PHYSICAL REVIEW B VOLUME 16, NUMBER 7 1 OCTOBER 1977

Effect of short-range interactions on the transverse dynamics of KD_2PO_4

H. Sompolinsky and S. Havlin
Department of Physics, Bar-Ilan University, Ramat-Gan, Israel

(Received 1 June 1977)

The dynamics of KD_2PO_4 along the transverse x direction is investigated using a pseudospin model which takes into account the transverse dipole moments of the hydrogen bonds and incorporates both short-range and long-range interaction effects. A four-cluster approximation to the Glauber equations of motion for the E-mode pseudospin fluctuations is employed. It is found that these fluctuations have three different relaxation times below T_c and two above T_c. However, in the low-frequency region the dynamical susceptibility has a Debye-type frequency dependence with one relaxation time τ_x. The temperature dependence of τ_x is calculated within the present model and is compared to that derived from the random-phase approximation (RPA). It is found that the relation between τ_x and the static transverse susceptibility χ_x is markedly different from the RPA result $\tau_x \propto T\chi_x$. The present theory explains in a consistent way the available experimental data on the dynamical properties of KD_2PO_4 in both the longitudinal and transverse directions.

I. INTRODUCTION

Dielectric and light-scattering measurements on KD_2PO_4 have recently demonstrated the anomalous behavior of the protonic E-mode fluctuations near the transition temperature.[1-4] Though several dynamical models for KD_2PO_4 have been extensively studied in order to explain the properties of the polarization fluctuations along the longitudinal z directions (B_2 modes),[5-7] very little theoretical work has been done on its dynamical properties along the transverse x direction. In the present paper we investigate the dynamical properties of KD_2PO_4 on the basis of a previously developed[8,9] pseudospin Hamiltonian which takes into account the transverse dipole moments of the hydrogen bonds. Relaxational processes are introduced through a Glauber[10] equation of motion for the transversely polarized pseudospins.

First, we apply the random-phase approximation (RPA) to the pseudospin equations of motion. Such an approximation was previously shown to be sufficient for explaining qualitatively some important dynamical properties of KH_2PO_4-(KDP-) type crystals along both the z and x directions.[11,12] However, we here show that it fails completely to explain the observed temperature dependence of the relaxation times in KD_2PO_4 particularly along the x direction. This failure is attributed to the neglect of protonic short-range interactions which are known to play an important role in the phase transition of this crystal.[9,13,14] In order to take into account the effect of these interactions on the transverse dynamical properties we use a time-dependent four-cluster model similar to that applied by Yoshimitsu and Matsubara[6] for the longitudinal case. Solution of this model results in a temperature dependence for the transverse relaxation time τ_x which is markedly different from that predicted by RPA. Finally, we show that the results of the present model fit well the available experimental data on the dynamical properties of KD_2PO_4 along both transverse and longitudinal directions.

II. TRANSVERSE DYNAMICAL MODEL

It is well known[13] that the static and the dynamical properties of KD_2PO_4 can be described by a pseudospin Ising Hamiltonian. In treating the dynamical properties of KD_2PO_4 in this model one should take into account the existence of four pseudospins per unit cell. This gives rise to three different modes with B_2, E, and A_2 symmetries.[1,15] However, when one considers only polarization fluctuations along the z direction (the B_2 mode), only one pseudospin need be assumed. The present work extends the dynamical treatment to include also polarization fluctuations along the x direction (the E modes). This is achieved by assuming the existence of two different pseudospins in each unit cell, which are labeled here as Z_i^+ and Z_i^-. With these assumptions the Hamiltonian can be written[9,16]

$$\mathcal{H} = -\sum_{\langle ij\rangle} J_{ij} Z_i Z_j - \mu_z E_z(t)\left(\sum_i{}^{+} Z_i^+ + \sum_i{}^{-} Z_i^-\right) - \mu_x E_x^{(t)}\left(\sum_i{}^{+} Z_i^+ - \sum_i{}^{-} Z_i^-\right). \tag{1}$$

It is assumed that the dynamical response of this spin system is due solely to interactions with the surrounding thermal bath and therefore is of a relaxational nature. A convenient way to treat these relaxational processes is by adopting the Glauber kinetic Ising model.[10] In this model only one spin is allowed to flip at a time, according to a transition probability which is a function of the various possible states of the surrounding spins. With these assumptions the spin equations of motion get the following form

$$-\tau_0 \frac{d}{dt} \langle Z_1 \cdots Z_n \rangle_t = 2 \left\langle Z_1 \cdots Z_n \sum_{j=1}^{n} P(Z_j) \right\rangle_t . \quad (2)$$

