferroelectric axis, and ω_0 is the frequency of the transverse optic mode as $q \rightarrow 0$. As $T \rightarrow T_c$, the transition temperature, $\omega_0 \rightarrow 0$. The constant B determines the dispersion of the transverse optic mode. (In principle B could be different for wave-vectors along the x, y and z directions, but such generality does not change the functional dependence of our results). The constant C is determined by the strength of the macroscopic electric field of the crystal and is the characteristic feature of uniaxial ferroelectrics. The singular part of the Debye-Waller factor is then proportional to

$$Y = \frac{k_B T}{N_S} \sum_{\underline{q}} \frac{1}{\omega(\underline{q})^2}, \quad (8)$$

where N_S is the number of temperature dependent modes in the summation.

The expression for Y may be evaluated by converting the summation to an integral over all $|\underline{q}| < Q$ to give

$$Y = \frac{k_B T \int_0^Q \int_0^\pi \frac{q^2 \sin \theta d\theta dq}{\omega_0^2 + B^2 q^2 + C^2 \cos^2 \theta}}{\int_0^Q \int_0^\pi q^2 \sin \theta d\theta dq} \quad (9)$$

Now if $X = BQ/\omega_0$ then

$$Y = \frac{3k_B T \omega_0^2}{B^3 Q^3 C} \int_0^X \frac{x^2}{\sqrt{1+x^2}} \tan^{-1} \left\{ \frac{C}{\omega_0 \sqrt{1+x^2}} \right\} dx \quad (10)$$

This result can only be further simplified if $C \gg BQ$ and $C \gg \omega_0$ when

$$Y = \frac{3\pi k_B T}{2BQC} \left[\frac{\sqrt{1+X^2}}{X} - \frac{1}{X^2} \log (X + \sqrt{1+X^2}) \right], \quad (11)$$

which close to T_c ($BQ \gg \omega_0$) gives

$$Y = \frac{3\pi k_B T}{2QBC} \left[1 - \frac{\omega_0^2}{B^2 Q^2} \log \left(\frac{2BQ}{\omega_0} \right) \right] \quad (12)$$

The first part of this expression is regular as $T \rightarrow T_c$. In uniaxial ferroelectrics ω_0^2 is both found experimentally⁷ and theoretically^{8,9} to vary as $(T - T_c)$. Consequently the singular part of Y varies as

$$Y^s = AT(T - T_c) \log (A'(T - T_c)), \quad (13)$$

where A and A' are constants.

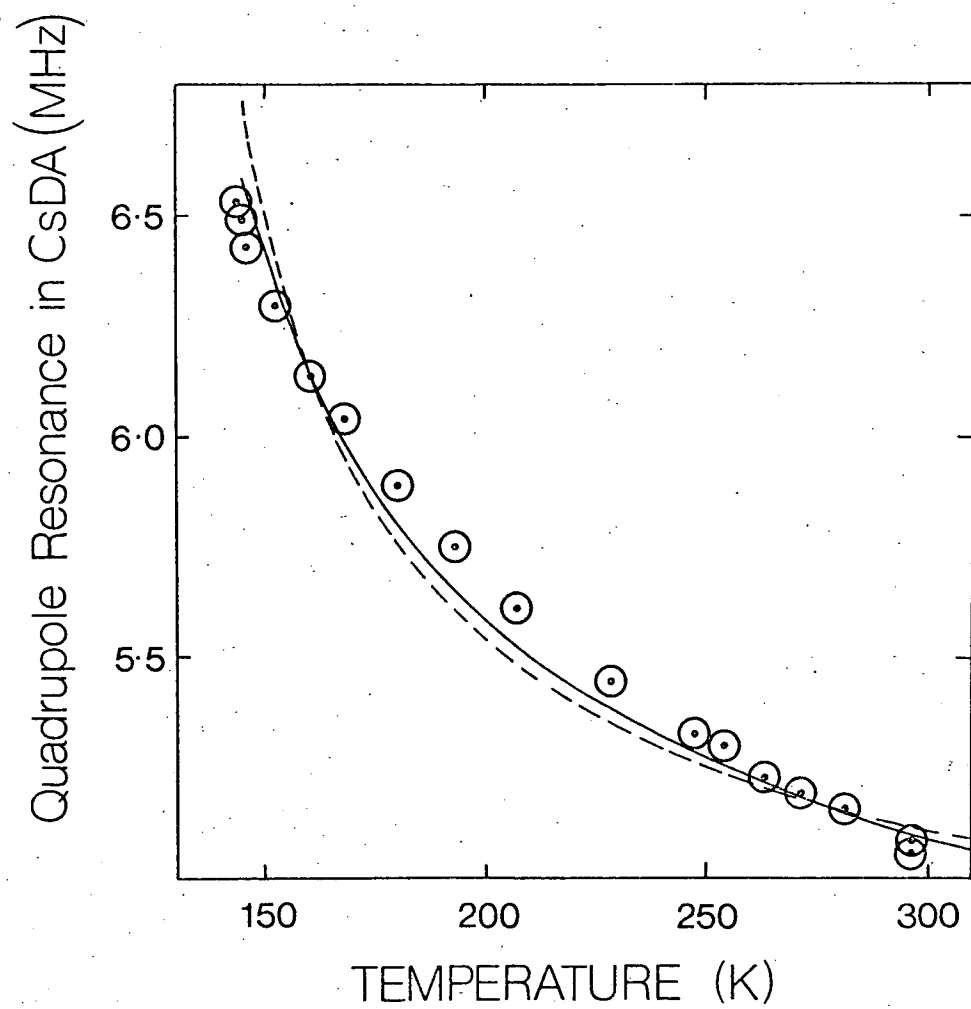
This result agrees with that obtained by Vaks et al.¹ for order-disorder ferroelectrics, but the above discussion shows it to be characteristic of uniaxial ferroelectrics whether they are of displacive or order-disorder character. It differs from the results of Blinc et al.² who assumed $\omega_0^2 = \omega(qj)^2$ for all wavevectors and of Scott and Worlock⁴ who neglected the effect of the macroscopic electric field.

The above results for Y have been compared with measurements² of the As^{75} nuclear quadrupole coupling coefficient of CsDA. In this case $B^2 Q^2 \gg C^2$, so that eqn. 3 was used and the integration performed numerically.

In the calculations ω_0^2 was put equal to $A(T - T_c)$ where in the calculations shown in Figure 1, T_c was set to either the clamped Curie temperature, 129K, or the free Curie temperature, 143K¹⁰. The agreement with the former choice of T_c is very satisfactory, with the parameters $C^2/A = 90K^{-1}$ and $(BQ)^2/A = 121K^{-1}$. Unfortunately the value of these parameters are highly correlated and similar agreement with

FIGURE 1.

The As^{75} nuclear quadrupole coupling coefficient of CsDA as a function of temperature. The experimental points are taken from the work of Blinc et al.², and the solid and dotted curves give the results of calculations using the clamped and free transition temperatures.



the experimental results can be obtained with other pairs of values which are quite different. The parameter values may, however, be compared with those deduced from neutron scattering measurements on DKDP¹¹, which yielded $C^2/A = 210 \pm 20K^{-1}$ and $B^2/A = 360 \pm 80K^{-1}$ if Q is expressed in reduced wavevector units ($\frac{aq}{2\pi}$). The cut-off, Q , is then estimated in CsDA to be a reasonable 0.6 of the Brillouin zone. This order of magnitude agreement between the values of these parameters for CsDA and DKDP supports the validity of the above analysis.

It is not surprising that the results shown in Figure 1. with the clamped Curie temperature are more satisfactory than those found with the free Curie temperature. The quadrupole resonance frequency is about 5 MHz, which is most probably above the acoustic resonance frequency of the crystal.

111. 3 PLANAR FERROELECTRICS.

In planar ferroelectrics the ferroelectric axis is confined to a plane. Above the phase transition there are two normal modes which describe the fluctuations of the dipole moments. The dynamical matrix for these modes may be written in the form

$$\begin{bmatrix} \omega_o^2 + B^2|\underline{q}|^2 + C^2 \frac{q_x^2}{|\underline{q}|^2} & C^2 \frac{q_x q_y}{|\underline{q}|^2} \\ C^2 \frac{q_x q_y}{|\underline{q}|^2} & \omega_o^2 + B^2|\underline{q}|^2 + C^2 \frac{q_y^2}{|\underline{q}|^2} \end{bmatrix} \quad (14)$$

where the ferroelectric axis is confined to the XY plane, and ω_o^2 , B^2 and C^2 describe the frequencies of the transverse optic modes as $q \rightarrow 0$, the dispersion of these modes, and the effect of the macroscopic elastic field. More complex forms of the dispersion can be included in the development without altering the functional dependence of the results.



The dynamical matrix may be diagonalised to yield two modes for each wavevector

$$\omega(\underline{q}1)^2 = \omega_0^2 + B^2 q^2 \quad (15)$$

$$\omega(\underline{q}2)^2 = \omega_0^2 + B^2 q^2 + c^2 (q_x^2 + q_y^2) / |\underline{q}|^2 \quad (16)$$

The singular part of the Debye-Waller factor is then proportional to

$$Y = \frac{K_B T}{N_s} \sum_{\underline{q}} \left[\frac{1}{\omega(\underline{q}1)^2} + \frac{1}{\omega(\underline{q}2)^2} \right] \quad (17)$$

The first term can be evaluated by replacing the summation by an integral over a sphere of radius Q to give

$$Y_1 = \frac{3K_B T}{B^2 Q^2} \left[1 - \frac{\omega_0}{BQ} \tan^{-1} \frac{BQ}{\omega_0} \right] \quad (18)$$

A similar treatment of the second term gives

$$Y_2 = \frac{3K_B T}{2Q^2} \int_0^Q \frac{q^2}{c \sqrt{\omega_0^2 + B^2 q^2 + c^2}} \log \left| \frac{\sqrt{\omega_0^2 + B^2 q^2 + c^2} + c}{\sqrt{\omega_0^2 + B^2 q^2 + c^2} - c} \right| dq \quad (19)$$

This integral can be performed analytically if $c^2 \gg \omega_0^2 + B^2 q^2$ to give

$$Y_2 = K_B T \left(\frac{\omega_0}{CBQ} \right)^2 \left[3\pi \left(\frac{\omega_0}{BQ} \right) - 6 \right] \quad (20)$$

These results show that as $T \rightarrow T_c$ and $\omega_0 \rightarrow 0$, the Debye-Waller factor does not diverge but tends to a finite value. Furthermore, since ω_0^2 is determined by the static susceptibility, $\omega_0^2 \propto (T - T_c)^{\gamma}$, then the Debye-Waller factor approaches its value at T_c asymptotically like $(T - T_c)^{\gamma/2}$. The contribution from the normal mode, $j = 2$, is smaller than that arising from the other mode. Comparatively little

work has been performed on planar ferroelectrics either experimentally or theoretically. Renormalisation group theory suggests that γ is larger than 1 (1.24 to $O(\epsilon)^5$).

111. 4 CUBIC FERROELECTRICS.

In cubic ferroelectrics the ferroelectric axis can be in any direction. There are three normal modes which describe the fluctuations in the dipole moment and the dynamical matrix is a 3×3 matrix with 9 components. The $(\alpha\beta)$ elements of the matrix are

$$(\omega_0^2 + B^2 q^2) \delta_{\alpha\beta} + C^2 \left| \frac{q_\alpha q_\beta}{|q|^2} \right|, \quad (21)$$

where the symbols stand for the same quantities as earlier and the same inessential approximation has been made in the form of the dispersion.

This dynamical matrix gives three normal modes; two transverse modes

$$\omega(q,1)^2 = \omega(q,2)^2 = \omega_0^2 + B^2 q^2, \quad (22)$$

and one longitudinal mode

$$\omega(q,3)^2 = \omega_0^2 + B^2 q^2 + C^2. \quad (23)$$

The contribution to the Debye-Waller factor is given by

$$Y = \frac{3K_B T}{B^2 Q^2} \left[3 - \frac{2\omega_0}{BQ} \tan^{-1} \frac{BQ}{\omega_0} - \frac{\sqrt{\omega_0^2 + C^2}}{BQ} \tan^{-1} \frac{BQ}{\sqrt{\omega_0^2 + C^2}} \right] \quad (24)$$

The temperature dependence of the Debye-Waller factor close to T_c is therefore dominated by the second term and is asymptotically $(T - T_c)^{5/2}$.

The best estimates of the critical exponents of a cubic ferroelectric are those found for the isotropic dipolar system⁵, $\gamma = 1.372$. Unfortunately we are unaware of any measurements on cubic ferroelectrics with which we can compare this prediction. The measurements on GeTe/SnTe alloys¹², for example, are qualitatively consistent but are not

of sufficient accuracy to provide a quantitative test.

111. 5 NON-FERROELECTRICS

At phase transitions other than ferroelectric ones, the dispersion relations for the normal modes are analytic in the region of wavevector space near the mode responsible for the phase transition. The temperature dependence of the Debye-Waller factor can then be obtained by considering each mode to have a dispersion relation of the form

$$\omega(\underline{q})^2 = \omega_0^2 + B^2 q^2 \quad (25)$$

The Debye-Waller factor is then given by Y_1 , equation 18. At T_c the Debye-Waller factor is finite and approaches this value asymptotically as $(T - T_c)^{1/2}$.

In principle the dispersion term can be considerably more complex than that given by equation 25. Physically reasonable but more complex forms also lead to a finite Debye-Waller factor at T_c and the same asymptotic form.

The value of γ is expected to vary with the number of different components for the soft mode. If there is only one mode γ is expected to be that of the three-dimensional Ising model. If there are two modes, the exponent of the XY model is appropriate, while if the mode is a triplet the Heisenberg model exponent is appropriate, whereas for higher degeneracy, renormalisation group theory suggests that other exponents may be appropriate.

111. 6 "REAL CRYSTALS"

In a parallel study of the effects of the Debye-Waller factor on structural phase transitions, Meissner et al.¹³ suggests that the forms derived in the previous sections may be incorrect. They reason that our form of $\omega(q, T)$ is derived from the results of renormalisation group theory. This technique is employed in the situation where

$t = \frac{T-T_c}{T_c} \rightarrow 0$ and $q \rightarrow 0$. However in calculating the singular part of the Debye-Waller factor, the integration is performed over a large region of reciprocal space - to approximately half way out in the Brillouin zone. In this situation Meissner et al.¹³ suggest that our forms still produce too strong a singularity at the transition. These forms need only be changed by replacing $\gamma/2$ in our expressions by $1-\alpha$. However, in deriving these altered results they are applying renormalisation group theory arguments outside their valid region. It is probably true to say that our exponents should be altered, but there must be some doubt about whether they should be replaced by $1-\alpha$.

Since the Debye-Waller factor varies relatively slowly with temperature, measurements will usually be made over an extended temperature range; perhaps $0 < t < 1$. Uniaxial ferroelectrics are known to show mean field theory type of behaviour, so we can expect our results for these materials to be most nearly correct. Deviations from our results, if they should exist, should be more apparent in the other ferroelectrics and antiferroelectrics.

To decide the contribution to the Debye-Waller factor from the other phonon branches, we assume the frequencies are temperature independent. The branches which contribute most, will have the lowest frequencies, so we make the approximation that the Bose-Einstein occupation number reduces to the form where it is proportional to temperature.

The subtraction of a background from the As⁷⁵ nuclear quadrupole resonance data for CsDA - proportional to temperature- does not improve the fit. In fact the fit is slightly poorer and some alterations in the parameters is required. The functional dependence of the data, suggests that the contribution from other phonon branches is small.

If the temperature dependent branch is coupled to other branches, we can expect the form of the Debye-Waller factor to be altered. Fits of Raman scattering data, show that it might be necessary to employ coupling of the "soft mode" to an optic branch^{14,15} and also to the acoustic branches^{8,16}. In the next section we look into the effect of the latter coupling.

III. 7 PIEZOELECTRIC COUPLING.

Measurements of the critical scattering in KDP (KH_2PO_4)¹⁷ have shown that the scattering in the [001] zone is not isotropic, as would be predicted by equation 7. This is most graphically displayed in Figure 10 of that paper (reproduced here as Figure 2). Cowley¹⁸ has been able to simulate this critical scattering pattern quite closely by including piezoelectric coupling of the acoustic modes to the polarisation fluctuations. We reproduce his simulation of the scattering in Figure 3.

Since the critical scattering is affected by the piezoelectric coupling, it follows that we should include this coupling in our calculation of the Debye-Waller factor.

To include piezoelectric coupling we must couple the polarisation fluctuations with the two acoustic modes polarised in the (xy) plane. This gives us a 3×3 response matrix

$$\underline{\underline{G}}(\underline{q}) = \underline{\underline{M}}(\underline{q})^{-1} \quad (26)$$

The terms in $\underline{\underline{M}}(\underline{q})$ are given in Table 1. The frequencies of the acoustic waves are given in terms of the elastic constants C_{11} , C_{12} , C_{66}^D (constant electric displacement) and the density ρ . The frequencies of the polarisation fluctuations are given by

$$\omega(q,1)^2 = A \left[(T - T_c^c) + b^2 |\underline{q}|^2 + c^2 \frac{q_z^2}{|\underline{q}|^2} \right] \quad (27)$$

FIGURE 2.

A contour map of the quasi-elastic neutron scattering close to the (510) reciprocal lattice point measured by Skalyo et al.¹⁷ in the (HK0) plane of DKDP at 225°K.

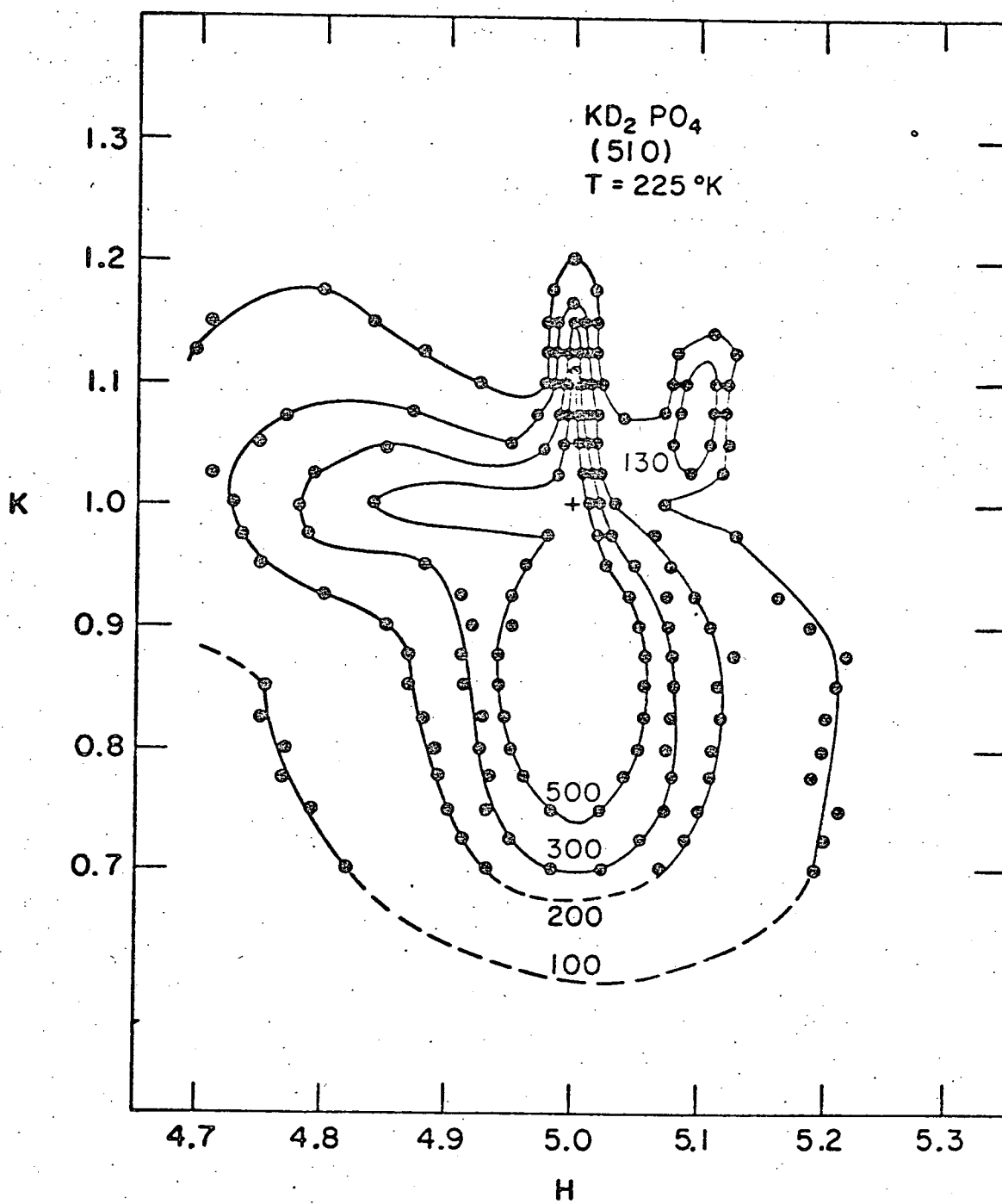


FIGURE 3.

A simulation of the scattering shown in Figure 2. by Cowley.¹⁸

KD_2PO_4 QUASI-ELASTIC CRITICAL SCATTERING

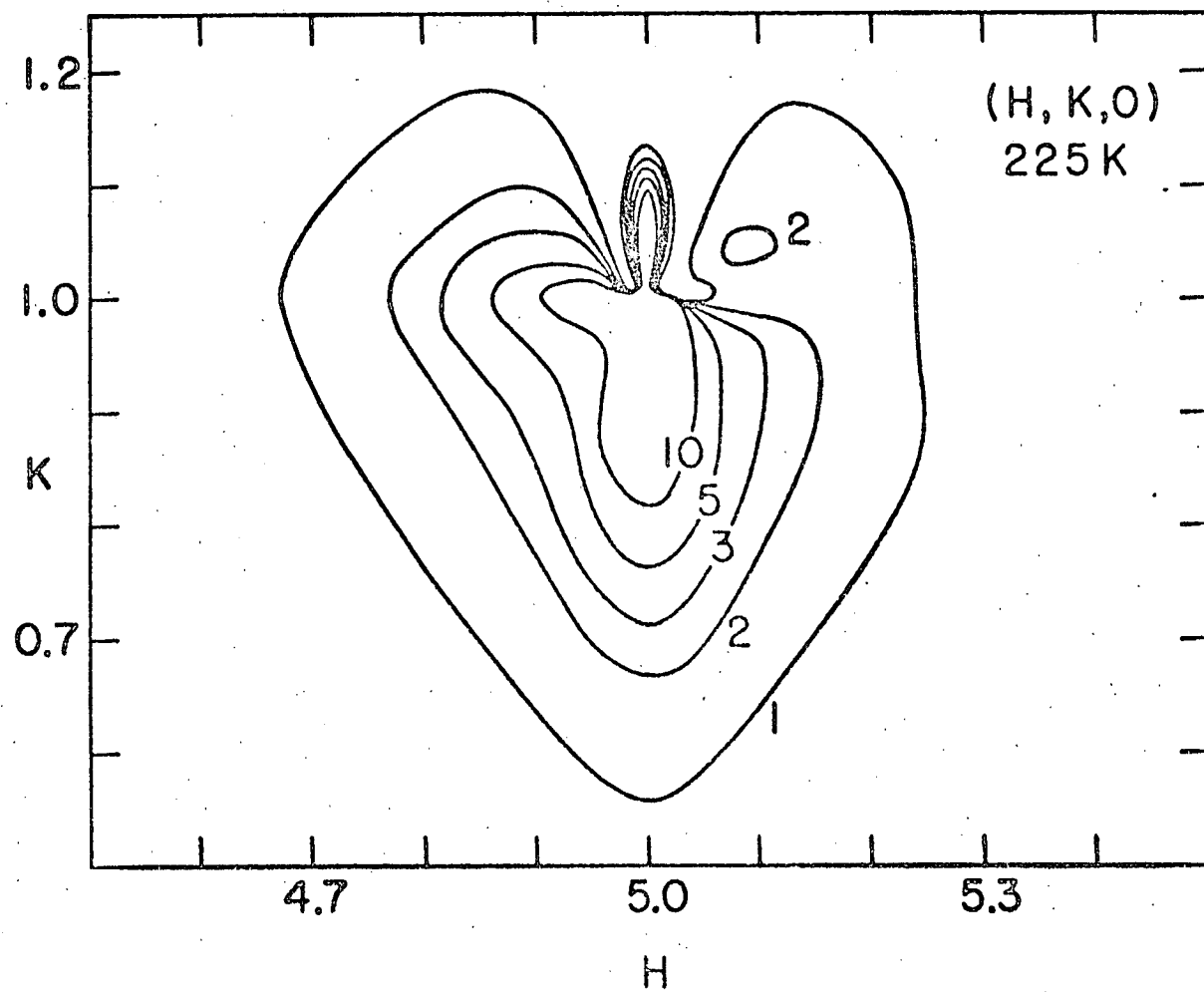


TABLE 1.

This gives the response matrix for a uniaxial ferroelectric, when the ferroelectric mode is coupled to the xy shear modes.

TABLE 1

$$\underline{\underline{M}} = \begin{bmatrix} \omega(q_1)^2 - \omega^2 - i\omega \gamma_0 & & \\ & Dq_y & Dq_x \\ & \frac{1}{\rho} (C_{11}q_x^2 + C_{66}q_y^2) - \omega^2 - i\omega \gamma_a & \frac{1}{\rho} (C_{12} + C_{66}) q_x q_y \\ & & \frac{1}{\rho} (C_{66}q_x^2 + C_{11}q_y^2) - \omega^2 - i\omega \gamma_a \end{bmatrix}$$

where T_c^c is the clamped crystal Curie temperature. The coupling between the modes is given by D , which is a measure of the piezoelectric coupling.

The leading term in the singular part of the Debye-Waller factor will now be proportional to

$$Y = \frac{k_B T}{N_s} \sum_{\mathbf{q}}^s G_{11}(\mathbf{q}) \quad (28)$$

Once again it proves more convenient to replace the cartesian co-ordinates of $\mathbf{q}$ by polar co-ordinates using

$$\begin{aligned} q_x &= q \sin \theta \cos \phi \\ q_y &= q \sin \theta \sin \phi \\ q_z &= q \cos \theta \end{aligned} \quad (29)$$

and converting the summation over $\mathbf{q}$ into an integral, we obtain

$$Y = \frac{8k_B T \int_0^{\frac{\pi}{4}} \int_0^Q \int_0^{\pi} \frac{q^2 \sin \theta d\theta dq d\phi}{A [(T - T_c^c) + b^2 q^2 + c^2 \cos^2 \theta] + f(\phi)} \quad (30)$$

$$\int_0^{2\pi} \int_0^Q \int_0^{\pi} q^2 \sin \theta d\theta dq d\phi$$

where

$$f(\phi) = \frac{e^{D^2} \left[-C_{11} + \frac{1}{2} (C_{11} + C_{12}) \sin^2 2\phi \right]}{\left[C_{11} C_{66} + \frac{1}{4} (C_{11} + C_{12}) (C_{11} - C_{12} - 2C_{66}) \sin^2 2\phi \right]} \quad (31)$$

we can express D in terms of measurable quantities through

$$A (T_c^F - T_c^c) = e^{D^2} / C_{66} \quad (32)$$

where T_c^F is the free crystal Curie temperature. Any one of the three integrals can be performed analytically, but then the remaining two integrals must be performed numerically. These numerical integrals are -

(a) Integrating over dq

$$Y = \frac{6k_B T}{\pi Q^3} \int_0^{\pi/4} \int_0^{\pi} \frac{1}{B^2} \left\{ 1 - \frac{\sqrt{\omega_o^2 + C^2 \cos^2 \theta + f(\phi)}}{BQ} \right. \\ \times \left. \tan^{-1} \left[\frac{BQ}{\sqrt{\omega_o^2 + C^2 \cos^2 \theta + f(\phi)}} \right] \right\} \sin \theta d\theta d\phi \quad (33)$$

(b) Integrating over dθ

$$Y = \frac{12k_B T}{\pi Q^3} \int_0^{\pi/4} \int_0^Q \frac{q^2 dq d\phi}{C \sqrt{\omega_o^2 + B^2 q^2 + f(\phi)}} \tan^{-1} \left[\frac{C}{\sqrt{\omega_o^2 + B^2 q^2 + f(\phi)}} \right] \quad (34)$$

(c) Integrating over dφ

$$Y = \frac{3k_B T}{2Q^3} \int_0^Q \int_0^{\pi} \left\{ \frac{1}{[\omega(q, \theta)^2 + e]} + \frac{[dc - eb]}{[e\omega(q, \theta)^2 + b]} \right. \\ \times \left. \frac{1}{[d\omega(q, \theta)^2 + b]^{\frac{1}{2}} [(d + e)\omega(q, \theta)^2 + b + c]^{\frac{1}{2}}} \right\} q^2 \sin \theta d\theta dq \quad (35)$$

where

$$\omega(q, \theta)^2 = \omega_o^2 + B^2 q^2 + C^2 \cos^2 \theta \quad (36)$$

$$\omega_o^2 = A(T - T_c^c) \quad (37)$$

$$b = -C_{11} \rho D^2 \quad (38)$$

$$c = \frac{1}{2}(C_{12} + C_{11}) \rho D^2 \quad (39)$$

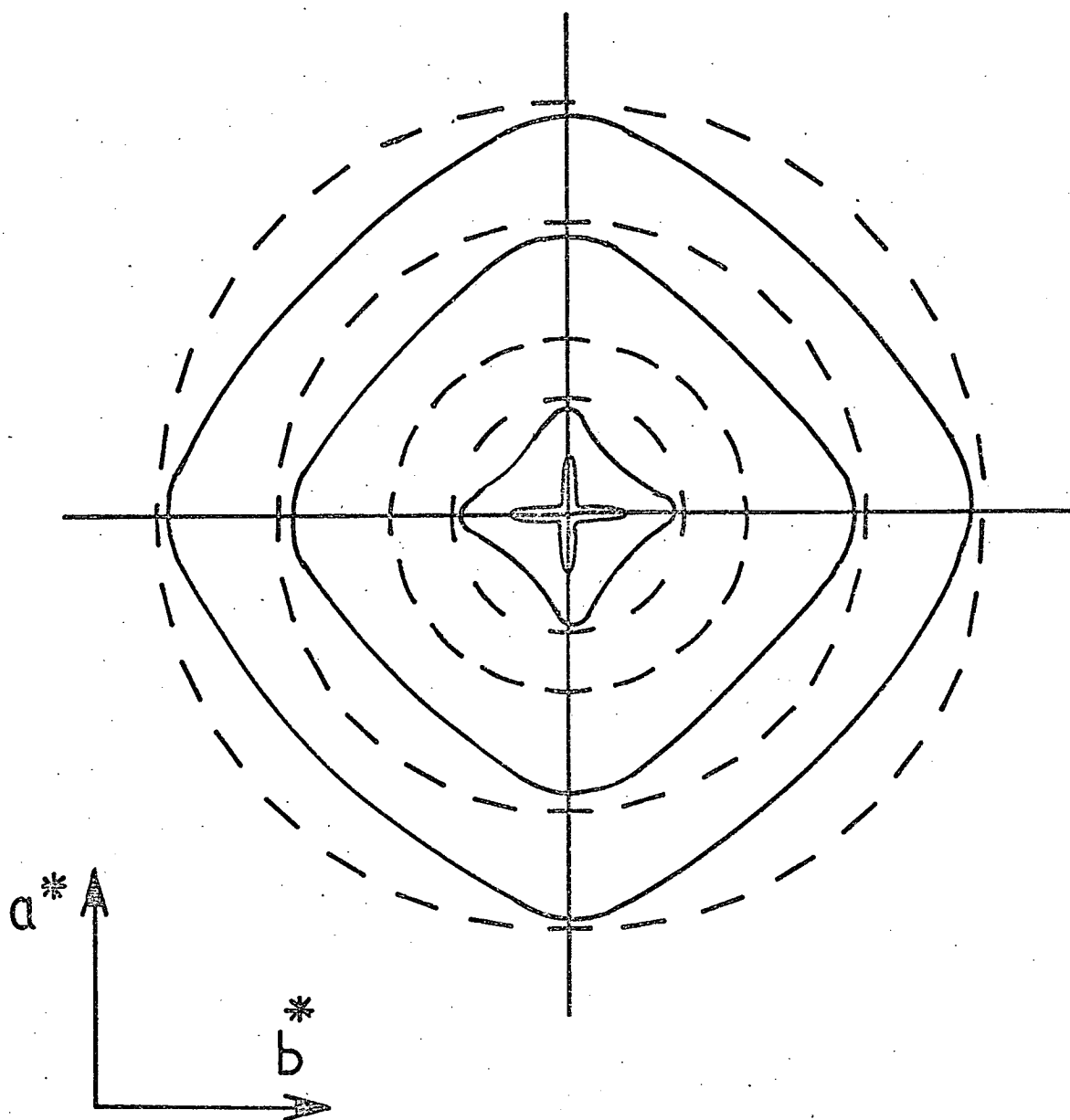
$$d = C_{11} C_{66} \quad (40)$$

$$e = \frac{1}{4}(C_{11} + C_{12}) (C_{11} - C_{12} - 2C_{66}) \quad (41)$$

and $f(\phi)$ is still given by equation 31.

FIGURE 4.

The form of $\omega^2(q)$ in the xy plane, shown with contours of constant frequency. Dotted line - without piezoelectric coupling. Continuous line - with piezoelectric coupling. (The diagram is only schematic).



Currently, all the parameters to make such a calculation are not available for any of the KDP type ferroelectrics for which the NQR resonance frequency has been measured. We expect the alteration of the form of $\omega^2(q, T)$ shown in Figure 4 to weaken the singularity given by equation 13.

111. 8 CONCLUSION.

In conclusion the temperature dependence of the Debye-Waller factor has been calculated close to structural phase transitions. It has been shown that the asymptotic behaviour provides a way of determining the critical exponent γ . If sufficient accuracy could be obtained, then careful measurements of the Debye-Waller factor or quadrupole coupling coefficient of systems undergoing continuous structural phase transitions would provide a means of testing the predictions of renormalisation group theory for different types of transition.

In particular the asymptotic behaviour of uniaxial ferroelectrics is found to be different from that of planar or cubic ferroelectrics, or of non-ferroelectrics. This is a direct consequence of the effect of the macroscopic electric field suppressing all the critical fluctuations in uniaxial ferroelectrics, except those with wavevectors perpendicular to the ferroelectric axis. A test of this prediction should be considerably easier than an accurate determination of γ .

Finally, throughout the paper, the dispersion of the normal modes has been assumed to be proportional to q^2 . Close to a phase transition, the dispersion is expected to be of the form $q^{2-\gamma}$. The critical exponent γ is, however, small, 0(0.02) and further, numerical calculations with different powers for the dispersion gave very similar results.

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CHAPTER IV

NEUTRON SCATTERING STUDIES ON CsDA AND DCsDA.

IV.1 INTRODUCTION

The ferroelectric properties of CsDA (CsH_2AsO_4) and DCsDA (CsD_2AsO_4) are in many ways similar to those of KDP (KH_2PO_4) and DKDP (KD_2PO_4). There have, however, been several reports that the transitions in the former materials may be more complex than in the latter¹⁻³. Neutron scattering measurements have therefore been made on CsDA and DCsDA in the hope of elucidating this behaviour. The measurements were made using a double axis spectrometer at the DR3 reactor at Risø.

Dietrich et al.¹ reported observing a satellite structure in the ferroelectric phase of DCsDA. Quasi-elastic peaks in the scattering were observed around a number of points in the (h0l) zone. These peaks appeared at reduced wavevectors 0.1 and 0.2 along the $[200]$ direction at (004) and (303), at 0, 0.034 and 0.067 for the systematic absence (002) and at combinations of these reduced wavevectors around other Bragg points. The indexing of the paraelectric phase is used throughout since this enables us to give a simpler description of the satellite intensities.

It was believed that the satellite intensities were distinct from the additional reflections caused by the domain structure since these are not expected to influence (00l) reflections. We have repeated the experiments in greater detail and with better vertical resolution on a 1 cm^3 crystal of CsDA. We provide an explanation for our observations.

Below the transition in CsDA, each Bragg reflection can split into four separate spots corresponding to the different domain types. Surprisingly in DCsDA a central Bragg reflection from the (tetragonal) paraelectric phase persists with decreasing intensity over a 60 degree temperature range before the crystal is completely in the (orthorhombic) ferroelectric phase. This effect has been observed with both neutron

and X-ray scattering and appears to be independent of crystal size.

We have measured the temperature dependence of the shear occurring in the ferroelectric phase of CsDA and show that the transition is first order. Finally we have measured one of the shear elastic constants of DCsDA.

