

Anisotropic polarisation fluctuations in KD_2PO_4 -type crystals

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Abstract. It is shown that the strong short-range interactions which exist in hydrogen bond ferroelectrics, produce strong anisotropy in the wavevector (q) dependence in the polarisation fluctuations in these systems. It is suggested that this anisotropy is the origin of the observed strong suppression of neutron intensity with wavevectors pointing along the ferroelectric axis of KD_2PO_4 . Calculations of the q -dependent susceptibility has been made using an Ising model which includes four spins per unit cell representing the motion of the four deuterons surrounding each PO_4 group. The short-range spin-spin interaction reproduces the known energies of the different hydrogen bonds configurations in KD_2PO_4 . The neutron scattering is then calculated using the mean-field approximation, and the anisotropy of the scattering is found to be in good agreement with experiments. Finally in the ice-rule limit of the model, the scattering has a dipolar singularity as $q \rightarrow 0$.

1. Introduction

Many theories of the phase transition and physical properties of KH_2PO_4 (KDP) have been developed by assuming that the dominant interactions are the short-range interactions between the protons. These interactions have been taken into account by models of the energies of the proton configurations (Slater 1941, Silsbee *et al* 1964) or by pseudo-spin models with strong short-range interactions (Tokunaga and Matsubara 1966, Blinc and Svetina 1966, Vaks *et al* 1975). In contrast the results of quasi-elastic neutron scattering experiments in KD_2PO_4 (Paul *et al* 1970, Skalyo *et al* 1970) have been interpreted as providing evidence for the existence of strong long-range dipolar interactions in these materials. In fact the wavevector dependence of the scattering has been interpreted in terms of a model of strong long-range dipolar forces and relatively weaker short-range forces.

In this present paper we suggest that a large part of the anisotropy in the scattering may arise from the strong short-range interactions between the hydrogen bonds. The wavevector dependence of the scattering is calculated from a pseudo-spin Ising model of KDP similar to that previously discussed by Montgomery and Paul (1971) and by Elliott and Young (1974). These earlier treatments did not however correctly take account of the 'Slater configuration' of the four protons surrounding each PO_4 group. When these are included the result is a strong anisotropy of the wavevector dependence of the scattering which is very similar to that observed experimentally.

A similar anisotropy in the scattering from copper formate tetrahydrate has been observed by Youngblood and Axe (1978), and associated with the strong correlations between the hydrogens caused by the ice rules. Using an exact solution to the six-vertex model, Youngblood *et al* (1980) and Youngblood and Axe (1981) were able to show that when the ice rule constraints were imposed on the hydrogen positions a singular scattering cross-section resulted at small wavevectors. They then phenomenologically extended their results to cases when the ice rules are weakly broken.

Our results are essentially similar except that we do not present an exact solution but show how the results can be obtained at least approximately by using standard techniques, as developed in the next section.

KDP is a relatively complicated material with four different types of hydrogen in each unit cell. Initially therefore we discuss in § 3 another model of a two-dimensional ferroelectric material in which it is possible to carry out the analysis in detail analytically, and which is similar to that used by Youngblood and Axe (1981). In the fourth section we describe similar calculations for DKDP and summarise the results in a final section.

2. Theory of the scattering

The system is assumed to consist of an arrangement of hydrogen bonds such as those shown in figure 1. The position of the hydrogen atom in each bond is specified by a spin $Z(l\kappa)$ describing the location of the atom of the κ th type of bond in the l th unit cell. It is assumed that the position of neighbouring hydrogen atoms are correlated by short-range interactions so that the Hamiltonian of the system is written in general as

$$\mathcal{H} = - \sum_{\substack{l \\ \kappa\kappa'}} J_{\kappa\kappa'}^{(l)} Z(l\kappa) Z(l'\kappa'). \quad (1)$$

This Hamiltonian can be written in terms of the Fourier transforms

$$Z(\kappa, \mathbf{q}) = \frac{1}{-\sqrt{N}} \sum_l Z(l\kappa) \exp[-i\mathbf{q} \cdot \mathbf{R}(l\kappa)] \quad (2)$$

where $\mathbf{R}(l\kappa)$ is the position of the $l\kappa$ atom, as

$$\mathcal{H} = - \frac{1}{2N} \sum_{\kappa\kappa'} \sum_{\mathbf{q}} D(\kappa\kappa', \mathbf{q}) Z(\kappa', -\mathbf{q}) \quad (3)$$

where

$$D(\kappa\kappa', \mathbf{q}) = \sum_l J_{\kappa\kappa'}^{(l)} \exp[i\mathbf{q} \cdot (\mathbf{R}(l\kappa) - \mathbf{R}(l\kappa'))]. \quad (4)$$