The moment $\langle Z_1 \cdots Z_n \rangle_t$ is the time-dependent average of the product of n pseudospins, the time constant τ_0 is the relaxation time of an individual proton in the high-temperature limit, and $P(Z_j)$ is the relative probability that the spin of the jth site takes the value $-Z_j$ while the other spins remain fixed in a given configuration. The probability $P(Z_j)$ is given by

$$P(Z_j) = \frac{\exp[-\beta E(Z_1, \ldots, -Z_j, \ldots, Z_N)]}{\exp[-\beta E(Z_1, \ldots, -Z_j, \ldots, Z_N)] + \exp[-\beta E(Z_1, \ldots, Z_j, \ldots, Z_N)]} \quad (3)$$

where the energies $E(Z_1, \ldots, \pm Z_j, \ldots, Z_N)$ are the eigenvalues of the Hamiltonian (Eq. (1)) for the eigen-states $(Z_1, \ldots, \pm Z_j, \ldots, Z_N)$, N being the number of spins in the system. It is readily seen that $P(Z_j)$ can be written

$$P(Z_j^{\pm}) = \frac{1}{2} \left\{ 1 - Z_j^{\pm} \tanh \left[\beta \left(\sum_{\langle ij \rangle} J_{ij} Z_i + \mu_z E_z \pm \mu_x E_x \right) \right] \right\} . \quad (4)$$

Evidently, Eq. (2) couples the amplitudes $\langle Z_i \rangle_t$ with amplitudes of moments of higher orders up to the Nth order, therefore in the following we apply approximation methods for the solution of Eq. (2).

III. RANDOM-PHASE APPROXIMATION (RPA)

A first-order approximation is achieved by replacing $\sum_{\langle ij \rangle} J_{ij} Z_i$ of Eq. (4) by the average term $\sum_{\langle ij \rangle} J_{ij} \langle Z_i \rangle_t$. Taking into account only linear terms in the time-dependent quantities, Eq. (2) becomes

$$-\tau_0 \frac{d}{dt} \left\langle \frac{Z^+ + Z^-}{2} \right\rangle_t = \left\langle \frac{Z^+ + Z^-}{2} \right\rangle_t - \beta (1 - \langle Z \rangle_0^2) \times \left(\mu_Z E_Z + J_{B_2} \left\langle \frac{Z^+ + Z^-}{2} \right\rangle_t \right) , \quad (5a)$$

$$-\tau_0 \frac{d}{dt} \left\langle \frac{Z^+ - Z^-}{2} \right\rangle_t = \left\langle \frac{Z^+ - Z^-}{2} \right\rangle_t - \beta (1 - \langle Z \rangle_0^2) \times \left(\mu_x E_x + J_E \left\langle \frac{Z^+ - Z^-}{2} \right\rangle_t \right) . \quad (5b)$$

The average $\langle Z \rangle_0$ is the spontaneous polarization which is zero above T_c, the constants J_{B_2} and J_E are the Fourier transforms of the interaction constants (for zero wave vectors) in the B_2- and E-mode configurations, respectively[16]:

$$J_{B_2} = \frac{1}{N} \sum_{\langle ij \rangle} J_{ij} ,$$
$$J_E = \frac{1}{N} \left(\sum_{\substack{\langle + + \rangle \\ \langle - - \rangle}} J_{ij} - \sum_{\substack{\langle + - \rangle \\ \langle - + \rangle}} J_{ij} \right) . \quad (6)$$

Solution of Eq. (5) yields the following dynamical susceptibility along the z direction:

$$\chi_Z(\omega) = \chi_Z(0) / (1 + i\omega\tau_{B_2}) , \quad (7)$$

where

$$\tau_{B_2} = \tau_0 \frac{T}{T - J_{B_2}(1 - \langle Z \rangle_0^2)} , \quad \chi_Z(0) = \frac{N\mu_Z^2}{T} \frac{\tau_{B_2}}{\tau_0} \quad (8)$$

and along the x direction:

$$\chi_x(\omega) = \chi_x(0) / (1 + i\omega\tau_E) , \quad (9)$$

where

$$\tau_E = \tau_0 \frac{T}{T - J_E(1 - \langle Z \rangle_0^2)} , \quad \chi_x(0) = \frac{N\mu_x^2}{2T} \frac{\tau_E}{\tau_0} . \quad (10)$$

The main result of Eq. (8) is that the longitudinal relaxation time τ_{B_2} critically slows down on approaching T_c. Such a behavior is clearly seen in experiment.[17-18] However, since $\chi_x(0)$ is known to vary very slowly with temperature, above T_c, the relation $\tau_E \propto T\chi_x(0)$, of Eq. (10) implies that τ_E increases with temperature. This result is in contradiction to experimental data[1,4] on KD_2PO_4 which clearly indicate that τ_E decreases significantly with increasing temperature. In Sec. IV we try to get a better approximation to the dynamical equations by considering a self-consistent four-cluster solution which takes into account also short-range interactions between the hydrogen bonds.