IV.2 THE SHEAR ANGLE OF CsDA - BACKGROUND

A number of theories have been put forward to explain the origin of ferroelectricity in KDP and its isomorphs⁴⁻⁷. In testing the validity of these theories it is important to know the order of the ferroelectric transition. Over the years there has been disagreement over whether the transition (usually in KDP or DKDP) is first⁸⁻¹² or second order¹³⁻¹⁵. In many cases the same technique has produced different results. For example, calorimetric measurements by Reese et al.^{10,13} gave different results, depending on whether a single crystal or multi-crystal method was used. Dielectric constant measurements have also been at variance with each other. These generally rely on the observance of thermal hysteresis. This is not conclusive since impurities (or concentration fluctuations in DKDP) may allow the co-existence of two phases over a short temperature interval. Both these methods rely on the observation of the transition through less direct means than should be obtained by measuring the temperature dependence of the lattice parameters. This is the technique employed by Zeyen et al.¹¹. They performed accurate measurement of the thermal expansion along the c axis, observing the existence of two phases in the DKDP transition up to $2\frac{1}{2}$ degrees below the transition temperature. There was no hysteresis ($< 10^{-3}$ °K), but there was a discontinuity in the lattice parameters.

In our experiments on CsDA the accuracy was insufficient to be

able to measure changes in the lattice parameters. However the crystal shears at the transition, so it is possible to get the desired accuracy by measuring the splitting of the Bragg reflections. The temperature dependence of this shows similar behaviour to the expansion of the crystal along the c axis. The accuracy of the temperature control was insufficient to confirm hysteresis found by Blinc et al.¹⁶ in the arsenates ($\lesssim 0.1$ °K).

IV.3 THE SHEAR ANGLE IN CsDA - EXPERIMENTAL

Although the true symmetry of the low temperature phase is orthorhombic, the cell can also be described in terms of pseudo-monoclinic axis a, forming an angle of $90^\circ + X_y$ with each other, and with the c axis perpendicular to the other two axis¹⁷. (see Figure 1b) The transition from the paraelectric to the ferroelectric form can then be regarded as a distortion of the cell by a shear X_y . When a single crystal of CsDA is taken from the tetragonal to the orthorhombic form the cell can shear in four separate ways (see Figure 1a), and in general four types of domain are produced.

The co-ordinates for the Bragg peaks of the four types of domain, in terms of the reciprocal cell dimensions of the paraelectric phase, are given by

$$(h \pm kd, k, 1) \quad (1)$$

$$(h, k \pm hd, 1) \quad (2)$$

where $a^* = b^* = 0.785 \text{ \AA}^{-1}$ and $c^* = 0.800 \text{ \AA}^{-1}$ are the reciprocal cell dimensions in the paraelectric phase and $d \lesssim 0.03$ takes account of the shearing of the crystal. The splitting of the Bragg peaks is shown schematically in Figure 2.

A 1 cm^3 crystal of CsDA, obtained from Quantum Technology,¹⁸ was placed with its c axis vertical in a variable temperature cryostat on a two axis spectrometer at the DR3 reactor, Risø. The temperature of

the crystal could be kept constant to an accuracy of 0.1°K . At each temperature, measurements of the splitting of the Bragg peaks, $2\text{d}b^*$, were made at (310), (220) and (400). A typical scan made at (310) is shown in Figure 3b. Compared to Figure 3a, it can be seen how important it is to choose the scans so as to take advantage of the instrumental resolution. The values of $\text{d}b^*$ obtained from the three scans were consistent to $0.0002 \text{ \AA}^{-1}$. Measurements were made both whilst cooling and warming the sample. These produced similar results, showing that sufficient time had been allowed for temperature stabilisation. Figure 4 shows a graph of $\text{d}b^*$ as a function of temperature. The shear angle is related to this through

$$\text{d}b^* = a^* \tan X_y \simeq 0.785 X_y \quad (3)$$

Below $0.85 T_c$ the shear angle is approximately constant at 1.75° ($\text{d}b^* = 0.0240 \pm 0.0003 \text{ \AA}^{-1}$). On warming to the transition temperature, the shear angle decreases to about 70 % of this value, before jumping discontinuously at the transition temperature of $145.9 \pm 0.2^{\circ}\text{K}$. This shows that the transition is first order.

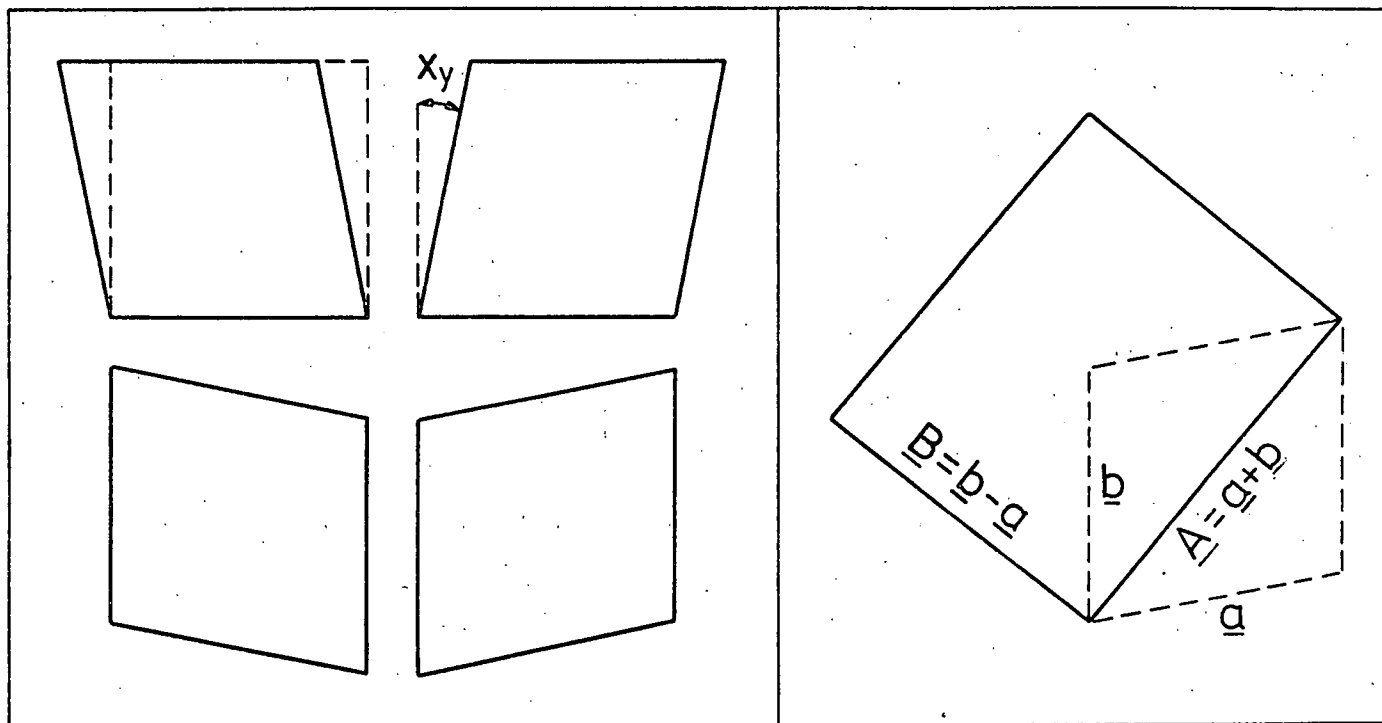
De Quervain¹⁹ found that the shear angle in KDP was less than 0.5° . The change in shear angle occurs over a wider temperature interval in KDP than in CsDA. More recent measurements of the shear angle in KDP²⁰ show a more rapid decrease in the shear angle close to the transition. This is perhaps related to the purity of the samples. If it is assumed that the more recent samples are better, it would appear that impurities produce a phase transition which is more strongly first order.

The shear angle in CsDA shows qualitatively the same behaviour as that found for the spontaneous polarisation²¹. There is, however, no direct proportionality between the two quantities.

It is to be expected that the shear angle in a deuterated sample would vary similarly. One such sample was measured 20 degrees below its transition temperature and the shear angle was slightly larger at 2.0° .

FIGURE 1

- (a) This shows the four ways the unit cell can shear on passing from the paraelectric to the ferroelectric phase.
- (b) After the shear, the cell appears to be pseudo-monoclinic, but it can be related to the orthorhombic cell which is more commonly employed.



THE FOUR WAYS THE UNIT CELL CAN DISTORT IN PASSING FROM THE PARAELECTRIC TO THE FERROELECTRIC PHASE. THIS CORRESPONDS TO A SHEAR X_y .

THE RELATION BETWEEN THE DISTORTED PSEUDO-MONOCLINIC CELL AND THE TRUE ORTHORHOMBIC CELL OF THE FERROELECTRIC PHASE.

FIGURE 2

A schematic diagram of the splitting of the Bragg points in the $(hk0)$ and parallel planes. In general four points are produced; along the principle axes $(h00)$ or $(0k0)$ only three are produced; no splitting occurs for points along $(00l)$.

$\uparrow$ OK(L)				
$1 + 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$
$1 + 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$
$1 + 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$	$1 \frac{2}{4} 3$
$*$	$\frac{2}{4}$	$\frac{2}{4}$	$\frac{2}{4}$	$\frac{2}{4} \xrightarrow{\text{HO(L)}}$

THE DOMAIN SPLITTING IN RECIPROCAL SPACE

FIGURE 3

Two scans through (310) in the ferroelectric phase of CsDA. This shows how advantage can be taken of both the experimental resolution and the increased splitting of the Bragg points in certain directions.

- (a) A scan in the $[2\ 0\ 0]$ direction.
- (b) A scan in the $[0\ \bar{1}\ 0]$ direction.

$T = 131^\circ \text{K}$

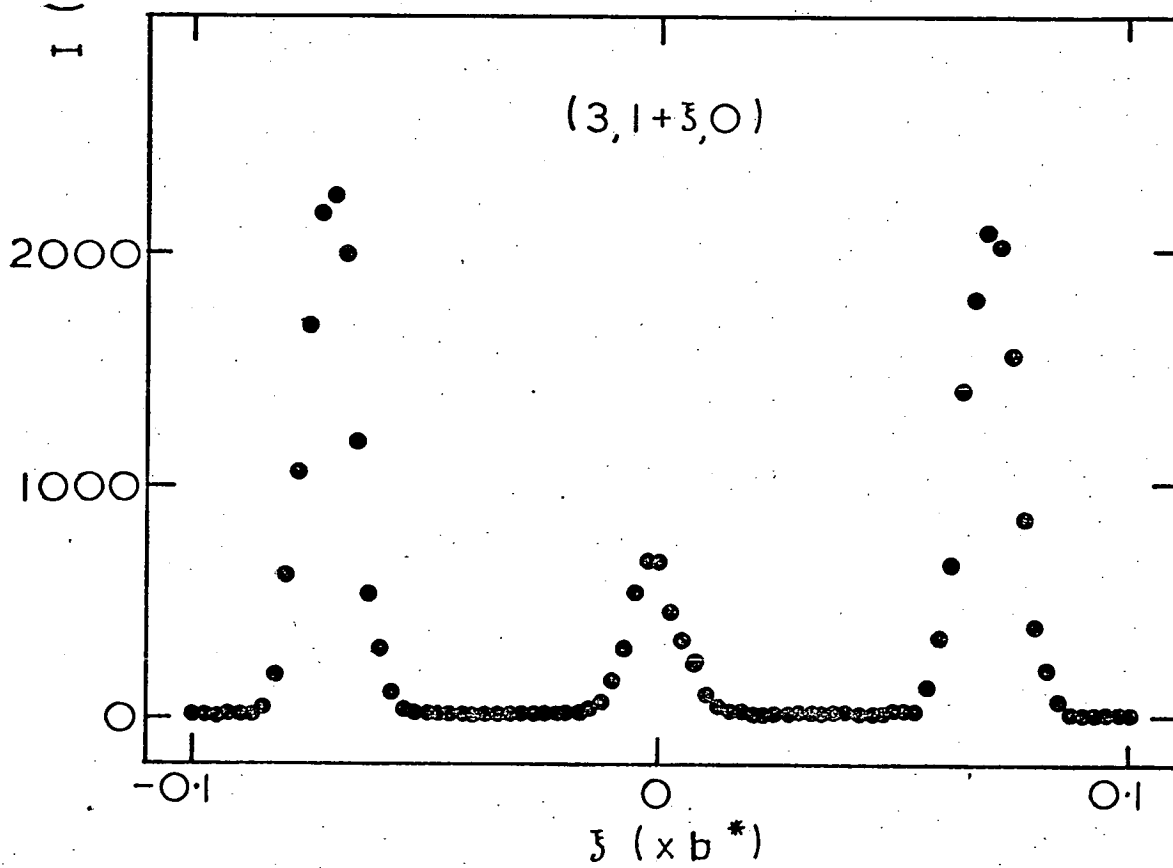
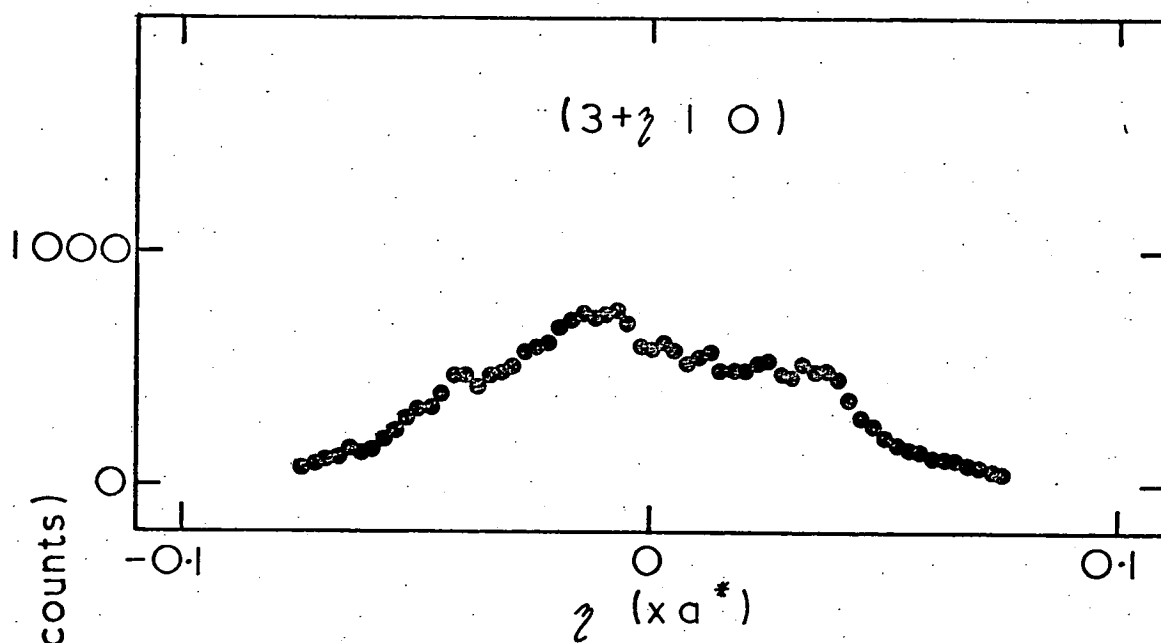
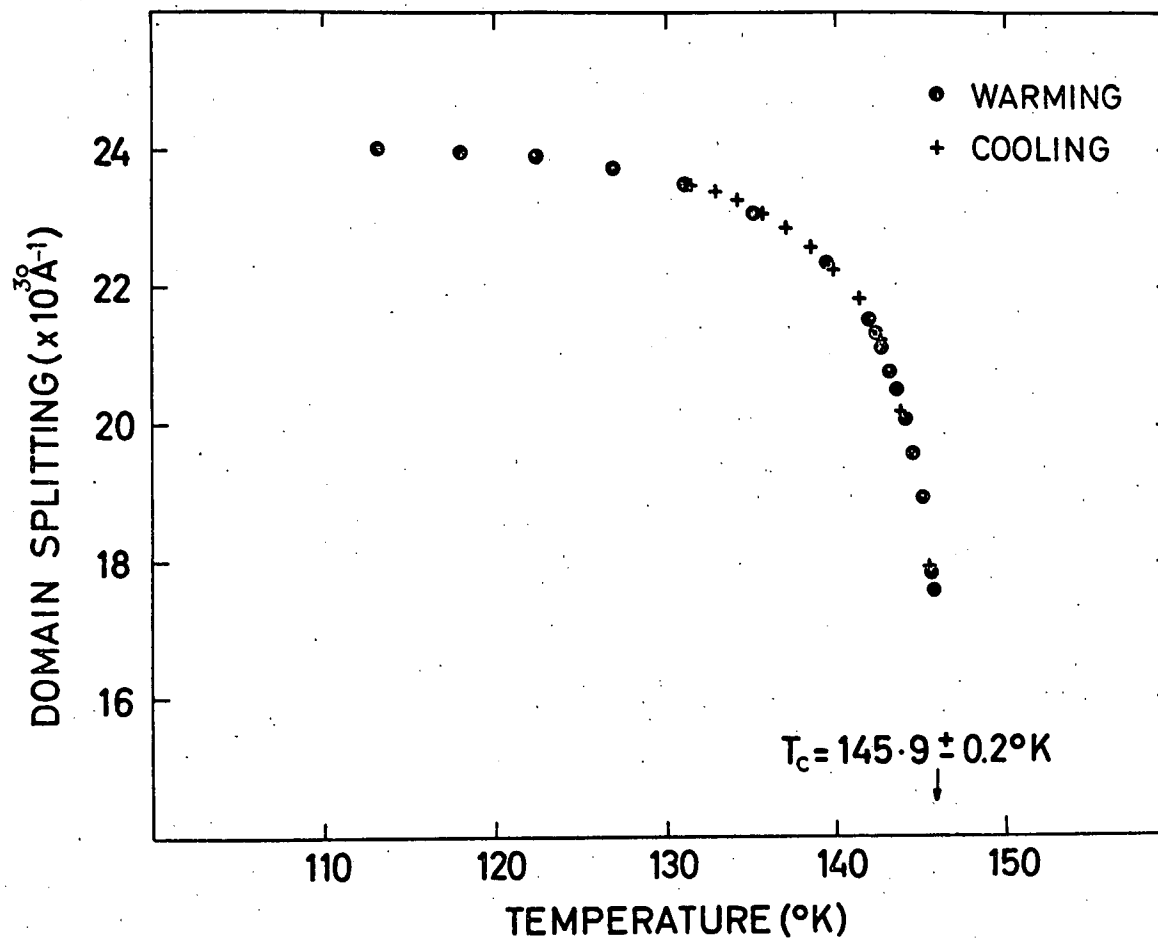


FIGURE 4

This shows the temperature dependence of the domain splitting in CsDA averaged over (400), (310) and (220) after being normalised by dividing through by the Miller index, h . At the transition the domain splitting is about 70% of its maximum value. The crystal transforms discontinuously between the two phases at 145.9 ± 0.2 °K, showing the transition is first order.



THE DOMAIN SPLITTING IN CsH_2AsO_4 . THIS IS RELATED TO THE SHEAR X_y BY DOMAIN SPLITTING = $a \cdot \tan X_y \approx 0.785 X_y$

IV.4. SATELLITE STRUCTURE -EXPERIMENTAL.

A 1 cm^3 crystal of CsDA was mounted with the $a - c$ plane horizontal and maintained in a cryostat at 115°K on a double axis spectrometer at the DR3 reactor, Risø. Elastic neutron scattering scans were made using neutrons of wavevector $k = 2.65\text{\AA}^{-1}$. Second order contaminant in the incoming beam was reduced by means of a graphite filter.

Scans were made in the $[\gamma 00]$ direction through all the Bragg points which had shown satellite peaks in the deuterated sample¹. Satellite intensities again appeared at approximately the same locations, but the intensities differed. Typical scans through (002) and (004) are shown in Figures 5 and 6.

One of the problems noted by Dietrich et al. (private communication) was that the structure measured on a triple axes spectrometer differed from when it was measured on a double axis spectrometer. These instruments have different resolutions. In particular, a triple axis spectrometer uses tall counters to improve efficiency, so it has poor resolution in the vertical direction.

The double axis spectrometer was set up with beam constraints so that the vertical resolution was comparable to that which could be obtained in the scattering plane.

The scattered intensity was sampled at $(h + \gamma, \xi, l)$ close to a number of Bragg points in the $(h 0 l)$ plane. Parallel scans were made in the $[\gamma 0 0]$ direction under the control of a PDP8 computer. At the end of each scan, ξ was incremented manually by tilting the counter vertically.

Contour maps of the scattered intensities observed at (002) and (004) are shown in Figure 7 and those observed at (103) and (303) are shown in Figure 8.

As we have already seen when a single crystal of CsDA is taken through

FIGURE 5

A typical scan through the systematic absence (002) in the $[300]$ direction, showing the satellite intensities in the ferroelectric phase of CsDA.

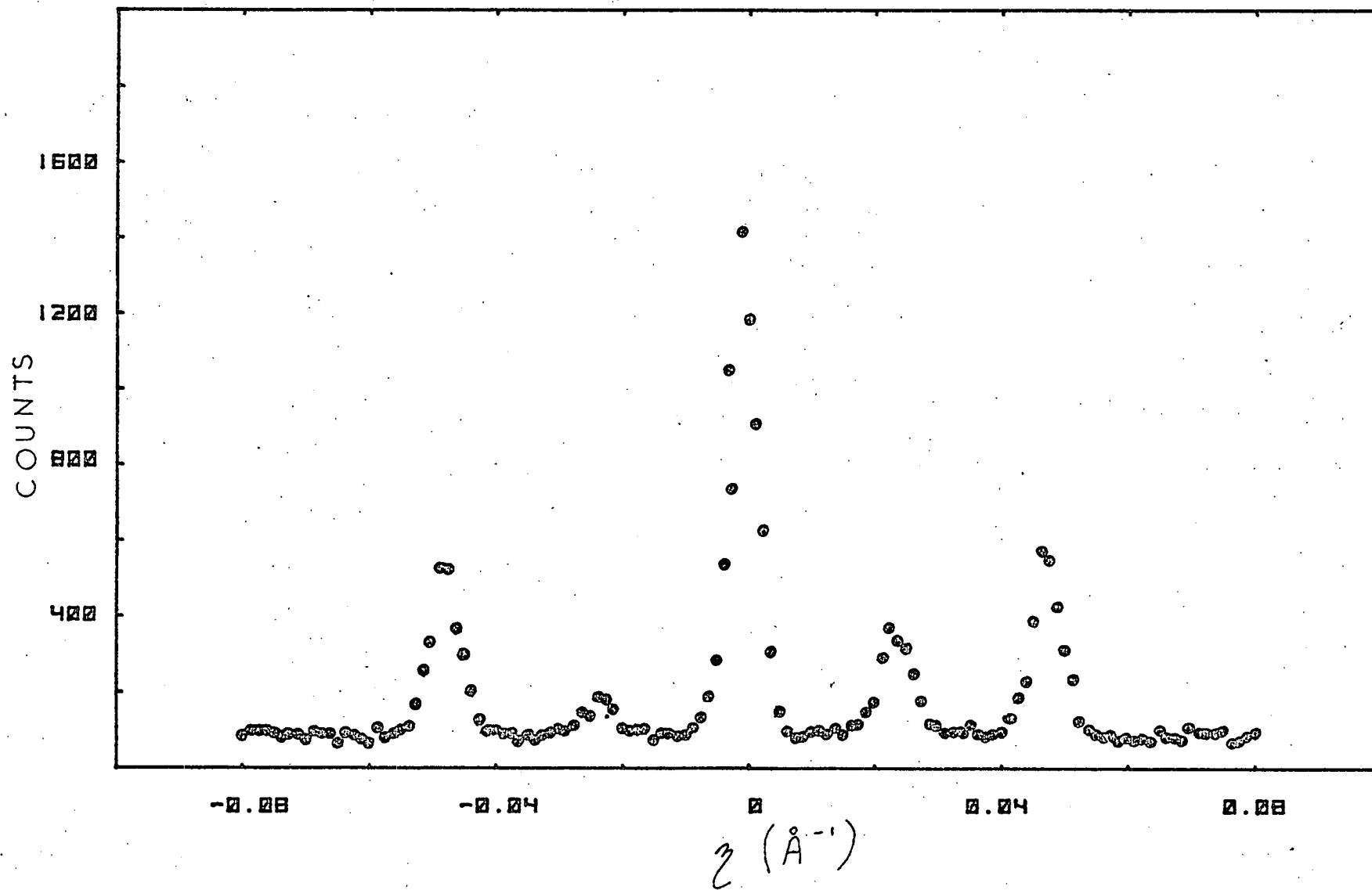


FIGURE 6

A typical scan through (004) in the $[200]$ direction showing the satellite intensities in the ferroelectric phase of CsDA. The Bragg peak is shown scaled down by a factor of 10.

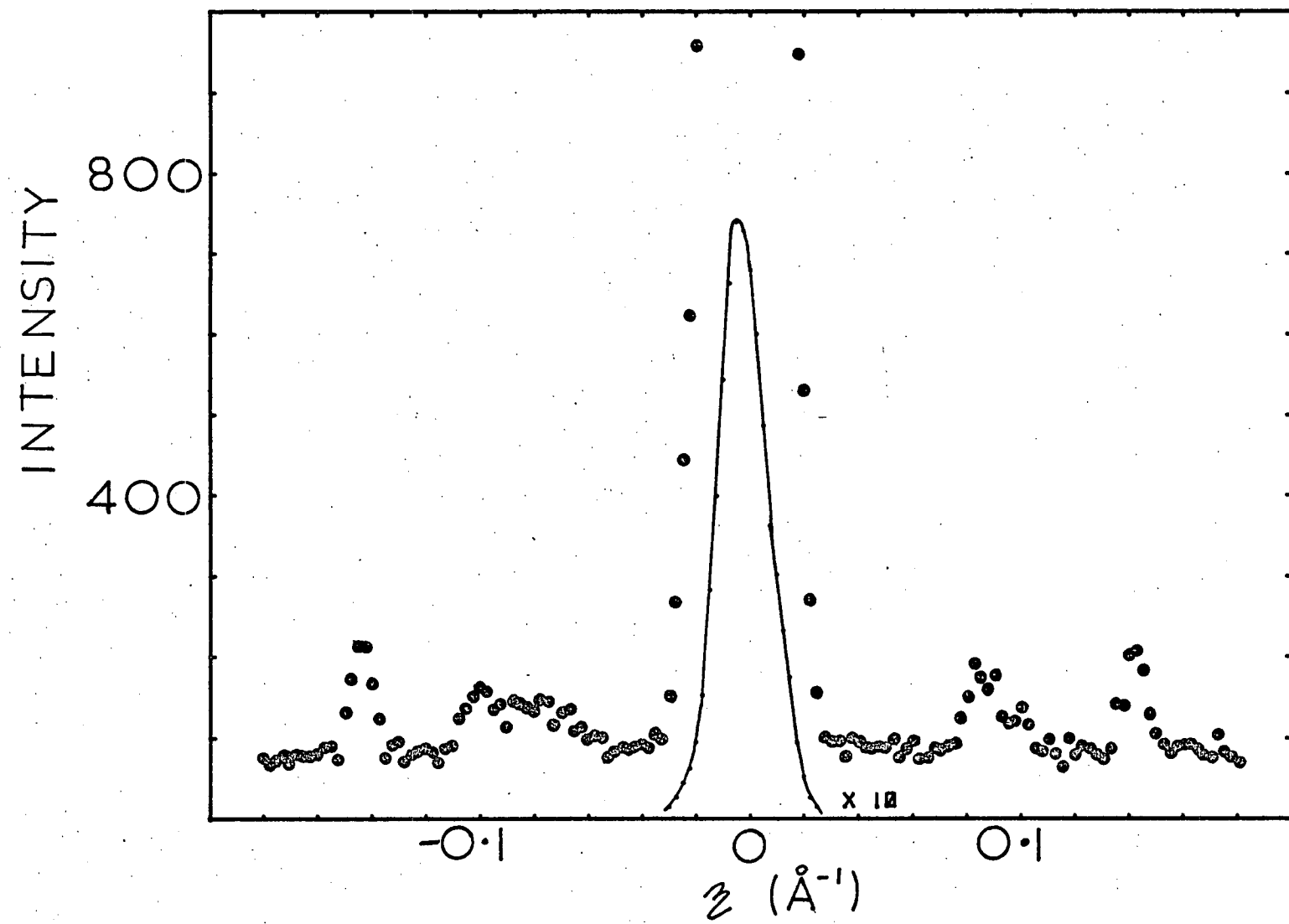


FIGURE 7

Complete $[2\ 5\ 0]$ contour maps of the intensities observed at 115 °K at (a) (002) and (b) (004). Contours are drawn at 10, 30, 100, 300, 1000 and 3000 counts above the background.

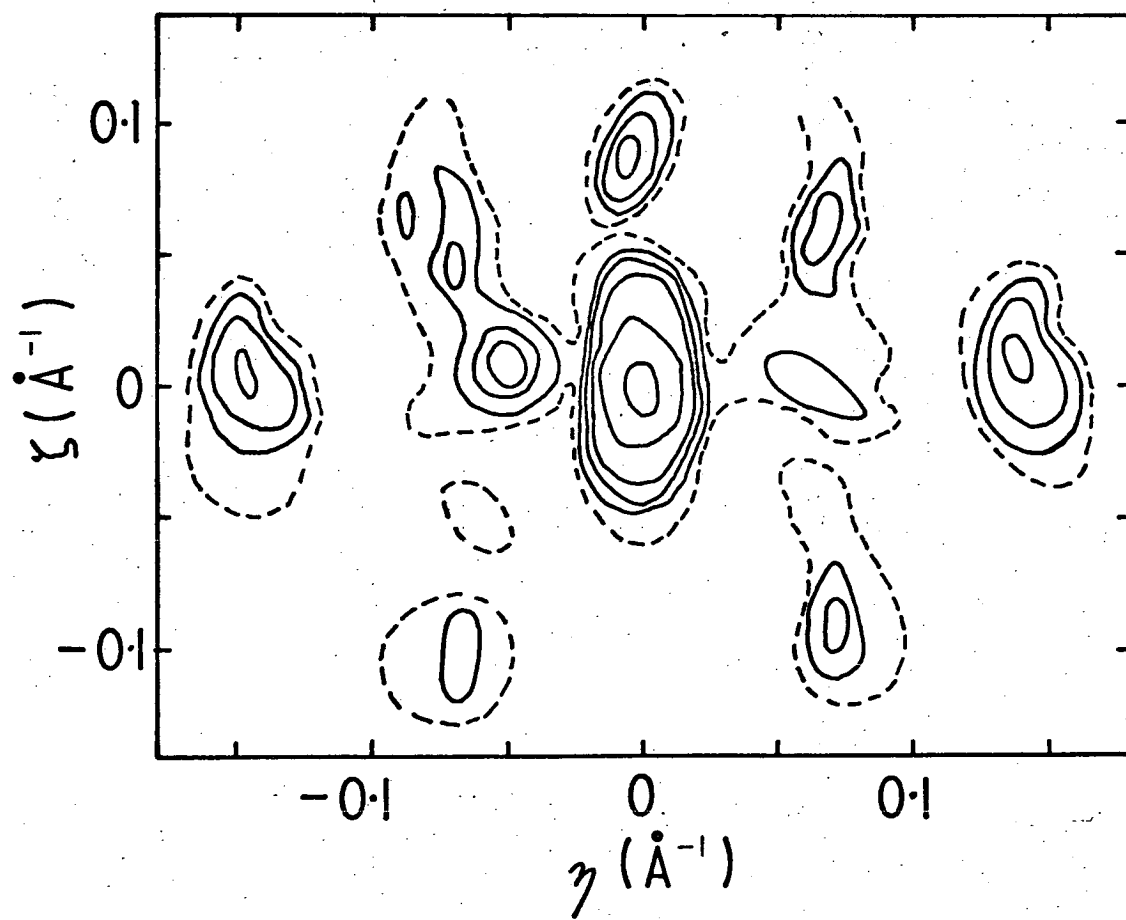
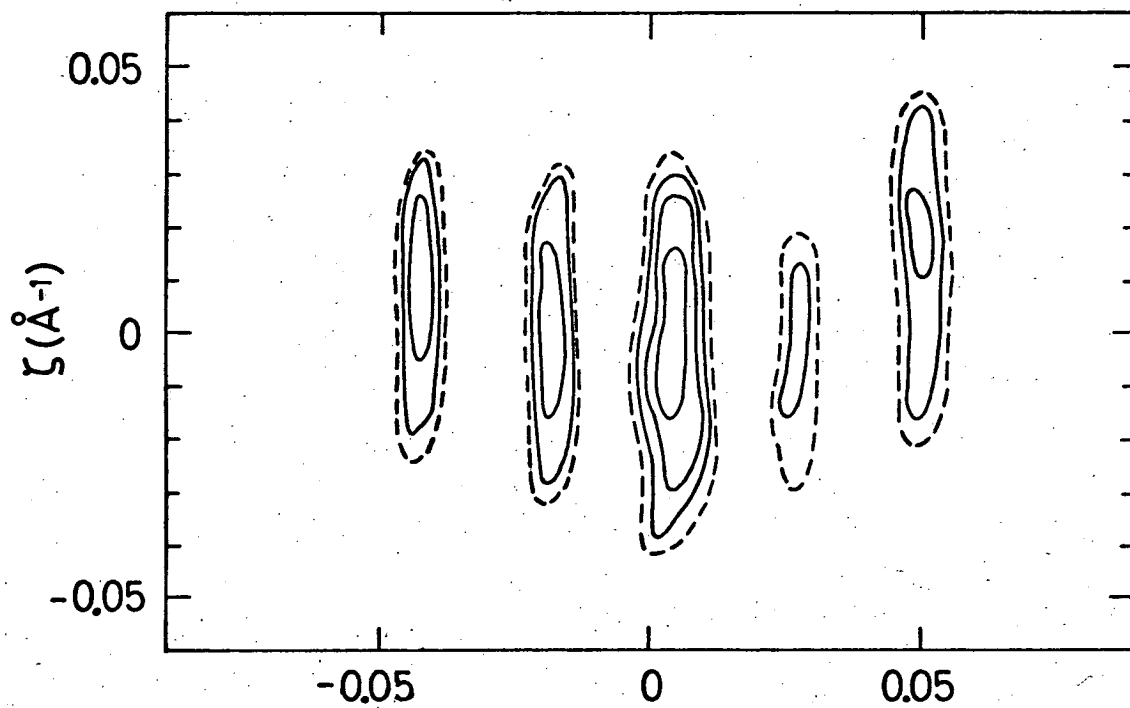
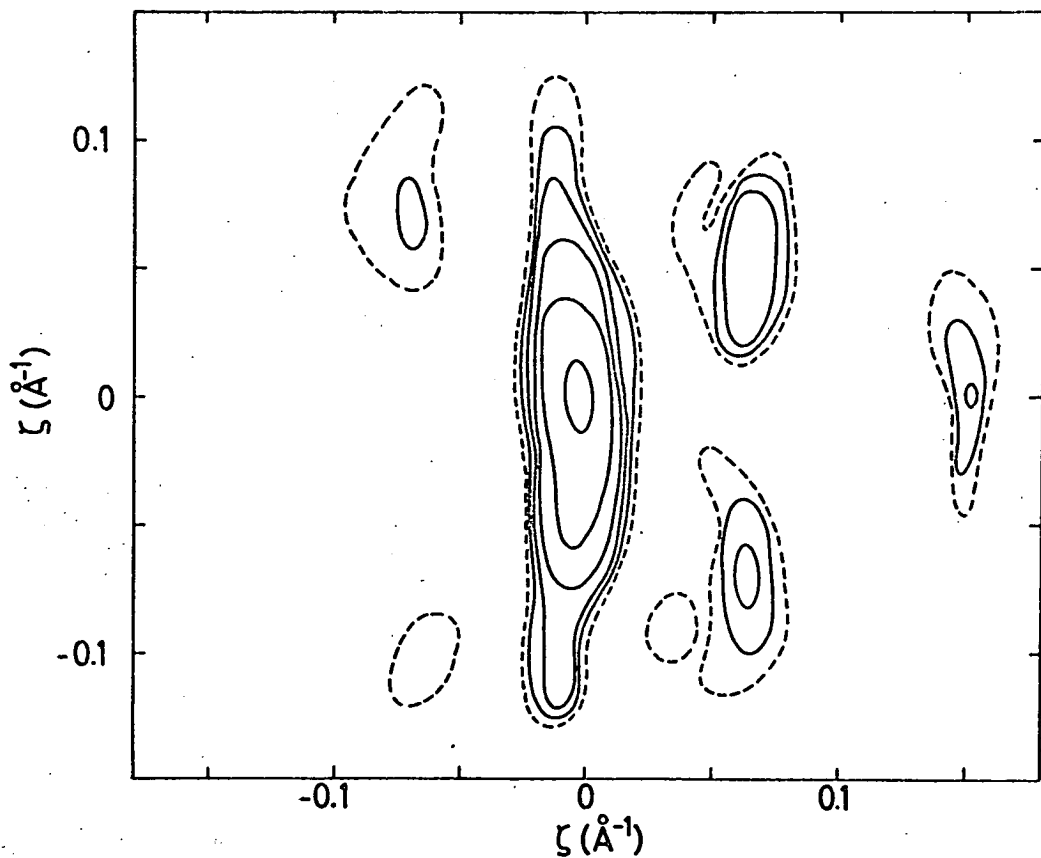
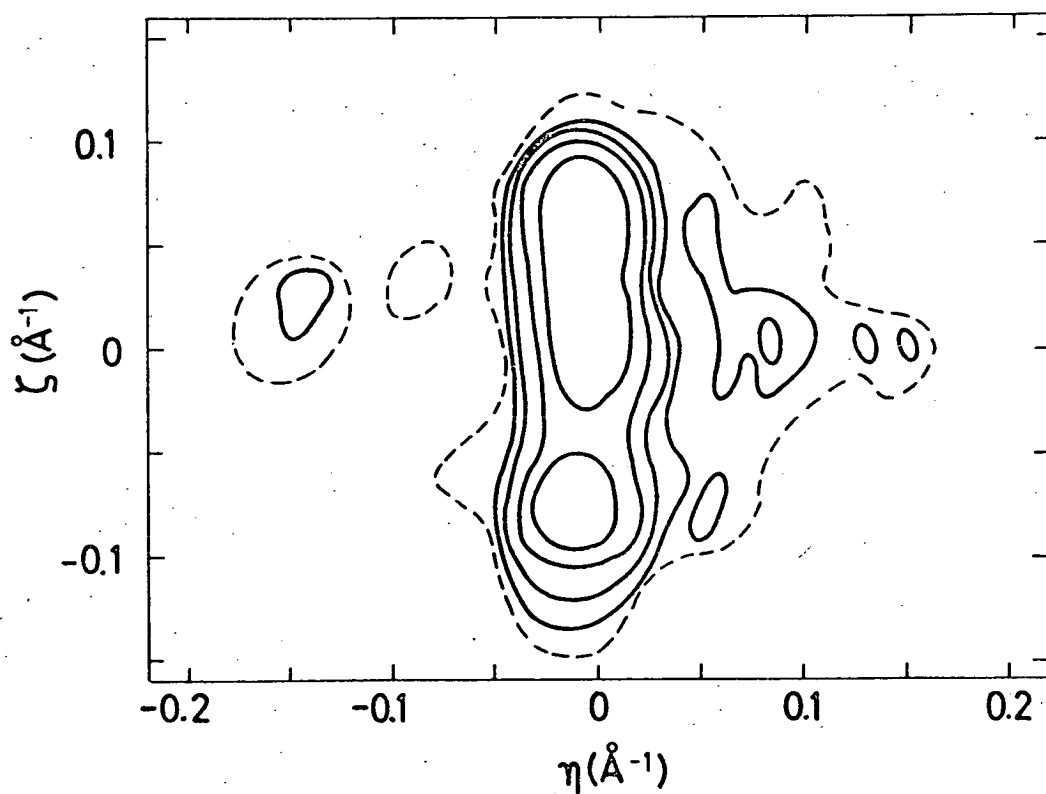


FIGURE 8

Complete $[2\ 5\ 0]$ contour maps of the intensities observed at 115 °K at (a) (103) and (b) (303). Contours are drawn at 10, 30, 100, 300, 1000 and 3000 counts above the background.