It is convenient to define a susceptibility matrix:

$$\chi(\kappa\kappa', \mathbf{q}) = \beta \langle Z(\kappa, \mathbf{q}) Z(\kappa', -\mathbf{q}) \rangle \quad (5)$$

where β is the reciprocal of the temperature, $1/k_B T$, and which can then be obtained using the mean-field approximation (Brout 1965) from the matrix equation

$$\sum_{\kappa''} [\delta_{\kappa\kappa''} - \beta + D(\kappa\kappa'', \mathbf{q})] \chi(\kappa''\kappa', \mathbf{q}) = \beta \delta_{\kappa\kappa'}. \quad (6)$$

The scattering for a wavevector transfer \mathbf{Q} can then be obtained from the susceptibility at high temperature as

$$I(\mathbf{Q}) = \frac{1}{\beta} \sum_{\kappa\kappa'} F(\kappa, \mathbf{Q}) F(\kappa', -\mathbf{Q}) \chi(\kappa\kappa', \mathbf{q}) \Delta(\mathbf{Q} - \mathbf{q}) \tag{7}$$

where, if $F(l\kappa)$ is the scattering amplitude associated with the $(l\kappa)$ bond,

$$F(\kappa, \mathbf{Q}) = \sum_l F(l\kappa) \exp[i(\mathbf{Q} - \mathbf{q}) \cdot \mathbf{R}(l\kappa)] \tag{8}$$

and $\Delta(\mathbf{Q} - \mathbf{q})$ is zero unless $\mathbf{Q} - \mathbf{q}$ is a reciprocal lattice vector, $\boldsymbol{\tau}$.

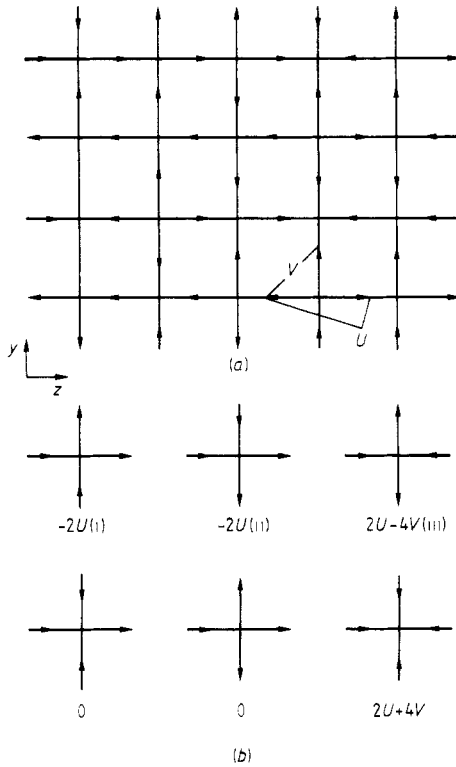


Figure 1. A two-dimensional model of a system of interesting hydrogen bonds. (a) the structure; (b) the energy of several Slater configurations.

Alternatively it is sometimes convenient to diagonalise the $D(\kappa\kappa', \mathbf{q})$ matrix to give the eigenvalues $D(\mathbf{q}j)$ and eigenvectors $E(\kappa, \mathbf{q}j)$, in terms of which the amplitudes of the normal mode $Z(\mathbf{q}j)$ are given by

$$Z(\kappa, \mathbf{q}) = \sum_j E(\kappa, \mathbf{q}j) Z(\mathbf{q}j). \tag{9}$$