IV. DYNAMICAL CLUSTER APPROXIMATION

In the four-cluster approximation of the Hamiltonian in Eq. (1), the exact short-range interactions between the four bonds surrounding a PO_4 group are taken into account, whereas the other

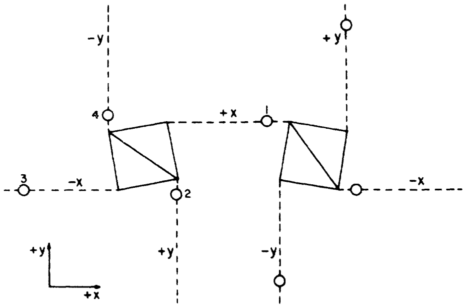

FIG. 1. z-axis projection of the hydrogen bonds connecting the K-PO$_4$ groups showing the different labels of the four spins surrounding each group.

interactions are averaged in a self-consistent way.[13] Thus we use here the following Hamiltonian[9]:

$$H_4 = -V(Z_1Z_2+Z_2Z_3+Z_3Z_4+Z_1Z_4) - U(Z_1Z_3+Z_2Z_4)$$
$$-[\mu_z E_z(t)+\gamma\langle Z\rangle_t+\tfrac{1}{2}\Delta_z(t)](Z_1+Z_2+Z_3+Z_4)$$
$$-[\mu_x E_x(t)+\tfrac{1}{2}\Delta_x(t)](Z_1+Z_2-Z_3-Z_4). \tag{11}$$

The one-particle Hamiltonians are

$$H_\pm = -[\mu_z E_z(t)+\gamma\langle Z\rangle_t+\Delta_z(t) \pm \mu_x E_x(t) \pm \Delta_x(t)]\, Z^\pm , \tag{12}$$

where Z^+ stands for the pseudospin of the bonds labeled 1 and 2 to which positive transverse dipole moments are assigned, and Z^- stands for the 3 and 4 bonds to which negative transverse dipole moments are assigned, see Fig. 1. The energies U and V are connected to the Slater energy parameters ϵ_0 and ϵ_1, through the relations: $U=-\frac{1}{2}\epsilon_1+\frac{1}{2}\epsilon_0$, $V=\frac{1}{2}\epsilon_1-\frac{1}{4}\epsilon_0$.[19]

In the above Hamiltonians the pseudospins interact with time-dependent effective fields which have components in both the longitudinal and the transverse directions. These effective fields are composed of external electric fields E_z and E_x, the longitudinal molecular field $\gamma\langle Z\rangle_t$, and short-range cluster fields Δ_z and Δ_x. The above Hamiltonians are the dynamical extension of the static cluster Hamiltonians of the type developed in detail in Ref. 9.

As indicated by the form of H_4 and $H_\pm$, the polarization along the x direction is represented by the E-mode fluctuation of $\langle Z_1\rangle_t - \langle Z_3\rangle_t$ (and $\langle Z_2\rangle_t - \langle Z_4\rangle_t$). In the four-cluster dynamical model this fluctuation is accompanied by the fluctuations of the higher pseudospin moments: $\langle Z_1Z_2Z_3\rangle_t - \langle Z_2Z_3Z_4\rangle_t$, and $\langle Z_1Z_2\rangle_t - \langle Z_3Z_4\rangle_t$. Therefore we define a vector $\vec{\mu}$ whose three components μ_α are the following transverse spin moments:

$$\mu_1 = \frac{1}{4}\Big(\sum_{i=1,2} Z_i - \sum_{i=3,4} Z_i\Big) ,$$
$$\mu_2 = \frac{1}{4}\Big(\sum_{i=1,4} Z_iZ_{i+1}Z_{i+2} - \sum_{i=2,3} Z_iZ_{i+1}Z_{i+2}\Big) , \tag{13}$$
$$\mu_3 = \frac{1}{4}\Big(\sum_{i=1,2} Z_iZ_{i+1} - \sum_{i=3,4} Z_iZ_{i+1}\Big),$$

where Z_5 and Z_6 are defined as Z_1 and Z_2, respectively. Thus we get the following three Glauber equations of motion for the four-cluster transverse moments.

$$-\tau_0 \frac{d}{dt}\langle \mu_\alpha\rangle_t = \langle m_\alpha\rangle_t , \tag{14}$$

where m_α are spin operators which are derived by multiplying each spin moment $Z_i \cdots Z_k$ in μ_α by the operators

$$\sum_{j=i}^{k} [1 - Z_j \tanh(\beta\epsilon_j^\pm)].$$

The operators $\epsilon_j^\pm$ are

$$\epsilon_j^\pm = \sum_{i=1}^{4} J_{ij}Z_i + \gamma\langle Z\rangle_0 + \tfrac{1}{2}\Delta_z(0) \pm [\mu_x E_x(t) + \tfrac{1}{2}\Delta_x(t)]. \tag{15}$$

The spontaneous polarization $\langle Z_0\rangle$, and the static cluster-field $\Delta_z(0)$ which have nonzero values only below T_c, are derived from the static four-cluster self-consistent equations,[9] whereas the fluctuating transverse cluster field $\Delta_x(t)$ is eliminated by comparison with the Glauber equation of motion of $H^\pm$:

$$-\tau_0 \frac{d}{dt}\langle Z^\pm\rangle_t = \langle Z^\pm\rangle_t - \tanh\{\beta(\Delta_z(0)+\gamma\langle Z\rangle_0 \pm[\mu_x E_x(t)+\Delta_x(t)]\} , \tag{16a}$$

and using the consistency condition

$$\frac{1}{2}\frac{d}{dt}\langle Z^+ - Z^-\rangle_t = \frac{d}{dt}\langle \mu_1\rangle_t . \tag{16b}$$

Expanding $\langle m_\alpha\rangle_t$ in linear terms of the transverse fluctuations $\langle \mu_\alpha\rangle_t$ and $\mu_x E_x(t)$ we obtain the following form for Eq. (14):

$$-\tau_0 \frac{d}{dt}\langle \mu_\alpha\rangle_t = \sum_{\alpha'} M_{\alpha\alpha'}\langle \mu_{\alpha'}\rangle_t + \beta\mu_x E_x(t) L_\alpha , \tag{17}$$

where $M_{\alpha\alpha'}$ and L_α are functions of the temperature and the energy parameters ϵ_0, ϵ_1, and γ. For detailed calculation of $M_{\alpha\alpha'}$ and L_α see Appendix.