THE OBSERVED INTENSITIES AT (013) CONTOURS 10,30, 100,300,1000,3000 ABOVE BACKGROUND.



THE OBSERVED INTENSITIES AT (033) CONTOURS 10,30,100,300 AND 1000 COUNTS ABOVE BACKGROUND.

the transition, in general, it is expected to shear up to four ways. The proportion of the crystal forming each type of domain can vary, but the process is otherwise reversible. In a sample of our dimensions, each type of domain was found to contain at least 5% of the total material of the crystal. In a much smaller X-ray sample (0.01mm^3), it was occasionally possible to obtain only two types of domain.

The effect of the domain splitting on Bragg peaks is shown schematically in Figure 9. The Bragg peaks split in the $a^* b^*$ plane, and in general into four points around each (hkl) position ($h \neq 0, k \neq 0$); for $h = 0$ or $k = 0$, two superpose, so that only three peaks are distinguished. The co-ordinates of the Bragg peaks are again given by equations 1 and 2.

IV.5 MULTIPLE BRAGG SCATTERING.

We would like to build on the hypothesis that these intensities could be caused by multiple Bragg scattering. Normally in a single crystal, only the intensities at reciprocal lattice vectors, γ , are affected. We will now show that this does not apply when the crystal is no longer single.

Multiple Bragg scattering is the term applied when scattering at (h,k,l) is affected because a further point (h', k', l') falls on the Ewald sphere and part of the beam is scattered once off this point and the beam is further scattered from a point $(h - h', k - k', l - l')$. How the intensity at (h,k,l) is affected, depends on the relative strengths of (h', k', l') and $(h - h', k - k', l - l')$. The intensity can be either increased or decreased by multiple Bragg scattering.

The problem is equivalent to that of comparing the positions of Bragg peaks from two parallel co-ordinate systems with the origins at either end of the scattering vector and seeing if they both lie on the Ewald sphere. Thus in CsDA, intensity at $(h + \frac{1}{2}, k + \frac{1}{2}, l)$ is seen

as scattering in one domain from one of the points at (h', k', l') followed by scattering in a different domain from one of the points at $(h' - h, k' - k, l' - l)$. For brevity, we will call this multiple scattering from $((h', k', l'))$.

A translation of the co-ordinate system along the c-axis by a reciprocal lattice vector like (002) leaves the splitting of the Bragg peaks unchanged. Peaks from the two co-ordinate systems will completely overlap (systematic absences in either system excepting).

If a scan in the $[\begin{smallmatrix} 2 \\ 0 \\ 0 \end{smallmatrix}]$ direction is made at (002), points in the two co-ordinate systems will "pass through" each other. A point such as (011), which splits into three co-linear Bragg peaks with spacing d , will have peaks from the two systems overlapping at five equi-spaced points on the scan. These are when the scan is at

$$(-2d \ 0 \ 2), (-d \ 0 \ 2), (0 \ 0 \ 2), (d \ 0 \ 2) \text{ and } (2d \ 0 \ 2) \quad (4)$$

where

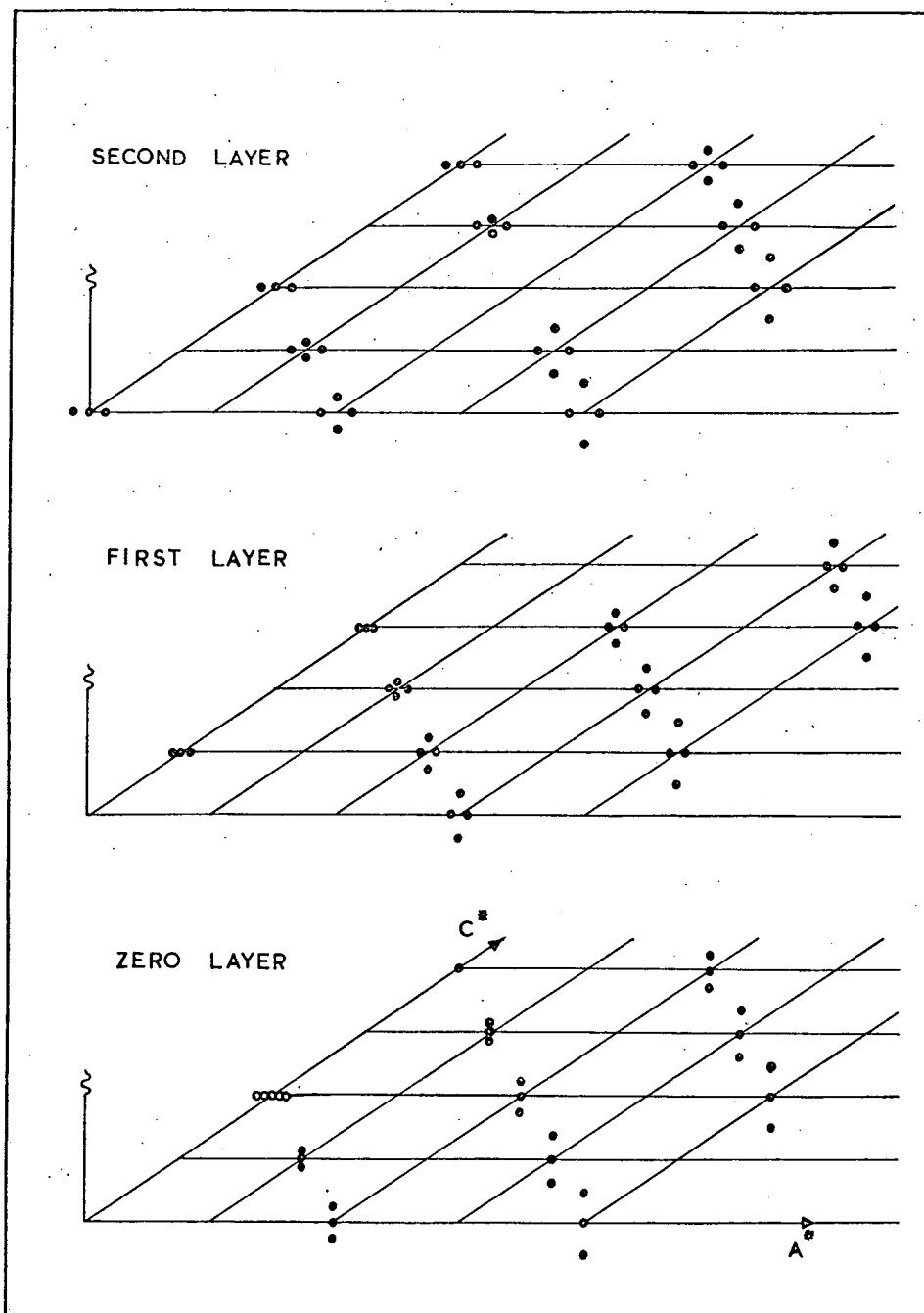
$$d = \tan x_y \simeq 0.03 \quad (5)$$

These are in the same positions as the satellites at (002), which are marked as open circles on Figure 9.

FIGURE 9

A schematic diagram of the splitting of Bragg points in the (h0l) and parallel planes. The points are split only in the a^*b^* plane. In addition, the satellite positions at (002) are shown as open circles.

THE DOMAIN SPLITTING FOR BRAGG POINTS IN THE $(h0l)$ PLANE



IV.6. TRACING RESPONSIBLE POINTS.

A computer simulation was set up to show that the necessary conditions for multiple scattering from two different domains applied in the case of $((0,1,1))$, and that other Bragg points were involved in producing the observed intensities.

Only the first four points on the $(\frac{1}{2} 0 2)$ scan also have the Ewald sphere intersecting the correct peaks at $((0,1,1))$. The first point also has a contribution from $((3,1,4))$. Multiple scattering off a single domain at $((5,2,3))$ and $((5,2, -1))$ meets the necessary conditions for the (3rd) centre point. There is probably a contribution to the centre point caused by second order reflection of the neutron beam at (004). (There is no first order reflection of the beam at (002)). The correct condition for the 5th and last point is met by multiple scattering from $((3, 1, -2))$.

It can similarly be shown that points such as $((4,3,3))$, $((4,3,1))$, $((1,3,2))$ and $((0,2,2))$ contribute towards the intensities observed around (004). The slight up-down asymmetry in the contour map is probably caused by incorrect alignment of the crystal. Multiple Bragg scattering is particularly sensitive to this.

Figure 8. shows the scattering close to (103) and (303). The complexity of the multiple scattering increases for points with $h \neq 0$ because there no longer exists a simple overlap of Bragg points from the two co-ordinate systems. Because of this additional complexity, and any possible misalignment of the crystal, we would probably not be justified in assigning responsibility for multiple scattering on any particular pair of Bragg points $((h', k', l'))$.

IV.7. EXPERIMENTAL VERIFICATION.

There are two methods of checking on whether or not an effect in neutron scattering is due to multiple scattering.

The wavelength of the monochromatic beam can be altered. This changes the relation of the Ewald sphere in the crystal, monochromator or analyser with the respective Bragg points from which undesirable scattering might occur. A beam of higher incident energy will also reduce higher order contaminant, but this is at the expense of resolution.

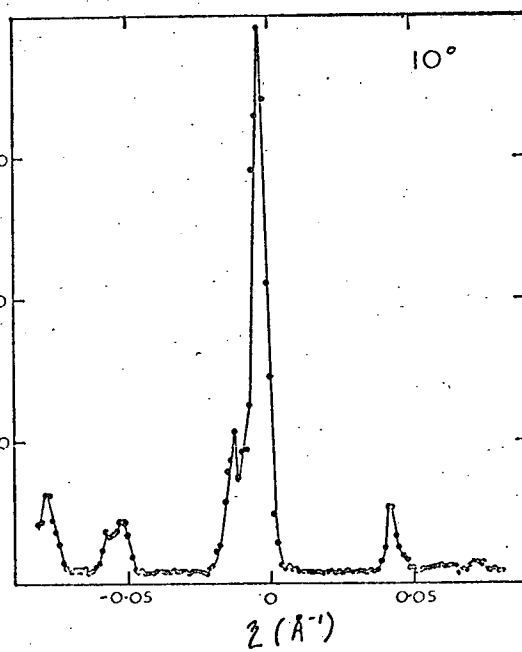
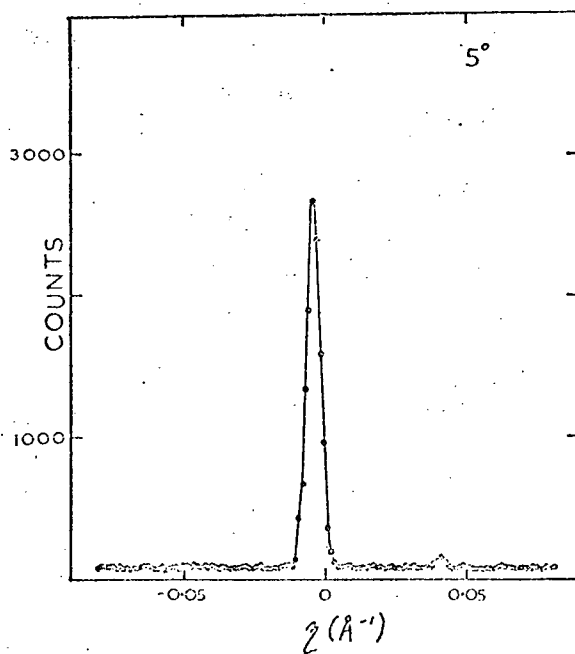
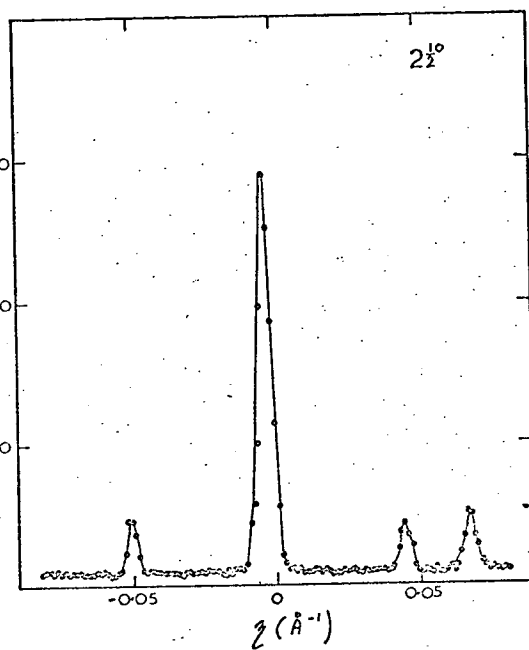
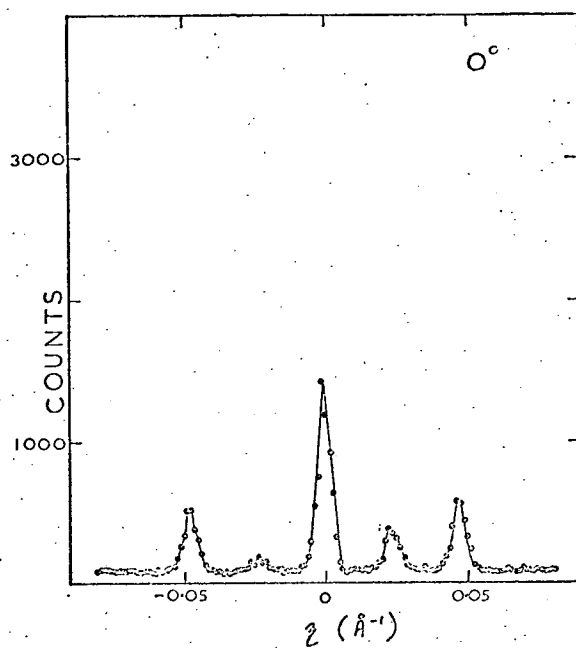
With the earlier experiments and these, the incident wavelength was chosen so that it was possible to use a graphite filter to reduce second order contaminant. It was difficult to change this wavelength.

An alternative method of removing undesirable reflections from the Ewald sphere is by rotating the crystal about the scattering vector. When the crystal was rotated about (002) and (004) a large variation in the intensity of the satellites near these points, was observed. Intensity disappeared and reappeared at different wavevectors. The result of a rotation of the crystal in $2\frac{1}{2}^\circ$ intervals about (002) is shown in Figure 10. This supports our conclusion that the satellite intensities can be explained in terms of multiple scattering.

FIGURE 10

A number of scans showing the variation in the satellite intensity at (002) when the crystal is rotated about γ by (a) 0° , (b) $2\frac{1}{2}^\circ$, (c) 5° and (d) 10° .

SCANS AT (002) - CRYSTAL ROTATED ABOUT τ



IV.8 TETRAGONAL BRAGG PEAK IN FERROELECTRIC DCsDA.

Deuteration changes a number of properties of CsDA. The shear angle, when measured away from the transition temperature, increases from 1.75° to 2.0° . The transition temperature increases from 146°K in CsDA to 227°K at a deuteration level of 85% ²².

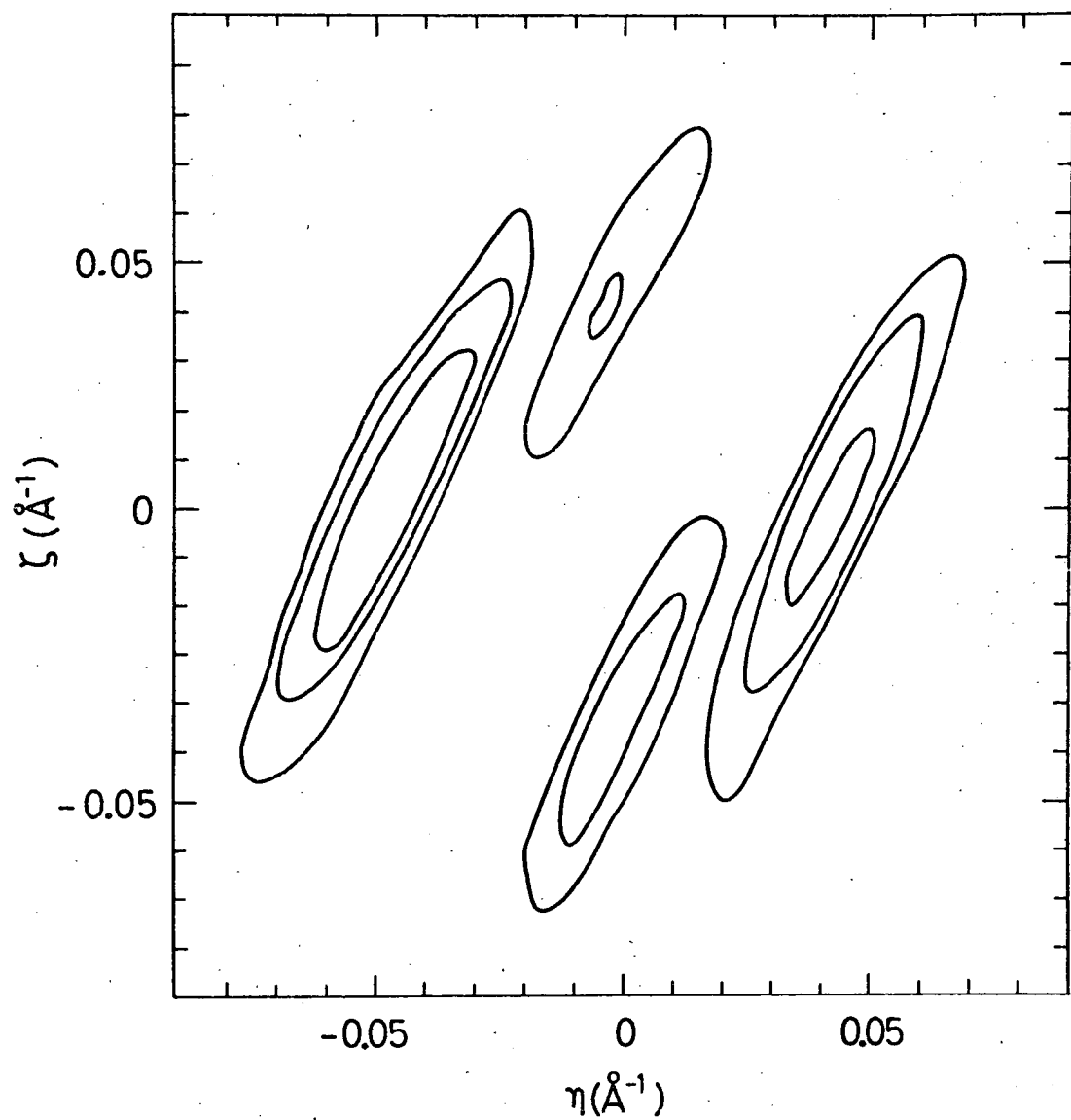
We find that in our samples of DCsDA, obtained from Quantum Technology ¹⁸, only part of the crystal transforms at the nominal transition temperature, with the remainder transforming over a 60 degree interval. In Figure 11 we show the expected splitting of the Bragg point at (220). However in DCsDA, the original Bragg peak remains, over a large temperature interval. A number of $(\frac{1}{2} 2 0)$ and $(2 \frac{1}{2} 0)$ scans at several temperatures showing this effect, are in Figures 12 - 14. In Figure 15 we show the neutron intensity, scattered in a 1cm^3 sample at the (220) tetragonal reciprocal lattice point, plotted against temperature. Obviously, only 40% of the intensity in the tetragonal high temperature phase disappears at 205°K ; the lost intensity is distributed over the four peaks of the orthorhombic low temperature phase. The remaining tetragonal peak intensity transfers to the orthorhombic peaks gradually, over a range extending nearly to the transition temperature of the hydrogenous compound.

Two smaller crystals (8mm^3 and 16mm^3) were investigated on a four-circle neutron diffractometer and showed quantitatively similar behaviour. Structure refinements ²³ indicate that the average deuteration of the 8mm^3 sample is 57%. Such a high hydrogen content is consistent with the unexpectedly intense incoherent neutron scattering found in the experiment on the 1cm^3 sample. $(h k 0)$ photographs of a 0.01mm^3 crystal taken with a Weissenberg X-ray camera again showed similar effects, and confirmed that all reflections were affected.

The fact that crystals of such diverse sizes exhibit quantitatively

FIGURE 11

A contour map of the splitting of the Bragg point (220) in CsDA.
Contours are at 100, 300 and 1000 above the background.



THE DOMAIN SPLITTING AT(220) CONTOURS
100,300 AND 1000 ABOVE BACKGROUND

FIGURE 12

Typical scans through (220) in DCsDA for (a) the $[2\ 0\ 0]$ direction and (b) the $[0\ \bar{1}\ 0]$ direction. The broken line was measured above the transition (212 °K) and the continuous line well below the transition (139 °K).

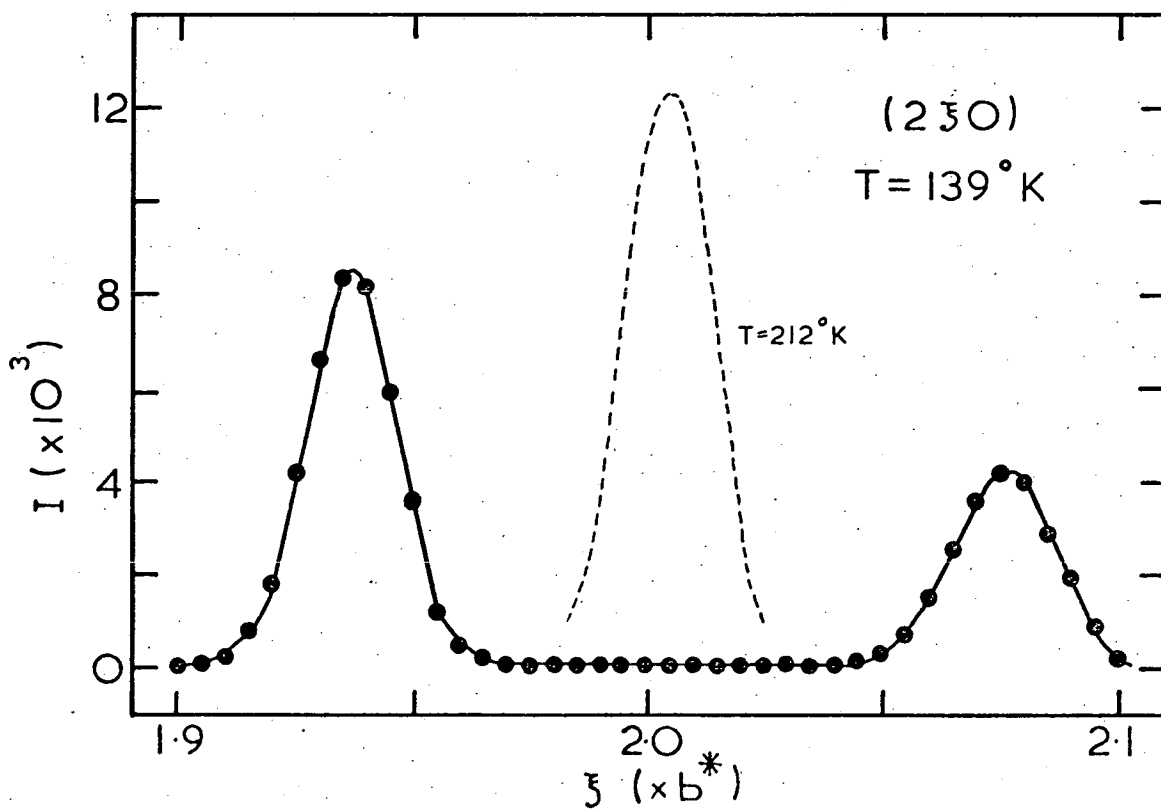
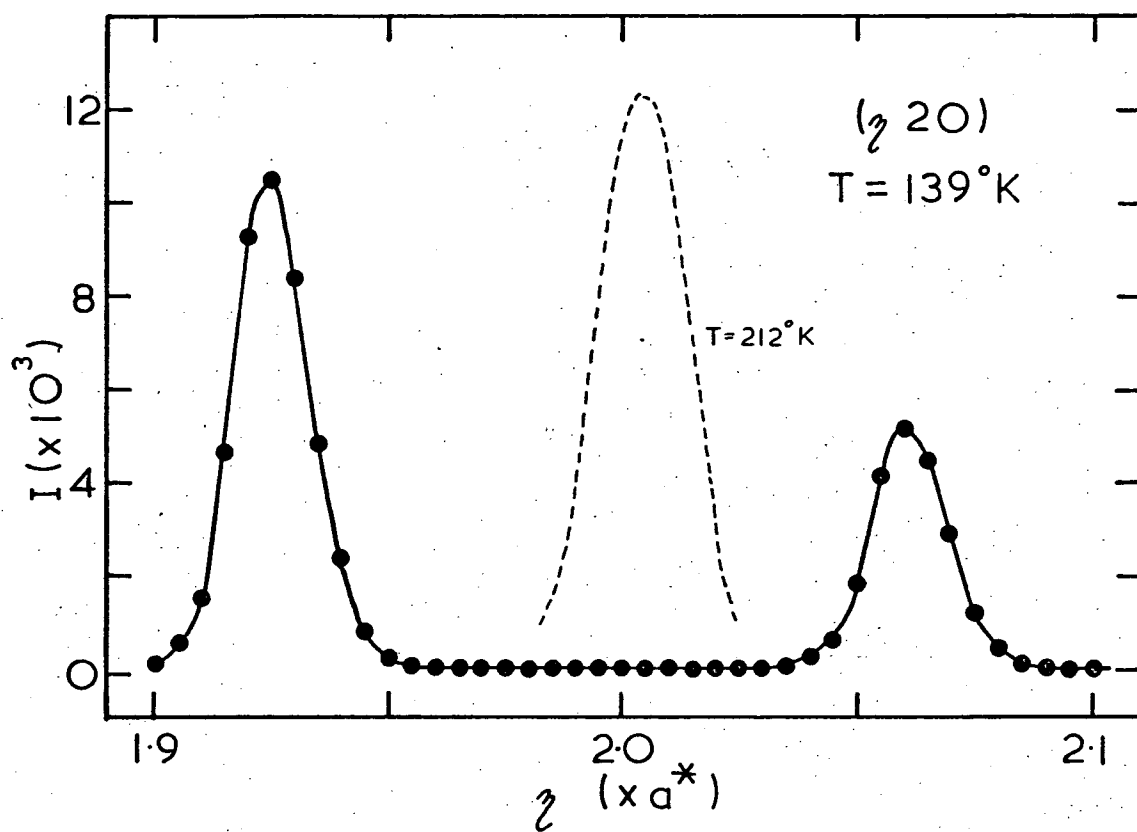


FIGURE 13

Scans through (220) in DCsDA at 185 °K in (a) the $[2\ 0\ 0]$ direction and (b) the $[0\ \bar{3}\ 0]$ direction showing the co-existence of the two phases.

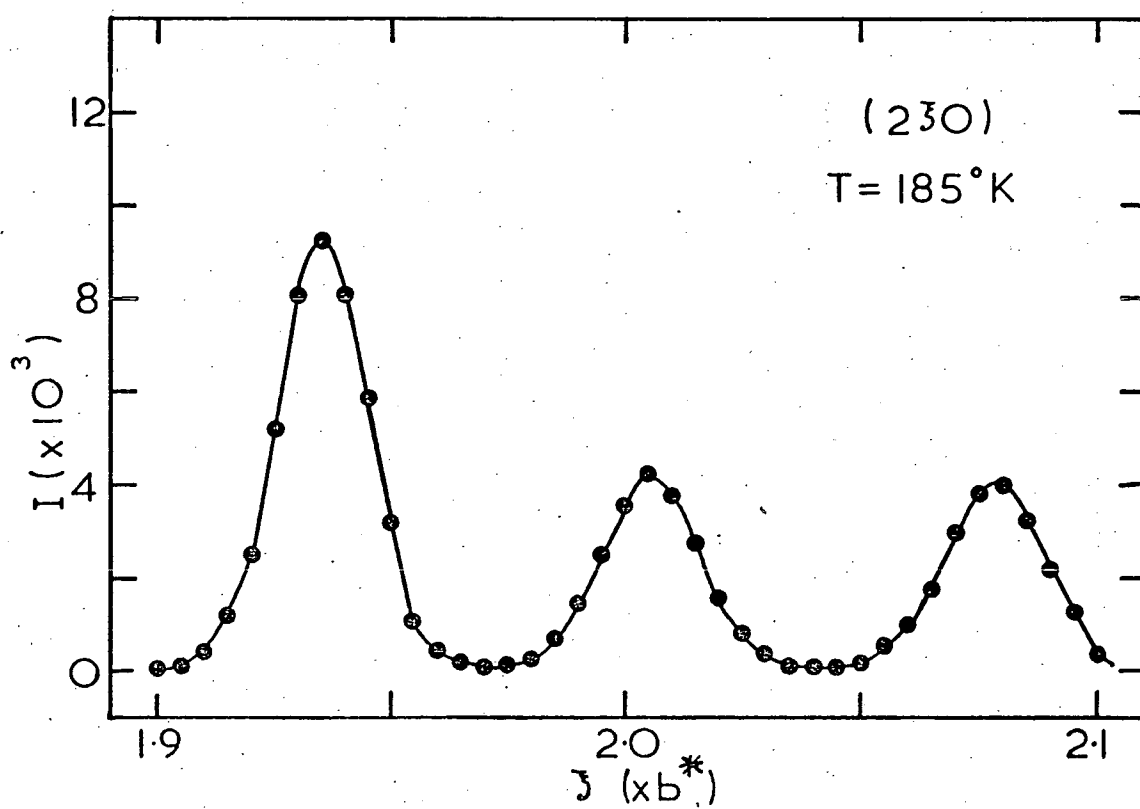
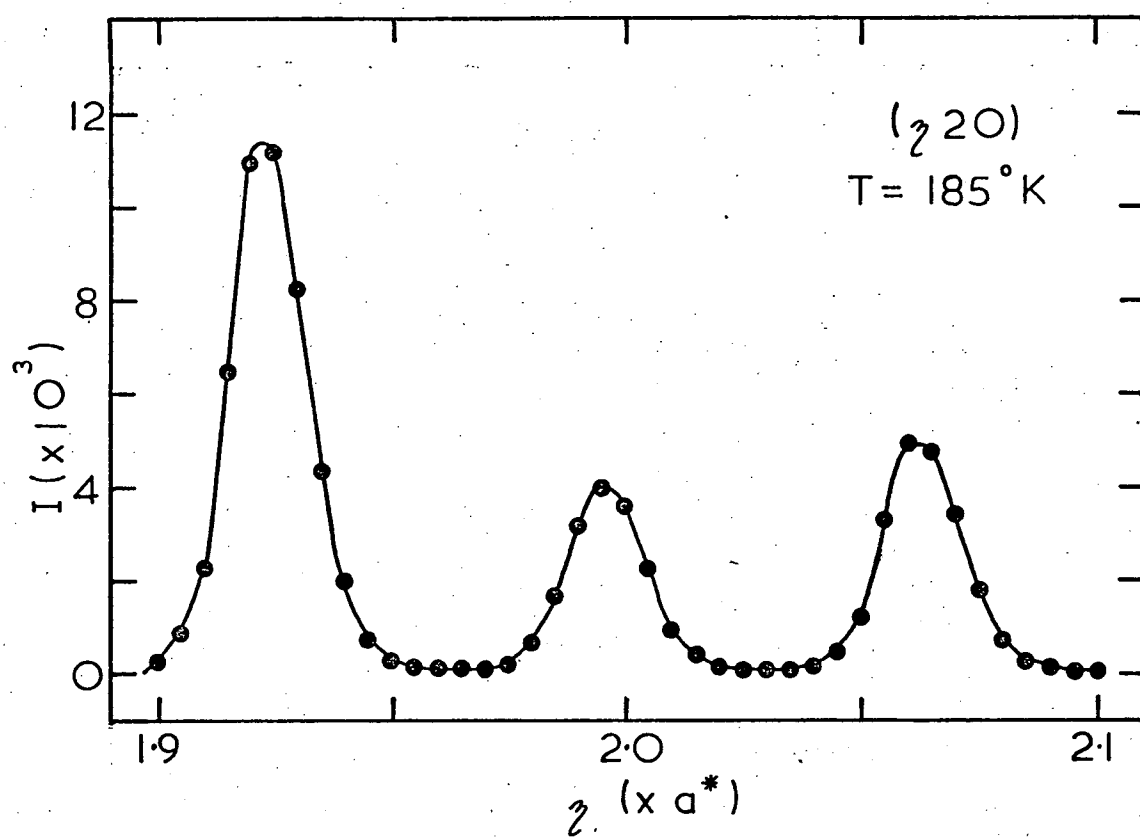


FIGURE 14

Scans through (220) in DCsDA at 197 °K in (a) the $[2\ 0\ 0]$ direction and (b) the $[0\ 5\ 0]$ direction showing the co-existence of the two phases.