The susceptibility of each mode is then defined by

$$\chi(\mathbf{q}j) = \beta \langle Z(\mathbf{q}j) Z(-\mathbf{q}j) \rangle \tag{10}$$

and is given by the mean-field theory as

$$\chi(\mathbf{q}j) = \beta / (1 - \beta D(\mathbf{q}j)). \tag{11}$$

The scattering is then given by

$$I(\mathbf{Q}) = \frac{1}{\beta} \sum_j F(\mathbf{Q}j) F(-\mathbf{Q}j) \chi(\mathbf{q}j) \Delta(\mathbf{Q} - \mathbf{q}) \quad (11)$$

where

$$F(\mathbf{Q}j) = \sum_{\kappa} E(\kappa, \mathbf{q}j) F(\kappa, \mathbf{Q}). \quad (12)$$

3. A two-dimensional model

The model consists of chains of hydrogen bonds along the x and y axes as illustrated in figure 1(a). The interaction between the hydrogen atoms is specified by $J_{(\kappa\kappa')}^{\prime\prime} = U$ between neighbouring hydrogen atoms on the same chains, and by $\pm V$ when the neighbouring hydrogen atoms are on different chains. The positive sign occurs if $Z(l, \kappa) = Z(l' \kappa') = 1$ and corresponds to only one of the hydrogen atoms close to the intersection of the chains and the minus sign in the other cases. The energies of the different configurations which can occur at an intersection are shown in figure 1(b). The model has two hydrogen atoms, κ , in each unit cell and it is convenient to label them x and y .

The matrix $D(\kappa\kappa', \mathbf{q})$ then becomes

$$\begin{pmatrix} D(xx, \mathbf{q}) & D(xy, \mathbf{q}) \\ D(yx, \mathbf{q}) & D(yy, \mathbf{q}) \end{pmatrix} = \begin{pmatrix} 2U \cos(q_x a) & -4V \sin(q_x a/2) \sin(q_y a/2) \\ -4V \sin(q_x a/2) \sin(q_y a/2) & 2U \cos(q_y a) \end{pmatrix}$$

and the susceptibilities become:

$$\begin{aligned} \chi(xx, \mathbf{q}) &= \frac{\beta}{D} (1 - 2\beta U \cos(q_x a)) \\ \chi(xy, \mathbf{q}) &= (\beta^2/D) (4V \sin(q_x a/2) \sin(q_y a/2)) \\ \chi(yy, \mathbf{q}) &= (\beta/D) (1 - 2\beta U \cos(q_y a)) \end{aligned} \quad (13)$$

where

$$\begin{aligned} D &= 1 - 4\beta^2 V^2 + (4\beta^2 V^2 - 2\beta U) (\cos(q_x a) + \cos(q_y a)) \\ &\quad + (4\beta^2 U^2 - 4\beta^2 V^2) \cos(q_x a) \cos(q_y a). \end{aligned}$$

These expressions become particularly simple if $\mathbf{q} = (q, 0)$ when:

$$\begin{aligned} \chi(xx, \mathbf{q}) &= \beta/(1 - 2\beta U \cos q) \\ \chi(yy, \mathbf{q}) &= \beta/(1 - 2\beta U) \\ \chi(xy, \mathbf{q}) &= 0 \end{aligned}$$

whereas if $\mathbf{q} = (0, q)$ then $\chi(xx, \mathbf{q}) = \beta/(1 - 2\beta U)$ while $\chi(yy, \mathbf{q}) = \beta/(1 - 2\beta U \cos q)$. These results illustrates that $\chi_{xx}(\mathbf{q})$ is not an isotropic function of (\mathbf{q}) but can be expected to be quite anisotropic. Close to a phase transition the susceptibility is large, so that $(1 - 2\beta U)$ is small compared with βU . In figure 2 we show $\chi(xx, \mathbf{q})$ for different values of the parameters U and V .