Above T_c, the third component of $\langle \mu_\alpha\rangle_t$ is not coupled to the other two and therefore there are only two modes which are polarized along the x direction. These two modes are determined by the upper 2×2 block of $M_{\alpha\alpha'}$ and the first two components of L_α which are

$$M_{\alpha\alpha'}=\begin{pmatrix} 1+P(1+L_1) & R(1+L_1) \\ -2P+3R+PL_2 & 3+P+RL_2 \end{pmatrix}, \tag{18}$$

$$\frac{2L_1}{1+L_1}=\frac{8ab}{1+2a+4ab+a^2b^4}\left(\frac{ab^3}{ab^3+1}+\frac{1}{ab+1}+\frac{2}{b+1}\right), \tag{19a}$$

$$\frac{2L_2}{1+L_1}=\frac{8ab}{1+2a+4ab+a^2b^4}\left(\frac{ab^3}{ab^3+1}+\frac{1}{ab+1}-\frac{2}{b+1}\right), \tag{19b}$$

where

$$P=\frac{1}{4}\left(\frac{1-ab}{1+ab}+2\frac{b-1}{b+1}+\frac{ab^3-1}{ab^3+1}\right), \quad R=P-\frac{b-1}{b+1} \tag{20}$$

and

$$a=\exp(-\beta\epsilon_0), \quad b=\exp[-\beta(\epsilon_1-\epsilon_0)]. \tag{21}$$

The solution of Eq. (17) for the relaxation times of the two modes above T_c, as well as numerical results for below T_c are given in Sec. V.

V. RESULTS AND COMPARISON WITH EXPERIMENT

Above T_c, diagonalization of Eq. (17), for $E_x = 0$, yields two relaxation times, τ_1^x and τ_2^x, which are approximately given by

$$(\tau_1^x)^{-1}\cong\frac{1}{\tau_0}\frac{8b}{3(1+2a)},$$

$$(\tau_2^x)^{-1}\cong\frac{1}{\tau_0}\left(3-\frac{b(2+3a+6a^2)}{3(1+2a)}\right). \tag{22}$$

A similar procedure gives, for the longitudinally polarized B_2 modes, the following two relaxation times:

$$(\tau_1^z)^{-1}\cong\frac{1}{\tau_0}\frac{8ab(2a-1-2\beta\gamma)}{3(1+2a)}$$

$$(\tau_2^z)^{-1}\cong\frac{1}{\tau_0}\left[3-\frac{b(6+7a-6a^2+2\beta\gamma a)}{3(1+2a)}\right], \tag{23}$$

Since it is known[9] that $b \ll 1$ for KD_2PO_4, we neglected in Eqs. (18) and (19) terms of the order of b^2. It should be noted that τ_0 is the same for both the longitudinal and transverse modes. It is also noted that, in the case of $\gamma = 0$, Eq. (23) reduces to the solution given in Ref. 6. It is seen from the above equations that, for both the E and B_2 modes, τ_1 has a strong temperature dependence and is much greater than τ_2 which is nearly independent of temperature. This significant difference between τ_1 and τ_2 stems from the fact that τ_1 is the lifetime of a mode in which the spin relaxation involves transitions from the low-energy levels which have the Slater energies 0 (in the longitudinal case) or ϵ_0 (in the transverse case) to the high-energy levels with the Slater energy ϵ_1. In contrast, τ_2 is the lifetime of a mode which involves transitions from the high-energy levels to the low ones. Since by approaching T_c from above the level with zero energy becomes stable, the longitudinal mode with the lifetime τ_1^z critically slows down, as evidenced from Eq. (23). However, the inclusion of the long-range interaction γ allows for a first-order transition[9] in which case, τ_1^z remains finite at T_c.

Below T_c, all three component of $\langle \mu_\alpha \rangle$ are coupled, and the elements of $M_{\alpha\alpha'}$ depend also on the spontaneous polarization. Numerical solution of Eq. (17), for $T < T_c$, shows that also in this region one relaxation time τ_1^x is much greater than τ_2^x and τ_3^x. A similar treatment of the longitudinal case yields four coupled ferroelectric modes with τ_1^z much higher than the other three.