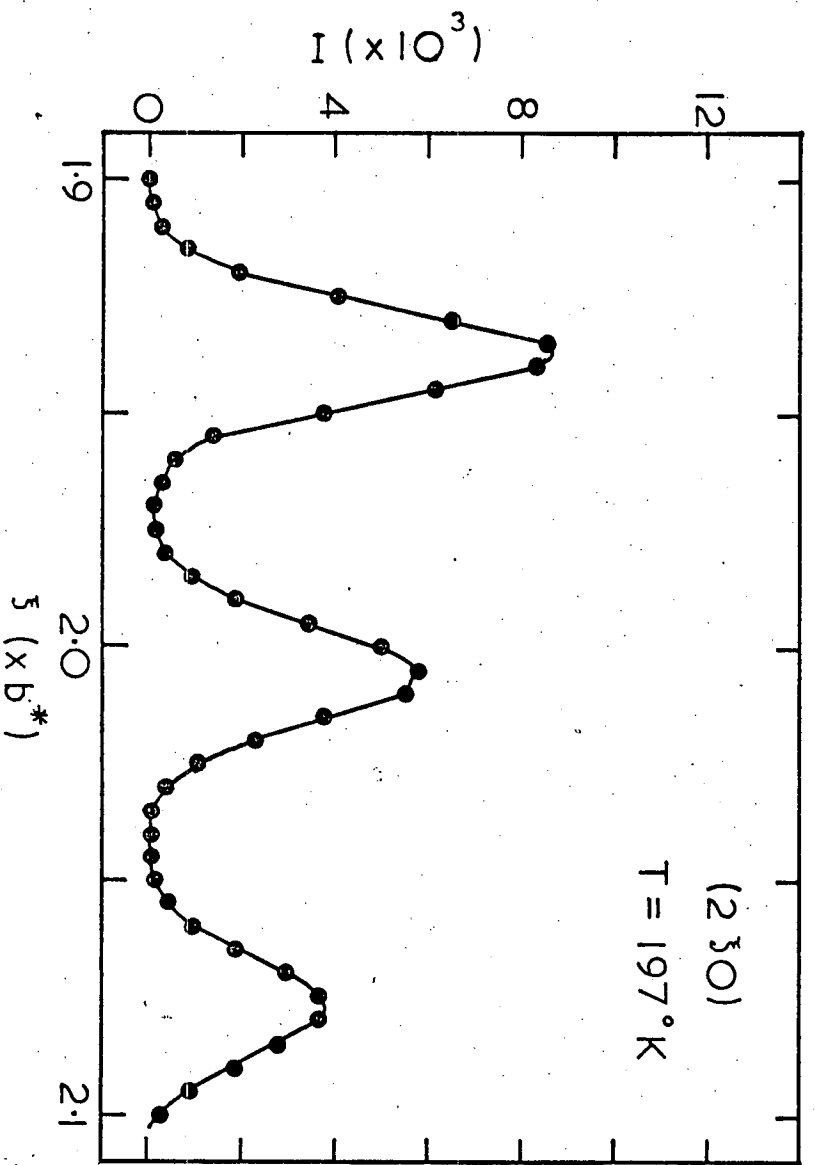
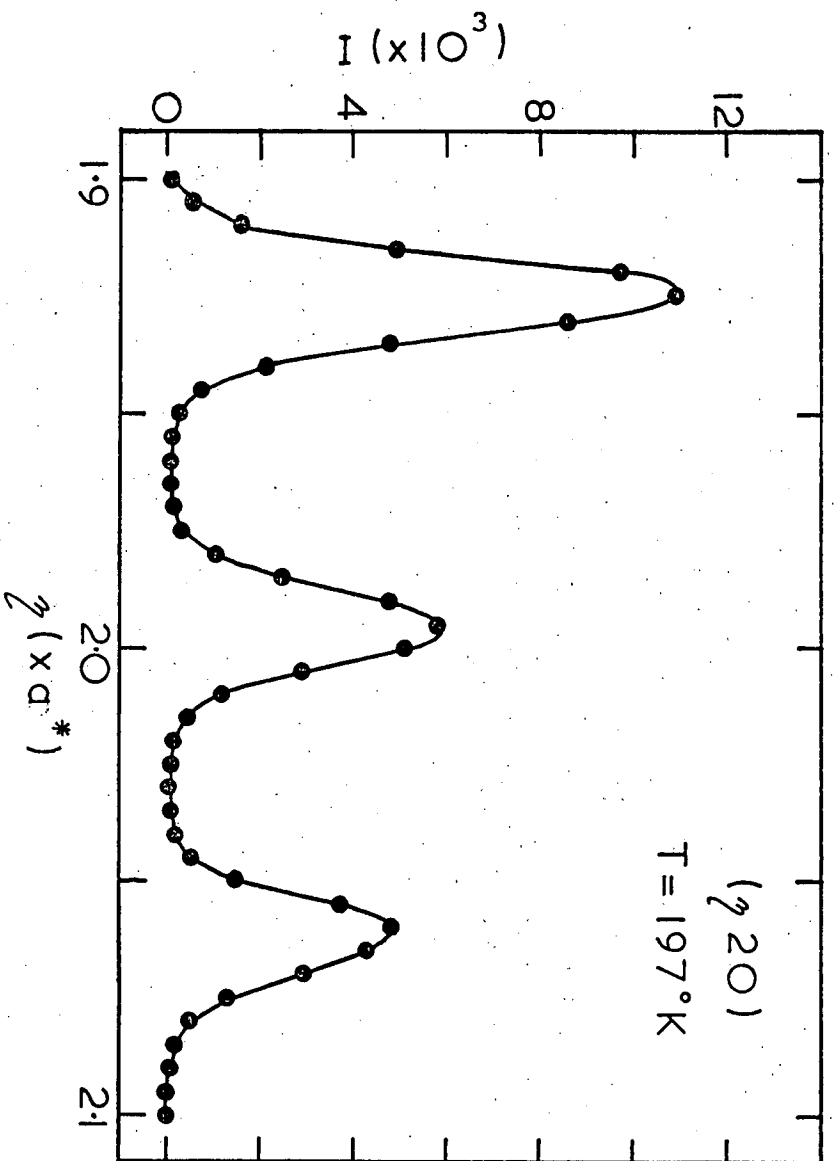
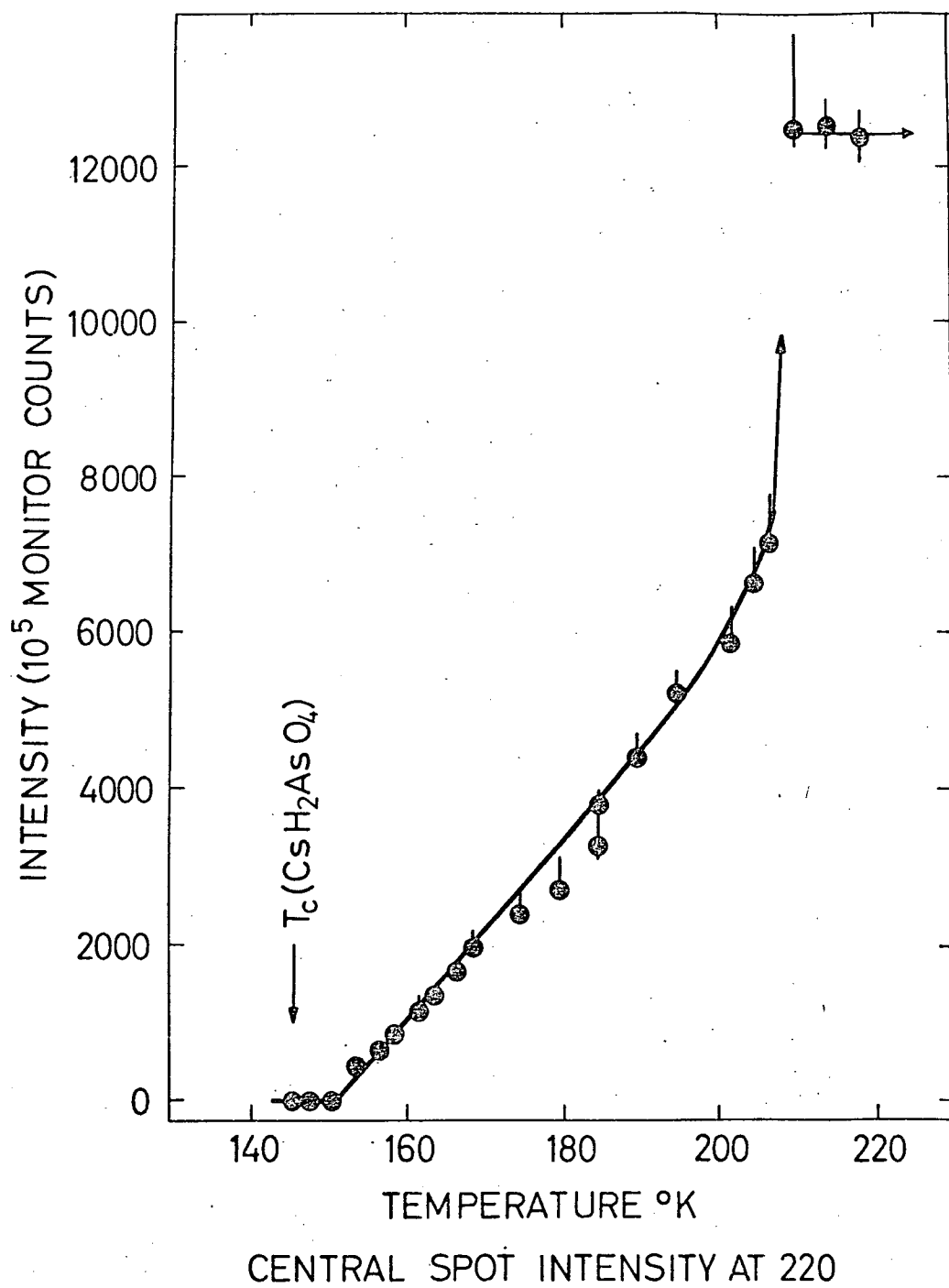


FIGURE 15

The intensity of the central tetragonal spot at (220) measured as a function of temperature in DCsDA. The crystal only partially transforms at $\sim 205^{\circ}\text{K}$. It is only completely in the ferroelectric phase at about the transition temperature of CsDA (146°K).



similar behaviour, makes surface rehydrogenation an unlikely explanation. We conclude rather that the observations suggest an inhomogeneity of the hydrogen-deuterium concentration over regions small in comparison to our smallest sample (0.2mm). This would be consistent with peculiar growth behaviour observed in DCsDA (G.M. Loiacono, private communication), and could be a characteristic common to all solution-grown samples.

The transition temperature of 227°K , given by Loiacono et al.²² for a deuteration level $\sim 85\%$, suggests that the deuteration levels for DCsDA samples quoted in the literature, have been grossly overestimated. If, in addition, the pronounced inhomogeneity of our specimens is a common characteristic, some further doubt must attach to the interpretation of the results of most previous experiments on DCsDA.

IV. 9 SHEAR ELASTIC CONSTANT - BACKGROUND.

It is well known that sound waves exhibit anomalous propagation characteristics in the neighbourhood of the phase transition in ferroelectric crystals^{3, 24-26}. This applies to ferroelectrics which are believed to be displacive, and to those that are of the order-disorder type. Cochran²⁷ has shown that there is a coupling of the ferroelectric mode with the X_y transverse acoustic modes in piezoelectric crystals, such as KDP. The acoustic mode frequency is then driven to zero by the interaction of the mode with the ferroelectric mode, with the result that the transition temperature is somewhat higher than the frequency at which the soft mode extrapolates to zero.

When the elastic constant is measured by neutron spectroscopy, the frequencies of the acoustic mode are no longer lower than those of the ferroelectric mode of the same wavevector. The result of this

is that at large wavevectors, the acoustic mode frequencies are no longer suppressed. The values of C_{66} obtained by this method, should then be similar to those obtained by measurement at constant polarization²⁸.

IV. 10 MEASUREMENT OF C_{66}

A 1cm^3 crystal of DCsDA, obtained from Quantum Technology¹⁸, was used for inelastic neutron scattering measurements. This crystal had a nominal transition temperature of $205 \pm 3^\circ\text{K}$. Although only half of the crystal seemed to transform at this temperature, this was deemed to be a sufficient quantity for this experiment.

The crystal was aligned in the $(h\ k\ 0)$ plane in a cryostat on the TAS 3 triple axis spectrometer at the DR3 reactor, Risø. Constant wavevector transfer inelastic neutron scattering scans were made, in which the outgoing energy was held fixed, initially at 14.5 meV, with a graphite filter used to suppress second order contaminant in the outgoing beam. A search for low energy branches near the reciprocal lattice points (510) , (400) , (310) and (200) gave only a large incoherent quasi-elastic background, which had a F.W.H.M. ~ 0.9 meV, in agreement with the value obtained for the resolution width. A typical scan, that at $(2, 0.24, 0)$, made at 203°K is shown in Figure 16. A number of scans made closer to the reciprocal lattice points showed that at temperatures below the transition temperature, there was too much elastic scattering from single and multiple Bragg scatterings.

The experiments were repeated with 5.52 meV scattered neutrons, which allowed further use of a graphite filter. This reduced the accessible region of reciprocal space, restricting measurements to those around the (200) reciprocal lattice point. The resolution was considerably improved, with the resolution width now ~ 0.2 meV, but the beam flux was down by a factor of 10, necessitating much longer counting times.

Constant wavevector scans were made at $(2, 0.075, 0)$, $(2, 0.1, 0)$, $(2, 0.125, 0)$ and $(2, 0.15, 0)$ at 224°K . The $\sum_2$ acoustic branch was observed and showed no signs of dispersion at these wavevectors. The scans at $(2, 0.1, 0)$ and $(2, 0.15, 0)$ were repeated at 213°K and the frequencies of the branch were unchanged. The latter scan is shown in Figure 17. The considerable quasi-elastic scattering is due to incoherent scattering - mainly from the hydrogen content. This scattering showed no temperature dependence and very little wavevector dependence, so it is unlikely that it can be associated with critical scattering. The $\sum_2$ branch can be seen at about 0.6 meV. The slope of the acoustic mode is therefore $5.2 \pm 0.6 \text{ meV} / \text{\AA}^{-1}$. A scan at $(2, 0.1, 0)$ is shown in Figure 18. This has the $\sum_2$ branch moved in to about 0.4 meV and there is additional scattering at 0.6 meV, which can be associated with the tail of the Bragg peak.

The shear elastic constant C_{66} is related to the $\sum_2$ mode through

$$\omega(q) = \sqrt{C_{66} / D} q \quad (6)$$

The density D was taken to be 3.6g/cm^3 as calculated from the known structure and the measured values of the reciprocal cell dimensions. This agrees with the values quoted in the literature ^{29, 30}. This gives a value of $C_{66} = 1.7 \times 10^{10} \text{ dynes / cm}^2$ (errors left out, but may be quite large $\pm 0.5 \times 10^{10} \text{ dynes / cm}^2$ ^{2,3}). This does not show the temperature dependent behaviour of the constant field elastic constant C_{66}^E , but it can be compared to the constant polarization elastic constant C_{66}^P ³¹ which in CsDA is temperature independent at $2.2 \pm 0.5 \times 10^{10} \text{ dynes / cm}^2$ ². The difference in the two results may be accounted for if deuteration lowers the shear stiffness of our crystal. The result is also consistent with the slightly larger value of shear angle found in DCsDA.

FIGURE 16

A typical scan made with 14.5 meV neutrons in DCsDA at (2, 0.24, 0).
Only the incoherent peak centered at $E = 0$ can be distinguished.

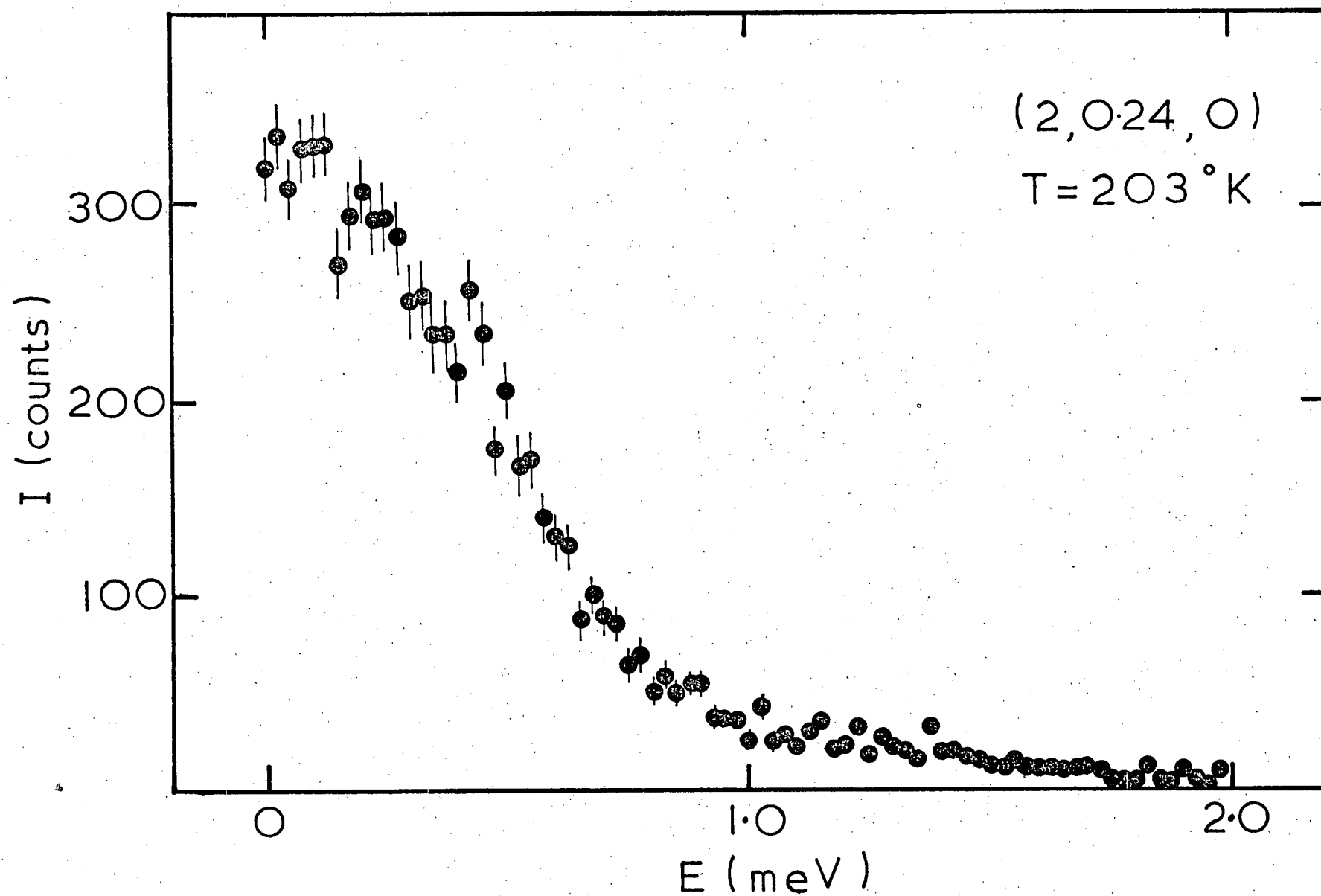
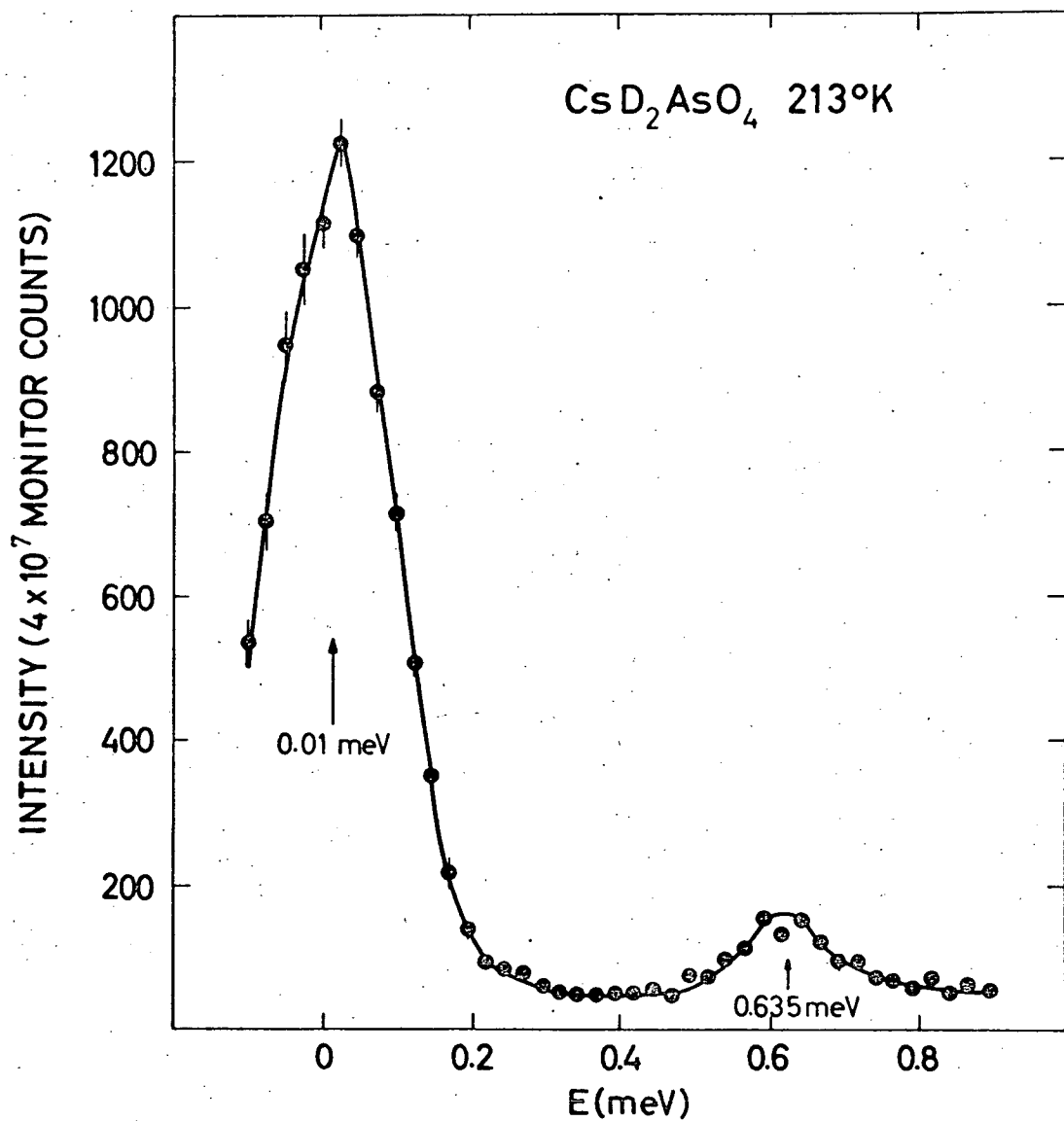


FIGURE 17

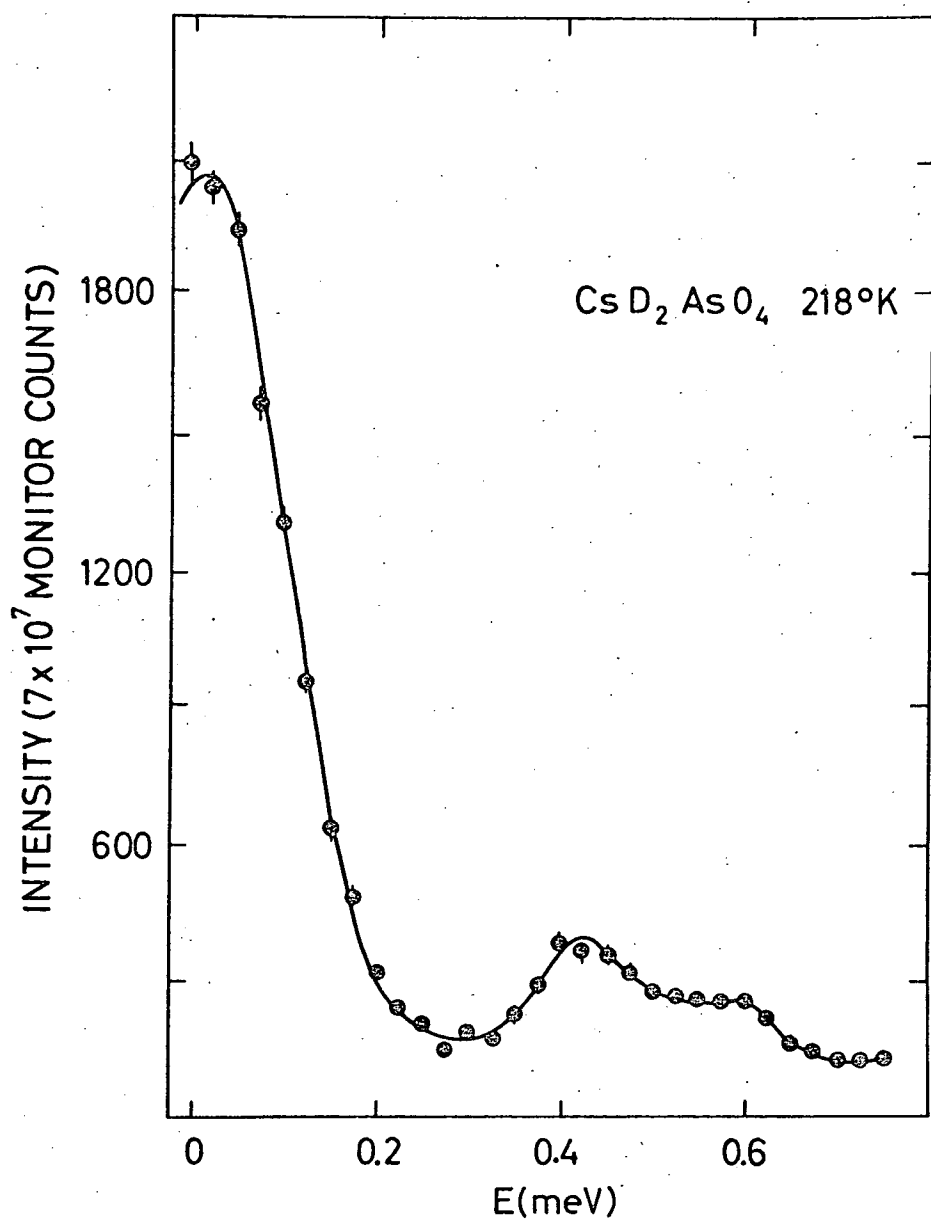
A typical scan made with 5.5 meV neutrons in DCsDA at (2, 0.15, 0)
As well as the incoherent peak at ~ 0 meV the Σ_2 acoustic phonon
is observed at 0.6 meV.



Σ_2 ACOUSTIC PHONON MEASURED AT (20·15,0)
THE PEAK AT $E \sim 0$ IS DUE TO INCOHERENT SCAT-
TERING FROM A LARGE HYDROGEN CONTENT

FIGURE 18

Moving in to $(2, 0.1, 0)$ brings the Σ_2 branch to ~ 0.4 meV.
Additional scattering from the tail of the Bragg peak is picked
up at ~ 0.6 meV.



Σ_2 ACOUSTIC PHONON MEASURED AT (2,0·1,0)
 THE PEAK AT $E=0$ IS DUE TO INCOHERENT
 SCATTERING FROM A LARGE HYDROGEN
 CONTENT. THE TAIL OF THE BRAGG PEAK
 IS AT $E \sim 0.6$ meV

IV.11 CONCLUSIONS

We have shown that the scattering arising at wavevectors away from Bragg reflections in CsDA and DCsDA arises, not because of any real periodic structure in these materials, but is most probably caused by multiple Bragg scattering in which two ferroelectric domains are involved. A phase transition in which a change of symmetry produces twinning, increases the probability of multiple Bragg scattering occurring. Evidence of this scattering is then no longer restricted to reciprocal lattice vectors, γ .

In the case of (D)CsDA the conditions for such scattering are particularly favourable for a number of reasons. The reciprocal cell dimensions quite closely approach that of a cubic system with $a^* = b^* = 0.785 \text{ \AA}^{-1}$ and $c^* = 0.800 \text{ \AA}^{-1}$. The splitting of the Bragg points below T_c is of the order of the difference between these reciprocal cell dimensions. This ensures that in many configurations, a reciprocal lattice point exists on the circular intersection between the sphere of reflection and a plane perpendicular to the scattering plane. In a situation like this, multiple Bragg scattering is guaranteed to occur, and changing the incident neutron energy will have little or no effect on the observed scattering.

All the samples of DCsDA in our possession have a smeared transition. Samples of greatly varying sizes, show the same quantitative behaviour. We believe that the smearing of the transition is due to concentration fluctuations. These fluctuations must occur over regions smaller than our smallest samples (0.2 mm).

Measurements of the elastic constant C_{66} made by neutron spectroscopy in CsDA are more akin to the "open circuit" ($P=0$) elastic constant in the free crystal, rather than the anomalously temperature dependent "closed circuit" ($E=0$) elastic constant in the clamped crystal. This

is because neutron scattering measurements are made at (relatively) large wavevectors where the frequencies of the ferroelectric mode are lower than those of the acoustic mode of the same wavevector. This allows the acoustic mode to follow the ferroelectric fluctuations.

The elastic constant in (D)CsDA is much smaller than that found in (D)KDP³² ($C_{66} = 7 \times 10^{10}$ dynes / cm²) and this explains the larger temperature difference found between the free and clamped Curie temperatures in CsDA². Further evidence for the low shear stiffness in CsDA comes from our measurements of the shear angle, which is a factor of four larger than that found in KDP. Deuterating CsDA slightly lowers the shear stiffness, and this shows up in the smaller value of the elastic constant and the larger shear angle found in the deuterated compound.

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CHAPTER V.

MIXED MAGNETIC SYSTEMS -- THE LINE SHAPE OF THE MAGNETIC

EXCITATIONS IN $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$.

V. 1 INTRODUCTION

The excitations in substitutionally disordered crystals have recently attracted a great deal of attention. The coherent potential approximation (CPA) has been applied in calculating the effect of disorder on a phonon density of states ¹. This is often complicated because of the long range of the harmonic forces and the presence of numerous branches in the spectrum. The CPA has also been applied to calculate the electron density of states when there is disorder ². However it is not possible to test the validity of the approximations by experiment on the electron systems.

In comparison, spin waves in magnetically disordered insulators can be characterised more simply than the other excitations. Additionally, single crystals can be grown at various defect concentrations and the growth properties are believed to be independent of the magnetic properties of the ions. In this way an impurity can be chosen so as to minimise the strain on the pure material.

Most of the early theories were on simple ferromagnetic insulators ³⁻⁶. However, in insulators the exchange interactions are short range, and the system usually orders antiferromagnetically.

Antiferromagnets of the rutile (eg. MnF_2) ⁷, perovskite (eg. KMnF_3) ⁸ and quadratic layer (eg. K_2MnF_4) structures are more common, and have been extensively studied in their pure forms. The magnetic excitations may be studied by light scattering and neutron scattering techniques. Only one spin wave branch is found in the pure systems because the two magnetic atoms in each unit cell are connected by time reversal and symmetry relations ¹⁰. An anisotropic Heisenberg Hamiltonian has been found to give a good description of these systems. The inclusion of anisotropy lifts the degeneracy for the spin wave branches, but the

splitting is sufficiently small to be obscured by resolution effects in experiments ⁷.

When a small concentration of defects are introduced into these antiferromagnetic insulators, variations of cluster or Ising models can be used to describe the excitations. The most successful method is to use Greens functions, which can be used to describe the host crystal exactly and they also give a good description of an isolated defect. At finite concentrations, the interactions can be treated by a series expansion. From the experience gained in these calculations, it appears that in the small concentration limit, an exact treatment of the longitudinal exchange interactions is more important than the inclusion of an accurate description of the transverse terms ¹¹. To what extent this carries over to systems with high concentrations of defects remains to be seen. It is partly justified by the structure we find in the line shapes of the excitations in Mn/ZnF_2 . Similar structure has been found by Svensson et al. ¹² and also by R.A. Cowley and R.J. Birgeneau in $\text{K}_2\text{Mn/MgF}_4$ (private communication). The structure in these materials is not as pronounced as would be expected from single site CPA theories, so perhaps some of the width arises from neglect of some of the transverse interactions.

When the defect concentration becomes larger, there is a finite probability (increasing rapidly with the concentration) that defects will be on adjacent sites and the theories can no longer be as exact as in the small concentration asymptotic limit. There is a choice in the approximations which have to be made and these have a varying effect on the results. Which choice of approximation is the most appropriate is not obvious. Neutron scattering experiments are perhaps able to differentiate between the theories, although in the past the instrumental resolution has not been good enough to indicate which theory is the

most appropriate¹³.

A single site coherent potential approximation theory has been derived by a number of authors^{10,15,16} as an extension of the earlier CPA theories of Soven¹ and Taylor², which were applied to electron and phonon density of states respectively. This type of approximation is expected to be most effective when only the exchange is affected by the inclusion of impurities and this can be treated exactly by CPA theory. However, the off-diagonal terms are usually also altered and these can only be treated approximately. The non diagonal terms are expected to be less important in the impurity rutile structure than in the impurity perovskite structure.

Another method of calculating the magnetic excitations in a dilute system is to replace the interactions in the crystal by an effective medium in which the scattering from a complex is on average zero^{6,16,17}. This type of approximation allows the transverse terms to be treated more exactly, so it is expected to be more appropriate when these terms are relatively large.

We might hope to differentiate between the theories, by observing the widths of the excitations in a neutron scattering experiment. If the resolution is sufficiently good, fine structure in the excitations predicted by single site CPA theories, but not present in the average site theories, should be observed. We have undertaken such an experiment on a dilute antiferromagnet of the rutile structure in which 32% of the (magnetic) manganese ions in MnF_2 are replaced by (non magnetic) zinc ions. When the impurities are non-magnetic there are no free parameters; these can all be taken from experiments on the pure system.

Because of the approximate nature of both types of theory, the calculations produce spurious structure at low energies, caused by an over-

flow of magnetic atoms onto the non-magnetic impurity sites. Two methods have been developed to overcome this problem; known as the hard core and empty core techniques. In the former case, the spurious zero frequency response is moved to frequencies high enough not to enter into the experimental conditions. In the latter case, calculations are restricted to the magnetic ions. These methods have some effect on the calculated line shapes of the magnetic excitations, but to a lesser extent than the differences due to making the single site or average site approximations.

In section 2, we briefly look at the form of the excitations in pure MnF_2 . In section 3 we discuss a simple cluster model which displays many of the features described by the more complex single site CPA theories discussed in section 4. A comparison is made with the average site CPA theories. In section 5 we describe an experiment on $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$.

V. 2 MANGANESE FLUORIDE.

The ground state of the free Mn^{2+} ion has orbital angular momentum $L = 0$ and spin angular momentum $S = \frac{5}{2}$. It is a good approximation to say that neither the crystal field environment nor spin orbit interactions influence the ground state. The effective spin in the Hamiltonian may thus be replaced by the true spin $S = \frac{5}{2}$.

The magnon dispersion relations in pure MnF_2 (Manganese Fluoride) have been measured by Okazaki et al.¹⁸ and by Nikotin et al.⁷. At low temperatures, they have shown that the system is well represented by the Heisenberg Hamiltonian for an antiferromagnet.

$$\hat{H} = - \sum_{ij} J_{ij} \underline{S}_i \cdot \underline{S}_j - \sum_{ij} K_{ij}^{ab} S_i^a S_j^b \quad (1)$$

Single ion anisotropy is negligible, so the term

$$K_{ij}^{ab} = g^2 \mu^2 (r_{ij}^2 \delta_{ab} - 3r_{ij}^a r_{ij}^b) / 2r_{ij}^5 \quad (2)$$

represents the magnetic dipole-dipole interactions. Using calculated values of this Nikotin et al.⁷ found that the three parameters

$J_1 = 0.028$ meV, $J_2 = -0.152$ meV and $J_3 = -0.004$ meV gave a good description of the dispersion curve which was not improved by the inclusion of interactions of more than third nearest neighbours. The dominant coupling, J_2 , is between second nearest neighbours. This is an interaction between neighbours along a body diagonal (see Figure 1) and the negative sign indicates that it is antiferromagnetic. Part of the effect of the dipolar interaction is the removing of the degeneracy on the spin wave branches. However, the estimated splitting of the frequencies is never large enough to be detected in a neutron scattering experiment ($\lesssim 0.005$ meV).

Figure 2 shows the general dispersion curve for an antiferromagnet such as MnF_2 . The general shape would be similar along $[001]$ and $[101]$ directions, but the energy at the zone boundary would differ, being slightly greater in both cases.

V. 3 CLUSTER MODEL

It is instructive to use a simple cluster model to show the approximate effect of the introduction of defects into a magnetic system. We use an Ising model, which differs from a Heisenberg model in that the transverse parts of the exchange interaction are neglected. Therefore

$$\hat{H} = - \sum_{mn} I_{mn} S_m^z S_n^z \quad (3)$$

where anisotropy has been neglected and only exchange between sublattices

is considered. I is the longitudinal or Ising exchange between the Z components of the spin S . With the introduction of magnetic or non-magnetic defects onto some of the magnetic lattice sites, the exchange will no longer depend solely on $\underline{r}(m) - \underline{r}(n)$.

The excitation energies are calculated on the basis of a molecular field, generated by the nearest neighbours. Cowley and Buyers¹¹ show that this type of model, although not expected to work well at general q values, provides a satisfactory description of the zone boundary excitations. In a dilute magnetic system such as Mn/ZnF_2 the excitation frequencies will be approximately

$$\omega(r) = (Z - r) IS \quad (4)$$

where we have only included the dominant exchange between the Z second nearest neighbours, and r of these positions are occupied by non-magnetic zinc ions. Inclusion of the other nearest neighbour interactions and taking some account of the dipolar anisotropy will of course alter these frequencies, but the principle of the model is unchanged. It only remains to calculate the probabilities of having the different number of defect configurations. These are given by

$$P(r) = \frac{Z!}{(Z - r)! r!} C^r (1 - C)^{Z - r} \quad (5)$$

where C is the concentration of defect ions and in the rutile structure, there are 8 neighbours along the body diagonal directions.

In Figure 3 we show a schematic diagram of the expected distribution of intensities from this model, when $C = 0.33$. The model is built up from a series of delta functions at the frequencies given by equation 5. We use a histogram to approximate the widths, which are not included in the theory, and also instrumental resolution.

FIGURE 1.

This shows the rutile structure for MnF_2 . The unit cell is tetragonal, with the c axis about $2/3$ of the length of the a and b axis. At low temperature, the magnetic manganese ions are ordered antiferromagnetically in layers along the c axis through the dominant exchange interaction along the body diagonals. The dilute system Mn/ZnF_2 is obtained by randomly replacing the manganese ions by zinc ions.

