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Low-frequency dynamics of KH_2PO_4-type crystals

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Abstract. The paraelectric low-frequency dynamics of KH_2PO_4-type crystals has been investigated on the basis of a new time-dependent pseudospin Hamiltonian which includes both long-range electrostatic interactions and strong short-range interactions which exist within clusters of four neighbouring bonds. The static limit of this model is the well-known four-particle cluster tunnelling Hamiltonian which gives a good account of the static properties of the first-order phase transition in these crystals. First-order time-dependent perturbation theory is used to calculate the dynamical linear response of the system.

The coupling between the collective excitation modes and the short-range energy levels of the clusters yields twelve collective B_2 mode frequencies, two of which contribute significantly to the dynamical response of the system. One major consequence of the model is that the protonic tunnelling integral of KH_2PO_4 is greater than 250 K, which is much higher than previous estimates. The temperature dependence of the low-lying modes is found to agree well with the observed temperature dependence of the soft mode, $\omega_0^2 \propto (T - T_c)$, in contrast to the RPA result $\omega_0^2 \propto (T - T_c)/T$. The best fit to the data on both static and dynamical properties is obtained with the set of Slater energy parameters $\epsilon_0 = 52$ K, $\epsilon_1 = 952$ K, $\gamma = 53{\cdot}4$ K and $\Gamma = 300$ K.

The results of the tunnelling cluster dynamical model of KH_2PO_4 shown to be consistent with data obtained from a previously developed cluster Glauber model of KD_2PO_4.

1. Introduction

The dynamical properties of ferroelectric KH_2PO_4 (KDP)-type crystals have attracted much interest in recent years (Blinc and Zeks 1974, Scott 1974, Cowley 1976, Fleury 1976, Courtens 1977, 1978, Durvasula and Gammon 1977). Particular attention has been paid to the low-frequency spectra which, in the vicinity of T_c, are dominated by the appearance of the soft mode and the so-called central peak.

It is well known that short-range interactions between hydrogen bonds play an important role in the phase transition of KH_2PO_4. However, whereas for the static features detailed theories have been developed (Slater 1941, Silsbee *et al* 1964, Blinc and Svetina 1966, Vaks *et al* 1975) that incorporate short-range interactions and successfully explain the experimental static properties of these crystals, most theories of the dynamics of KDP are based on molecular-field-type approximations which neglect short-range interactions. Although these theories give a good qualitative description of some of the important dynamical features that are observed, they fail to describe adequately the temperature dependence of the soft-mode frequency and they do not account for the

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appearance of the central peak in the very-low-frequency limit in the immediate vicinity of T_c. Recently several models (Krumhansl and Schrieffer 1975, Binder *et al* 1975, 1977, Schneider and Stoll 1976, 1978) have been proposed which explain the onset of the central mode in structural phase transitions in terms of non-linear cluster dynamics. This approach suggests that fluctuating clusters which result from strong short-range interactions may also be important in the linear dynamical response of these crystals. Indeed, it has been shown very recently (Sompolinsky and Havlin 1977) that a linear small-cluster dynamical approximation which incorporates the characteristic short-range interactions of KD_2PO_4 yields a good quantitative description of the relaxational dynamics of this crystal. In the present work, the paraelectric low-frequency dynamics of KDP-type crystals is investigated, based on a new time-dependent pseudospin Hamiltonian which includes both long-range electrostatic and strong short-range interactions which exist within clusters of four neighbouring hydrogen bonds. The static limit of this model is the well-known four-particle cluster tunnelling Hamiltonian (Blinc and Svetina 1966, Vaks *et al* 1975) which gives a good description of the static properties of the first-order phase transition in these crystals. First-order time-dependent perturbation theory is used to calculate the dynamical linear response of the system.

Instead of the one soft tunnelling B_2 mode which appears in the usual RPA method (Brout *et al* 1966, Kobayashi 1968), several collective protonic B_2 modes are obtained in our model. These modes are the result of the strong coupling of the collective excitations to the short-range energy levels of the four clusters. Of these various modes, only the two low-lying modes contribute significantly to the dynamical susceptibility; one in the high-temperature region and the other in the vicinity of T_c. A major consequence of this dynamical cluster model is that the short-range interactions and correlations tend to screen the protonic tunnelling and reduce its contribution to the protonic mode frequencies. Thus, in order to explain the measured value of the soft-mode frequency, the value of the tunnelling must be greater than 250 K which is much higher than previous estimates (Kaminow and Damen 1968, Kaminow 1969, Fairall and Reese 1975, Vaks *et al* 1975, Blinc *et al* 1976). Indeed, it is shown here that this large value of the tunnelling integral is also supported by measurements of some static properties of KDP in the paraelectric region. Furthermore, it is shown that the calculated temperature dependence of the low-lying modes in this model agrees well with the observed (Lagakos and Cummins 1974, Gauss *et al* 1975) temperature dependence of the soft mode, $\omega_0^2 \propto (T - T_c)$, in contrast to the RPA prediction $\omega_0^2 \propto (T - T_c)/T$.