In order to calculate the dynamical transverse susceptibility, $\chi_x(\omega)$, we introduce $E_x(t) = E_x \exp(i\omega t)$ in Eq. (17). Solution of Eq. (17) for $\chi_x(\omega) \equiv N\mu_x \langle \mu_1 \rangle / 2E_x$ yields

$$\chi_x(\omega)=\frac{\chi_1}{1+i\omega\tau_1^x}+\frac{\chi_2}{1+i\omega\tau_2^x}+\frac{\chi_3}{1+i\omega\tau_3^x}, \tag{24}$$

where each χ_i represents the temperature-dependent relative contribution of one of the three E modes to the transverse susceptibility. Above T_c, χ_3 is zero, and χ_1 and χ_2 are given by

$$\chi_1\cong\frac{N\mu_x^2}{T}\frac{a}{1+2ab}\left(1+\frac{b(8+18a)}{9(1+2a)}\right), \tag{25}$$

$$\chi_2\cong\frac{N\mu_x^2}{T}\frac{ab}{9(1+2a)(1+2ab)},$$

where, again, terms of the order of b^2 were neglected.

Since the high-energy levels have relatively small Boltzmann factors, their contribution to the susceptibility χ_2 and χ_3 is much smaller than that of the low-energy levels, which is χ_1. Thus in the low-frequency region, $\chi_x(\omega)$ is dominated by χ_1 and therefore can be written in both the paraelectric and ferroelectric phases as

$$\chi_x(\omega)\cong\chi_x(0)/(1+i\omega\tau_x), \tag{26}$$

where $\chi_x(0) \simeq \chi_1$ and $\tau_x \simeq \tau_1^x$. This result shows that, in the low-frequency region, not only in the RPA but also in the dynamical four-cluster approximation, $\chi_x(\omega)$ has a monodispersive Debye-type frequency dependence. This behavior is actually seen in experiment.[4,20]

A very interesting consequence of the above theory is the relation between τ_x and the static susceptibility $\chi_x(0)$, which is very different from the

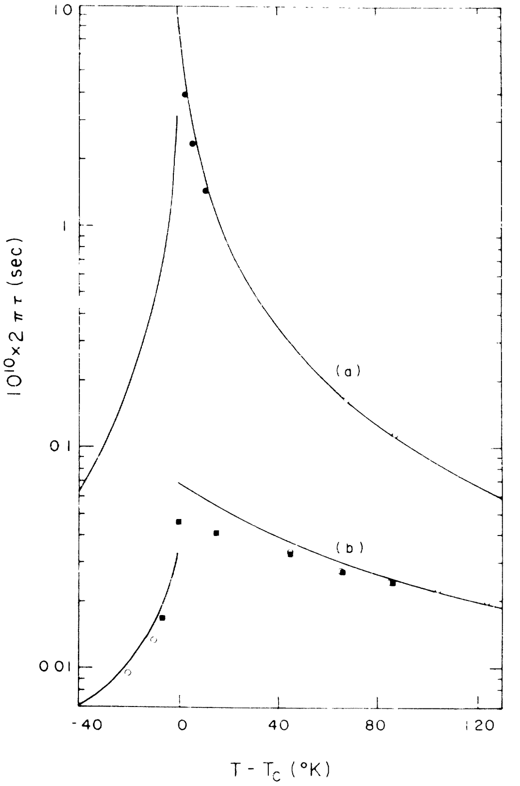

FIG. 2. Pseudo spin relaxation times in KD_2PO_4 as a function of $T - T_c$. (a) Longitudinal relaxation time, (b) transverse relaxation time. The open circles are the results of Kaminow's (Ref. 1) measurements of $\tan\delta_z$ on fully deuterated KD_2PO_4 and $\tan\delta_x$ on 76% deuterated KD_2PO_4. The full circles are the experimental data of Reese *et al.* (Ref. 12) for fully deuterated KD_2PO_4. The full squares are the data of Gauss and Happ (Ref. 4). The line represents the theoretical calculations of τ_1 in Eqs. (7) and (8) with $\epsilon_0 = 92$ °K, $\epsilon_1 = 907$ °K, and $\gamma = 36.9$ °K. These energy values give best fit to the static dielectric properties of KD_2PO_4 (Ref. 6).

relation $\tau_x \propto T\chi_x(0)$ which was derived above in the RPA. In effect, in the cluster model, this relation turns out to be

$$\tau_x \propto T\chi_x(0)/L_1 , \tag{27}$$

where L_1 [Eq. (A5)] has strong temperature dependence. For example, above $T_c, L_1 \simeq ab/(1+2a)$. Similar results have been obtained, for the longitudinal z direction, using a phenomenological dynamical version of the Slater-Takagi model.[7]

As mentioned above, measurements of $\tan\delta_x = \text{Im}\chi_x/\text{Re}\chi_x$, which is equal to $\omega\tau_x$ in the Debye model, yields for $T > T_c$ in KD_2PO_4 a strongly *decreasing* function of T.[1,4] Indeed, due to the temperature dependence of L_1, τ_x of Eq. (27) is a decreasing function of T, in constrast to its behavior in the RPA. Moreover, the solution of both τ_x and τ_z in the four-cluster approximation is in good quantitative agreement with the available experimental data of Kaminow,[1] Reese *et al.*,[17] and Gauss and Happ.[4] Comparison between the present theory and the experimental data for τ_x and τ_z above as well as below T_c is given in Fig. 2. The slight discrepancy between the theory and Kaminow's data of τ_x is attributed to the fact that that data was obtained from a not fully deuterated DKDP and therefore the value of τ_x is expected to be smaller than that of a fully deuterated crystal. It should be noted that the good agreement was achieved with the same individual proton relaxation time $\tau_0 = 0.31 \times 10^{-13}$ sec, for both the x and the z directions.