Mn



F

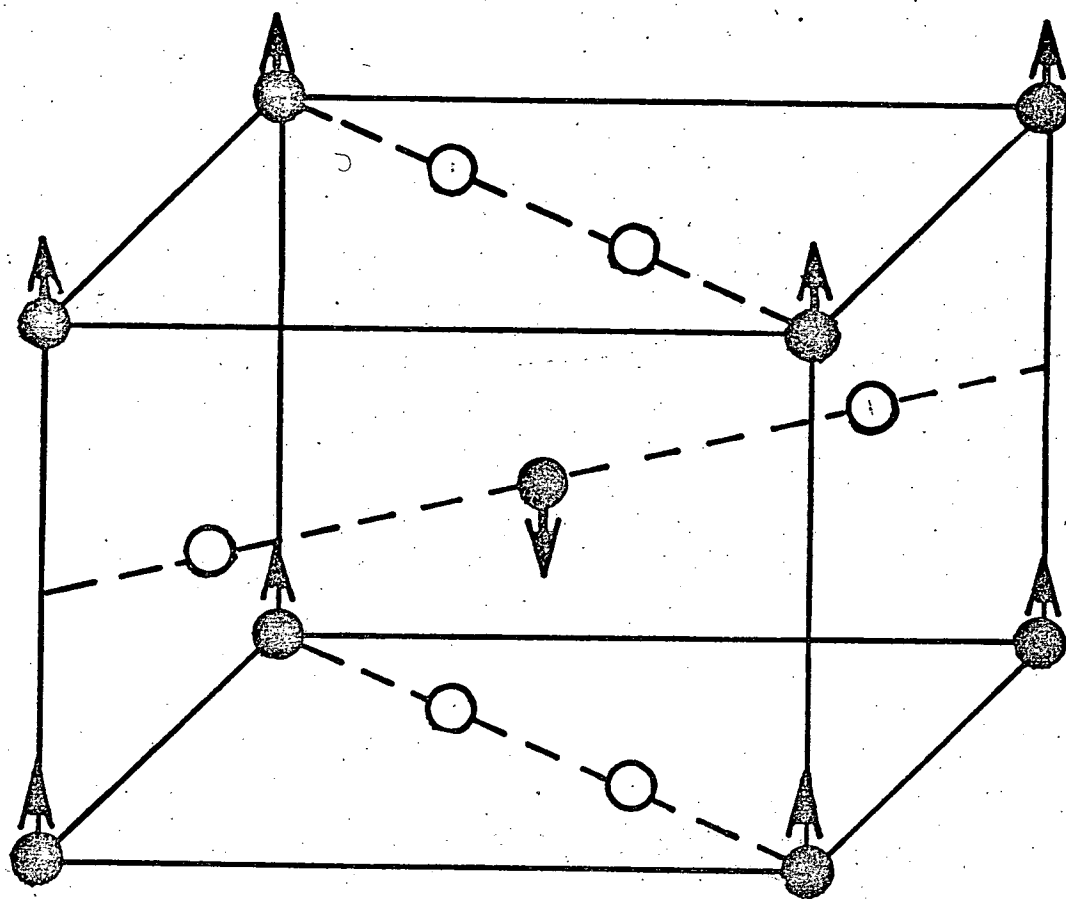


FIGURE 2.

A typical dispersion relation for the spin waves in the antiferromagnet MnF_2 .

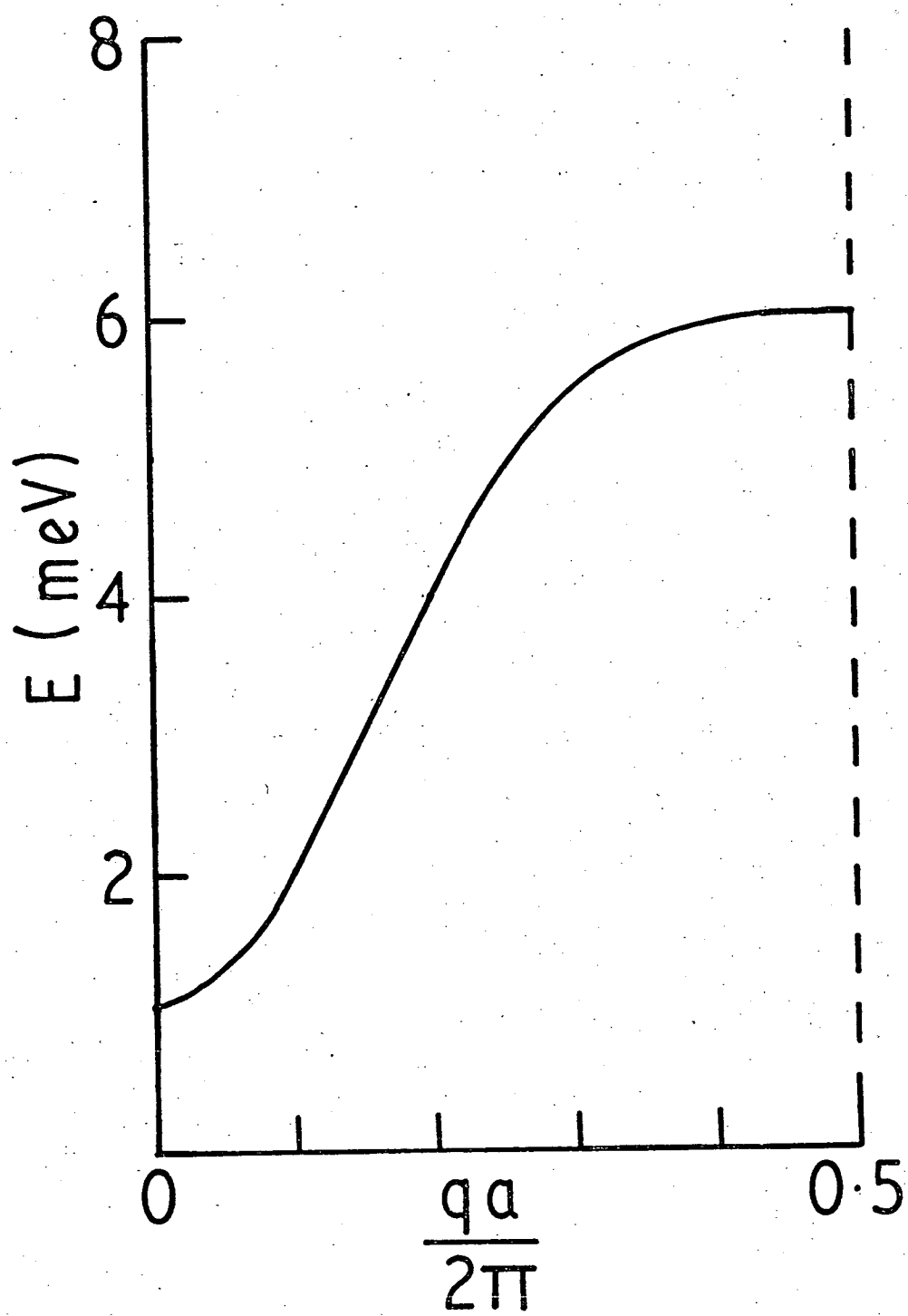
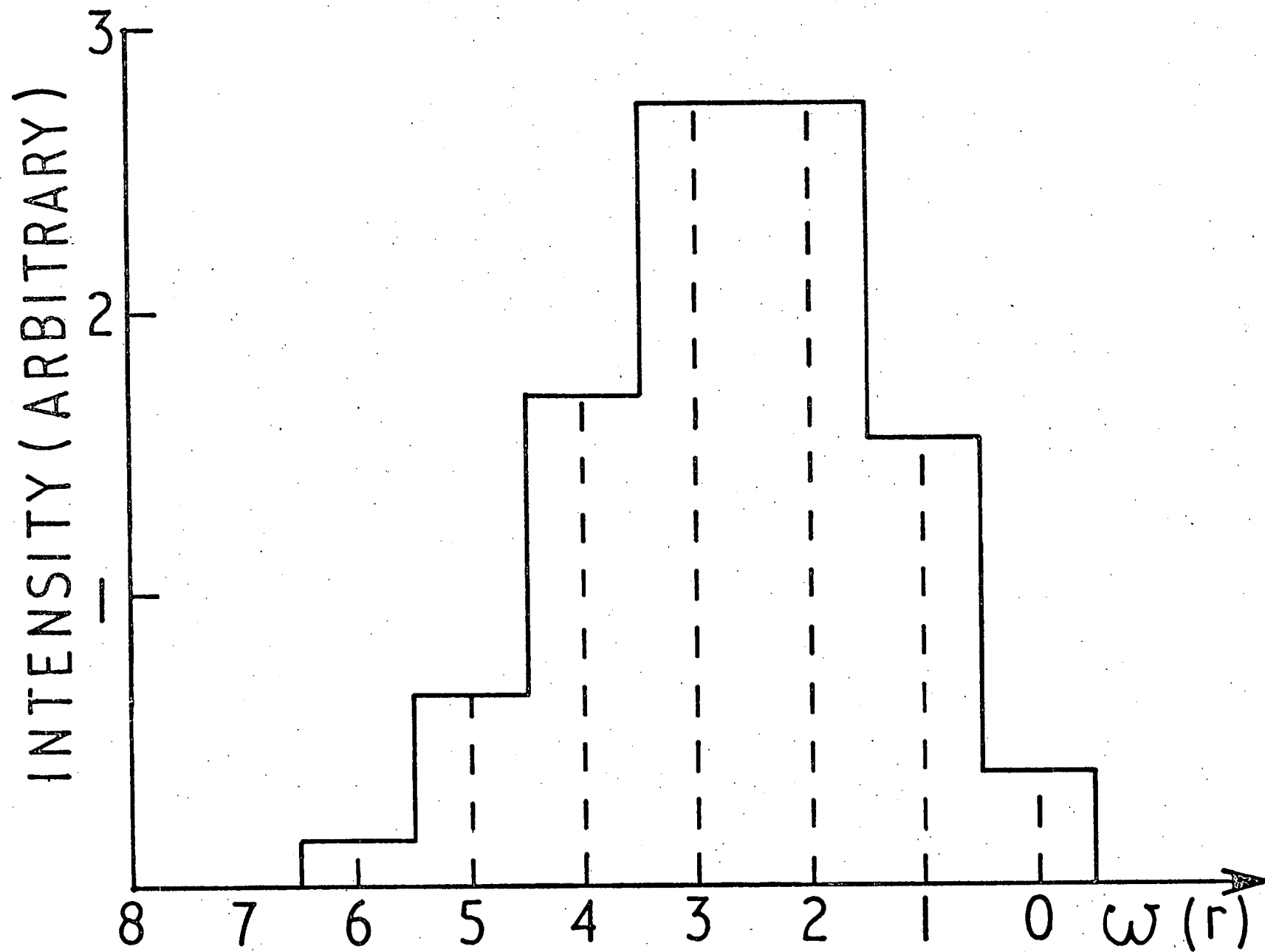


FIGURE 3.

Using a simple cluster model, the Ising modes can be weighted according to

$$P(r) = \frac{Z!}{(Z-r)! r!} c^r (1-c)^{Z-r}$$

The widths are provided by using a histogram. This type of model may be used to give a rough idea of the energies and widths of the excitations.



Birgeneau et al.⁹ show that in some ways this provides a good description of the random quadratic layer antiferromagnet $\text{Rb}_2 \text{Mn}_{0.5} \text{Ni}_{0.5} \text{F}_4$. This has two branches because the impurity is magnetic. The individual peaks within a branch, can be well represented by this type of model, but the relative intensities of the two branches differ considerably from the predicted values. They suggest that the transverse terms can transfer intensity between the Mn^{++} and Ni^{++} branches without having much effect on the energies. This shows that more sophisticated models are required to describe some of the finer features of the excitations.

V. 4 THE THEORIES.

A defect system, such as that with the rutile structure can be described in terms of an anisotropic Heisenberg Hamiltonian

$$\hat{H} = \sum_{mn} I_{mn} S_{mu}^Z S_{nd}^Z + \frac{1}{2} J_{mn} (S_{mu}^+ S_{nd}^- + S_{mu}^- S_{nd}^+) \quad (6)$$

where m and n are unit cells and u and d are the up-spin and down-spin sublattices. The spins can take on two values corresponding to a host or defect ion; and the exchange interactions can take on three values corresponding to host-host, host-defect and defect-defect interactions. The system is normally studied using Green functions¹⁹ which for an impure lattice are defined as

$$G^{ab}(mn, \omega) = \frac{(-1)^{1+a}}{2(S_{ma} S_{nb})^{\frac{1}{2}}} \langle\langle S_{ma}^+ S_{nb}^- \rangle\rangle_{\omega} \quad (7)$$

where a and b can take on the values 1 or 2 (ie. up or down) and

$\langle\langle S_{ma}^+ S_{nb}^- \rangle\rangle_{\omega}$ is the frequency Fourier transform of the retarded Green function. If the equation of motion for the Green function in the pure

crystal is written in matrix form as

$$\omega \underline{g} = \underline{I} + \underline{A} \underline{g} \quad (8)$$

where $\underline{A}$ is the dynamical matrix;

then an equivalent expression can be written for the Green function in the defect crystal as

$$\omega \underline{G} = \underline{I} + (\underline{A} + \underline{V}) \underline{G} \quad (9)$$

These are all $2N$ by $2N$ matrices where N is the number of unit cells.

The two equations may be combined to form a Dyson equation

$$\underline{G}(\omega) = \underline{g}(\omega) + \underline{g}(\omega) \underline{V} \underline{G}(\omega) \quad (10)$$

The matrix $\underline{V}$ is only non zero on the elements for the sites which are affected by an impurity. The introduction of defects into the system has removed the translational symmetry of the system, but this can be restored by summing over all the sites and taking a configurational average

$$\langle \underline{G}(\underline{q}, \omega) \rangle = \underline{g}(\underline{q}, \omega) + \underline{g}(\underline{q}, \omega) \sum \underline{V}(\underline{q}, \omega) \langle \underline{G}(\underline{q}, \omega) \rangle \quad (11)$$

In the single site approximation these are 2×2 matrices and in the initial calculations, the self energy matrix is assumed to be diagonal with the elements related by

$$\sum^{11}(\omega) = -\sum^{22}(-\omega) = \sum^1(\omega) \quad (12)$$

Since $\sum^1(\omega)$ is independent of $\underline{q}$ we can return to the site representation and define a perturbation at particular sites away from the effective average crystals as

$$\tilde{V}^a(m) = V^a(m) - \sum_a(\omega) \quad (13)$$

The coherent potential approximation is to find an effective Green function in which the random perturbations on average give no scattering of the excitations. The multiple scattering from an individual site is given by the T matrix whose elements are given by

$$T^a(m) = \frac{V^a(m)}{1 - V^a(m)g^a} \quad (14)$$

and the effective Green function is given by

$$g^a = \frac{1}{N} \sum_q \langle G^{aa}(q, \omega) \rangle \quad (15)$$

In the single site approximation, the self energy is calculated under the condition that $\langle T^a(m) \rangle = 0$. This can be expressed in terms of the concentration of defects as the condition

$$\sum_{r=0}^Z P(r) [C T_D^a(r) + (1-C) T_H^a(r)] = 0 \quad (16)$$

where $P(r)$ is given by equation 5. The self energy is obtained by an iterative solution of equations 11, 14, 15 and 16.

So far, only a solution for the diagonal elements of the self energy matrix has been obtained. The off diagonal elements in the matrix can only be obtained approximately. In the virtual crystal approximation (VCA) of Coombs and Cowley¹⁵ the elements are chosen to be independent of frequency as

$$\sum_{l=1}^{12} (q, \omega) = - \sum_{l=1}^{21} (q, \omega) = W \sum_{\text{neighbours}} \exp(iq \cdot R) \quad (17)$$

The constant W is obtained from the rotation symmetry of the Hamiltonian which requires that at $q = 0$ and $\omega = 0$ with an average anisotropy $\bar{H}$

$$\sum_{12}^{12} (0,0) = \sum^1 (0) - \bar{H} \quad (18)$$

Buyers et al. (BPE) assume that the frequency dependence of the off-diagonal terms is related to the frequency dependence of the diagonal terms through

$$W(\omega) = \frac{1}{Z} \left(\sum^1 (\omega) - \bar{H} \right) \quad (19)$$

These approximations produce slightly different results which shall be illustrated later.

Added complications arise when the defect ion is non magnetic, as is the case for zinc. Two methods have been developed to overcome the problem which is apparent when $S^1 = 0$ is inserted into equation 7. The method favoured by Buyers et al.¹⁴ is the hard core approximation. A fictitious large repulsive potential is introduced on the non-magnetic ions which keeps the spin waves from propagating via the zinc sites. The impurity spin can then be given as $S^1 = \frac{1}{2}$ and $I(\text{Mn} - \text{Mn}) \ll I(\text{Zn} - \text{Zn}) < I(\text{Mn} - \text{Zn})$. The magnetic excitations on these ions are then moved to very high frequencies, where they have little effect on the low frequency excitations on the magnetic ions. Coombs and Cowley¹⁵ have also tried what is known as the empty core method in which the calculations are only made for the magnetic ions.

We therefore have four variants on the single site coherent potential approximation as applied to dilute antiferromagnets - two involving a hard core approximation which we can label BPEH and VCAH and two which

use the empty core approximation which we label as BPCE and VCAE.

The characteristic of all these single site theories is that the frequencies are decreased in comparison to those found in the pure crystal. At a concentration of defect ions above about 0.7, the magnetic scattering becomes disordered - there is no long range order and the spin waves are replaced by an overdamped response. At smaller defect concentrations, the line shapes of the excitations are predicted to be structured. The structure should be most apparent at the zone boundaries, where the average frequency of the response is greatest, and peaks in the structure are predicted at approximately the frequencies given by the simple Ising cluster model, discussed in section 3. The four variants predict slightly different frequencies with a slight variation in the weighting of the cluster model theories.

A recent Monte Carlo computer simulation of the system has been developed by Holcomb and Harris²⁰ using an array of 8192 sites. The line shape of the excitations has a structure similar to those obtained by the CPA theories discussed above, although the frequencies of the peaks in the line shape are somewhat shifted.

An alternative use of the CPA in this type of system has been made by Harris et al.⁶ and by Holcomb¹⁷. The former paper considered dilute ferromagnets whereas the latter was restricted to the dilute system Mn/ZnF_2 . This use of the CPA produces an unstructured lineshape with a peak frequency approximately that of the "average" frequency in the single site theories. The differences between the single site theories and average theories arise because in the latter case all the magnetic ions are treated equivalently. However, this allows the transverse interactions to be included more satisfactorily.

V. 5 EXPERIMENTAL RESULTS

The crystal used for the experiments was a single crystal of $\text{Mn}_{1-C}\text{Zn}_C\text{F}_2$ with $C = 0.32 \pm 0.02$. The crystal was used in earlier low resolution measurements by Coombs and Jones^{21,22} and a comparison was made with various single site and average site CPA theories. The experimental resolution was such that any structure in the line shape was obscured so only a comparison with the gross structure predicted by the theories was made.

With the introduction of the cold source at Risø an opportunity arose to repeat the experiment making use of the greatly improved flux at low neutron energies to improve the resolution.

The experiments were performed at 6K on the TAS 1 triple axis spectrometer at the DR3 reactor. Pyrolytic graphite crystals were used for the monochromator and analyser. The scattered energy was held fixed at either 3.5 meV, configuration A or 5.0 meV configurations B and E. In all configurations, a beryllium filter was placed between the specimen and analyser to eliminate neutrons which might be reflected by higher order planes in the analyser. A flat background was subtracted from the raw neutron groups, before compensating the results for the number of higher order neutrons reflected by the monochromator and counted by the monitor. This correction factor varied smoothly between 1.4 at low energy transfers to 1.1 at the highest energy transfers. This gives the distributions for a constant incident flux of the first order desired neutrons.

Figure 4 shows some of the results obtained for the $[100]$ and $[001]$ zone boundaries for a variety of different experimental arrangements. On each scan the experimental resolution (FWHM) is indicated for some typical energies, while below the distributions are shown a set of equally

spaced arrows corresponding to the approximate positions for the fine structure. The line shape for $(0\ 0\ 0.5)A$ as well as having the obvious maximum at 4.5 meV, appears to have two shoulders on the high frequency side. When the models were fitted to this line shape, they were not found to have the necessary width to follow the line shape. This was particularly so at the low frequency side where there appears to be excess scattering of unknown origin.

The line shape of $(1.5\ 0\ 0)B$ and $(0.5\ 0\ 1)B$ have a flat topped or two peaked response but individually the rest of the line shape shows no significant departures from a smooth curve other than those that could be accounted for by statistical fluctuations.

In Figure 5 we show the line shape at $(0.5\ 0\ 0)$ configuration E with the predictions of four of the models when broadened by the appropriate resolution functions. In part (a), we show a comparison with the theory of Holcomb¹⁷. Clearly the shape is in detail incorrect, being considerably more peaked than that observed experimentally. The deviations are most apparent on the high frequency side, although quite good account can be taken of the low frequency side.

In parts (b) and (c) are shown two of the single site CPA calculations. In these calculations, it is necessary to add an imaginary part, ξ , to the frequency to aid the numerical integration. The results become more and more sharply structured as ξ is reduced, but the iteration does not converge so readily. For the mesh size used, convergence could be obtained with ξ as low as 0.1 meV, but as is shown in Figure 5, the VCAE and BPEH variants of the single site theories, provide good descriptions of the observations with the much smoother line shapes calculated for $\xi = 0.3$.

The fourth diagram on Figure 5 shows a computer simulation of the system by Holcomb and Harris²⁰ in which the concentration of defects

FIGURE 4.

Neutron scattering distribution from the $[100]$ and $[001]$ zone boundary excitations in $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$. The horizontal bars give the experimental resolution for the various different experimental configurations described in the text. The vertical arrows denote the approximate positions of the fine structure.

NEUTRON DISTRIBUTIONS FROM $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$

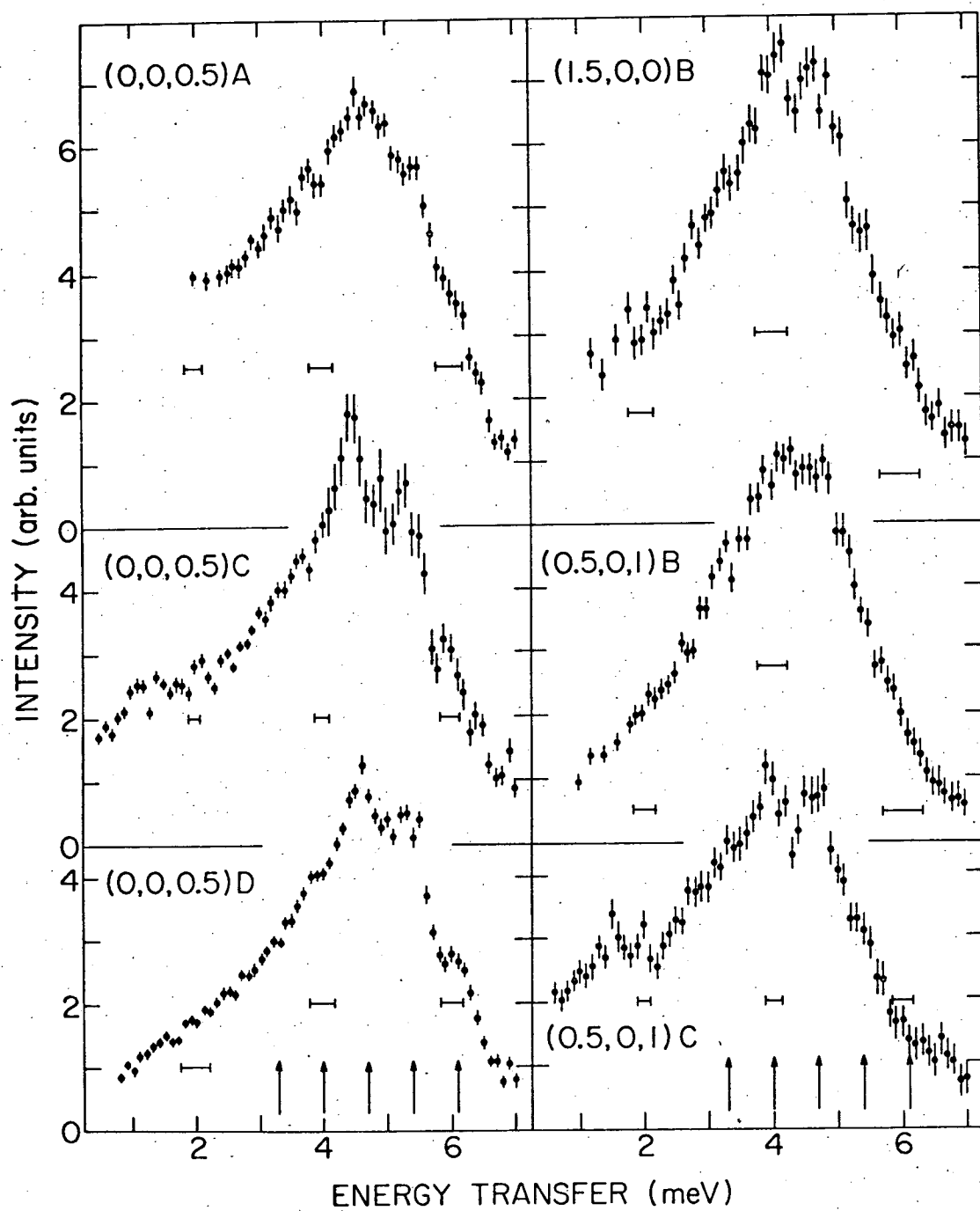
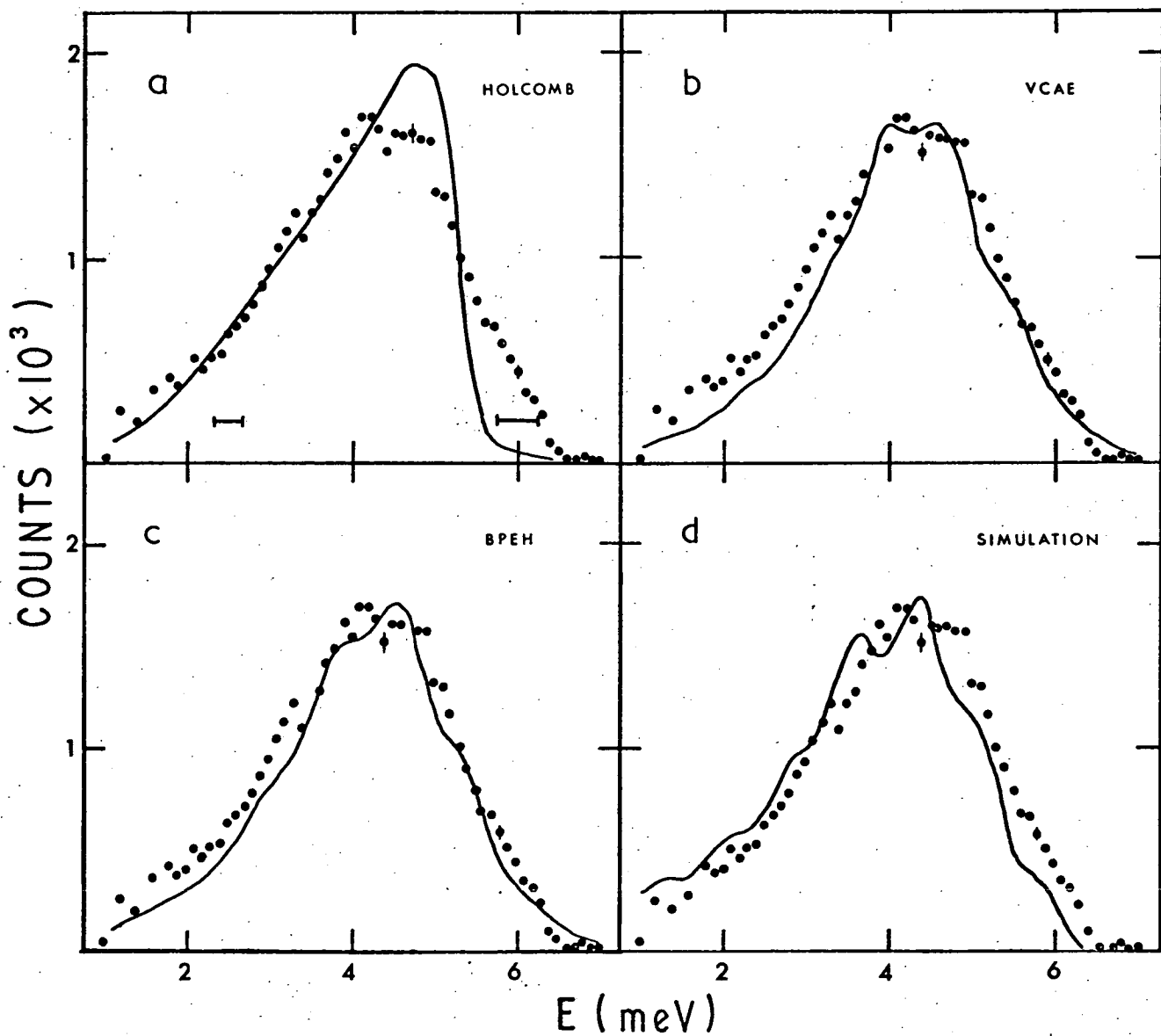


FIGURE 5.

The neutron scattering distribution at (0.5 0 0) from the magnetic excitations in $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$ compared with the predictions of the theories of Holcomb¹⁷, Coombs and Cowley¹⁵, Buyers et al.¹⁴ and computer simulations by Holcomb and Harris²⁰.

(0.500)E



was $C = 0.35$. This model also predicts structure, but the whole line shape appears to be displaced with respect to the measured line shape.

The experimental line shape again appears to be flat topped or possibly shows two of the Ising like levels. The rest of the line shape shows no significant departure from a smooth line shape.

These experimental line shapes show signs of being well fitted by single site CPA theories and there is indication of structure in the line shape in the form of a double peak or broad topped response. It appeared that if the experiments could be repeated using better resolution, some more of the structure might be resolved.

Subsequently, a number of experiments have been performed on the same crystal by O.W. Dietrich and G. Shirane at the High Flux Beam reactor at Brookhaven in which better resolution was used.

In configuration C the scattered neutron energy was held fixed at 4.5 meV and similar corrections to those stated earlier were made to obtain the experimental line shape. In configuration D, the incident neutron energy was held fixed at 13.97 meV with a pyrolytic graphite filter used to remove higher order neutrons from the incident beam. The results were also corrected to obtain the correct form for the partial differential cross section when doing this type of scan.

Three scans over the excitations are shown in Figure 4. The results for the $[001]$ zone boundary performed using configurations C and D are in very reasonable agreement with each other except that in the former scan there is some extra scattering for energy transfers of about 1.5 meV. Comparing these to the scan made at Risø, configuration A, we see there is considerable additional scattering at low energies of unknown origin. Despite these discrepancies, we believe these results show definite evidence of structure at energy transfers of 6.0, 5.3 and 4.5 meV. with a suggestion of structure at 3.9 meV.

Comparing the result at the $[100]$ zone boundary with those obtained at Risø, it can be seen that the agreement is quite good, apart from excess intensity at energy transfers of about 1.5 meV in configuration C not present in the other two scans. Taken together, these results provide evidence for structure at energy transfers of 4.0 and 4.7 meV and less conclusively at 3.3 and 5.4 meV.

In Figure 6, a comparison is made between the scattering distributions at the bottom of Figure 4 and various theoretical calculations. These are three of the same methods used for comparison in Figure 2. BPE again stands for results of calculations based on the single site CPA theory of Buyers et al.^{10,14} in which the hard core approximation is used. For the line shapes shown in this figure, the imaginary part added to the energy was reduced to $\xi = 0.2$ meV so the structure is more pronounced. The structure in the theory is very similar in magnitude to that observed experimentally. Other variations on the single site theories, discussed earlier, produce similar results. The position of the peaks do not exactly agree, but this might be accounted for by a change in the exchange constants due to a lattice parameter change. The theory does not provide such a good account of the low energy transfer side of the distributions. This has been noted in earlier low resolution results²² and is a definite discrepancy between the single site theories and experiment.

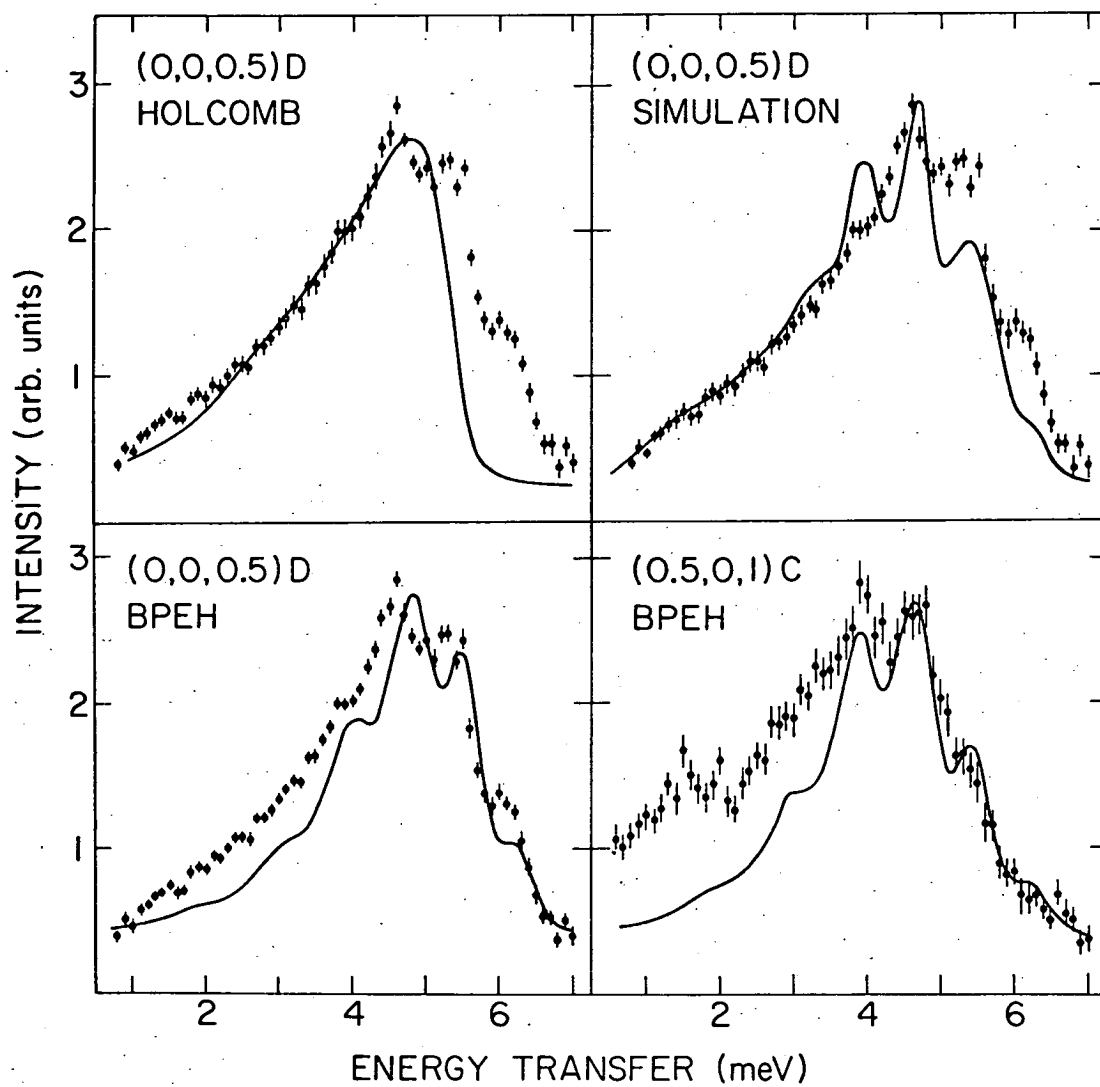
In contrast, the theory of Holcomb¹⁷ gives an excellent account of the low frequency side of the peak, but fails to account for the high frequency side or the structure.

At least some of the discrepancy in the overall position of the line shape calculated in the computer simulation by Holcomb and Harris²², arises from their use of a slightly larger concentration, 0.35, of empty sites than was present in our specimen. The calculations predict

FIGURE 6.

Neutron Scattering distributions from the magnetic excitations in $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$ compared with the predictions of the theories of Buyers et al.¹⁴ (BPEH), of Holcomb¹⁷ and computer simulations of Holcomb and Harris²⁰.

NEUTRON DISTRIBUTIONS AND THEORY FOR $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$



somewhat more structure than was observed. In part, this may arise, as the authors remark, from their neglect of the weak nearest-neighbour ferromagnetic exchange interactions. These interactions were included at least approximately in the CPA calculations.