Finally it is shown that the value of the free protonic relaxation time of KH_2PO_4 obtained in the present cluster dynamic model is consistent with the results obtained previously for KD_2PO_4, using a four-particle cluster Glauber kinetic model (Sompolinsky and Havlin 1977).

2. Description of the dynamics of KDP by the RPA

The dynamical and the static properties of KDP-type crystals are commonly described by a pseudospin Ising Hamiltonian with a transverse field (de Gennes 1963, Brout *et al* 1966, Blinc and Zeks 1974):

$$H = -\Gamma \sum_i X_i - \tfrac{1}{2} \sum_{i \neq j} J_{ij} Z_i Z_j. \tag{2.1}$$

Calculation of the dynamical properties of the above Hamiltonian is usually done on the

basis of RPA. This 'first-order' approximation yields the well-known protonic tunnelling soft mode with a frequency ω_0 which in the paraelectric phase is given by (Brout *et al* 1966, Blinc and Zeks 1974)

$$\omega_0^2 = 4\Gamma(\Gamma - J_0\langle X\rangle) \tag{2.2a}$$

where

$$\langle X\rangle = \tanh \beta\Gamma \qquad J_0 = \sum_j J_{ij} = \Gamma/\tanh \beta_c\Gamma. \tag{2.2b}$$

The main features of the RPA soft-mode frequency ω_0 are the following: (i) ω_0 vanishes at $T = T_c$; (ii) the high-temperature limit of ω_0 is 2Γ; (iii) $\omega_0^2 \propto (T - T_c)/T$ for $\beta\Gamma < 1$.

Since the soft mode is known to be heavily overdamped, a relaxation process must also be included in the model. The simplest way to take that into account is by using an overdampled harmonic oscillator model with the following dynamical susceptibility:

$$\chi(\omega) = \chi(0)\,\omega_0^2/(\omega_0^2 - \omega^2 + 2i\omega\Delta). \tag{2.3}$$

A more comprehensive way is to solve the Bloch-type equations of motion for the pseudospin fluctuations, as was done by Blinc and Zeks (1974). However, in the paraelectric phase and the low-frequency region this model reduces approximately to that of a damped harmonic oscillator (Blinc and Zeks 1972). Indeed, light scattering experiments (Lagakos and Cummins 1974, Scott 1974, Gauss *et al* 1975) show that the low-frequency response of KDP is adequately described by taking into account strong coupling between the above protonic overdamped soft mode (equation 2.3) and a lattice optic B_2 mode. If the experimental data (Cochran 1969, Kaminow 1969, Lagakos and Cummins 1974) for ω_0 are fitted to equation (2.2), the following numerical values for the energy parameters are obtained:

$$\Gamma \sim 50\,\mathrm{cm}^{-1}, \qquad J_0 \sim 90\,\mathrm{cm}^{-1}, \qquad \Delta \sim 80\,\mathrm{cm}^{-1}. \tag{2.4}$$

Although the above model gives a good qualitative account of the main features of the low-frequency dynamical response of KDP, it has some serious limitations. First, as already noted by previous authors, the analysis of the light scattering spectra by the model involving two coupled modes (She *et al* 1972, Lagakos and Cummins 1974, Scott 1974, Gauss *et al* 1975. Azoulay *et al* 1977) shows that the temperature dependence of the pure tunnelling soft-mode frequency deviates significantly from $[(T - T_c)/T]^{1/2}$; near T_c it behaves like $(T - T_c)^{1/2}$ as indicated in figure 3. The deviation from the temperature dependence predicted by the RPA is also evident in the very low-frequency measurements (Kaminow 1965, Gauss *et al* 1975) of the loss tangent $\tan\delta$ given by

$$\tan\delta = \mathrm{Im}\,\chi/\mathrm{Re}\,\chi \simeq 2\omega\Delta/\omega_0^2. \tag{2.5}$$

This is of particular importance since the quantity $2\pi\tau = 2\Delta/\omega_0^2$ is more readily extracted from the experimental data (Scott 1974) than ω_0 or Δ. Also the analysis of the data in the very low-frequency region does not depend significantly on the coupling to the lattice mode.