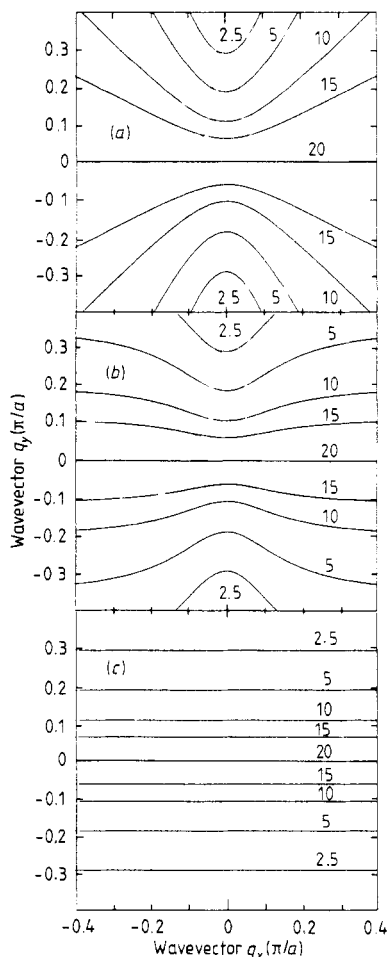


Figure 2. Constant contours for the susceptibility, $\chi(xx, \mathbf{q})$, for the two-dimensional model and $2\beta U = 0.95$ and (a) $V = U$, (b) $\beta V = 0.4$, (c) $V = 0$.

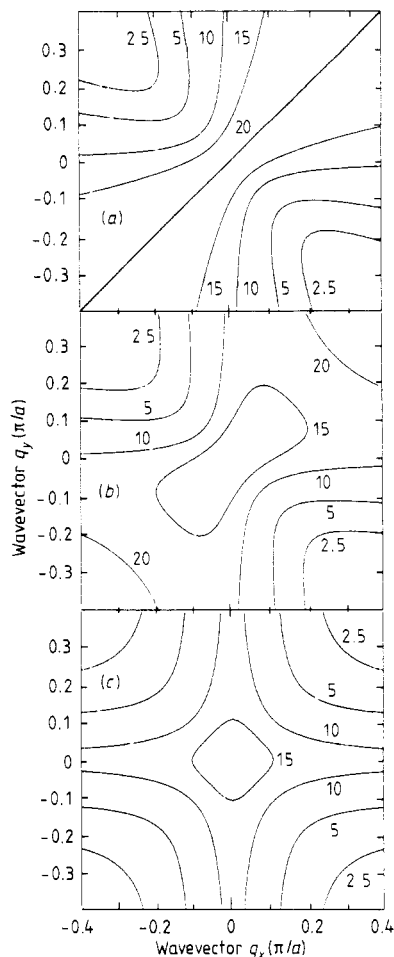


Figure 3. Constant contours for the susceptibility $\frac{1}{2}(\chi(xx, \mathbf{q}) + \chi(yy, \mathbf{q}) + 2\chi(xy, \mathbf{q}))$, for the two-dimensional model with $2\beta U = 0.95$ and (a) $V = U$, (b) $\beta V = 0.4$, (c) $V = 0$.

The scattering for this type of system is given by equation (7). If we consider a phonon system and consider the scattering around a reciprocal lattice vector, $\boldsymbol{\tau}$, along the x axis, $F(y, \mathbf{Q})$ is negligibly small compared with $F(x, \mathbf{Q})$, which is then assumed to be independent of \mathbf{Q} . The scattering is then proportional to $\chi^{xx}(\mathbf{q})$ which is shown in figure 2. The scattering is independent of q_x when $q_y = 0$ for all values of the ratio V/U . This is a result of the energy of the vertices being independent of the orientation of the aligned chains as shown in configurations (i) and (ii) of figure 1(b). In the model we have further assumed, unrealistically, that $Z(l\mathbf{k})$ is a continuous variable. Consequently the model gives identical energies for all values of q_y although in practice we might expect that the intensity would decrease as $|q_y|$ increases because $Z(l\mathbf{k})$ is limited to ± 1 . In the case $V = 0$ the scattering is independent of q_x , but for positive $V < U$ the scattering becomes pinched in when $q_x = 0$. Clearly the scattering is very anisotropic in \mathbf{q} .

A similar pattern is obtained if \mathbf{Q} is along the y axis but in this case the x and y axes in figure 2 must be interchanged. A very different set of patterns may emerge if the

scattering is determined near a lattice point along the (110) direction when $F(x, Q) = F(y, 0) = F$ and the scattering is proportional to $\frac{1}{2}(\chi(xx, q) + \chi(yy, q) + 2\chi(xy, q))$, which is shown in figure 3. In the isotropic case $U = V$, the scattering pattern is similar to that given by $\chi(xx, q)$ except rotated by 45° . This is essentially because the vertex (iii), figure 1(b), has the same energy as vertices (i) and (ii) and because $Z(l\kappa)$ is allowed to be a continuous variable. When $V = 0$, the pattern has fourfold symmetry corresponding to the scattering from decoupled linear chains while a more complex pattern results for intermediate values of V .