The effect of the spontaneous polarization on the transverse dynamics below T_c is manifested by the discontinuity of τ_x at T_c and its rapid decrease below it, as shown in Fig. 2. Evidence for such anomalous behavior of τ_x below T_c is found in the measurements of Kaminow[1] and Gauss and Happ.[4]

Finally, it is noted that the temperature dependence of τ_x can be deduced also from the T dependence of $\text{Re}\chi_x(\omega, T)$. Very recent measurements[4] of the temperature dependence of this quantity in KD_2PO_4 at $\omega/2\pi = 4.6$ cm^{-1} have shown that T_c, $\text{Re}\chi_x(\omega, T)$ *increases* with T up to room tem-

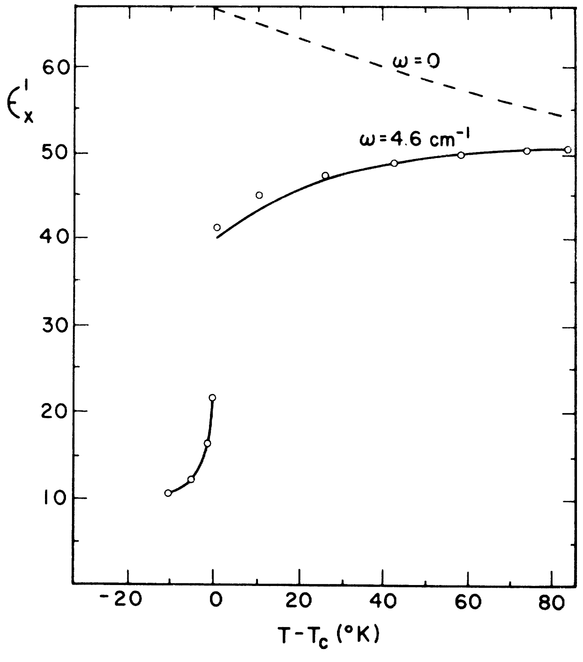

FIG. 3. Real part of the transverse dielectric constant in KD_2PO_4 at $\omega/2\pi = 4.6$ cm^{-1} as a function of $T - T_c$ the circles are the experimental data of Gauss and Happ (Ref. 4). The full line is the theoretical result. For comparison we also bring the static transverse dielectric constant (Ref. 9) presented by the dashed line.

perature. This result indicates that (a) $\omega\tau_x \gtrsim 1$ at 4.6 cm^{-1}, and (b) τ_x strongly decreases with temperature, thus causing an increase in $\text{Re}\chi_x(\omega, T) = \chi_x(0)/(1+\omega^2\tau_x^2)$, in spite of the decrease of $\chi_x(0)$. Both conclusions fit well with our theoretical results. Indeed, calculation of $\text{Re}\chi_x(\omega, T)$, based on Slater energy values previously deduced from static measurements on KD_2PO_4,[9] resulted in a peak which is located at $T=300\,^\circ\text{K}$ for $\omega/2\pi = 4.6\ \text{cm}^{-1}$, see Fig. 3.

In conclusion, we have shown that the observed transverse dynamical properties of KD_2PO_4 clearly indicate that both long-range and short-range interactions play an important role in the dynamics of KDP-type crystals. We have also shown that a four-cluster theory which takes both interactions into account does explain the low-frequency dynamical properties of KD_2PO_4 in both the longitudinal and transverse directions.

ACKNOWLEDGMENTS

The authors wish to thank Professor H. Happ for providing a preliminary version of his work prior to publication, Professor M. Luban for critically reading the manuscript, and Mrs. A. Vishnia for helping with the computer calculations. One of the authors (H.S.) gratefully acknowledges the generous financial support afforded to him by a stipend from the Jerome Stern family.

APPENDIX

In this Appendix we derive the explicit form of the equations of motion, represented by Eqs. (14) and (17). Retaining in m_α only linear terms in the dynamical transverse field $\xi_x(t) = \mu_x E_x(t) + \Delta_x(t)$, m_α is written

$$m_\alpha = m_\alpha^0 + m'_\alpha \beta\, \xi_x\,, \quad m'_\alpha = \frac{1}{\beta}\,\frac{\partial m_\alpha}{\partial \xi_x}\,. \tag{A1}$$

The field ξ_x can be written as a linear function of the amplitudes $\langle \mu_\alpha \rangle_t$ and the external field $\mu_x E_x(t)$, in the following way:

$$\xi_x(t) = \sum_\alpha \xi_\alpha \langle \mu_\alpha \rangle_t + \xi_\epsilon\, \beta \mu_x E_x(t)\,. \tag{A2}$$