Another point of interest is the comparison between the relaxation time τ_0 of a non-interacting proton and that of a deuteron in KD_2PO_4. This relaxation time is actually calculated by taking the high-temperature limit of the collective relaxation time τ or of $2\Delta/\omega_0^2$ for KH_2PO_4. Analysis of various experiments in conjunction with the RPA formula yielded values around 0·02 cm (Kaminow and Damen 1968, Garland and Novotny 1969, Litov and Garland 1970, Lahajnar *et al* 1974, Gauss *et al* 1975) for $2\pi\tau_0$ in KH_2PO_4 and around 0·2 cm for KD_2PO_4 (Kaminow 1965, Litov and Uehling 1968, 1970, Litov

and Garland 1970). There is no theoretical explanation for the order of magnitude difference between τ_0 for KH_2PO_4 and that for KD_2PO_4.

Furthermore, as has been shown previously (Sompolinsky and Havlin 1977), the analogue of equation (2.2) in KD_2PO_4, according to the RPA (i.e. $\tau \propto T/(T-\theta)$) fails to describe adequately the observed temperature dependence of τ in that crystal in both the z and x directions. Finally, it is noted that both the RPA dynamical and static results are not consistent with the well-known Slater–Takagi microscopic description of the short-range interaction energies of the KH_2PO_4 groups. For instance, the inclusion of these strong short-range interactions in J_0 in equation (2.2) would increase its value to at least 500 K, which yields an unrealistically high value for T_c (Tokunaga and Matsubara 1966).

From the above discussion it is evident that the well-known short-range interactions which are crucial to the description of the static properties of KDP-type crystals are also important for the description of their dynamical properties. Elliott and Young (1974) have proposed a dynamical model which includes these short-range interactions by adding a four-spin interaction term to the pseudospin Hamiltonian (equation 2.1). However, since their approach is limited to simple RPA treatment they obtain, in the paraelectric region, the same results as are given by equation (2.2*a*).

We have shown previously (Sompolinsky and Havlin 1977) that the effect of these short-range interactions can be properly taken into account by a relaxational four-particle cluster dynamical model. In KDP however, collective tunnelling modes play the important role in its dynamics and therefore we present in the following section a tunnelling cluster dynamical model which takes into account the effect of the short-range interactions on these tunnelling modes.

3. Dynamical tunnelling cluster model

Previous treatments of the static properties of KDP have shown that by applying a four-particle cluster approximation to the Hamiltonian of equation (2.1), the effects of both the long-range electrostatic interactions and the important strong short-range interactions which exist between the four neighbouring hydrogen bonds surrounding the PO_4 groups can be successfully taken into account (Blinc and Svetina 1966, Vaks *et al* 1975).

In the present work we extend the static four-particle cluster approximation into the dynamical region by using the following new time-dependent four-particle cluster tunnelling Hamiltonian H_4:

$$H_4 = -U(Z_1Z_3 + Z_2Z_4) - V(Z_1Z_2 + Z_2Z_3 + Z_3Z_4 + Z_4Z_1) - \xi(t)\sum_{i=1}^{4} Z_i - \tilde{\Gamma}(t)\sum_{i=1}^{4} X_i - \tfrac{1}{2}\alpha(t)\sum_{i=1}^{4} Y_i . \tag{3.1}$$

The first two terms represent the short-range energies of the four pseudospins within the cluster which represent the four hydrogen bonds around a PO_4 group. The energies U and V are connected to the Slater energy parameters ϵ_0 and ϵ_1, through the relations (Vaks *et al* 1975)

$$U = -\epsilon_1/2 + \epsilon_0/2 \qquad V = \epsilon_1/2 - \epsilon_0/4$$

The effective time-dependent field $\xi(t)$ is given by

$$\xi(t) = \mu_Z E_Z(t) + \gamma\langle Z\rangle_t + \tfrac{1}{2}\Delta_Z(t) \tag{3.2}$$

where $E_Z(t)$ is a small fluctuating external electric field, $\gamma\langle Z\rangle_t$ is a molecular-field term resulting from long-range dipole–dipole interaction and Δ_Z is a cluster field which represents the short-range interactions with the neighbouring spins outside the clusters. The tunnelling term $\tilde{\Gamma}(t)$ is

$$\tilde{\Gamma}(t) = \Gamma - \tfrac{1}{2}\eta(t) \tag{3.3}$$

where $\eta(t)$ stands for the modification of the single-spin tunnelling arising from its short-range interaction with the neighbours outside the cluster. It should be noted that the transverse cluster field does not vanish in the static limit, even for $T > T_c$ (Blinc and Svetina 1966, Vaks and Zinenko 1973). Finally, the new effective transverse cluster field $\alpha(t)$ acting on Y_i is a dynamical contribution from the short-range interactions and vanishes in the static limit.