V. 6 CONCLUSIONS

In conclusion, the line shape of the zone boundary excitations in a specimen of $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$ have been studied under a number of high resolution inelastic scattering configurations. The results show that the line shapes are not smooth, but have structure very similar to that predicted by the single site CPA theory of Buyers et al.¹⁴ and by computer simulations²⁰. Similar results have now been obtained by Svensson et al.¹² in a crystal of $\text{Mn}_{0.32}\text{Zn}_{0.68}\text{F}_2$. Similar, but more pronounced structure, has also been observed in $\text{Rb}_2\text{Mn}_{0.5}\text{Mg}_{0.5}\text{F}_4$ by R.A. Cowley and R.J. Birgeneau (Private Communication).

The structure is more apparent in this material because each ion is coupled to only four neighbours on the opposite sublattice, so the excitations are expected to show a four peaked structure in comparison to the eight peaked structure predicted for the rutile structure.

These results show that the effect of the different environments in modifying the Ising energy of the different magnetic ions must be an essential aspect of a successful theory of these systems.

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CHAPTER VI.

CRITICAL SCATTERING IN $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$

V1. 1 INTRODUCTION

Over the last decade it has become apparent that widely varying physical systems which exhibit co-operative phenomena show remarkably similar behaviour in their critical regions ¹⁻⁴. The behaviour of the systems depends on

- (1) the dimensionality of the system d
- (2) the dimensionality of the order parameter space n
- (3) the range and angular dependence of the interactions
- (4) the symmetry of the system.

The system can then be characterised by a set of ' Universal Quantities ' determined by the above conditions. Series expansion or renormalisation group methods are able to predict the development of the order parameter as a function of the reduced temperature

$$t = \frac{(T - T_N)}{T_N} \quad (1)$$

The order parameter is some quantity which is only non-zero below a transition temperature. In an (anti-) ferromagnetic system this will be the (staggered) spontaneous magnetisation. Critical exponents can be obtained which define the behaviour of the susceptibility (γ), correlation length (ν), specific heat (α), correlation function (η) and magnetisation (β) in terms of power laws in the reduced temperature. These exponents are related through the scaling relations

$$d\nu = 2 - \alpha \quad (2)$$

$$\alpha + 2\beta + \gamma = 2 \quad (3)$$

$$\gamma = (2 - \eta)\nu \quad (4)$$

Amplitude ratios such as those for the susceptibility

$$\chi_{||}(T_N + |\Delta T|) / \chi_{||}(T_N - |\Delta T|) \quad (5)$$

and inverse correlation length

$$K_{||}(T_N - |\Delta T|)/K_{||}(T_N + |\Delta T|) \quad (6)$$

are also known to be Universal and can be obtained using renormalisation group calculations ⁵.

Systems may possess different critical exponents in different ranges of the reduced temperature with a region between in which the critical exponents are uncertain ^{6,7}. The change from one set of exponents to another need not necessarily be well behaved. Riedel ⁸ has shown that MnF_2 crosses over from a system in which the exponents should be those of an isotropic system, to one at small values of the reduced temperature in which the exponents should be those of an anisotropic system. The cross over takes place at a reduced temperature $t_{c.o.}$ approximately given by

$$K_{||}(t_{c.o.}) = K_{\perp}(0) \quad (7)$$

where these are the inverse correlation lengths of the divergent parallel and non-divergent perpendicular fluctuations.

Interest has also centred on the effects of annealed ⁹ and quenched ¹⁰⁻¹² disorder on the critical behaviour of the systems. A heuristic argument by Harris ¹³ shows that we might expect to find altered critical behaviour in a quenched impurity system if the specific heat exponent (α) in the pure system is positive. Renormalisation group results ¹⁰⁻¹² support this view.

Our current problem is; what happens to the critical exponents of MnF_2 when 32% of the manganese ions are randomly replaced by non-magnetic zinc ions. In the remainder of this chapter we look at the theoretical predictions and make a comparison of our neutron scattering results with those found in the pure system MnF_2 .

VI. 2 DILUTION - THE THEORETICAL VIEWPOINT

A dilute system is expected to behave like an ensemble of systems with a distribution of transition temperatures resulting from fluctuations in the concentration of defect ions. Using an Ising model, Harris¹³ has shown that the transition temperature reduces in proportion to the concentration of defects until no transition occurs when the concentration of defects becomes greater than $\sim 70\%$.

Experimental verification of the proportionality comes from measurements on $\text{CoF}_2/\text{ZnF}_2$ mixtures¹⁷.

Harris¹³ has looked more closely at the problem which might arise from the random fluctuations in the concentration of defect ions. This problem is in addition to any "chemical" variation in the concentration arising from non isotropic growth of the crystal -- normally one hopes that the growth is isotropic.

Many of the critical properties of magnetic transitions can be expressed as a power law in the reduced temperature. For example, the distance over which spins are expected to be correlated is given by an expression for the correlation length of the form

$$\xi \sim |t|^{-\nu} \quad (8)$$

In a dilute system the reduced temperature is uncertain due to the spread in the values of the transition temperature for different correlated regions. The system can be divided into regions having ξ^d spins; where d , the dimensionality of our system, is 3. On average, each volume element will have

$$\langle\langle n \rangle\rangle = c \xi^d \quad (9)$$

missing interactions with a deviation

$$[\langle\langle (dn)^2 \rangle\rangle]^{1/2} = [c(1-c) \xi^d]^{1/2} \quad (10)$$

in the number of missing interactions. It follows that the variation in the concentration found in any volume element will vary by

$$\Delta c \sim [\xi^d c(1-c)]^{1/2} / \xi^d \quad (11)$$

The linear relationship between T_N and c gives the condition that the assumed value of ξ is self consistent if

$$\Delta c \sim \left| \frac{\Delta T_N}{T_N} \right| < |t| = \left| \frac{T - T_N}{T_N} \right| \quad (12)$$

for all t . Substitution of equations 8 and 11 into equation 12 shows that self consistency is entirely governed by the exponents such that the condition

$$\alpha = 2 - d\nu < 0 \quad (13)$$

ensures a sharp transition, where α is the specific heat exponent.

From the heuristic approach of Harris¹³ outlined above the system will appear to have a sharp or smooth transition according to how quickly the regions of correlation develop in relation to approaching the transition temperature. If the increase in volume is faster than a certain rate; in a 3-dimensional system the rate being determined by the exponent $\nu > \frac{2}{3}$; the transition should appear smooth and the critical exponents are expected to be unchanged. On the other hand if $\nu < \frac{2}{3}$, the transition may be smeared or the critical exponents may be altered.

More recent renormalisation group studies¹⁰⁻¹² confirm the importance of the specific heat condition on the behaviour of disordered systems. When α is positive, new values of the critical exponents have been obtained. Grinstein and Luther¹² point out that the new exponents are known only to $O(\xi^{1/2})$ and the inclusion of further terms in the ξ -expansion may reduce the differences between the exponents in the pure and disordered systems. The prevailing theor-

etical viewpoint¹¹ is that transitions are not expected to be rounded; but in all cases a stable fixed point with new critical exponents should (eventually) always be found. The rounding found in experiments on disordered systems is then explained as a chemical smearing of the transition temperature arising from gradients in the concentration of defects throughout the crystal.

V1. 3 EXPERIMENTAL APPARATUS

The $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$ crystal was relatively unshaped and had a volume of $\sim 8 \text{ cm}^3$. It was mounted in a variable temperature cryostat with the $[0\ 1\ 0]$ axis vertical on a triple axis spectrometer at Risø. For the experiments reported in this chapter the spectrometers — TAS 6 and TAS 3 — were operated in a two axis spectrometer mode. A number of scans were made through $(0\ 0\ 1)$ and $(1\ 0\ 0)$ both in the $[1\ 0\ 0]$ and $[0\ 0\ 1]$ directions at a series of temperatures around the transition temperature.

The scans in the $[1\ 0\ 0]$ direction through $(0\ 0\ 1)$ were made on TAS 6. The temperature could be measured to an accuracy of 100 mK with similar stability. The remaining scans were made on TAS 3 with the temperature measurement improved to ± 10 mK and the stability over a scan of 11 or 21 points was $\lesssim 30$ mK. The scans were confined to a distance of 0.2 reduced wavevector in both directions. The conditions in all the experiments were similar. An incident neutron wavevector of $2.636 \text{ \AA}^{-1}$ (14.38 meV) was obtained using a graphite monochromator. The two axis resolution function was measured using the long range order at $(1\ 0\ 0)$ at low temperatures; and also at high temperature at $(0\ 0\ 1)$ using second order neutrons. These resolution functions were compared with those based on calculations made using the method of Møller and Nielsen¹⁸, and with slight

alterations we obtained the following effective collimations from the reactor to the detector — 42 min, 33 min and 31 min and the mosaic spread of the monochromator was estimated to be 24 min. These gave the following semi-axis for the resolution function (in $\text{\AA}^{-1}$).

	MAJOR	MINOR	VERTICAL	
(1 0 0)	0.0142	0.0033	0.0367	(14)
(0 0 1)	0.0175	0.0043	0.0368	(15)

Some masking of the collimation tubes using cadmium was required to obtain the figures shown for the vertical resolution. These were obtained by tilting the crystal through the reciprocal lattice point.

Second order contaminant in the incident neutron beam was reduced by means of 5 cm of pyrolytic graphite placed before the sample. The filter was aligned by minimising the neutron scattering from the sample when the spectrometer was set on (0 0 1).

VI. 4 NEUTRON SCATTERING CROSS SECTION

Van Hove ¹⁹ gives the neutron scattering cross section for scattering from magnetic systems as

$$\frac{d^2\sigma}{d\Omega dE} = N \frac{k_2}{k_1} \left(\frac{\gamma_e^2}{mc^2} \right)^2 \left(\left| \frac{1}{2} g F(Q) \right| \right)^2 \exp(-2W(Q)) \times$$

$$\times \sum_{ab} \left(\delta_{ab} - \hat{Q}_a \hat{Q}_b \right) S^{ab}(Q, \omega) \quad (16)$$

where $F(Q)$ is the magnetic form factor which decreases rapidly with increasing wavevector transfer. The response function $S^{ab}(Q, \omega)$ is the Fourier transform of the spin pair correlation function

$$S^{ab}(Q, \omega) = \frac{1}{2\pi} \sum_{\underline{r}} \int_{-\infty}^{\infty} dt \exp(i(Q \cdot \underline{r} - \omega t)) \langle S_o^a(0) S_{\underline{r}}^b(t) \rangle \quad (17)$$

The response function may be divided into two parts, the first of which gives the long range order part of the response. If the quantisation axis is chosen to be parallel to $\underline{z}$, the mean direction of the spins, we find

$$\left(\frac{d\sigma}{d\Omega} \right)^{\text{Bragg}} \propto |F(\underline{Q})|^2 |F_M(\underline{Q})|^2 \langle S_z^2 \rangle^2 \sum_{\underline{\gamma}} (\underline{Q} - \underline{\gamma}) (1 - (\underline{\gamma} \cdot \underline{z})^2) \quad (18)$$

$F_M(\underline{Q})$ is the magnetic unit cell structure factor which in the rutile structure is

$$F_M(\underline{Q}) \sim (1 - \exp(i\pi(t_1 + t_2 + t_3))) \quad (19)$$

where

$$\underline{\gamma} = \frac{2\pi}{a} (t_1, t_2, \frac{a}{c} t_3) \quad (20)$$

The structure factor is non zero if $(t_1 + t_2 + t_3)$ is an odd integer. We might expect to find purely magnetic Bragg scattering at reciprocal lattice points such as

$$(H \ 0 \ 0), (H \ 0 \ 2) \quad ; \ H \text{ odd} \quad (21)$$

$$(0 \ 0 \ L), (2 \ 0 \ L) \quad ; \ L \text{ odd} \quad (22)$$

However the last term in the scattering formula (eq. 18) provides an additional factor varying between zero for $\underline{\gamma}$ along $[0 \ 0 \ 1]$ to unity for $\underline{\gamma}$ perpendicular to $[0 \ 0 \ 1]$. Therefore reflections such as $(0 \ 0 \ 1)$ and $(0 \ 0 \ 3)$ are absent and $(1 \ 0 \ 2)$ and $(2 \ 0 \ 1)$ are weaker than might otherwise be expected.

The magnetic scattering at the Bragg points is proportional to the square of the (staggered) magnetisation. Neutron scattering allows us to make a direct measurement of the long range ordering of the spins in (anti-) ferromagnetic systems. Above the Néel temperature, there is no ordering; below the transition temperature the magnetic Bragg scattering is expected to increase as $|t|^{2\beta}$ where β , the exponent of

the order parameter, varies between 0.33 and 0.37 in 3-dimensional systems.

Results of measurements of the scattered intensity at (1 0 0), (3 0 0) and (2 0 1) indicated that the results were unreliable because of the presence of extinction.

Using the fluctuation-dissipation theorem, the response function can be related to the susceptibility.

$$S^{ab}(\underline{Q}, \omega) = S_{\text{Bragg}}^{ab}(\underline{Q}, \omega) + \frac{\omega \exp(\frac{\hbar\omega}{kT})}{(\exp(\frac{\hbar\omega}{kT}) - 1)} \left(\frac{1}{g\mu_B}\right)^2 \chi^{ab}(\underline{Q}) F^{ab}(\underline{Q}, \omega) \quad (23)$$

For convenience, the susceptibility has been written as the product of a purely wavevector dependent susceptibility $\chi^{ab}(\underline{Q})$ and a spectral shape function $F^{ab}(\underline{Q}, \omega)$. The latter is chosen so as to satisfy the condition

$$\int_{-\infty}^{\infty} F^{ab}(\underline{Q}, \omega) d\omega = 1 \quad (24)$$

The spectral shape function has sometimes been assumed to be approximately a Lorentzian ^{14,16}.

$$F(\underline{Q}, \omega) = \frac{1}{\pi} \frac{\Gamma(\underline{q}, T)}{\omega^2 + \Gamma(\underline{q}, T)^2} \quad (25)$$

cut off at some frequency ω_m . The frequency ω_m being chosen to compensate for the Lorentzian having the incorrect form of higher moments. Tucciarone et al.²⁰ show that a Lorentzian becomes a very poor approximation at large values of q/K in RbMnF_3 where K is the inverse correlation length. Marshall and Lovesey²¹ discuss several semi-empirical alternatives to a Lorentzian.

Since our main interest is in the wavevector dependent susceptibility, we adopt an experimental approach in which the frequency integration is automatically performed over the spectral weight function. Tucciarone et al.²⁰ outline the conditions under which a two axis spectrometer may be used to perform this integration. The problem involved in using

a two axis spectrometer becomes apparent when we consider that the wavevector transfer and energy transfer are correlated through

$$Q(\omega) = k_1 - \hat{k}_2 (|k_1|^2 - \frac{2m\omega}{\hbar})^{\frac{1}{2}} \quad (26)$$

where $\hat{k}_2$ is a unit vector in the direction of the scattered neutrons.

This is illustrated in Figure 1.

One of the requirements is that

$$Q(\omega) \approx Q(0) = \gamma + q_0 \quad (27)$$

or in effect that the inelasticity is much smaller than the neutron energy

$$\hbar\omega \ll \frac{\hbar^2}{2m} k_1^2 \quad (28)$$

A further requirement is that the Bose-Einstein factor is approximately unity for all energies at which there is appreciable scattering. The effect of this term is reduced by a partial cancelling out of the energy gain and energy loss terms.

In this chapter we shall assume that any inelasticity can be ignored. As a justification, we note that the scattering observed at $(|\gamma| \ 0 \ |q|)$ differs only slightly from that observed at $(|\gamma| \ 0 \ -|q|)$. Trial inelasticity corrections show that if the inelasticity is significant we would expect noticeable asymmetries in the scans perpendicular to the scattering vector. The effect of inelasticity corrections is expected to be smaller on scans parallel to the scattering vector — in the $[1 \ 0 \ 0]$ direction through $(1 \ 0 \ 0)$ and in the $[0 \ 0 \ 1]$ direction through $(0 \ 0 \ 1)$.

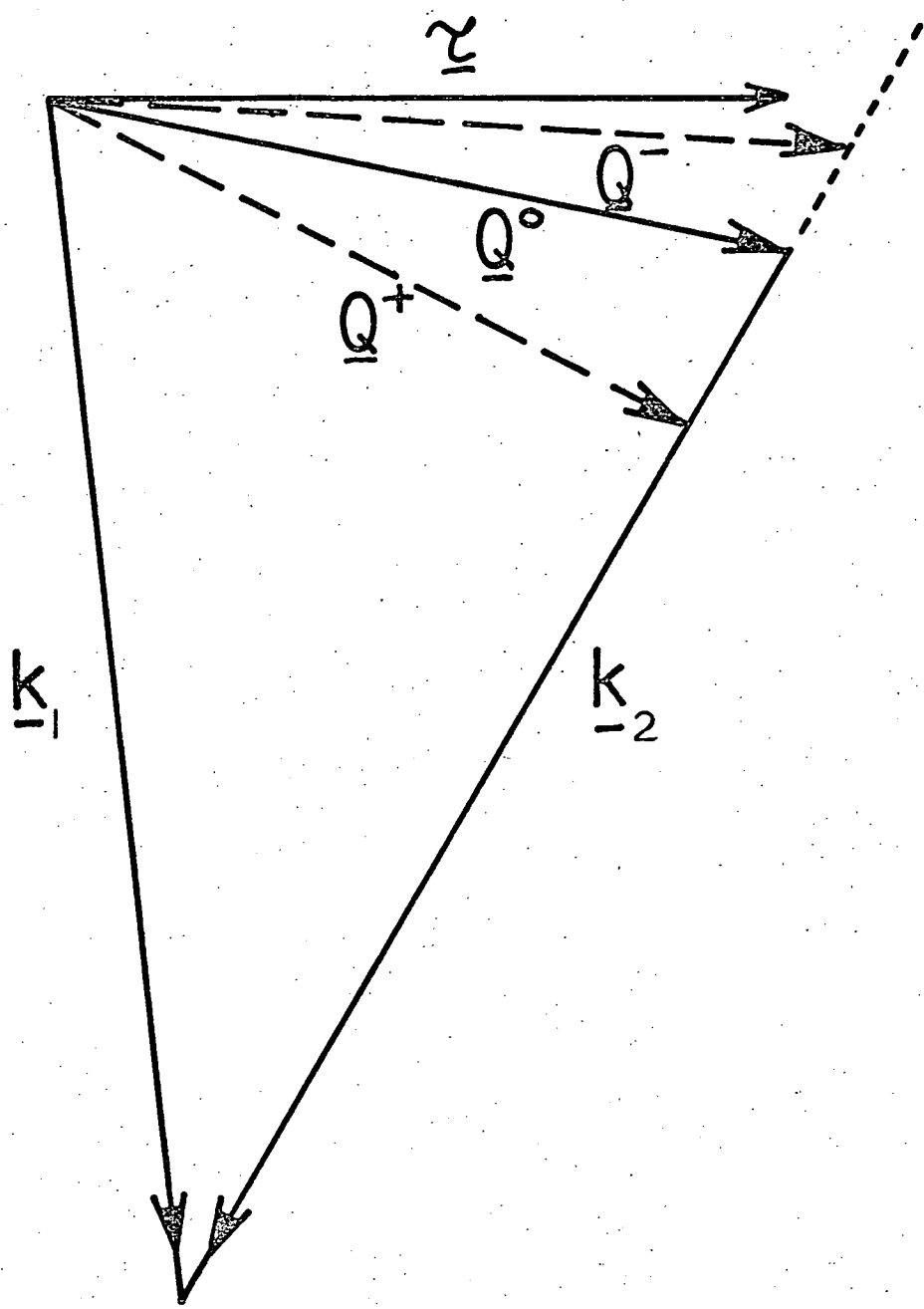
The main effect of inelasticity in the scattering is to alter the critical amplitudes rather than the ratios between the amplitude terms or the critical exponents.

FIGURE 1.

In an experiment on a two axis spectrometer , both the magnitude and direction of $\underline{k}_1$ and $\underline{\gamma}$ are specified. The direction of the vector $\underline{k}_2$ is specified by the setting of the instrument but its magnitude depends on the energy transfer. If we allow $|\underline{k}_2| = |\underline{k}_1|$ we can obtain $\underline{Q}^0$ the scattering vector for elastic scattering. The inelastic neutron scattering is detected at a different wavevector transfer given by

$$\underline{Q}^{\pm} = \underline{Q}(\pm|\omega|) = \underline{k}_1 - \hat{\underline{k}}_2 (|\underline{k}_1|^2 \pm \frac{2m|\omega|}{\hbar})^{\frac{1}{2}}$$

These wavevector transfers are illustrated in the diagram.



In the quasi-elastic approximation, the scattering detected in an experiment on a two axis spectrometer becomes

$$\frac{d\sigma}{d\Omega} \propto kT |F(Q)|^2 (1 + (\hat{Q} \cdot \hat{z})^2) \chi^{xx}(Q) + (1 - (\hat{Q} \cdot \hat{z})^2) \chi^{zz}(Q) \quad (29)$$

where the cross terms in a and b are sufficiently small and can be ignored. The form of the equation allows us to select out the purely transverse (xx) component by measuring the scattering close to for example (0 0 1). Near (1 0 0) we obtain a known mixture of the transverse component and the longitudinal (zz) component.

Fisher and Burford²² have shown that the wavevector dependent susceptibility has a functional dependence like

$$\chi_{||,\perp}(Q,T) = \left[\frac{A_{||,\perp}(T)}{K_{||,\perp}^2(T) + q^2} \right]^{1 - \frac{2}{2}} \quad (30)$$

where $A_{||,\perp}(T)$ is a relatively slowly varying function of temperature and $K_{||,\perp}(T)$ is the inverse correlation length. In a non isotropic system, following Moriya²³, we adopt

$$q^2 = q_x^2 + q_y^2 + \left(\frac{c}{a}\right)^2 q_z^2 \quad (31)$$

where the q_a are in $\text{\AA}^{-1}$. The contours of equal susceptibility are therefore expected to fall on ellipsoids with a minor to major ratio of $\frac{c}{a} = 0.68$. Dietrich¹⁴ verified that this is a valid approximation in MnF_2 . In the Ornstein-Zernike approximation $\eta = 0$ but the application of series expansion or renormalisation group methods suggests that $0.02 \lesssim \eta \lesssim 0.06$ with the more recent renormalisation group estimates favouring the lower value.

For the purposes of our experiment we can replace equation 30 by

$$\chi_{||,\perp}(Q,T) = \frac{A'_{||,\perp}(T)}{K_{||,\perp}^2(T) + q^2} \quad (32)$$

with the effects of the exponent γ being absorbed into the scale factor $A'_{||,\perp}(T)$.

Our main interest lies in the temperature dependence of the variables as $|t| = |(T - T_N)/T_N| \rightarrow 0$. In particular, there are four quantities associated with the divergent longitudinal fluctuations which can be expressed as power laws in the reduced temperature

$$K^{\pm}(T) = K^{\pm}(\pm t)^{\gamma^{\pm}} \quad (33)$$

and

$$\chi^{\pm}(\gamma, T) = \frac{A^{\pm}(T)}{(K^{\pm}(T))^2} t^{-\gamma^{\pm}} = S^{\pm}(\pm t)^{-\gamma^{\pm}} \quad (34)$$

Similar relations can be given for the non divergent transverse fluctuations but only for $T > T_N$. Below T_N , the transverse fluctuations develop into spin waves. To measure the temperature dependence of these requires an inelastic neutron scattering experiment on a triple axis spectrometer.

Application of the renormalisation group shows us that we might expect to find

$$\gamma_{||}^+ = \gamma_{||}^- \neq \gamma_{\perp}^+ \quad (35)$$

$$\gamma_{||}^+ = \gamma_{||}^- \neq \gamma_{\perp}^+ \quad (36)$$

and the static scaling relation

$$\gamma = (2 - \gamma) \nu \quad (37)$$

which assumes that the term $A(T)$ in equation 30 is constant over any range of values for which the critical exponents might be expected

to hold.

Other universal quantities we might expect to measure would be the ratios of the critical amplitudes above and below the transition.

$$\frac{K^-}{K^+} ; \quad \frac{S^+}{S^-} ; \quad \frac{A^+}{A^-} \quad (38)$$

VI. 5 EXPERIMENTAL PREAMBLE

An estimate of the Néel temperature might be obtained from a measurement of the critical scattering close to the (1 0 0) reflection. In Figure 2 we show the scattered intensity at (1.05 0 0) and (1.10 0 0) as a function of temperature. The scattering at (1.05 0 0) is peaked at 38.85 ± 0.15 K. Because of the form of the wavevector dependent susceptibility above and below the transition, at finite values of $q = Q - \gamma$, this gives a higher apparent transition than the real Néel temperature. This is particularly so if the transition is suspected of being "chemically" smeared.

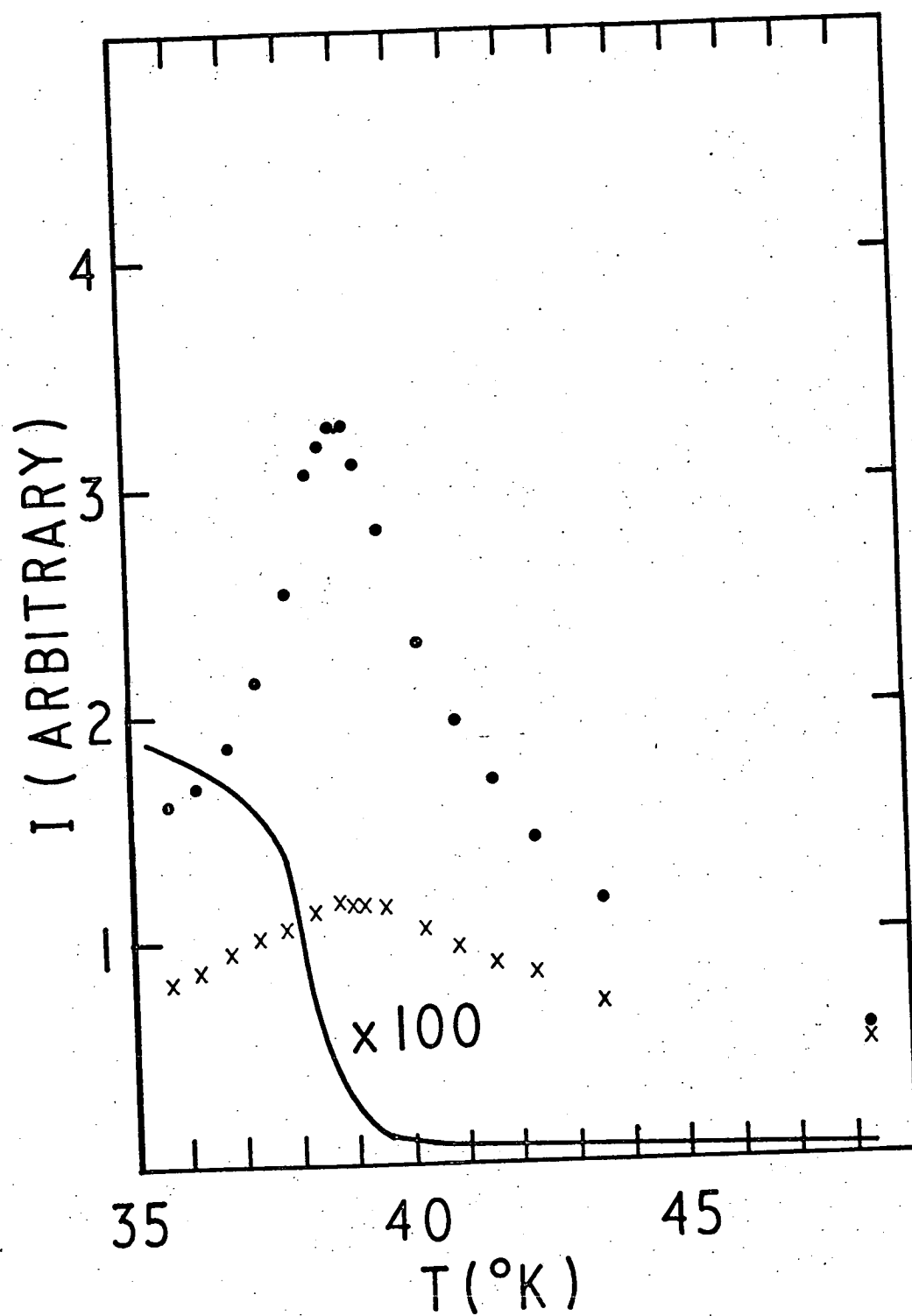
Also shown in Figure 2 is the development of the long range order at (1 0 0). The long tail above the transition temperature is partly due to critical scattering. Some additional intensity results from higher order or multiple Bragg scattering of the incident neutron beam. On subtraction of the effects mentioned above, there still remains some localised temperature dependent scattering up to ~ 10 K above the transition. The variation of this scattering with temperature is small and can probably be accounted for by variations in the defect concentration at the surface of the crystal.

FIGURE 2.

This shows the scattering obtained in Mn/ZnF_2 at

(1 0 0)	continuous line
(1.05 0 0)	closed circles
(1.10 0 0)	crosses

The scattering at (1.05 0 0) peaks at 38.85 ± 0.15 K. The scattering at (1 0 0) is the long range order component with some contribution from the susceptibility and second order scattering of the neutrons at (2 0 0).



VI. 6 TRANSVERSE FLUCTUATIONS

The transverse fluctuations may be measured close to (0 0 1) without any contamination from the longitudinal fluctuations. To begin with, we assume that there is no smearing of the transition temperature. The scattering cross section is then the convolution of the wavevector dependent susceptibility with the two axis resolution function.

$$\frac{d\sigma}{d\Omega} \propto \int k_B T |F(\underline{r} + \underline{q})|^2 \chi_{\perp}(\underline{r} + \underline{q}, T) R(\underline{q} - \underline{q}_0) d\mathbf{q} \quad (39)$$

where $\chi_{\perp}(\underline{r} + \underline{q}, T)$ is given by equation 32 and the resolution function $R(\underline{q} - \underline{q}_0)$ is a Gaussian in three dimensions. The half height contour of the resolution function is the resolution ellipsoid with semi-axis given by equation 15. The convolution was performed over a grid of 1728 points covering two half-widths of the resolution function in all directions.

The scattering cross section was sampled at 21 points on each scan. A number of representative scans are shown in Figure 3 for temperatures below and above the Néel temperature. Below the transition, the scattering increases roughly proportional to temperature so that when $k_B T$ is divided out the susceptibility is fairly constant over a large temperature range. Above the transition, the scattering and the susceptibility decrease with temperature.

The scans were least squares fitted with equation 39 to obtain values of $A'_{\perp}(T)$, $K_{\perp}(T)$, and $\chi_{\perp}(\underline{r}, T)$. In Figure 4 we show the values of $K_{\perp}(T)$ obtained for scans through (0 0 1) parallel to $[0 0 1]$ and perpendicular to $[0 0 1]$. There is some difference between the results. The main difference is that $K_{\perp}(T)$ on the scans parallel to $[0 0 1]$ takes on slightly lower values than on the scans perpendicular to $[0 0 1]$. There are a number of reasons why the results could differ.

We know that the form of q^2 (equation 31) is only an approximation. It remains sufficiently good for the unfolding of the instrumental resolution. Neglect of the inelasticity corrections may also introduce differences between the measured inverse correlation lengths. Trial inclusions of such corrections show that the inverse correlation length will be smaller, with the main effect being on the scans perpendicular to the $[0\ 0\ 1]$ direction.

The scans were made on different spectrometers so we have no guarantee that the backgrounds are matched — an increase in the background by 20% (about 10-15 counts) varied the values of $K_{\perp}$ and $A'_{\perp}$ by about -5% and -5% respectively. Some or all of these effects may combine to reduce the slight differences found between the parallel and perpendicular scans.

Figure 4 also shows values of $A'_{\perp}$ for the scans parallel to $[0\ 0\ 1]$. The values for the scans perpendicular to $[0\ 0\ 1]$ showed the same functional dependence but a direct comparison on an absolute basis could not be made because of the differences caused by changing spectrometers.

It should be pointed out that the values of $K_{\perp}$ obtained below the Néel temperature are not values of the transverse inverse correlation length but $A'_{\perp}$ and $K'_{\perp}$ are just effective parameters which describe the observed lineshape.

Figure 5 shows a log-log plot of the transverse susceptibility versus temperature for both sets of scans. The temperatures have been measured using 37.0 K as a base. This is calculated as the temperature at which the transverse correlations would diverge based on the value of $T_N - T_{\perp}$ obtained by Schulhof et al.¹⁵. We have used

$$T_N - T_{\perp} \sim 2.8 \frac{T_N(\text{Mn/ZnF}_2)}{T_N(\text{MnF}_2)} = 1.6 \text{ K} \quad (40)$$

FIGURE 3.

Typical scans in the $[1\ 0\ 0]$ direction through $(0\ 0\ 1)$ at a number of temperatures giving the transverse fluctuations.

- (A) 22.8 K
- (B) 35.0 K
- (C) 38.8 K
- (D) 40.3 K
- (E) 43.2 K
- (F) 45.8 K

(001)

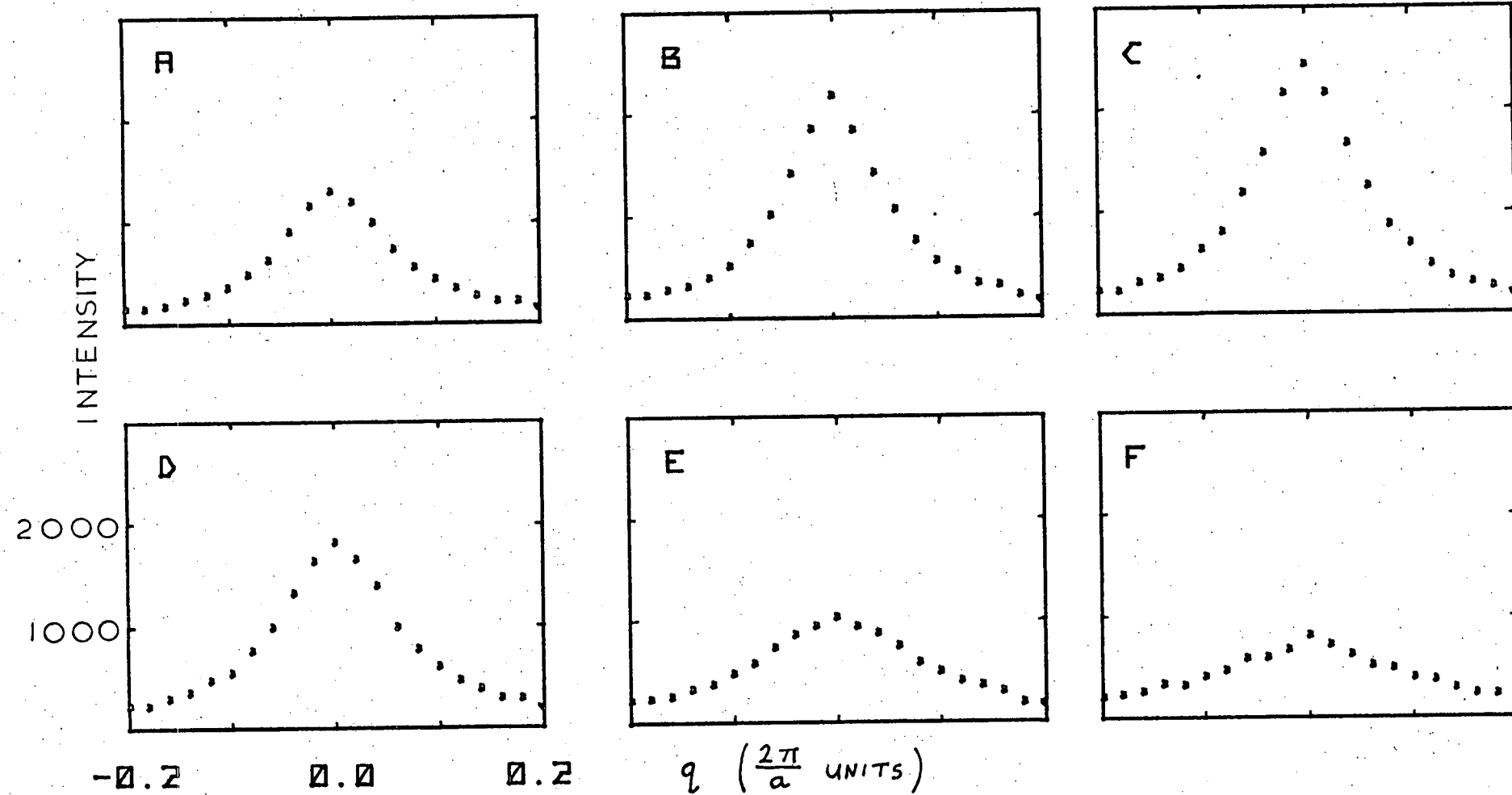


FIGURE 4.

This shows the inverse correlation length for the transverse fluctuations measured near (0 0 1).

Open circles — from scans made in the $[0\ 0\ 1]$ direction

Closed circles — from scans made in the $[1\ 0\ 0]$ direction

We also show the scale factor (or parameter $A'_{\perp}$) for the scans made in the $[0\ 0\ 1]$ direction.