Substituting Eq. (A2) in Eq. (A1), and averaging, yield:

$$\langle m_\alpha \rangle_t = \sum_{\alpha'} M_{\alpha\alpha'} \langle \mu_{\alpha'} \rangle_t + L_\alpha \beta \mu_x E_x(t)\,, \tag{A3}$$

where

$$\begin{aligned} M_{\alpha\alpha'} &= \frac{\langle m_\alpha^0 \mid \mu_{\alpha'} \rangle}{\langle \mu_{\alpha'} \mid \mu_{\alpha'} \rangle} + \langle m'_\alpha \rangle_0 \beta \xi_\alpha \\ &= \tfrac{1}{4}\, \text{Tr}(m_\alpha^0 \mu_{\alpha'}) + \langle m'_\alpha \rangle_0 \beta \xi_\alpha \end{aligned} \tag{A4}$$

and

$$L_\alpha = \langle m'_\alpha \rangle_0 \beta \xi_\epsilon\,. \tag{A5}$$

Note that the quantity $\langle m'_\alpha \rangle_0$ is a static average, i.e., calculated for $\xi_x = 0$. In the following, we present explicit expressions for $\text{Tr}(m_\alpha^0 \mu_{\alpha'})$, $\langle m'_\alpha \rangle_0$, ξ_α, and ξ_ϵ.

Using the definitions of m_α of Eq. (14) and μ_α of Eq. (13), we obtain

$$\tfrac{1}{4}\text{Tr}(m_\alpha^0 \mu_{\alpha'}) = \begin{pmatrix} 1+P & R & M \\ 3R-2P & 3+P & M+N-L \\ 2(M+N-L) & 0 & 2(1+R) \end{pmatrix}, \tag{A6}$$

where

$$\begin{aligned} P &= \tfrac{1}{16}\text{Tr}[Z_{i+2} \tanh(\beta\epsilon_i^0)]\,, \\ R &= \tfrac{1}{16}\text{Tr}[Z_{i+1} Z_{i+2} Z_{i+3} \tanh(\beta\epsilon_i^0)]\,, \\ L &= \tfrac{1}{16}\text{Tr}[\tanh(\beta\epsilon_i^0)]\,, \\ M &= \tfrac{1}{16}\text{Tr}[Z_{i+1} Z_{i+2} \tanh(\beta\epsilon_i^0)]\,, \\ N &= \tfrac{1}{16}\text{Tr}[Z_{i+1} Z_{i+3} \tanh(\beta\epsilon_i^0)]\,. \end{aligned} \tag{A7}$$

The energy operator ϵ_i^0 in Eqs. (A7), is the operator $\epsilon_i^\pm$, defined in Eq. (15) with a zero transverse field. Thus $\tanh(\beta\epsilon_i^0)$ of Eqs. (A7) is a 16×16 diagonal matrix, which has the quantities $\tanh(\beta\epsilon_i^0)$ as diagonal entries.

Calculating the static thermodynamic average of the operators m'_α we obtain:

$$\begin{aligned} \langle m'_1 \rangle_0 = -[&l + (2p+q)\langle Z_i \rangle_0 + r\langle Z_i Z_{i+1} Z_{i+2} \rangle_0 \\ &+ 2m\langle Z_i Z_{i+1} \rangle_0 + n\langle Z_i Z_{i+2} \rangle_0] \\ \langle m'_2 \rangle_0 = -[&n + (2q+r)\langle Z_i \rangle_0 + p\langle Z_i Z_{i+1} Z_{i+2} \rangle_0 \\ &+ 2m\langle Z_i Z_{i+1} \rangle_0 + l\langle Z_i Z_{i+2} \rangle_0]\,, \\ \langle m'_3 \rangle_0 = -[&2q + 2(l+m+n)\langle Z_i \rangle_0 + 2m\langle Z_i Z_{i+1} Z_{i+2} \rangle_0 \\ &+ 2(r+p)\langle Z_i Z_{i+1} \rangle_0 + 2q\langle Z_i Z_{i+2} \rangle_0]\,, \end{aligned} \tag{A8}$$

where

$$\begin{aligned} p &= \tfrac{1}{16}\text{Tr}[Z_{i+2}\, \text{sech}^2(\beta\epsilon_i^0)]\,, \\ q &= \tfrac{1}{16}\text{Tr}[Z_{i+1}\, \text{sech}^2(\beta\epsilon_i^0)]\,, \\ r &= \tfrac{1}{16}\text{Tr}[Z_{i+1} Z_{i+2} Z_{i+3}\, \text{sech}^2(\beta\epsilon_i^0)]\,, \\ l &= \tfrac{1}{16}\text{Tr}[\text{sech}^2(\beta\epsilon_i^0)]\,, \\ m &= \tfrac{1}{16}\text{Tr}[Z_{i+1} Z_{i+2}\, \text{sech}^2(\beta\epsilon_i^0)]\,. \\ n &= \tfrac{1}{16}\text{Tr}[Z_{i+1} Z_{i+3}\, \text{sech}^2(\beta\epsilon_i^0)]\,. \end{aligned} \tag{A9}$$

In order to calculate the transverse field coefficients ξ_α and ξ_ϵ we use the dynamical consistency condition of Eqs. (16). Expanding Eq. (16a) in linear terms of $\langle\mu_\alpha\rangle_t$ and $\mu_x E_x(t)$ and using Eq. (A2), we obtain the following form for Eq. (16b):

$$\sum_{\alpha'} \delta_{1\alpha'}\langle\mu_{\alpha'}\rangle_t - 2\beta[1-\langle Z\rangle_0^2]\left[\sum_{\alpha'} \xi_{\alpha'}\langle\mu_{\alpha'}\rangle_t - (\beta\xi_\epsilon - \tfrac{1}{2})\mu_x E_x(t)\right] = \sum_{\alpha'} M_{1\alpha'}\langle\mu_{\alpha'}\rangle_t + L_1\beta\mu_x E_x . \tag{A10}$$