The determination of Δ_Z, η and α depends on the specific consistency method which is used in the cluster approximation (Strieb *et al* 1963). Here we use a dynamical consistency relation which is an extension of that used previously for the static problem (Blinc and Svetina 1966) namely

$$\langle \boldsymbol{S}_1\rangle_1 = \langle \boldsymbol{S}_1\rangle_4 \tag{3.4}$$

where $\langle \boldsymbol{S}_1\rangle_4$ is the time-dependent average of the three-component spin operator calculated by the equations of motion of H_4 (equation 3.1) and $\langle \boldsymbol{S}_1\rangle_1$ is the corresponding average calculated by the equations of motion of the effective one-spin cluster Hamiltonian which is given by

$$H_1 = -(\mu_Z E_Z(t) + \gamma\langle Z\rangle_0 + \Delta_Z(t))Z_1 - (\Gamma - \eta(t))X_1 - \alpha(t)Y_1. \tag{3.5}$$

The difference between the effective fields in H_1 and H_4 stems from the fact that in H_4 only half of the nearest neighbours of each spin add a contribution to the effective fields acting on it, while its interaction with the other half is taken into account in H_4 explicitly.

The usual procedure of calculating the dynamics of the spin waves consists of writing the Heisenberg equations of motion $\mathrm{d}\langle \boldsymbol{S}\rangle/\mathrm{d}t = -\langle|H, \boldsymbol{S}|\rangle$. This yields the following equations of motion for H_4:

$$\tfrac{1}{2}(\mathrm{d}/\mathrm{d}t)\langle X_1\rangle_t = V(\langle Z_0 Y_1\rangle_t + \langle Z_2 Y_1\rangle_t) + U\langle Z_3 Y_1\rangle_t + \xi(t)\langle Y_1\rangle_t + \tfrac{1}{2}\alpha(t)\langle Z_1\rangle_t \tag{3.6a}$$

$$\tfrac{1}{2}(\mathrm{d}/\mathrm{d}t)\langle Y_1\rangle_1 = -V(\langle Z_0 X_1\rangle_t + \langle Z_2 X_1\rangle_t) - U\langle Z_3 X_1\rangle_t + (\Gamma - \tfrac{1}{2}\eta(t))\langle Z_1\rangle_t - \xi(t)\langle X_1\rangle_t \tag{3.6b}$$

$$\tfrac{1}{2}(\mathrm{d}/\mathrm{d}t)\langle Z_1\rangle_t = -(\Gamma - \tfrac{1}{2}\eta(t))\langle Y_1\rangle_t - \tfrac{1}{2}\alpha(t)\langle X_1\rangle_t \tag{3.6c}$$

and for H_1:

$$\tfrac{1}{2}(\mathrm{d}/\mathrm{d}t)\langle X_1\rangle_t = (2\xi(t) - \mu_Z E_Z - \gamma\langle Z\rangle)\langle Y_1\rangle_t + \alpha(t)\langle Z_1\rangle_t \tag{3.7a}$$

$$\tfrac{1}{2}(\mathrm{d}/\mathrm{d}t)\langle Y_1\rangle_t = (\Gamma - \eta(t))\langle Z_1\rangle_t - (2\xi(t) - \mu_Z E_Z - \gamma\langle Z\rangle)\langle X_1\rangle_t \tag{3.7b}$$

$$\tfrac{1}{2}(\mathrm{d}/\mathrm{d}t)\langle Z_1\rangle_t = -(\Gamma - \eta)\langle Y_1\rangle_t - \alpha\langle X_1\rangle_t \tag{3.7c}$$

and similar equations for the higher moments $\langle Z_0 Y_1\rangle_t$, $\langle Z_0 X_1\rangle_t$ etc.

For the sake of simplicity, we will limit ourselves to the paraelectric phase, $T > T_c$. In this region the polarisation $\langle Z\rangle$ and the longitudinal fields are small fluctuating quantities. Hence from linearisation of the above equations it is found that both $\langle X\rangle$ and η do not have fluctuating parts and their values are determined through the

solution of the static problem (Blinc and Svetina 1966, Vaks *et al* 1975). As for $\xi(t)$ and $\alpha(t)$, if we assume $E_Z(t) = E_Z \exp(i\omega t)$ and use the consistency relation equation (3.4), we obtain

$$\xi(t) = (1/2\langle X\rangle)(\Gamma - \eta - \tfrac{1}{4}\omega^2)\langle Z_1\rangle_t + \tfrac{1}{2}\gamma\langle Z_1\rangle_t + \tfrac{1}{2}\mu_Z E_Z(t) \tag{3.8}$$

$$\alpha(t) = (i\omega\eta/2\Gamma\langle X\rangle)\langle Z_1\rangle_t \tag{3.9}$$

where $\langle X\rangle = \tanh\beta(\Gamma - \eta)$.