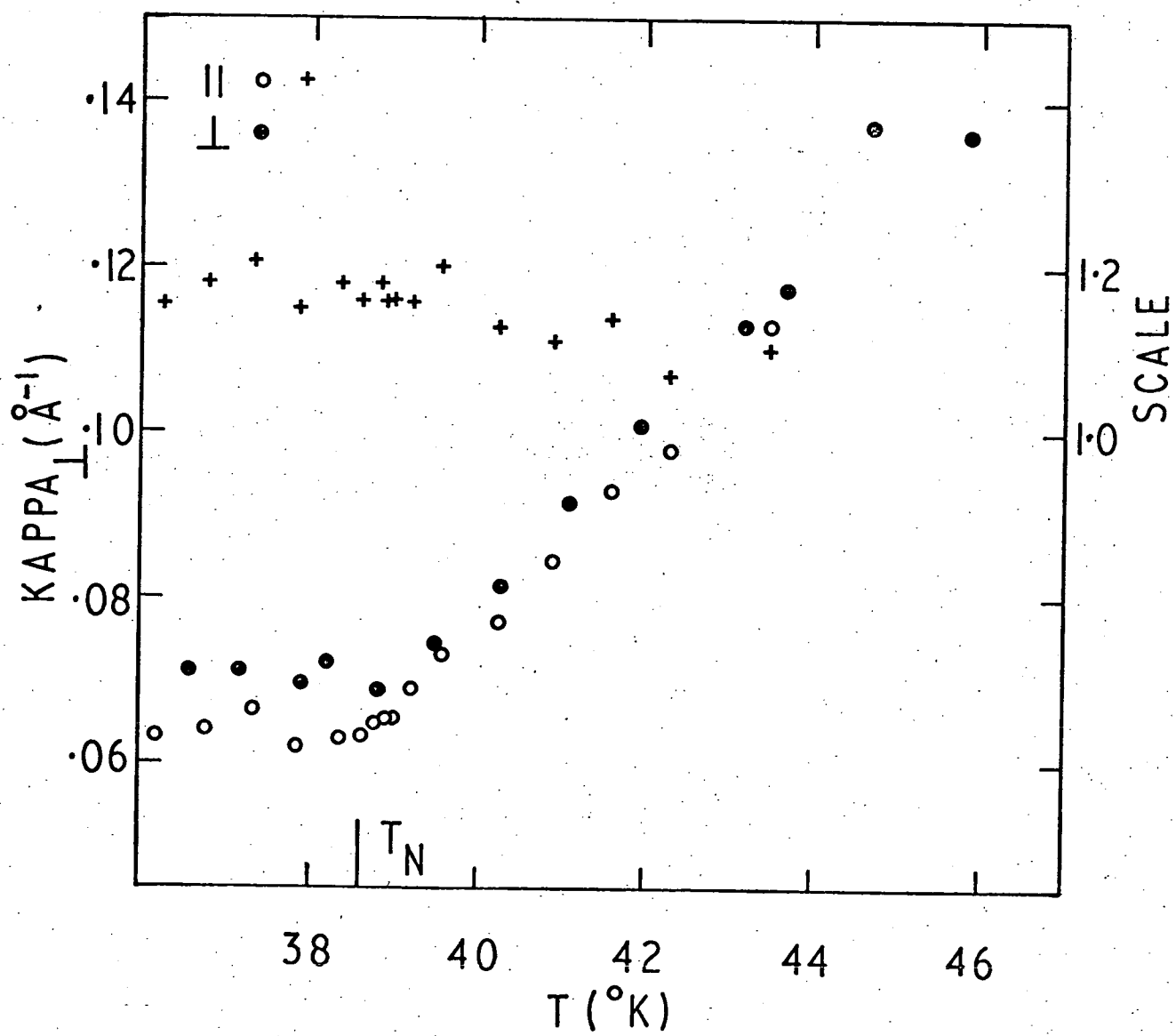
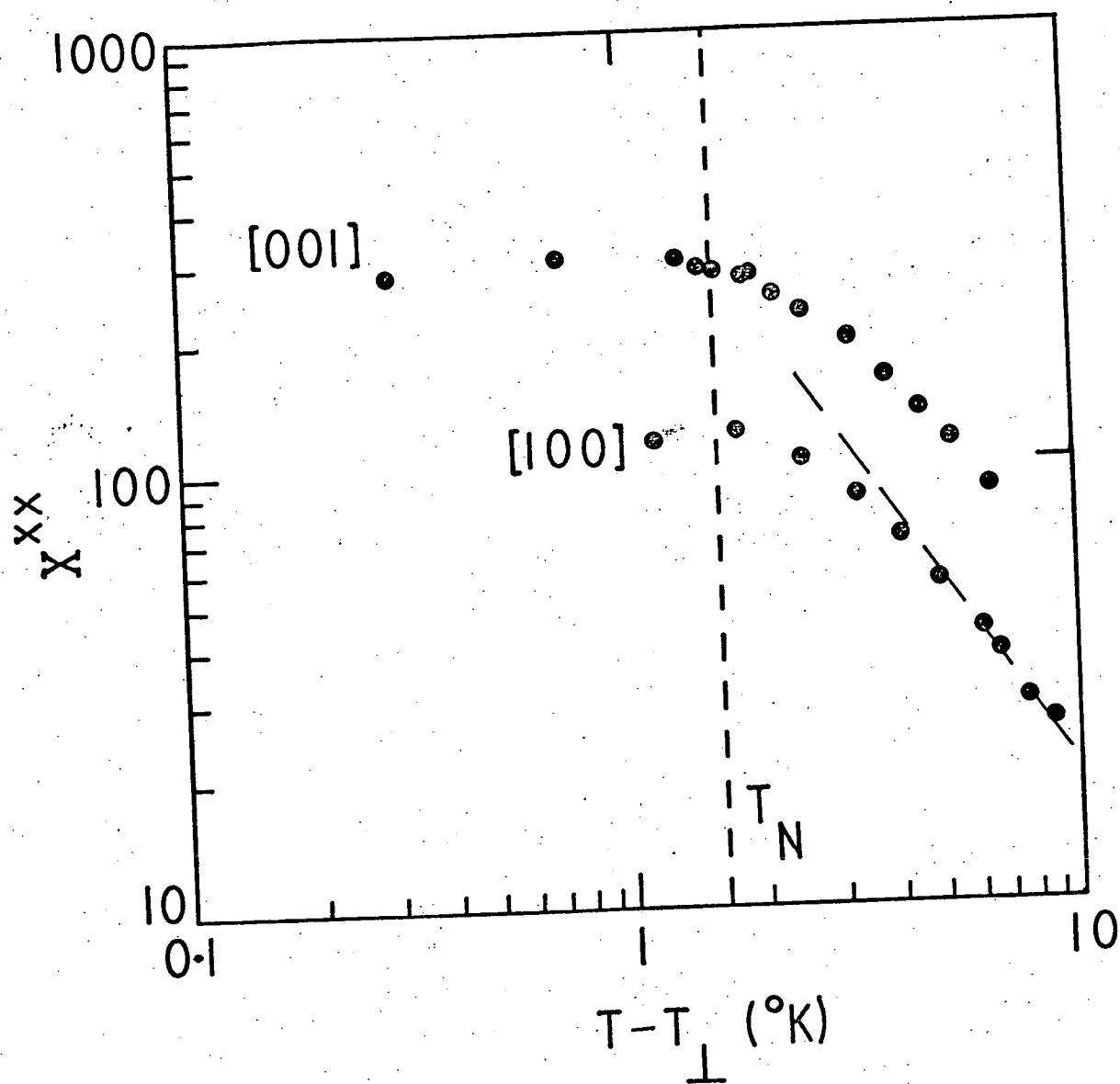


FIGURE 5.

This shows the susceptibility for the transverse fluctuations for scans made in the $[0\ 0\ 1]$ and $[1\ 0\ 0]$ directions through $(0\ 0\ 1)$. The plot is log-log using $T_{\perp} = 37.0\text{ K}$; $T_N = 38.6\text{ K}$. A line at a slope of -1.47 is the value obtained for $-\chi$ in pure MnF_2^{15} . Under these constraints the results are obviously not consistent with a simple power law fit.



with T_N taken as ~ 38.6 K. A line is drawn with a slope of -1.47 corresponding to the exponent γ obtained for MnF_2 ¹⁵. As $T \rightarrow T_N$, it can be seen that using these parameters our data is not consistent with those obtained in the pure system. A better fit to the data could be obtained by adopting a lower value for $T_\perp$ but in no case could a straight line be obtained which fitted all the data for $T > T_N$. This is an indication that the transition temperature is smeared.

It is the author's opinion that the addition of a term convoluting the transverse susceptibility with a smearing of the Néel temperature would lead to no clarification of the exponents $\gamma_\perp$ and $\gamma_\parallel$. The problem with trying this type of approach on the transverse data is that we have no means of knowing how the parameters above the transition temperature in an unsmeared transition transform over to the effective parameters below the transition. The convolution with the smearing of the transition temperature produces results which are highly correlated with the choice of the effective parameters below the transition.

VI. 7 LONGITUDINAL FLUCTUATIONS

Unlike the transverse fluctuations, the longitudinal fluctuations cannot be measured on their own. However by making the measurements in the vicinity of (1 0 0) we can detect a known, convenient mixture of the longitudinal and transverse fluctuations. The scattering cross section near (1 0 0), including a convolution with the two axis resolution function, becomes

$$\begin{aligned} \frac{d\sigma}{d\Omega} \propto & \int k_B T |F(\underline{\tau} + \underline{q})|^2 \chi_{\parallel}(\underline{\tau} + \underline{q}, T) R(\underline{q} - \underline{q}_0) d\underline{q} \\ & + \int k_B T |F(\underline{\tau} + \underline{q})|^2 \chi_{\perp}(\underline{\tau} + \underline{q}, T) R(\underline{q} - \underline{q}_0) d\underline{q} \end{aligned} \quad (41)$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are of the form of equation 32 and $R(\underline{q} - \underline{q}_0)$ is a

resolution function, whose resolution ellipsoid is defined by the parameters in equation 14.

The transverse fluctuations can be treated as a background which can be calculated from the values of $A'_{\perp}$ and $K_{\perp}$ obtained in the measurements near (0 0 1). If we had a good knowledge of the magnetic form factor and a spherical or cylindrical crystal the contribution from the transverse fluctuations could be calculated directly using these parameters. Since neither of these conditions is really met it is fortunate that we can calculate the contribution by another method.

For weakly anisotropic systems we expect that the transverse and longitudinal fluctuations will behave similarly at large values of the reduced temperature ⁸. Thus

$$K_{\parallel}^{+} \approx K_{\perp}^{+} \quad (42)$$

and also

$$A_{\parallel}^{+} \approx \frac{T_N}{T_{\perp}} A_{\perp}^{+} \quad (43)$$

Applying this criterion to our high temperature data, we find that

$$A'_{\perp}(1\ 0\ 0) = 0.96 \pm 0.06 A'_{\perp}(0\ 0\ 1) \quad (44)$$

The transverse fluctuations can then be treated as a conventional background -- subtracted off along with the incoherent scattering.

Figure 6 shows some raw neutron groups for scans in the [0 0 1] direction through (1 0 0). The scattering is noticeably different from that found for the pure transverse fluctuations measured in the scans through (0 0 1) (Figure 3). The scattering is intense at small wavevector near the transition temperature and falls away rapidly in

($q, |t|$) parameter space. We would have expected that by diagrams E and F all the long range order component at $q = 0$ would have disappeared. What remains could be attributable to crystallites of Mn/ZnF_2 on the surface of the crystal which have a lower concentration of zinc.

In Figures 7 and 8 we show values of the inverse correlation length (closed circles) and susceptibility (open circles) obtained for the longitudinal fluctuations above and below the Néel temperature. From later calculations T_N is taken to be 38.62 K. The vertical bars shown on Figure 7 show the effects of varying the contribution to the scattering of the transverse fluctuations by 10% (about twice the amount we believe to be our uncertainty as given by equation 44).

Since at small values of the reduced temperature, in both the Figures for the data above and below the Néel temperature, the susceptibility is smaller than anticipated and the inverse correlation length is bigger than anticipated, this indicates that the transition is probably smeared. Unfortunately we know of no way of measuring the concentration of zinc in Mn/ZnF_2 to a sufficient accuracy to be able to determine a profile for the smearing of the transition temperature in a crystal with long range fluctuations in the concentration. We have chosen to use a Gaussian spread in the transition for no reason other than that it is a well behaved function. One could visualise several simple plausible alternatives such as a square wave pulse or a wedge shape brought on by a simple one dimensional gradient through the crystal -- one can also visualise a multitude of other less agreeable alternatives.

Having conceded that the crystal is "chemically" smeared, the introduction of a Gaussian spread in the transition temperature tends to over parameterise the fits to the data. The form of the scattering cross section we use is

$$\frac{d\sigma}{d\Omega} \propto \iint k_B T |F(\underline{\tau} + \underline{q})|^2 \chi_{\parallel}(\underline{\tau} + \underline{q}, T, T_N) G(T_N) R(\underline{q} - \underline{q}_0) d\underline{q} dT_N \\ + \int k_B T |F(\underline{\tau} + \underline{q})|^2 \chi_{\perp}(\underline{\tau} + \underline{q}, T) R(\underline{q} - \underline{q}_0) d\underline{q} \quad (47)$$

The parameters $A'_{\perp}$ and $K_{\perp}$ obtained from the (0 0 1) data without any smearing are then carried over and used as effective parameters to describe the transverse fluctuations near (1 0 0). The transition temperatures are given a weighting

$$G(T_N) = G \exp(-\ln(2) \left(\frac{T_{NO} - T_N}{\Delta T_N} \right)^2) \quad (48)$$

where T_{NO} is the best estimate of the Néel temperature and the smearing in the transition temperature is given by a Gaussian of width $2\Delta T_N$. The susceptibility now depends explicitly on T_N .

$$\chi_{\parallel}(\underline{\tau} + \underline{q}, T, T_N) = \frac{A'_{\parallel}(T, T_N)}{K_{\parallel}^2(T, T_N) + q^2} \quad (49)$$

If the smearing in the transition temperature is sufficiently small, the parameter $A'_{\parallel}(T, T_N) \approx A'_{\parallel}(T)$ is effectively constant over the region of integration.

$$T_N - 2\Delta T_N < T_{NO} < T_N + 2\Delta T_N \quad (50)$$

The main variation caused by the smearing can then be introduced through a variation in the inverse correlation length.

$$K_{\parallel}^{\pm}(T, T_N) = K_{\parallel}^{\pm} \left| \frac{T - (T_N - T_{NO})}{(T_N - T_{NO})} \right|^{\nu_{\parallel}^{\pm}} \quad (51)$$

The introduction of a smearing in the transition temperature can then be seen to be equivalent to replacing $\chi_{\parallel}(\underline{\tau} + \underline{q}, T)$ in

equation 41 by

$$\int \frac{A'_{||}(T)}{K_{||}^2(T, T_N) + q^2} G \exp(-\ln(2) \left(\frac{T_N - T_{NO}}{\Delta T_N} \right)^2) dT_N \quad (52)$$

There are several problems with this approach. We have to guess values of T_N , ΔT_N , $\nu_{||}^+$, $\nu_{||}^-$, $K_{||}^-/K_{||}^+$ and $A_{||}^+/A_{||}^-$ to be inserted into equations 51 and 52. The resulting values of $K_{||}(T, T_{NO})$ and $\chi_{||}(\underline{\nu}, T, T_{NO})$ can then be fitted to a power law in the reduced temperature with T_{NO} held fixed. This provides us with a new set of values for $\nu_{||}^+$, $\nu_{||}^-$, $K_{||}^-/K_{||}^+$ and $A_{||}^+/A_{||}^-$. This is obviously very wasteful on computing time since these variables are also highly correlated with the choice of T_{NO} and ΔT_N . One can only proceed by trial and error with no guarantee that convergence to a consistent solution can be obtained.

However we can adopt a second approach which is to fit equation 41 to all the data at once in which case we can let many more parameters vary. Replacing $\chi_{||}(\underline{\nu} + \underline{q}, T)$ by

$$\int \Delta T_N \left(\frac{A'_{||}(T)}{K_{||}^2(T, T_N) + q^2} \right)^{1 - \frac{2}{2}} \exp(-\ln(2) \left(\frac{T_N - T_{NO}}{\Delta T_N} \right)^2) \quad (53)$$

we can obtain convergent solutions by varying $A_{||}^+$, $A_{||}^+/A_{||}^-$, $K_{||}^+$, $K_{||}^-/K_{||}^+$, T_{NO} and ΔT_N whilst fixing $\nu^+ = \nu^-$ and $\underline{\nu}^+ = \underline{\nu}^-$ (from scaling) at a number of trial values. We can also look at the effects of varying $A'_{\perp}(1\ 0\ 0)/A'_{\perp}(0\ 0\ 1)$. All the estimates of the errors in our results are based on values obtained in these fits. Generally the largest uncertainty arises from the uncertainty in the value of $A'_{\perp}(1\ 0\ 0)/A'_{\perp}(0\ 0\ 1)$ and we have transformed our uncertainty in this quantity into an uncertainty in the other parameters.

Hence we obtain the results:

$$\text{Néel temperature} \quad T_{NO} = 38.62 \pm 0.05 \text{ K} \quad (54)$$

$$\text{Gaussian smearing} \quad \Delta T_N = 0.52 \pm 0.05 \text{ K} \quad (55)$$

Fixing these values we can return to the first method we described and varying $A'_{||}^+/A'_{||}^-$, $K_{||}^-/K_{||}^+$, $\nu_{||}^+$, $\nu_{||}^-$ we obtain fairly consistent results. These are the susceptibility (crosses) and inverse correlation length (open triangles) which are shown in Figures 7 and 8. We find that it is necessary to slightly break the condition $\nu_{||}^+ = \nu_{||}^-$ to obtain consistency. This is probably not significant since we have rather too few scans below the transition temperature and the uncertainty in the background becomes more important for these scans.

Best straight lines through the data are then obtained with the following values for the inverse correlation length (with $T_{NO} = 38.62 \text{ K}$ and $T_N = 0.52$ held fixed)

$$\nu_{||}^+ = 0.63 \pm 0.05 \quad (56)$$

$$K_{||}^+ = 0.38 \pm 0.05 \quad (57)$$

$$\nu_{||}^- = 0.68 \pm 0.15 \quad (58)$$

$$K_{||}^- = 0.66 \pm 0.15 \quad (59)$$

Since the condition $\nu_{||}^+ = \nu_{||}^-$ is not met exactly, although the results are still consistent with this result, the quantity $K_{||}^-/K_{||}^+$ can no longer be regarded as universal. However applying the constraint $\nu_{||}^+ = \nu_{||}^-$ and varying $\nu_{||}$ and $A'_{\perp}(100)/A'_{\perp}(001)$ in a reasonable manner we obtain the result

$$\frac{K_{||}^-}{K_{||}^+} = 1.55 \pm 0.15 \quad (60)$$

We can also obtain the following results for the longitudinal susceptibility

FIGURE 6.

Typical scans in the $[0\ 0\ 1]$ direction through $(1\ 0\ 0)$ at a number of temperatures giving the scattering from both the longitudinal and transverse fluctuations.

- (A) 22.8 K
- (B) 36.0 K
- (C) 38.8 K
- (D) 40.3 K
- (E) 43.5 K
- (F) 45.8 K

These are approximately the same temperatures as those shown in Figure 3 for the purely transverse component near $(0\ 0\ 1)$. The vertical scale is a factor of 4 different.

(100)

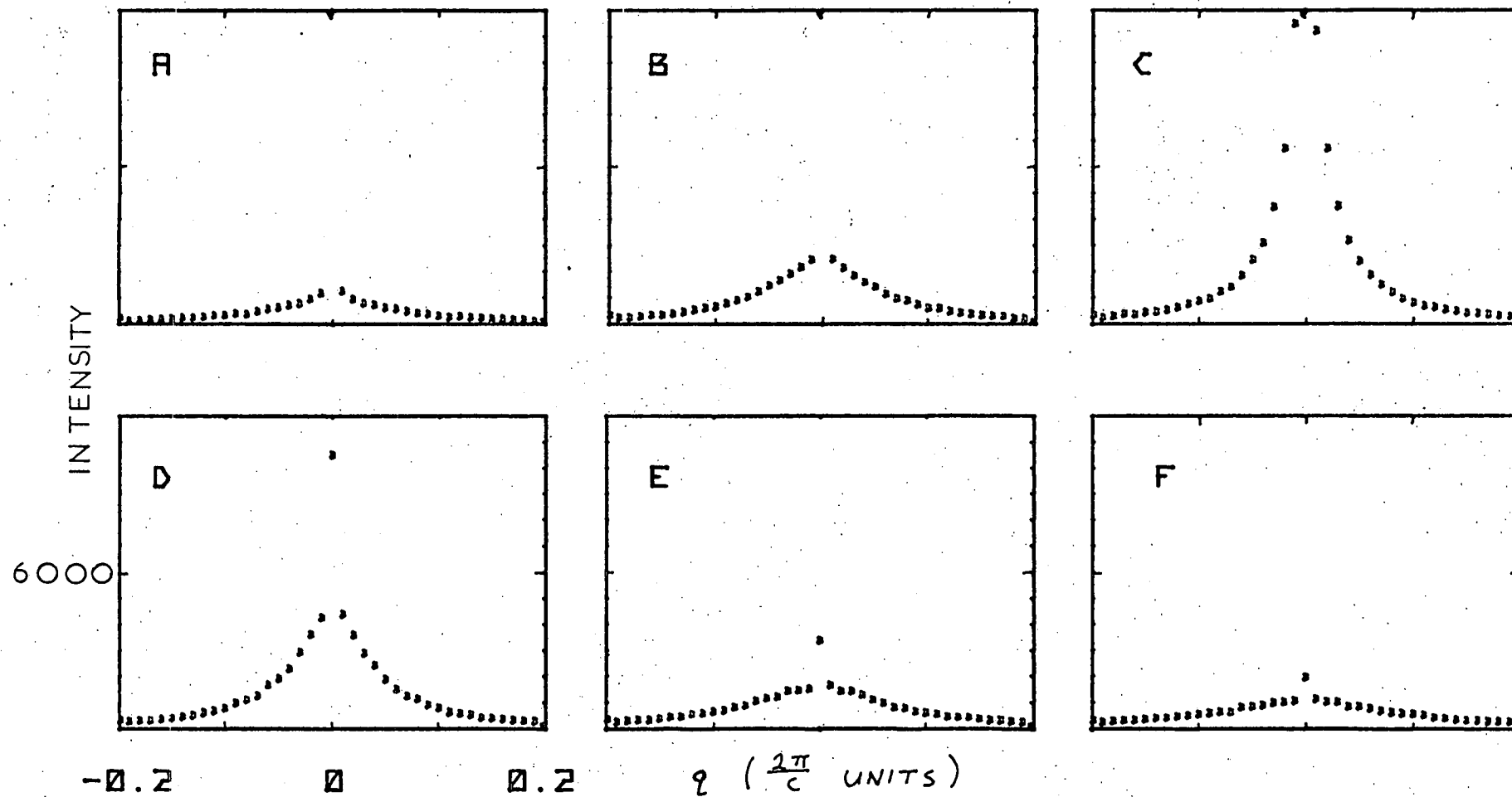


FIGURE 7.

The inverse correlation length and susceptibility of the longitudinal fluctuations ($T > T_{NO}$) measured from scans in the $[1\ 0\ 0]$ direction through $(1\ 0\ 0)$. The closed and open circles are the values obtained without any smearing of the transition temperature ($T_N = 38.62\text{ K}$). Using a further convolution of the scattering function with a Gaussian spread in the transition temperature of half width 0.52 K , the values shown with open triangles and crosses are obtained (only shown where they noticeably differ from the unsmeared values). The vertical bars are uncertainties brought about by an uncertainty in what to subtract for the transverse fluctuations (shown for about twice what we believe the actual uncertainty is).

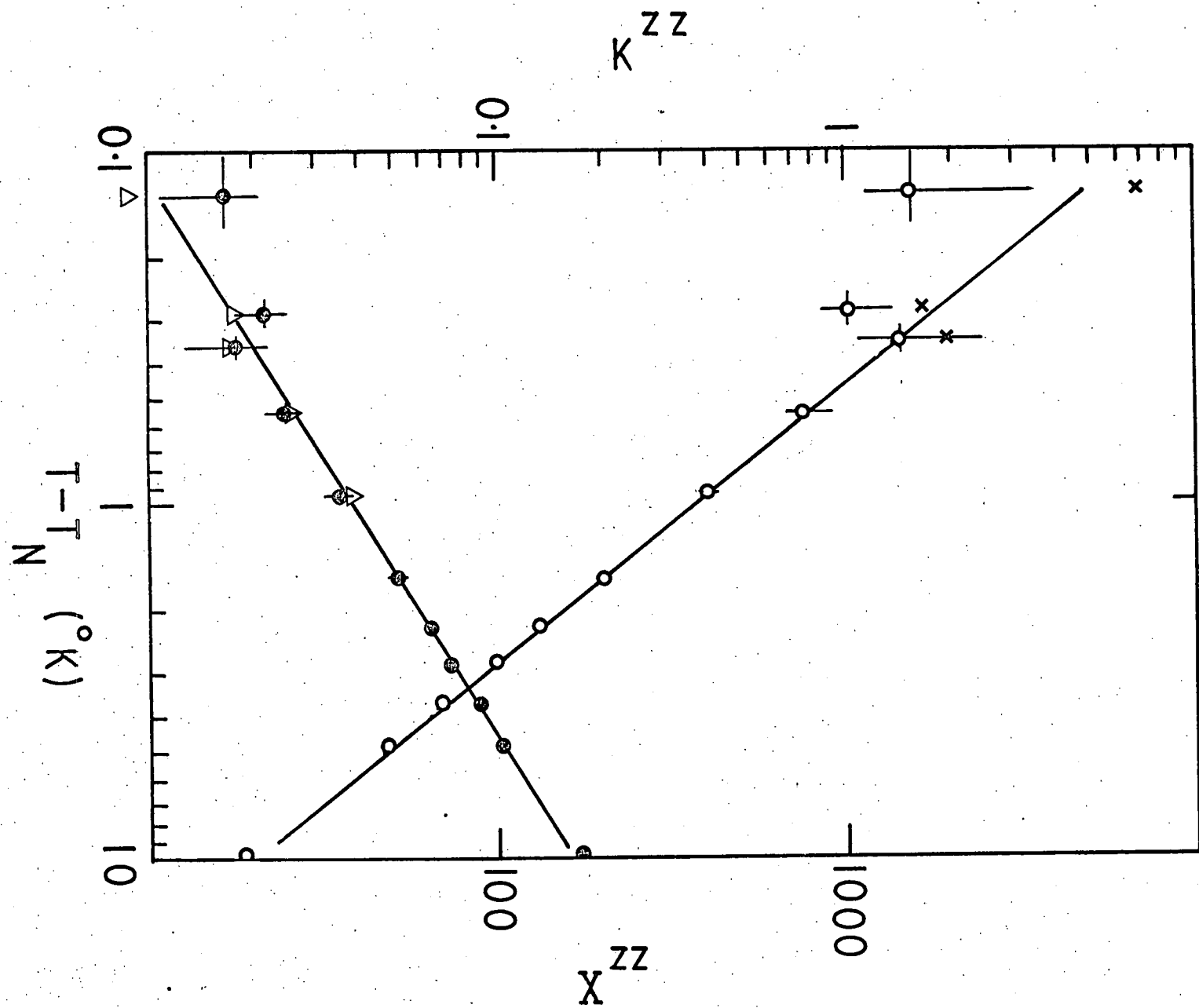
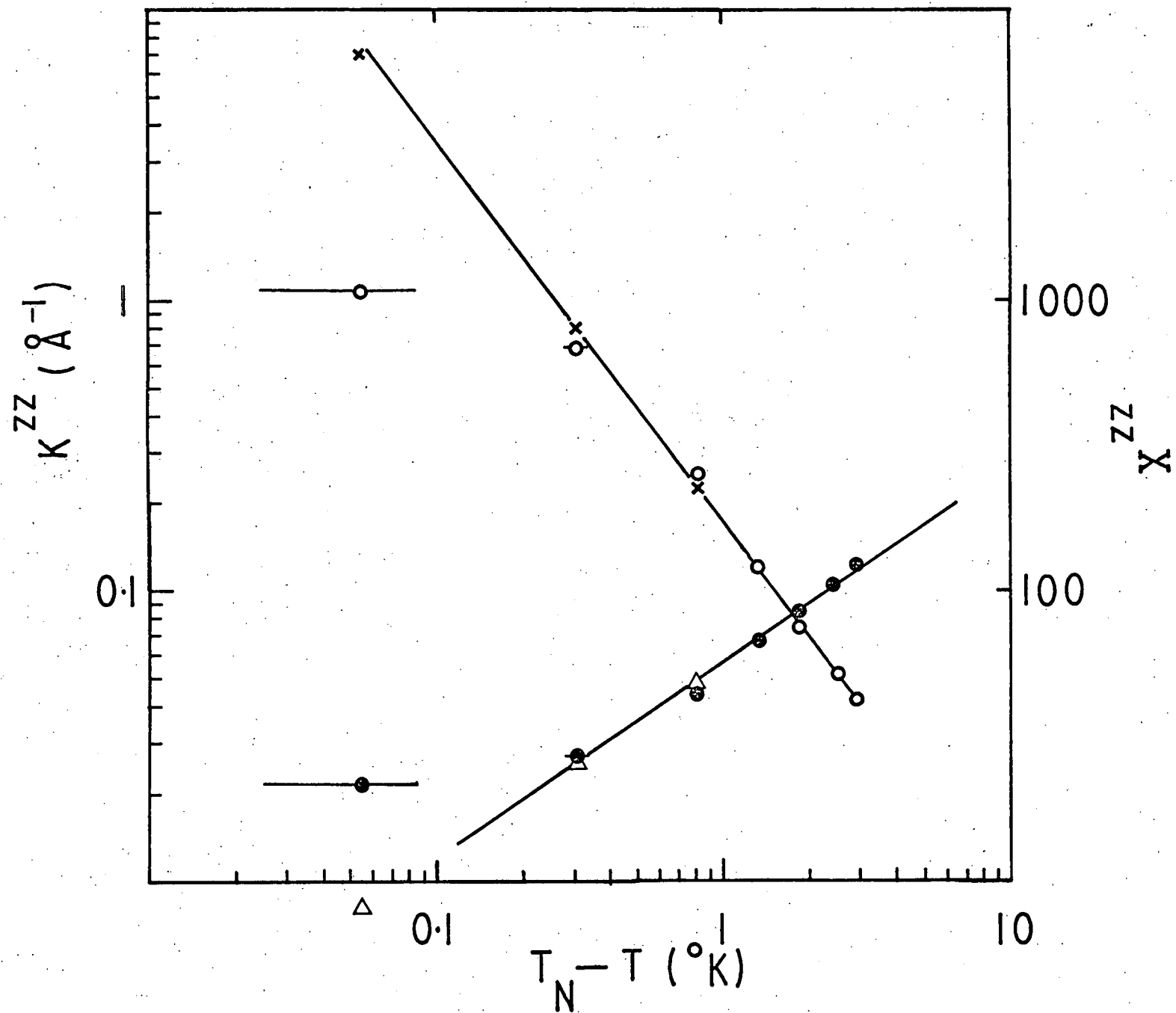


FIGURE 8.

The inverse correlation length and susceptibility of the longitudinal fluctuations ($T < T_{NO}$) measured from scans in the $[1\ 0\ 0]$ direction through $(1\ 0\ 0)$. The closed and open circles are the values obtained without any smearing of the transition temperature ($T_{NO} = 38.62\text{ K}$). Using a further convolution of the scattering function with a Gaussian spread in the transition temperature of half width 0.52 K the values shown with open triangles and crosses are obtained (only shown where they noticeably differ from the un-smeared values).



$$\chi_{||}^{+} = 1.25 \pm 0.15 \quad (61)$$

$$S_{||}^{+} = 3.7 \pm 0.5 \quad (62)$$

$$\chi_{||}^{-} = 1.31 \pm 0.25 \quad (63)$$

$$S_{||}^{-} = 1.4 \pm 0.3 \quad (64)$$

Applying the constraint $\chi_{||}^{+} = \chi_{||}^{-}$ and $S_{||}^{+} = S_{||}^{-}$ we obtain the universal ratio

$$\frac{S_{||}^{+}}{S_{||}^{-}} = 2.5 \pm 0.5 \quad (65)$$

VI. 8 CONCLUSIONS

We have performed a neutron scattering experiment on the random antiferromagnetic system $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$. Values of the susceptibility and inverse correlation length, derived assuming the transition to be sharp, are not consistent with power law fits in the reduced temperature indicating that the transition is smeared. We have proceeded on the assumption that the apparent smearing of the transition temperature is due to macroscopic variations in the concentration of zinc ions. Unfortunately we are only able to guess at the form of the macroscopic fluctuations in the concentration. We have employed a Gaussian spread in the transition temperature to obtain the exponents for the longitudinal fluctuations.

Our results may be compared to the results¹⁶ of the pure system, MnF_2 , which in turn appears to be consistent with the exponents for the 3 dimensional Ising model.

$$\chi_{||}^{+} = \chi_{||}^{-} = 0.63 \quad (66)$$

$$S_{||}^{+} = S_{||}^{-} = 1.25 \quad (67)$$

Recent renormalisation group calculations¹² show that we might

expect these results to be altered in a ($d = 3$; $n = 1$) disordered system to

$$\gamma_{||}^{+} = \gamma_{||}^{-} = 0.58 \quad (68)$$

$$\gamma_{||}^{+} = \gamma_{||}^{-} = 1.17 \quad (69)$$

Further terms in the ϵ -expansion may alter the exponents slightly, bringing them closer to those in the pure Ising model. It therefore appears that our results are consistent with both these models. It should be pointed out that the cross-over from the system with pure Ising model exponents to one with the ($d = 3$; $n = 1$) disordered type exponents is expected at quite small values of the reduced temperature ¹².

Again we may compare our values of $K_{||}^{-}/K_{||}^{+}$ and $S_{||}^{+}/S_{||}^{-}$ with those predicted for the Ising model ⁵.

$$\frac{K_{||}^{-}}{K_{||}^{+}} = 1.9 \quad (70)$$

$$\frac{S_{||}^{+}}{S_{||}^{-}} = 4.8 \quad (71)$$

The values we obtain do not appear to be really consistent with those values — so far as the author is aware, no estimates for these critical ratios have been derived for the disordered ($d = 3$; $n = 1$) system. If the ratios in this system are sufficiently different, this could provide a better method of testing for the predicted behaviour.

In conclusion, we have shown that the exponents in our disordered system are not inconsistent with those found in the pure system and the errors in our values are sufficiently large that the exponents are also consistent with the predictions for the ($d = 3$; $n = 1$) disordered system.

The values of the parameters are perhaps embarrassingly close to those found in the pure system considering the errors with which we quote the results. These we hope take into account the uncertainties brought about by the necessary inclusion of constraints. In particular the first method of fitting requires input of some of the parameters which are then compared with the output parameters. The new parameters are then reinserted into the program in an attempt to obtain consistency. There is no unique choice of parameters which can be selected from the output values, so it may well be that the choice is such that the type of exponents one is looking for are probably more likely to turn up in the highly parameterised fits. Never-the-less we believe that if different options were chosen at the stages towards a solution, the results would almost certainly have fallen within our quoted error limits.

A large part of the problem in analysing the Mn/ZnF_2 data is in making the choice of $A'_{\perp}(1\ 0\ 0)/A'_{\perp}(0\ 0\ 1)$ to which the results are particularly sensitive. To some extent the ratio depends on whether we believe the difference in the $[0\ 0\ 1]$ and $[1\ 0\ 0]$ scans through $(0\ 0\ 1)$ is the result of the form of q^2 or is caused by the neglect of the inelasticity corrections. In hindsight to test for the predictions of the $(d = 3 ; n = 1)$ disordered model one should have chosen to use neutrons of higher incident energy. Choosing a system with a higher transition temperature would allay doubts about replacing the Bose-Einstein population factor by unity. The best solution, to reduce uncertainties in the exponents, is to choose a system in which the transverse fluctuations are small, as would be the case for Co/ZnF_2 mixtures where because of the large anisotropy one would not need to worry about the factor $A'_{\perp}(1\ 0\ 0)/A'_{\perp}(0\ 0\ 1)$.

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Line Shape of the Magnetic Excitations in Substitutionally Disordered Antiferromagnets

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The neutron scattering from the magnetic excitations in the substitutionally disordered antiferromagnet, $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$, has been measured. The results show structure in the line shape which is similar to that predicted by some of the calculations based on the coherent-potential approximation and to that obtained in recent computer simulations.

The magnetic excitations in dilute antiferromagnets are ideal systems with which to test the predictions of theories for the excitations in disordered systems, because they may be studied in detail with neutron inelastic scattering techniques. The coherent-potential approximation (CPA) has been applied to these systems in several different ways. In the approach adopted by Buyers, Pepper, and Elliott,¹ each magnetic ion is treated as having an Ising energy determined by the number of neighboring magnetic ions, and the single-site CPA is used to evaluate the scattering of the excitations from these different energy levels. The line shape of the neutron scat-

tering is then calculated and has considerable structure corresponding to these different possible single-ion energies. Similar structure has also been found in computer simulations of these systems.² In another approach^{3,4} each magnetic ion is treated equivalently and the calculated line shape is smooth. Earlier experiments on these systems⁵⁻⁸ have had insufficient experimental resolution to observe the fine structure and hence have been unable to distinguish clearly between these two theoretical predictions. In this Letter, we report on measurements with considerably improved experimental resolution which has enabled us to observe fine structure in the line

shapes.