Combining the terms of $\langle\mu_{\alpha'}\rangle_t$ and $\mu_x E_x(t)$ and substituting (A4) and (A5) one obtains

$$\begin{aligned} \beta\xi_{\alpha'} &= \frac{\delta_{1\alpha'} - \frac{1}{4}\,\mathrm{Tr}(m_1^0\mu_{\alpha'})}{2(1-\langle Z\rangle_0^2) - \langle m_1'\rangle_0} , \\ \beta\xi_\epsilon &= \frac{1-\langle Z\rangle_0^2}{2(1-\langle Z\rangle_0^2) - \langle m_1'\rangle_0} . \end{aligned} \tag{A11}$$

Finally for $T>T_c$, Eqs. (A7) and (A9) reduce to the following analytical form:

$$\begin{aligned} P &= \frac{1}{4}\left(\frac{1-ab}{1+ab} + \frac{2(b-1)}{b+1} + \frac{ab^3-1}{ab^3+1}\right) , \\ R &= \frac{1}{4}\left(\frac{1-ab}{1+ab} - \frac{2(b-1)}{b+1} + \frac{ab^3-1}{ab^3+1}\right) , \\ l &= \frac{ab}{(ab+1)^2} + \frac{2b}{(b+1)^2} + \frac{ab^3}{(ab^3+1)^2} , \\ m &= \frac{ab}{(ab+1)^2} - \frac{ab^3}{(ab^3+1)^2} , \\ n &= \frac{ab}{(ab+1)^2} - \frac{2b}{(b+1)^2} + \frac{ab^3}{(ab^3+1)^2} , \\ L &= M = N = p = q = r = 0 , \end{aligned} \tag{A12}$$

where $a=\exp(-\beta\epsilon_0)$ and $b=\exp[-\beta(\epsilon_1-\epsilon_0)]$.

Also, the averages appearing in Eq. (A8) reduce for $T>T_c$, to

$$\begin{aligned} \langle Z_i\rangle_0 &= \langle Z_i Z_{i+1} Z_{i+2}\rangle_0 = 0 , \\ \langle Z_i Z_{i+1}\rangle &= \frac{1-a^2b^4}{1+2a+4ab+a^2b^4} , \\ \langle Z_i Z_{i+2}\rangle &= \frac{1-2a+a^2b^4}{1+2a+4ab+a^2b^4} . \end{aligned} \tag{A13}$$

Using the above expressions one obtains the simple form of $M_{\alpha\alpha'}$ and L given in Eqs. (18) and (19).

---

[1] I. P. Kaminow, Phys. Rev. 138, A1539 (1965).

[2] C. M. Wilson and H. Z. Cummins, *Proceedings of the Second International Conference on Light Scattering in Solids* (Flammarion, Paris, 1971), p. 420.

[3] Y. Takagi and T. Shigenari, J. Phys. Soc. Jpn. 39, 440 (1975); T. Shigenari and Y. Takagi, The Fifth International Conference on Raman Spectroscopy, Paris, September, 1976 (unpublished).

[4] K. E. Gauss, H. Happ, and G. Rother, Phys. Status Solidi B 72, 613 (1975); K. E. Gauss and H. Happ, *ibid.* 78, 133 (1976).

[5] R. Blinc and B. Zeks, Adv. Phys. 21, 693 (1972).

[6] K. Yoshimitsu and T. Matsubara, Prog. Theor. Phys. Suppl. 109 (1968).

[7] V. H. Schmidt, Phys. Rev. 164, 749 (1967).

[8] S. Havlin, E. Litov, and E. A. Uehling, Phys. Rev. B 9, 1024 (1974).

[9] S. Havlin, E. Litov, and H. Sompolinsky, Phys. Rev. B 13, 4999 (1976).

[10] R. J. Glauber, J. Math. Phys. 4, 294 (1963).

[11] R. Blinc and B. Zeks, *Soft Modes in Ferroelectricity and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[12] S. Havlin and H. Sompolinsky, Phys. Lett. A 57, 171 (1976).

[13] R. Blinc and S. Svetina, Phys. Rev. 147, 430 (1966).

[14] V. G. Vaks, N. E. Zein, and B. A. Strukov, Phys. Status Solidi A 30, 801 (1975).

[15] R. J. Elliott, Ferroelectrics 7, 23 (1974).

[16] S. Havlin, E. Litov, and H. Sompolinsky, Phys. Lett. A 53, 41 (1975).

[17] R. L. Reese, I. J. Fritz, and H. Z. Cummins, Phys. Rev. B 7, 4165 (1973).

[18] E. Litov and E. A. Uehling, Phys. Rev. B 1, 3713 (1970).

[19] H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. 133, A 165 (1964).

[20] G. Luther, Ferroelectrics 12, 243 (1976).