As can be seen from equations (3.6), the single-spin averages $\langle S_1\rangle_t$ are coupled to high-order moments of spins which belong to the same cluster. In contrast to the RPA in the dynamical cluster model we do not couple these moments, and therefore a whole set of equations of motion must be derived and solved for all the relevant spin moments. In the paraelectric region there are 24 fluctuating spin moments in the four-particle cluster and therefore 12 different doubly degenerate modes of fluctuation of polarisation (B_2 modes) are obtained. Before calculating the eigenfrequencies ω_α, it is perhaps instructive to write down the general form of ω_α which is obtained by resubstituting equations (3.8) and (3.9) into equations (3.6) and (3.7). The result is

$$\omega_\alpha^2 = 4\Gamma(\Gamma - J^\alpha\langle X\rangle) \tag{3.10}$$

where

$$J^\alpha = \gamma + \{[4V(\langle Z_0X_1\rangle_t^\alpha + \langle Z_2X_1\rangle_t^\alpha) + 2U\langle Z_3X_1\rangle_t^\alpha]/\langle Z_1\rangle_t^\alpha\langle X\rangle\}. \tag{3.11}$$

It can be seen that the improvement in the present treatment compared with the RPA arises from the fact that the effective interaction constants J^α of each mode contain contributions from both mean-field long-range interactions and short-range interactions. While the long-range interactions provide a constant contribution to all J^α, similar to J_0 in the RPA (equation 2.2*b*), the contribution of the short-range interactions is affected by the spin–spin short-range correlations within the cluster and therefore it is different for each mode and is also temperature-dependent.

Instead of deriving and solving the set of equations of motion, which is rather cumbersome, we calculate the dynamical quantities of the system by using a first-order time-dependent perturbation technique. Thus $\xi(t)$ and $\alpha(t)$ are treated as small time-dependent perturbations of the form $\xi(t) = \xi\exp(i\omega t)$, $\alpha(t) = \alpha\exp(i\omega t)$, which cause an induced oscillating polarisation in the various unperturbed stationary energy levels of H_4. The induced polarisation of each energy level is calculated by a first-order time-dependent perturbation theory and $\langle Z_1\rangle_t$ is then derived by taking the thermal average of these polarisations. Thus we obtain the equation

$$\langle Z_1\rangle_t = \frac{2}{\mathscr{Z}_4}\sum_{j,m>j}\frac{\exp(-\beta E_m)[1-\exp(-\beta\Delta E_{jm})]}{(\Delta E_{j,m})^2 - \omega^2}\left[\tfrac{1}{4}\Delta E_{jm}\left(\langle j|\sum_{i=1}^{4} Z_1|m\rangle\right)^2\xi - \tfrac{1}{8}\omega\langle j|\sum_{i=1}^{4} Y_i|m\rangle\langle j|\sum_{i=1}^{4} Z_i|m\rangle\alpha\right]\exp(i\omega t) \tag{3.12}$$

where E_m and E_j are the energy levels of the unperturbed H_4 corresponding to the eigenstates $|m\rangle$ and $|j\rangle$ respectively and $\Delta E_{jm} = E_j - E_m$. The quantity $\mathscr{Z}_4$ is the four-particle function defined as $\mathscr{Z}_4 = \sum_j \exp(-\beta E_j)$.

Substitution of equations (3.8) and (3.9) into equation (3.12) yields a closed equation for $\langle Z_1\rangle_t$. The eigenfrequencies ω_α are calculated through equation (3.2) by substituting $E_Z = 0$ in equation (3.8). Since there are 12 different transition energies ΔE_{jm}, equation (3.12) yields 12 solutions for ω_α. Numerical results for a chosen set of energy parameters

ϵ_0, ϵ_1, Γ and γ are presented in figure 1. It can be seen that the collective eigenfrequencies can be interpreted as the modification of the transition energies of the cluster caused by its interaction with the collective motion of surrounding spins.

It is also seen that the values of most of the frequencies ω_α are nearly equal to one of the ΔE_{jm}, for all temperatures above T_c. Only the two low-lying frequencies ω_1 and ω_2 differ significantly from the corresponding transition energies and are strongly temperature-dependent: the higher frequency ω_2 decreases with decreasing T but freezes out to a

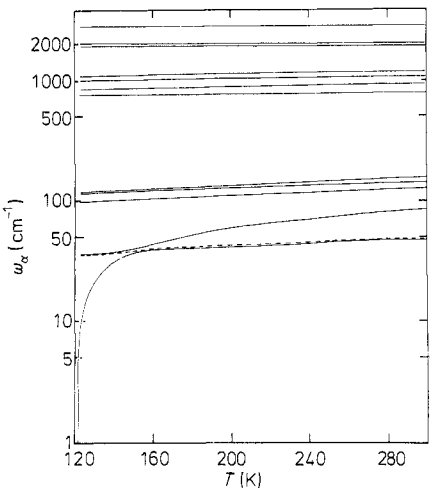

Figure 1. Numerical results for the different transition energies ΔE_{jm} and for the 12 eigenfrequencies ω_α calculated with the energy parameters given in Set I (see table 1). The 10 high eigenfrequencies are nearly equal to their corresponding transition energies and both are represented by full curves. The two low-lying eigenfrequencies ω_1 and ω_2 differ significantly from the corresponding transition energies and are represented by full curves whereas the lowest transition energy is represented by a broken curve.