We used a single crystal of $\text{Mn}_{1-c}\text{Zn}_c\text{F}_2$ with $c = 0.32 \pm 0.02$, which was the same as that used in earlier low-resolution measurements,⁹ and which has an antiferromagnetic ordering temperature of 38.7 ± 0.3 K. The experiments were performed at 6 K with triple-axis crystal spectrometers on the cold source of the DR3 reactor at Risø and on the high-flux beam reactor at Brookhaven. All of the experiments were performed with pyrolytic graphite crystals as both monochromator and analyzer. In the experiments at Risø the scattered-neutron energy was held fixed at either 3.5 meV, configuration A, or 5.0 meV, configuration B, while in the experiments at Brookhaven, either the scattered-neutron energy was held fixed at 4.5 meV, configuration C, or the incident-neutron energy fixed at 13.97 meV, configuration D. In configurations A-C, a beryllium filter was placed between the specimen and analyzer to eliminate neutrons which might be reflected by the higher-order planes of the analyzer, and a correction applied to the results to compensate for the effect on the monitor in the incident neutron beam of higher-order contaminant neutrons from the monochromator. In configuration D, a tuned pyrolytic graphite filter was used to eliminate higher-order contaminant neutrons from the monochromator and a correction applied for the varying analyzer efficiency across the distribution.

Results for the [100] and [001] zone-boundary excitations are shown in Fig. 1 for a variety of different experimental arrangements. On each scan the experimental resolution (full width at half-maximum) is indicated for some typical energies, while below the distributions are shown a set of equally spaced arrows corresponding to the approximate positions of the fine structure. The results for the [001] zone boundary performed with configurations C and D are in very reasonable agreement with each other except that there is some excess intensity for energy transfers of about 1.5 meV. There is considerable additional scattering at low energies in configuration A but the origin of this is unknown. Despite these discrepancies, we believe these results provide definite evidence for structure at energy transfers of 6.0, 5.3, and 4.5 meV and a suggestion of structure at 3.9 meV.

The results for the [100] zone boundary are all in reasonable accord with one another except that there is excess intensity at energy transfers of 1.5 meV in configuration C which is absent from

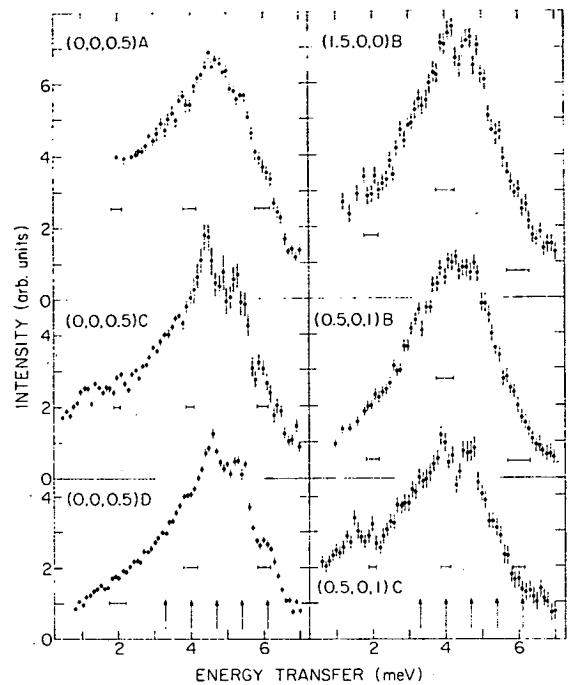


FIG. 1. Neutron scattering distributions from the [100] and [001] zone-boundary excitations in $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$. The horizontal bars give the experimental resolution for the various different experimental configurations described in the text. The vertical arrows denote the approximate positions of the fine structure.

the other results. These results provide evidence for structure at energy transfers of 4.0 and 4.7 meV and suggest that there is also slight structure at 3.3 and 5.4 meV.

In Fig. 2, we compare the distribution shown at the bottom of Fig. 1 with various theoretical calculations. The calculations labeled BPE are the results of the theory developed by Buyers, Pepper, and Elliott¹ in which each magnetic ion has an energy determined by the number of neighboring magnetic ions, and the single-site CPA is used to evaluate the scattering of the excitations by these different energies. The transverse parts of the exchange interactions are included approximately as suggested by Buyers, Pepper, and Elliott and the excitations are kept off the non-magnetic sites by placing a large repulsive potential on them. Other variants of this type of theory¹⁰ give very similar results for the zone boundaries. In the calculations it is necessary to add an imaginary part, ϵ , to the energy to obtain convergence, but the larger ϵ is, the less structure there is in the results. In our calculations, we put $\epsilon = 0.2$ meV for which convergence could be obtained although considerably more

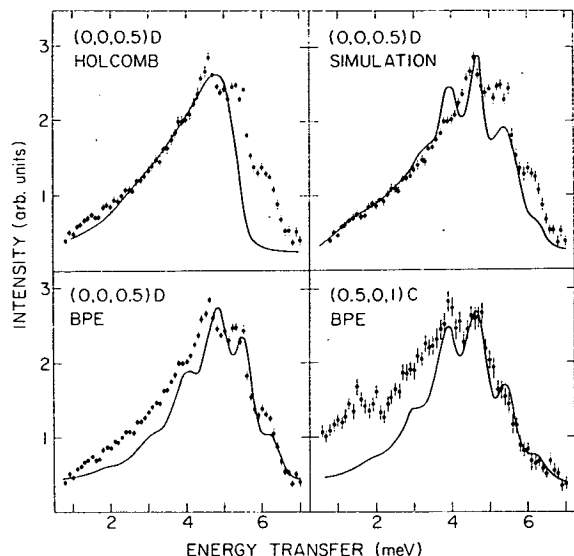


FIG. 2. Neutron scattering distributions from the magnetic excitations in $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$ compared with the predictions of the theories of Buyers, Pepper, and Elliott (Ref. 1) and of Holcomb (Ref. 4) and with computer simulations of Holcomb and Harris (Ref. 2).

slowly than for $\epsilon = 0.3$ meV. The results were convoluted with the experimental resolution, scaled, and a constant background added before comparison with the experimental results. Figure 2 shows that the structure in the theory is very similar in magnitude to that observed experimentally. The positions of the peaks do not exactly agree but this might be accounted for by a change in the exchange constants due to a lattice parameter change. The theory fails to account adequately for the low-energy-transfer side of the distributions. This discrepancy was apparent in the earlier low-resolution measurements⁹ and is a definite discrepancy between the theory and experiment.

The CPA has also been applied to this system by Holcomb.⁴ In his approach, the transverse part of the exchange interactions is included more satisfactorily than in the other development but at the expense of treating all the magnetic ions equivalently. His theory when convoluted with the experimental resolution gives an excellent account of the low-frequency side of the peak but fails to account for the structure or shape of the high-frequency side.

A computer simulation of this system has been performed by Holcomb and Harris² using an array of 8192 sites. Their calculations for $c = 0.35$ were convoluted with the experimental resolution

functions, and are shown in Fig. 2. At least some of the discrepancy in overall position arises from their use of a slightly larger concentration, 0.35, of empty sites than was present in our specimen, 0.32. Their calculations do seem to predict somewhat more structure than was observed. In part, this may arise, as the authors remark, from their neglect of the weak nearest-neighbor ferromagnetic exchange interactions. These interactions were included at least approximately⁸ in the two CPA calculations described above.

In conclusion, the line shape of the zone-boundary excitations in a specimen of $\text{Mn}_{0.68}\text{Zn}_{0.32}\text{F}_2$ have been studied with high-resolution neutron inelastic scattering techniques. The results show that the line shapes are not smooth but have structure very similar to that predicted by the CPA theory of Buyers, Pepper, and Elliott¹ and by computer simulations.² We understand that similar results have been obtained with a crystal of $\text{Mn}_{0.25}\text{Zn}_{0.75}\text{F}_2$ by Buyers, Holden, and Svensson.¹¹ These results then show that the effect of the differing environments in modifying the Ising energy of the different magnetic ions must be an essential aspect of a successful theory of these systems.

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THE DEBYE-WALLER FACTOR AND STRUCTURAL PHASE TRANSITIONS

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As continuous structural phase transitions are approached, an increase in both the Debye-Waller factor and the nuclear quadrupole coupling coefficient is predicted. The behaviour of these is dependent upon the nature of the fluctuations associated with the structural phase transition. In particular in uniaxial ferroelectrics the macroscopic electric field suppresses some of the fluctuations so that the Debye-Waller factor has a form different from that at other phase transitions. It is shown that the predicted form for uniaxial ferroelectrics is consistent with the observed temperature dependence of the quadrupole resonance in CsDA when reasonable values are used for the parameters in the theory. At other phase transitions the measurement of the Debye-Waller factor would enable the critical exponent, γ , to be determined and compared with the various predictions of renormalization group theory.

INTRODUCTION

In recent years there has been considerable interest in the understanding of critical phenomena occurring at structural phase transitions. Unfortunately many of the experiments in this field are difficult, time consuming and possible only when large single crystals are available. The Debye-Waller factor does not provide nearly such detailed information about the critical fluctuations as many other quantities, but it has the advantage that it can be measured readily by x-ray diffraction, neutron diffraction or Mossbauer spectroscopy and a closely related quantity can be measured by magnetic resonance techniques. In this paper we discuss the effect on the Debye-Waller factor of the critical fluctuations occurring close to a structural phase transition, and suggest that some interesting information can be obtained by measuring it.

The behaviour of the Debye-Waller factor close to structural phase transitions has been discussed previously by several authors.¹⁻⁴ It is appropriate, however, to re-examine the topic partly because of the variety of results obtained by these authors, but also because of the recent advances made as a result of applying renormalization group theory to these transitions.⁵ In particular these results have emphasized that the critical fluctuations are dependent upon the degeneracy of the fluctuations and whether or not the transition is to a ferroelectric phase.

The Debye-Waller factor of an atom of type K in the l th unit cell is given by

$$W_{\alpha\beta} = \langle U_{\alpha}(lK)U_{\beta}(lK) \rangle,$$

where $U(lK)$ is the displacement vector of the atom. It is usually more convenient to rewrite the displacement in terms of the frequencies $\omega(qj)$ and eigenvectors $e(K|qj)$ of the harmonic normal modes of vibration when

$$W_{\alpha\beta} = \frac{\hbar}{2NM_K} \sum_{qj} \frac{e_{\alpha}(K|qj)e_{\beta}^*(K|qj)}{\omega(qj)} (2n(qj) + 1), \quad (1)$$

where $n(qj)$ is the Bose-Einstein occupation number of the normal mode. In an anharmonic crystal the leading corrections to this expression are obtained by replacing the harmonic frequencies by the renormalized frequencies which include the effects of the anharmonicity.⁶

Structural phase transitions may frequently be treated as instabilities of the crystal against particular normal modes of vibration. It is convenient to divide $W_{\alpha\beta}$ into two terms; a part which is regular at the phase transition and a part which is singular and which arises from those terms in Eq. (1) for which the mode (qj) is a temperature dependent mode associated with the phase transition. These modes are then expected to have a low frequency compared with $k_B T/\hbar$ so that the Debye-Waller factor becomes

$$W_{\alpha\beta} = W_{\alpha\beta}^R + W_{\alpha\beta}^S,$$

where at high temperatures $W_{\alpha\beta}^R$ is proportional to temperature and

$$W_{\alpha\beta}^S = k_B T \sum_{qj} \frac{C_{\alpha\beta}(qj)}{\omega(qj)^2}, \quad (2)$$

and the summation is only over the temperature dependent modes and the $C_{\alpha\beta}$ are temperature independent constants.

Although Eq. (2) was obtained within the framework of weakly anharmonic lattice dynamics, it is also applicable to order-disorder transitions if $\omega(\mathbf{q}j)^2$ is identified with the inverse of the static susceptibility for wavevector, $\mathbf{q}$.

The frequency of the nuclear quadrupole resonance is determined by the electric field gradient at the nucleus. The gradient may be expanded in terms of the normal mode displacements when their contribution to the gradient may be written² as

$$V_{\alpha\beta} = \frac{1}{N} \sum_{\mathbf{q}j} \frac{V_{\alpha\beta}(\mathbf{q}j)}{\omega(\mathbf{q}j)} (2n(\mathbf{q}j) + 1).$$

In a similar way to the Debye-Waller factor this may be separated into a regular and singular part close to T_c and the latter written as

$$V_{\alpha\beta}^S = \frac{2k_B T}{N\hbar} \sum_{\mathbf{q}j} \frac{V_{\alpha\beta}(\mathbf{q}j)}{\omega(\mathbf{q}j)^2}.$$

In the remainder of this paper we discuss the form of $W_{\alpha\beta}^S$ and $V_{\alpha\beta}^S$ at different phase transitions. The results are clearly dependent upon the form of $\omega(\mathbf{q}j)^2$ allowed by the symmetry of the crystal so that different results are obtained for different types of structural phase transitions.

UNIAXIAL FERROELECTRICS

Uniaxial ferroelectrics have a unique ferroelectric axis and consequently only one branch, j , which is anomalously temperature dependent. For small wavevectors the eigenvector of these modes may be taken as independent of wavevector, while the frequencies of the mode are given by

$$\omega(\mathbf{q}j)^2 = \omega_0^2 + B^2 |\mathbf{q}|^2 + C^2 \frac{q_z^2}{|\mathbf{q}|^2},$$

where z is the ferroelectric axis, and ω_0 is the frequency of the transverse optic mode as $q \rightarrow 0$. As $T \rightarrow T_c$, the transition temperature, $\omega_0 \rightarrow 0$. The constant B determines the dispersion of the transverse optic mode. (In principle B could be different for wavevectors along the x , y and z directions, but such generality does not change the functional dependence of our results.) The constant C is determined by the strength of the macroscopic electric field of the crystal and is the characteristic feature of uniaxial ferroelectrics. The singular

part of the Debye-Waller factor is then proportional to

$$Y = \frac{k_B T}{N_s} \sum_{\mathbf{q}}^s \frac{1}{\omega(\mathbf{q}j)^2},$$

where N_s is the number of temperature dependent modes in the summation.

The expression for Y may be evaluated by converting the summation to an integral over all $|\mathbf{q}| < Q$ to give

$$Y = \frac{k_B T \int_0^Q \int_0^\pi \frac{q^2 \sin \theta d\theta dq}{\omega_0^2 + B^2 q^2 + C^2 \cos^2 \theta}}{\int_0^Q \int_0^\pi q^2 \sin \theta d\theta dq}.$$

Now if $X = BQ/\omega_0$ then

$$Y = \frac{3k_B T \omega_0^2}{B^3 Q^3 C} \int_0^X \frac{x^2}{\sqrt{1+x^2}} \tan^{-1} \left[\frac{C}{\omega_0 \sqrt{1+x^2}} \right] dx \quad (3)$$

This result can only be further simplified if $C \gg BQ$ and $C \gg \omega_0$ when

$$Y = \frac{3\pi k_B T}{2BQC} \left[\frac{\sqrt{1+X^2}}{X} - \frac{1}{X^2} \log(X + \sqrt{1+X^2}) \right],$$

which close to T_c ($BQ \gg \omega_0$) gives

$$Y = \frac{3\pi k_B T}{2QBC} \left[1 - \frac{\omega_0^2}{B^2 Q^2} \log \left(\frac{2BQ}{\omega_0} \right) \right] \quad (4)$$

The first part of this expression is regular as $T \rightarrow T_c$. In uniaxial ferroelectrics ω_0^2 is both found experimentally⁷ and theoretically⁸ to vary as $T - T_c$. Consequently the singular part of Y varies as

$$Y^S = AT(T - T_c) \log(A'(T - T_c)),$$

where A and A' are constants.

This result agrees with that obtained by Vaks *et al.*¹ for order-disorder ferroelectrics, but the above discussion shows it to be characteristic of uniaxial ferroelectrics whether they are of displacive or order-disorder character. It differs from the results of Blinc *et al.*² who assumed $\omega_0^2 = \omega(\mathbf{q}j)^2$ for all wavevectors and of Scott and Worlock⁴ who neglected the effect of the macroscopic electric field.

The above results for Y have been compared with measurements² of the As⁷⁵ nuclear quadrupole coupling coefficient of CsDA. In this case $B^2 Q^2 \approx C^2$,

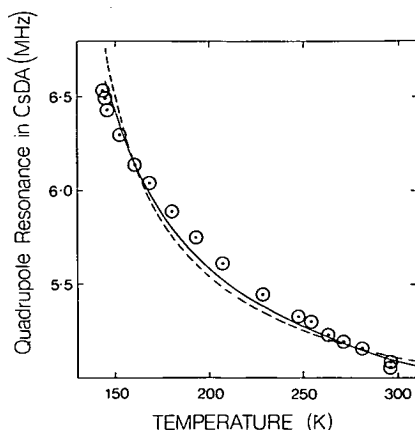


FIGURE 1 The As^{75} nuclear quadrupole coupling coefficient of CsDA as a function of temperature. The experimental points are taken from the work of Blinc *et al.*,² and the solid and dotted curves give the results of calculations using the clamped and free transition temperatures.

so that Eq. (3) was used and the integration performed numerically.

In the calculations ω_0^2 was put equal to $A(T - T_c)$ where in the calculations shown in Figure 1, T_c was set to either the clamped Curie temperature, 129 K, or the free Curie temperature, 143 K.⁹ The agreement with the former choice of T_c is very satisfactory, with the parameters $C^2/A = 90 \text{ K}^{-1}$ and $(BQ)^2/A = 121 \text{ K}^{-1}$. Unfortunately the value of these parameters are highly correlated and similar agreement with the experimental results can be obtained with other pairs of values which are quite different. The parameter values may, however, be compared with those deduced from neutron scattering measurements on DKDP,¹⁰ which yielded $C^2/A = 210 \pm 20 \text{ K}^{-1}$ and $B^2/A = 360 \pm 80 \text{ K}^{-1}$ if Q is expressed in reduced wavevector units ($aq/2\pi$). The cut-off, Q , is then estimated in CsDA to be a reasonable 0.6 of the Brillouin zone. This order of magnitude agreement between the values of these parameters for CsDA and DKDP supports the validity of the above analysis.

It is not surprising that the results shown in Figure 1 with the clamped Curie temperature are more satisfactory than those found with the free Curie temperature. The quadrupole resonance frequency is about 5 MHz which is most probably above the acoustic resonance frequency of the crystal.

PLANAR FERROELECTRICS

In planar ferroelectrics the ferroelectric axis is confined to a plane. Above the phase transition there are

two normal modes which describe the fluctuations of the dipole moments. The dynamical matrix for these modes may be written in the form

$$\begin{pmatrix} \omega_0^2 + B^2|q|^2 + C^2 \frac{q_x^2}{|q|^2} & C^2 \frac{q_x q_y}{|q|^2} \\ C^2 \frac{q_x q_y}{|q|^2} & \omega_0^2 + B^2|q|^2 + C^2 \frac{q_y^2}{|q|^2} \end{pmatrix}$$

where the ferroelectric axis is confined to the XY plane, and ω_0^2 , B^2 and C^2 describe the frequencies of the transverse optic modes as $q \rightarrow 0$, the dispersion of these modes, and the effect of the macroscopic elastic field. More complex forms of the dispersion can be included in the development without altering the functional dependence of the results.

The dynamical matrix may be diagonalized to yield two modes for each wavevector

$$\omega(q_1)^2 = \omega_0^2 + B^2 q^2$$

$$\omega(q_2)^2 = \omega_0^2 + B^2 q^2 + C^2(q_x^2 + q_y^2)/|q|^2$$

The singular part of the Debye-Waller factor is then proportional to

$$Y = \frac{k_B T}{N_s} \sum_{\mathbf{q}} \left[\frac{1}{\omega(q_1)^2} + \frac{1}{\omega(q_2)^2} \right]$$

The first term can be evaluated by replacing the summation by an integral over a sphere of radius Q to give

$$Y_1 = \frac{3k_B T}{B^2 Q^2} \left[1 - \frac{\omega_0}{BQ} \tan^{-1} \frac{BQ}{\omega_0} \right] \quad (5)$$

A similar treatment of the second term gives

$$Y_2 = \frac{3k_B T}{2Q^2} \int_0^Q \frac{q^2}{C \sqrt{\omega_0^2 + B^2 q^2 + C^2}} \times \log \left| \frac{\sqrt{\omega_0^2 + B^2 q^2 + C^2} + C}{\sqrt{\omega_0^2 + B^2 q^2 + C^2} - C} \right| dq$$

This integral can be performed analytically if $C^2 \gg \omega_0^2 + B^2 q^2$ to give

$$Y_2 = k_B T \left(\frac{\omega_0}{CBQ} \right)^2 \left[3\pi \left(\frac{\omega_0}{BQ} \right) - 6 \right]$$

These results show that as $T \rightarrow T_c$ and $\omega_0 \rightarrow 0$, the Debye-Waller factor does not diverge but tends to a finite value. Furthermore, since ω_0^2 is determined by the static susceptibility, $\omega_0^2 \propto (T - T_c)^\gamma$, then the

Debye-Waller factor approaches its value at T_c asymptotically like $(T - T_c)^{\gamma/2}$. The contribution from the normal mode, $j = 2$, is smaller than that arising from the other mode. Comparatively little work has been performed on planar ferroelectrics either experimentally or theoretically. Renormalization group theory suggests that γ is larger than 1 (1.24 to $0(\epsilon)^5$).

CUBIC FERROELECTRICS

In cubic ferroelectrics the ferroelectric axis can be in any direction. There are three normal modes which describe the fluctuations in the dipole moment and the dynamical matrix is a 3×3 matrix with 9 components. The $(\alpha\beta)$ elements of the matrix are

$$(\omega_0^2 + B^2 q^2) \delta_{\alpha\beta} + C^2 \frac{q_\alpha q_\beta}{|q|^2},$$

where the symbols stand for the same quantities as earlier and the same inessential approximation has been made in the form of the dispersion. This dynamical matrix gives three normal modes; two transverse modes

$$\omega(q, 1)^2 = \omega(q, 2)^2 = \omega_0^2 + B^2 q^2,$$

and one longitudinal mode

$$\omega(q, 3)^2 = \omega_0^2 + B^2 q^2 + C^2.$$

The contribution to the Debye-Waller factor is given by

$$Y = \frac{3k_B T}{B^2 Q^2} \left[3 - \frac{2\omega_0}{BQ} \tan^{-1} \frac{BQ}{\omega_0} - \frac{\sqrt{\omega_0^2 + C^2}}{BQ} \right. \\ \left. \times \tan^{-1} \frac{BQ}{\sqrt{\omega_0^2 + C^2}} \right]$$

The temperature dependence of the Debye-Waller factor close to T_c is therefore dominated by the second term and is asymptotically $(T - T_c)^{\gamma/2}$. The best estimates of the critical exponents of a cubic ferroelectric are those found for the isotropic dipolar system⁵, $\gamma = 1.372$. Unfortunately we are unaware of any measurements on cubic ferroelectric with which we can compare this prediction. The measurements on GeTe/SnTe alloys,¹¹ for example, are qualitatively consistent but are not of sufficient accuracy to provide a quantitative test.

NON-FERROELECTRICS

At phase transitions other than ferroelectric ones, the dispersion relations for the normal modes are analytic

in the region of wavevector space near the mode responsible for the phase transition. The temperature dependence of the Debye-Waller factor can then be obtained by considering each mode to have a dispersion relation of the form

$$\omega(q)^2 = \omega_0^2 + B^2 q^2 \quad (6)$$

The Debye-Waller factor is then given by Y_1 , Eq. (5). At T_c the Debye-Waller factor is finite and approaches this value asymptotically as $(T - T_c)^{\gamma/2}$.

In principle the dispersion term can be considerably more complex than that given by Eq. (6). Physically reasonable but more complex forms also lead to a finite Debye-Waller factor at T_c and the same asymptotic form.

The value of γ is expected to vary with the number of different components for the soft mode. If there is only one mode γ is expected to be that of the three-dimensional Ising model. If there are two modes the exponent of the XY model is appropriate, while if the mode is a triplet the Heisenberg model exponent is appropriate, whereas for higher degeneracy renormalization group theory suggests that other exponents may be appropriate.

In conclusion the temperature dependence of the Debye-Waller factor has been calculated close to structural phase transitions. It has been shown that the asymptotic behaviour provides a way of determining the critical exponent γ . If sufficient accuracy could be obtained then careful measurements of the Debye-Waller factor or quadrupole coupling coefficient of systems undergoing continuous structural phase transitions would provide a means of testing the predictions of renormalization group theory for different types of transition.

In particular the asymptotic behaviour of uniaxial ferroelectrics is found to be different from that of planar or cubic ferroelectrics, or of non-ferroelectrics. This is a direct consequence of the effect of the macroscopic electric field suppressing all the critical fluctuations in uniaxial ferroelectrics except those with wavevectors perpendicular to the ferroelectric axis. A test of this prediction should be considerably easier than an accurate determination of γ .

Finally throughout the paper the dispersion of the normal modes has been assumed to be proportional to q^2 . Close to a phase transition the dispersion is expected to be of the form $q^{2-\eta}$. The critical exponent η is, however, small, (0.02) and further numerical calculations with different powers for the dispersion gave very similar results.

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LETTER TO THE EDITOR

The structure of ferroelectric DCsDA

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Abstract. In further neutron scattering experiments on the (orthorhombic) ferroelectric phase of DCsDA and CsDA, a study has been made of the scattering arising at wavevectors along the a^* direction at positions away from Bragg reflections. It is shown that this most probably arises from Bragg scattering in which two different ferroelectric domains are involved.

Below T_c each Bragg reflection can split into four separate spots corresponding to the different domain types. Surprisingly in DCsDA a central Bragg spot from the (tetragonal) paraelectric phase persists with decreasing intensity over a 60 K temperature range. This effect has been observed with both neutron and x-ray scattering techniques and is independent of crystal size.

1. Satellites in CsDA

Dietrich *et al* (1974) reported observing a satellite structure in the ferroelectric phase of DCsDA (CsD_2AsO_4). Peaks in the scattering were observed around a number of Bragg points in the $(h0l)$ zone. These peaks appeared at reduced wavevectors 0.1 and 0.2 along the $[\eta 00]$ direction at (004) and (303), at 0, 0.034 and 0.067 for (002) and at combinations of these reduced wavevectors around other Bragg points. The indexing of the tetragonal phase is used throughout this paper.

The experiments have been repeated in greater detail on a 1 cm^3 crystal of the corresponding hydrogenous compound, CsDA (CsH_2AsO_4), obtained from Quantum Technology§. The crystal was mounted with the ac plane horizontal and maintained at a temperature of 115 K in a cryostat on a double-axis spectrometer at the DR3 reactor, Risø. Elastic neutron scattering scans of the type $(h + \eta, \xi, l)$ were made using neutrons of wavevector $k = 2.65\text{ \AA}^{-1}$. η was varied under the control of a PDP 8 computer and at the end of each scan ξ was incremented manually by tilting the counter vertically. Contour maps of the intensities observed at the systematic absence (002) and at (004) are shown in figure 1. These are similar to those observed in DCsDA, but in the present study the vertical resolution has been improved.

The ferroelectric cell can be described as a distortion of the paraelectric cell by a spontaneous shear x_y (Jona and Shirane 1962). The shear angle is about 1.8° and decreases to 70% of this value close to the transition temperature (Meyer and Dietrich 1975). When

§ Quantum Technology, 60 Nugget Avenue, Unit 5 Agincourt (Toronto), Ontario, Canada.

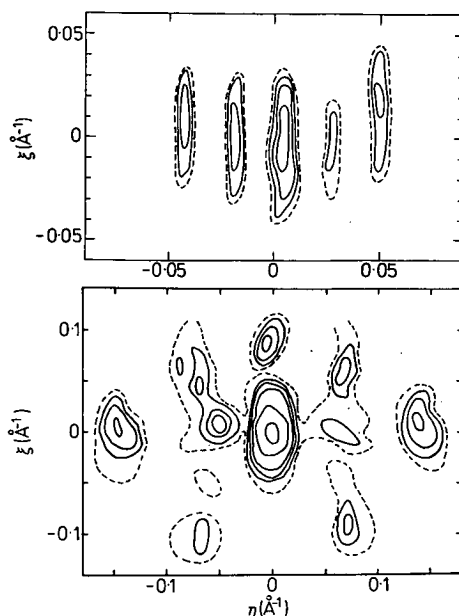


Figure 1. The intensities observed in the ferroelectric phase of CsDA at 115 K. Maps of (002) and (004) with contours at 10, 30, 100, 300, 1000 and 3000 above background.

a single crystal of CsDA is taken through the transition it is expected in general to shear four different ways. There are thus four types of ferroelectric domain distinguished by their mutual orientation. The proportion of the crystal forming each type of domain can

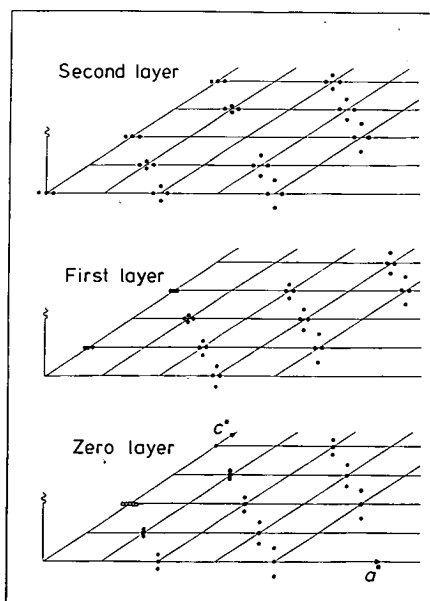


Figure 2. The domain splitting for Bragg points in ($h0l$) and parallel planes. The points are split only in the a^*b^* plane. In addition the satellite positions at (002) are shown as open circles.

vary but the process is otherwise reversible. The effect of the domain splitting on Bragg peaks is shown schematically in figure 2. At the position of each Bragg peak of the paraelectric phase there appear in general four separate peaks, lying in the a^*b^* plane: for $a^* = 0$ or $b^* = 0$, two superpose so that only three peaks are distinguished.

In a single crystal, multiple Bragg scattering affects only the intensities at reciprocal lattice vectors. But when the crystal consists of domains with a number of different orientations, multiple scattering can give rise to scattering at points other than those permitted by a single scattering process—as we shall now demonstrate. The problem is equivalent to determining whether reciprocal lattice points from two parallel co-ordinate systems, with origins at either end of the scattering vector, simultaneously lie on the Ewald sphere. Thus intensity seen at $(h + \eta, k + \xi, l)$ can result as scattering from a Bragg point (h', k', l') in one domain type followed by scattering from a Bragg point $(h' - h, k' - k, l' - l)$ in a different domain type. For brevity we shall refer to this scattering as multiple scattering from $((h', k', l'))$.

A translation of the co-ordinate system along the c -axis by a reciprocal lattice vector like (002) leaves the splitting of the Bragg peaks unchanged. Peaks from the two co-ordinate systems will completely overlap (systematic absences in either system excepting). If a scan in the $[\eta 00]$ direction is made at (002), points in the two co-ordinate systems will 'pass through' each other. For example, a reciprocal lattice point such as (011), which splits into three collinear Bragg peaks with spacing d , will have peaks from the two systems overlapping at five equispaced positions in the scan, namely at $(-2d, 0, 2)$, $(-d, 0, 2)$, $(0, 0, 2)$, $(d, 0, 2)$ and $(2d, 0, 2)$ where

$$d = \tan x, \simeq 0.03.$$

These positions are the same as those at which the satellites were observed around (002). They are marked as open circles on figure 2. The above, however, only provides a necessary condition for multiple scattering—to make the condition sufficient, we must ensure that pairs of points, designated by $((0, 1, 1))$, simultaneously lie on the Ewald sphere.

A computer simulation was set up to investigate all the possible ways that multiple scattering from two different domain types can produce satellites. This shows that only the first four points on the $(\eta 02)$ scan listed above have contributions from $((0, 1, 1))$ multiple scattering. The first point has a further contribution from $((3, 1, 4))$. Normal multiple scattering (i.e. in a *single* domain type)—at $((5, 2, 3))$ and at $((5, 2, -1))$ —also meets the necessary conditions for the centre point at $(0, 0, 2)$. The correct condition for the last point is only met by multiple scattering from $((3, 1, -2))$. There is no first-order reflection at (002), but a slight second-order contamination of the neutron beam reflected at (004) contributes to the intensity observed at $(0, 0, 2)$.

It can similarly be shown that multiple scattering from $((4, 3, 3))$, $((4, 3, 1))$, $((1, 3, 2))$ and $((0, 2, 2))$ contribute towards the intensities observed round (004). The slight up-down asymmetry in the contour map, figure 1, is probably caused by incorrect alignment of the crystal, since multiple Bragg scattering is particularly sensitive to correct alignment.

There are two ways of checking whether an effect observed in a neutron scattering experiment is due to multiple scattering. Firstly the wavelength of the monochromatic beam can be altered. Thereby the radius of the Ewald sphere in the crystal, monochromator or analyser changes and so do the conditions for the multiple scattering. Unfortunately with the present experimental set-up it was difficult to change the wavelength of the incident beam.

Alternatively, rotation of the crystal about the scattering vector also changes the conditions for multiple scattering. When the crystal was rotated about (002) and (004) a large variation in the intensity of the satellites was observed. This supports our conclusion that the appearance of satellites is caused by multiple Bragg scattering.

2. Tetragonal Bragg peak in ferroelectric DCsDA

Deuteration changes a number of properties of CsDA. The shear angle, when measured away from the transition temperature, increases from 1.75° to 2.0° . The transition temperature increases from 146 K in CsDA to 227 K at a deuteration level of $\sim 85\%$ (Loiacono *et al* 1976).

We have now found that in our samples of DCsDA, obtained from Quantum Technology, only part of the crystal transforms at the nominal transition temperature with the remainder transforming over a 60 K temperature range. In figure 3 we show the neutron

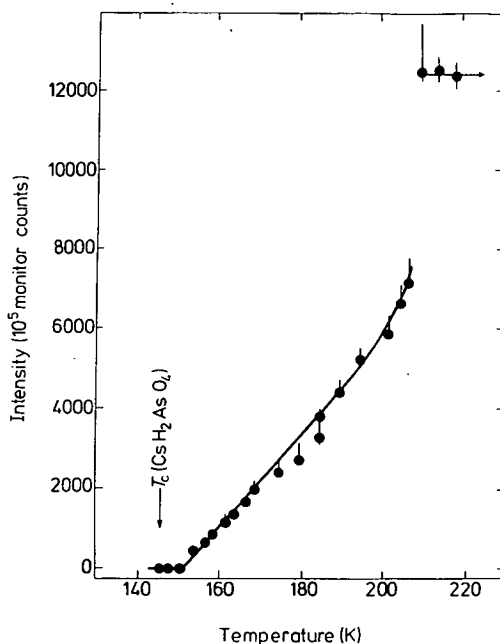


Figure 3. The temperature dependence of the central Bragg peak intensity at (220). T_c (CsDA) was measured as 145.9 ± 0.2 K.

intensity scattered in a 1 cm^3 sample at the (220) tetragonal reciprocal lattice point, plotted against temperature. Obviously, only 40% of the intensity in the tetragonal high-temperature phase disappears at 205 K; the lost intensity is distributed over the four peaks of the orthorhombic low-temperature phase. The remaining tetragonal peak intensity transfers to the orthorhombic peaks gradually, over a range extending nearly to the transition temperature of the hydrogenous compound.

Two smaller crystals (8 mm^3 and 16 mm^3) were investigated on a four-circle neutron diffractometer and showed quantitatively similar behaviour. Structure refinements (Hay

and Nelmes 1976) indicate that the average deuteration of the 8 mm^3 sample is 57%. Such a high hydrogen content is consistent with the unexpectedly intense incoherent neutron scattering found in the experiment on the 1 cm^3 sample. (*hk0*) photographs of a 0.01 mm^3 crystal taken with a Weissenberg x-ray camera again showed similar effects and confirmed that all reflections were affected.

The fact that crystals of such diverse sizes exhibit quantitatively similar behaviour makes surface rehydrogenation an unlikely explanation. We conclude rather that the observations suggest an inhomogeneity of the hydrogen-deuterium concentration over regions small in comparison with our smallest sample (0.2 mm). This could be consistent with peculiar growth behaviour observed in DCsDA (G M Loiacono, private communication) and could be a characteristic common to all solution-grown samples.

The transition temperature of 227 K given by Loiacono *et al* (1976) for a deuteration level $\sim 85\%$ suggests that the deuteration levels for DCsDA samples quoted in the literature have been grossly overestimated. If, in addition, the pronounced inhomogeneity of our specimens is a common characteristic, some further doubt must attach to the interpretation of the results of most previous experiments in DCsDA.

We are making further studies of the nature and reproducibility of the observed inhomogeneity.

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