The results are essentially similar to the low- q results obtained by Youngblood and Axe (1981) in their model when they allow for violations of the ice rules. Our model corresponds in their notation to allowing longitudinal fluctuations in the polarisation, $D \neq 0$. The fact that our result reduces to this shows the success of the mean field arguments of § 2 in reproducing the correct functional form for the scattering. This form of scattering has been observed in copper formate tetrahydrate (Youngblood and Axe 1978).

4. The model of KDP

The structure of KDP is illustrated in figure 4 and there are four hydrogen bonds in each unit cell ($\kappa = 1 \dots 4$). The interactions are between neighbouring hydrogen atoms and symmetry allows us to reduce the $J(\kappa\kappa')$ to only two values

$$J(\frac{1}{12}) = J(\frac{1}{21}) = U$$

and

$$J(\frac{1}{32}) = J(\frac{1}{32}) = J(\frac{1}{23}) = J(\frac{1}{24}) = V$$

as illustrated in figure 4. Each hydrogen bond interacts with the three other hydrogen bonds in the same cell and three others in an adjoining cell. The constants U and V can be related to the Slater energies ϵ_0 and ϵ_1 of the PO_4 units as:

$$4U = -2\epsilon_1 + 2\epsilon_0 \quad \text{and} \quad 4V = 2\epsilon_1 - \epsilon_0$$

where ϵ_0 and ϵ_1 are known to be approximately 90 K and 800 K respectively (Havlin *et al* 1976, Sompolinsky and Havlin 1977, Havlin and Sompolinsky 1981).

The matrix $D(\kappa\kappa', q)$ can be simplified by a unitary transformation shown in figure 5 which corresponds to moving the hydrogen atoms. The result is

$$D(\kappa\kappa', q) = \begin{pmatrix} 0 & C_1 & C_2 & C_3 \\ C_1 & 0 & C_4 & C_5 \\ C_2 & C_4 & 0 & C_6 \\ C_3 & C_5 & C_6 & 0 \end{pmatrix}$$

where

$$\begin{aligned} C_1 &= 2U \cos(\pi\eta_x) & C_2 &= 2V \cos[(\pi/2)(\eta_x - \eta_y + \eta_z)] \\ C_3 &= 2V \cos[(\pi/2)(\eta_x + \eta_y + \eta_z)] & C_4 &= 2V \cos[(\pi/2)(\eta_x + \eta_y + \eta_z)] \\ C_5 &= 2V \cos[(\pi/2)(\eta_x - \eta_y - \eta_z)] & C_6 &= 2U \cos(\pi\eta_y) \end{aligned}$$

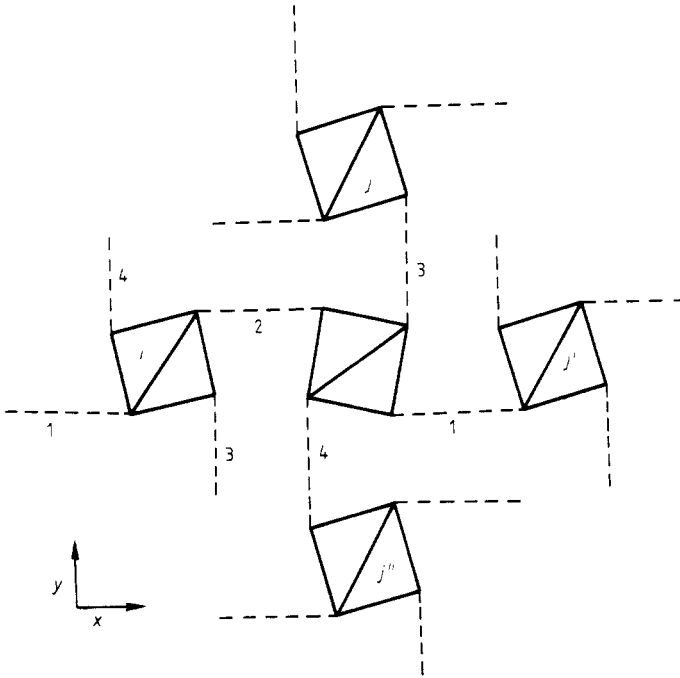


Figure 4. z-axis projection of the hydrogen bonds connecting K- PO_4 groups showing the different labels of the four pseudospins.