finite value while the lower frequency ω_1 becomes soft on approaching T_c and extrapolates to zero at the Curie temperature T_0. This already indicates that only these two low-lying modes are important in the collective dynamical response of the system. Indeed, calculation of $\chi(\omega)$ by solution of equation (3.12) with $E_Z \neq 0$ yields the following:

$$\chi(\omega) = N\mu_Z\langle Z_1\rangle/E_Z = \sum_{\alpha=1}^{12} \chi_\alpha\omega_\alpha^2/(\omega_\alpha^2 - \omega^2) \tag{3.13}$$

where χ_α is the relative contribution of each mode to the total susceptibility. Calculation of χ_α shows that only χ_1 and χ_2, which correspond to ω_1 and ω_2 contribute significantly over the whole range of temperatures. Another general feature of the results is that over most of the temperature range, only one of the susceptibilities χ_1 and χ_2 is dominant. Although in the region of high temperatures only the relative susceptibility of the higher mode χ_2 is important, the susceptibility χ_1 of the low-lying mode is dominant in the region of about 30 K above T_c. This is illustrated by the numerical results presented in figure 2.

It is noted that ω_1 and ω_2 go to zero when Γ vanishes; hence they are recognised as tunnelling modes. The appearance of two dominant low-lying polarisation fluctuation

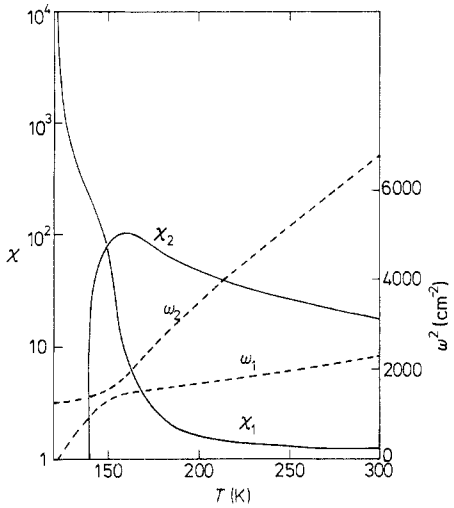

Figure 2. The temperature dependence of the two low-lying eigenfrequencies ω_1 and ω_2 and their corresponding susceptibilities χ_1 and χ_2.

tunnelling modes with B_2 symmetry is in marked contrast to the RPA result where only one soft tunnelling B_2 mode exists. This interesting result of our model is due to the inclusion of short-range interactions which induces a coupling between the collective modes and the internal energy structure of the four-particle clusters. The qualitative dynamical features of the model which were described above are independent of the specific energy parameters ϵ_0, ϵ_1, γ and Γ over a wide range of values. However, the quantitative results of the model are sensitive to the specific choice of parameters which should be fixed by a quantitative comparison with the experimental results. This is done in the following section.

4. Determination of the energy parameters of KH_2PO_4

One of the main results of the cluster dynamical model is that the dominant eigenfrequency is much smaller than 2Γ, even in the high-temperature region. This arises from the screening of the tunnelling by the short-range interactions, which appear in J^{α} of equation (3.11). Because of this effect, the values of the eigenfrequencies ω_1 and ω_2 depend strongly on the values of both the tunnelling integral Γ and the Slater high-energy parameter ϵ_1. In fact, the increase in Γ as well as the decrease in ϵ_1 increases the values of ω_1 and ω_2. On the other hand, the dependence of these eigenfrequencies on the values of ϵ_0 and γ is rather weak and is significant only in the vicinity of T_c. Indeed, in order to fit the dominant frequency ω_2 to the experimental value $\omega_0 \simeq 110$ K at room temperature (Kaminow 1969, Gauss *et al* 1975), the value of Γ must be in the range 250–300K, with ϵ_1 varying between 750 and 950 K. The only way to obtain a smaller value of Γ which would be consistent with the experimental value of ω_0 is to choose correspondingly low values for ϵ_1, which would not be compatible with the well-known (Reese 1969, Vaks *et al* 1975) first-order nature of the phase transition.