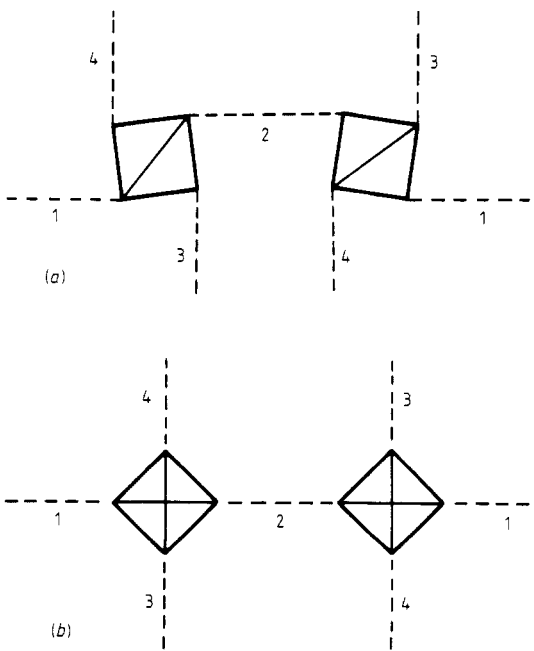


Figure 5. The hydrogen bonds in one unit cell are shown in figure 5(a). The unitary transformation used in obtaining equation (9) changes the coordinates of the hydrogen bonds of figure 5(a) to the structure described in figure 5(b).

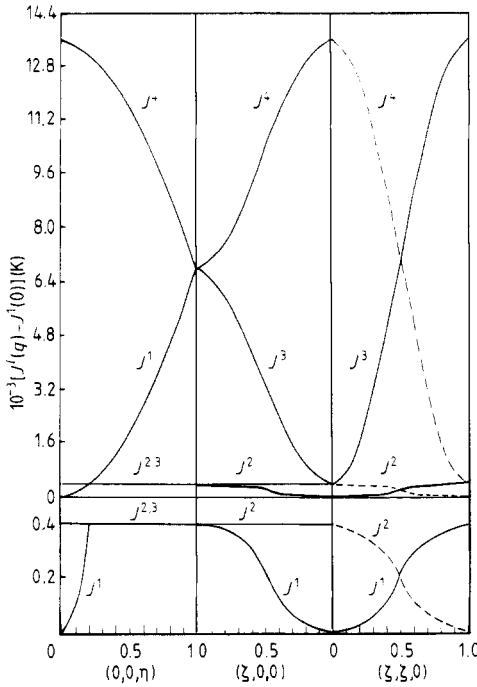


Figure 6. The wavevector dependence of the four eigenvalues of the interaction matrix. The lower part of the figure shows the enlargement for J^1 and J^2 .

and $q_x a = 2\pi\eta_x$, $q_y a = 2\pi\eta_y$ and $q_z c = 2\pi\eta_z$. The matrix $D(\kappa\kappa', \mathbf{q})$ can be diagonalised to obtain the eigenvalues and eigenvectors and the results for the eigenvalues $D(\mathbf{q}j)$ are shown in figure 6. The ferroelectric fluctuations are associated with the lowest eigenvalue, $J(\mathbf{q}1)$. The results, shown in figure 6, show that $J(\mathbf{q}1)$ is very anisotropic for small \mathbf{q} and this is confirmed by a small- \mathbf{q} expansion of $J(\mathbf{q}1)$ which gives

$$J(\mathbf{q}1) = J(01) - \pi^2 V \eta_z^2 - \pi^2 (U + V)(\eta_x^2 + \eta_y^2). \tag{14}$$

Using the Slater energies to obtain the coefficients of η_z^2 and $(\eta_x^2 + \eta_y^2)$ gives $(U + V)/V \approx 0.05$. Consequently the eigenvalue increases and susceptibility decreases with increasing η_z much more rapidly than with increasing η_x or η_y .