The high value of Γ mentioned above is in marked contrast to the RPA result (Kaminow 1969), $\Gamma \simeq 70$ K which corresponds to the experimental value of ω_0 at room

temperature. Previous estimates of Γ were also obtained by comparing the static properties, especially in the ferroelectric region, with the static cluster model (Blinc and Svetina 1966, Fairall and Reese 1975, Vaks *et al* 1975, Chabin and Gilleta 1977). These estimates yielded a value of Γ which is close to the above-mentioned RPA result. However it is interesting to note that quantitative fitting of the static properties in the paraelectric region also favours the high values of Γ and ϵ_1 which are similar to those deduced above from our dynamical cluster model. In particular, the experimental high value of the paraelectric Curie constant cannot be adequately explained (Vaks *et al* 1975) unless it is assumed that Γ is in the range 250–300 K. Also the weak temperature dependence of the paraelectric susceptibility in the transverse X direction (Havlin *et al* 1975) can be explained within the cluster model only by a value of Γ greater than 250 K (Havlin and Sompolinsky 1979).

Table 1. Comparison between the predictions of the cluster model and the experimental results for the dynamical and static properties of KH_2PO_4. The theoretical results of these sets of parameters are given. Set I: $\Gamma = 300$ K, $\epsilon_1 = 952$ K, $\epsilon_0 = 52$ K, $\gamma = 53{\cdot}4$ K; Set II: $\Gamma = 250$ K, $\epsilon_1 = 750$ K, $\epsilon_0 = 50$ K, $\gamma = 50{\cdot}6$ K; Set III (Vaks *et al* 1975): $\Gamma = 74$ K, $\epsilon_1 = 550$ K, $\epsilon_0 = 61$ K, $\gamma = 17$ K.

	ω_2 (cm^{-1}) ($T = 300$ K)	C_z (K)	$\chi_x(300\text{ K})/\chi_x(150\text{ K})$	P_c	$T_c - T_0$ (K)
Set I ($\Gamma = 300$ K)	82	2960[b]	0·65	0·25	0·06
Set II ($\Gamma = 250$ K)	81	2560[b]	0·62	0·27	0·05
Set III ($\Gamma = 74$ K)	10	2200[b]	0·57	0·4	0·01
Experiment	79[a]	2850–3200[c]	0·67[d]	0·30–0·36[e]	0·05–0·08[f]

a Kaminow and Damen (1968), Kaminow (1969).
b The Curie constant C_z was calculated by assuming $\mu_z = P_0/2N$ where P_0 is the experimental saturated polarisation (Samara 1973).
c Samara (1973), Gauss *et al* (1975).
d Havlin *et al* (1975).
e Benepe and Reese (1971), Vaks *et al* (1975).
f Vaks *et al* (1975).

Table 1 summarises the main predictions of the static and dynamic cluster models for the two sets of parameters which correspond to $\Gamma = 250$ and 300 K, respectively. These results are compared to those obtained from sets of parameters described previously (Vaks *et al* 1975, $\Gamma = 70$ K) and also to the corresponding experimental data. It can be seen from table 1 that both Sets I and II are a good fit to the dynamic and the static properties in the paraelectric region, whereas Set III does not fit the static experimental results well and yields a completely wrong value for the frequency of the soft mode. However, it should be noted that the temperature dependence of the spontaneous polarisation in the low-temperature region calculated with the aid of Set I or II does not give a good fit to the observed results. This discrepancy is attributed to the failure (Blinc and Svetina 1966, Vaks and Zinenko 1973) of the self-consistent cluster approximation in describing the thermodynamic properties of the Ising model with a transverse field in the low-temperature region.

Finally, it is noted that the value of ϵ_1 in Set I is nearly the same as that for KD_2PO_4 (Silsbee *et al* 1964, Sompolinsky and Havlin 1977), whereas ϵ_0 turns out to be different from the value for KD_2PO_4 by the same factor as the corresponding transition temperatures. As has already been pointed out (Blinc and Svetina 1966), an isotope effect of this type is also expected from simple physical arguments. In the following section we adopt Set I as the basis for a quantitative comparison between the theoretical results of the dynamical cluster model and experimental data.

5. Comparison with experimental dynamical data

As mentioned previously (§ 2), in order to obtain a realistic description of the dynamics of KDP the effects of relaxation processes must be incorporated in the theoretical calculations. For our dynamical cluster model, the simplest way to do this is by assuming that each mode with frequency ω_α behaves as a damped harmonic oscillator of width Δ_α. Thus, instead of equation (3.13), we obtain for the dynamical susceptibility the expression

$$\chi(\omega) = \sum_{\alpha=1}^{12} \chi_\alpha \omega_\alpha^2/(\omega_\alpha^2 + \omega^2 + 2i\omega\Delta_\alpha). \tag{5.1}$$