It is of interest to examine the form of $J(\mathbf{q}1)$ in the limit that the ice rules are exactly obeyed $U \rightarrow -\infty$, $V \rightarrow +\infty$, $U + V = \epsilon_0$. In this case the expansion given in equation (14) is no longer valid and a more careful analysis gives

$$J(\mathbf{q}1) = J(01) - 4(U + V) \frac{\eta_z^2}{2(\eta_x^2 + \eta_y^2) + \eta_z^2}.$$

Thus the ice rules lead to a singularity as $\mathbf{q} \rightarrow 0$ in the eigenvalue which is similar to that produced by long-range dipolar forces (Paul *et al* 1970).

This behaviour is illustrated in figure 7 which shows the anisotropic behaviour of $J(\mathbf{q}1)$ for KDP calculated both if the ice rules are satisfied and using the Slater configurations to estimate the parameters. The two models give very similar results except for small \mathbf{q} where the former have a singular behaviour which the latter do not. This anisotropic behaviour of $J(\mathbf{q}1)$ is reflected in an anisotropic behaviour of the susceptibility

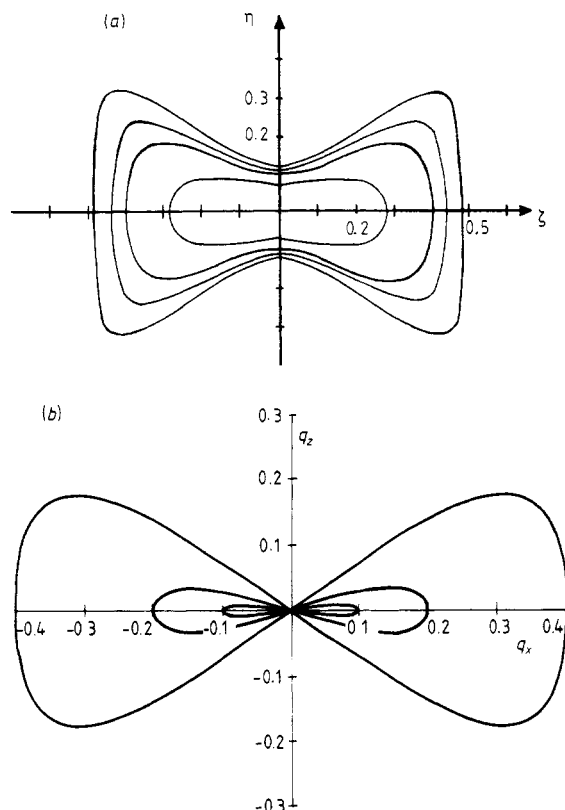


Figure 7. Constant contours of $J^i(q) - J^i(0)$ for: (a) the parameters $U + V = 45$ K and $V = 860$ K estimated from the energies of the Slater configurations; and (b) in the ice-rule limit $U + V = 45$ K, $V \rightarrow \infty$.

and scattering cross section. This anisotropic scattering has been observed in DKDP (Paul *et al* 1970, Skalo *et al* 1970), and the magnitude of the anisotropy is very similar to that which is obtained from equations (11) and (14) and figure 7. The origin of this anisotropy cannot therefore be immediately attributed to long-range dipolar forces but may arise from short-range ice-rule constraints on the position of the hydrogen atoms.

5. Summary

We have shown that strong short-range interaction between the hydrogen bonds in ferroelectrics can give rise to very anisotropic critical scattering as observed in copper formate tetrahydrate and in DKDP. As pointed out by Youngblood and Axe (1981), the suppression of the ferroelectric fluctuations along certain directions is not necessarily the result of long-range dipolar forces but may result from short-range correlations. Numerical calculations including only short-range interactions reproduce the magnitude of the anisotropy which has been observed experimentally.

These results were obtained using the mean-field approximation. They are, however, of the same form as those found using exact calculations and phenomenological arguments by Youngblood and Axe (1981) and by using cluster models by Havlin and

Sompolinsky (1981). We therefore believe that the functional forms are not greatly changed by more rigorous calculations even if the numerical results change in detail.

Since in practice the ice rules are not satisfied exactly it is possible to determine the magnitude of the anisotropy induced by the dipolar forces and by the short-range forces separately, by a careful measurement of the form of the scattering at small q . Our calculations, figure 7, suggest this is impossibly difficult using the available resolution of a neutron scattering experiment but may be possible using high resolution x-ray scattering techniques.

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