However, as has already been pointed out above, over almost the whole temperature range, only one of the two dominant modes contributes significantly to the total susceptibility and therefore the right hand side of equation (5.1) can be approximated by a single damped harmonic oscillator:

$$\chi(\omega) \simeq \chi(0)\omega_0^2/(\omega_0^2 - \omega^2 + 2i\omega\Delta) \tag{5.2}$$

where the effective eigenfrequency ω_0 is equal to ω_1 in the temperature range $T_c \leqslant T \lesssim 150$ K and to ω_2 for higher temperatures. (In the limited region around $T = 150$ K where $\omega_1 \sim \omega_2$ their relative susceptibilities are nearly equal and therefore ω_0 is here taken to be their average.) The temperature dependence of ω_0 was calculated with the

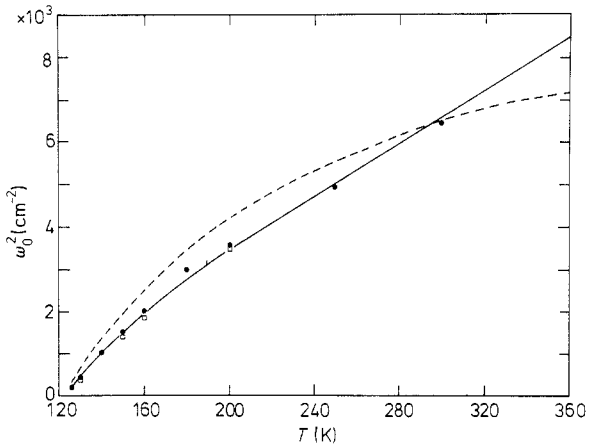

Figure 3. The temperature dependence of the soft-mode eigenfrequency. The broken curve represents the RPA result; the full curve is the present cluster dynamical results. The experimental data of Lagacos and Cummins (1974, □) and the data of Gauss *et al* (1975, ●) are also shown.

energy parameters of Set I (see table 1). The results are shown in figure 3 together with the experimental data obtained by Lagakos and Cummins (1974) and Gauss *et al* (1975) from the analysis of light scattering data through the lattice proton-coupling method. Also shown in figure 3 is the RPA result, the energy parameters of which were chosen so that it coincided with the measured value of ω_0 at room temperature. It can be clearly seen that in contrast to the RPA results, the cluster dynamical results agree very well with the experimental data. In effect, both our theoretical results and the experimental data indicate a linear variation of ω_0^2 with T over a wide range of temperatures above T_0. This contrasts with the RPA result, $\omega_0^2 \propto (T - T_c)/T$. As can be seen in figure 3, this difference between the two models becomes especially evident above room temperatures where the RPA soft-mode frequency rapidly approaches its high-temperature limit, whereas the cluster soft-mode frequency still increases linearly with temperature.

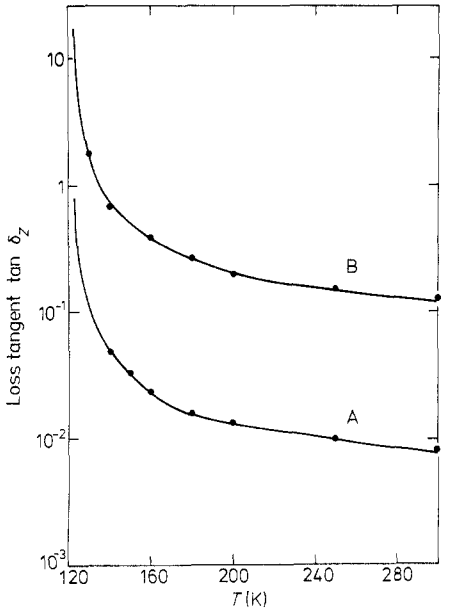

Figure 4. The temperature dependence of the loss tangent tan δ_z. The full curve represents the theoretical results and the circles represent the experimental data of Kaminow (1965; ω = 0·306 cm^{-1}, curve A) and Gauss *et al* (1975; ω = 4·6 cm^{-1}, curve B).

The theoretical predictions of the present model are also compared to the very low-frequency measurements (Kaminow 1965, *Gauss et al* 1975) of the loss tangent tan δ_z which is related to $\chi(\omega)$ of equation (5.2) through equation (2.5). The results are shown in figure 4, where we have used the value $\Delta = 80\ cm^{-1}$, which is the width extracted from Raman experiments (Kaminow 1969, Lagakos and Cummins 1974). It can be seen that very good agreement is achieved for both the temperature dependence of tan δ_z and its absolute value.

Finally, it should be noted that in the present model the non-interacting protonic relaxation time calculated by taking the high-temperature limit of $2\Delta/\omega_0^2$ is 0·007 cm. It is interesting to compare this to the value $2\pi\tau_0 = 0{\cdot}006$ cm previously obtained (Sompolinsky and Havlin 1977) in KD_2PO_4 by using a four-particle cluster Glauber

kinetic model. This agreement supports the basic assumption of the importance of four-particle cluster short-range interactions in the dynamics of both KDP and DKDP-type crystals.

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