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Green's-function theory of phase transitions in H-bonded antiferroelectric $NH_4H_2PO_4$, $ND_4D_2PO_4$, and $NH_4H_2AsO_4$ crystals with a pseudospin model: A unified model for the transverse electrical susceptibilities of ADP- and KDP-type crystals

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A double-time temperature-dependent Green's-function technique has been used for the first time to study the static and the dynamic behavior of antiferroelectric ADP ($NH_4H_2PO_4$), DADP ($ND_4D_2PO_4$), and ADA ($NH_4H_2AsO_4$) crystals with a four-sublattice pseudo-spin-cluster model. The spin-phonon interaction has been included, and the renormalized energy spectrum and the transverse and the longitudinal electrical susceptibilities have been calculated. It has been shown that the temperature-dependent "hard" E mode and the "soft" B_2 symmetry mode are strongly coupled in the ADP antiferroelectrics. Like the ferroelectric soft mode in KDP (KH_2PO_4), a linearly temperature-dependent antiferroelectric mode is also present in ADP, agreeing with the neutron-diffraction results of Meister, Skalyo, Frazer, and Shirane. Unlike KDP, the antiferroelectric mode should occur at the z point $[\vec{q} \approx (2\pi/c)\hat{c}]$ in ADP. "Pseudo-soft-mode" behavior of the E mode, similar to that observed earlier in KDP, has been predicted in the present antiferroelectric system. Furthermore, the transverse electrical susceptibilities of KDP and ADP which are assumed to be associated with the "hard" E mode behave in a similar way, indicating the validity of a unified theory applicable to both KDP and ADP. From fitting the transverse and longitudinal susceptibilities of ADP, DADP, and ADA it is observed that the proton-proton interaction is much stronger in ADA compared with those of ADP and DADP, which might be responsible for the positive value of the Slater configurational energy in ADA. Our derived expresssions for the longitudinal and transverse susceptibilities which fit the respective experimental data very well are found to be quite different from those of Havlin, Litov, and Sompolinsky. This is partly due to the inclusion of spin-lattice and tunneling terms in the Hamiltonian and partly due to the different method of their calculations.

I. INTRODUCTION

Compared with the hydrogen-(H-) bonded ferroelectric (FE) crystals like KDP (KH_2PO_4), very little theoretical work has been done on the isomorphous antiferroelectric (AFE) crystal like ADP ($NH_4H_2PO_4$). The latter crystal undergoes a first-order transition[1,2] at about 148 K. The AFE transition in ADP causes a change of structure from tetragonal[3,4] ($D_2-\overline{4}2m$) to orthorhombic (D_2-222) below T_C. The main structural feature of both KDP and ADP in their two phases is the $(H_2PO_4)^{-1}$ network in which each phosphate group is linked by O—H $\cdots$ O bonds to a tetrahedral arrangement of phosphate-group neighbors. But the significant difference between the two structures as shown in Fig. 1 is that in ADP each ammonium group is tetrahedrally connected to four phosphate groups by N—H $\cdots$ O bonds. The large isotope shift in the transition temperature from 148 to 242 K in ADP indicates that the tunneling effect in ADP is as important as in the KDP crystal. However, this isotope dependence of T_C and the dynamical behavior of ADP have not yet been studied theoretically. Even the tunneling effect has been completely neglected in the previous theoretical work.[5-7] For this an attempt has been made in this paper to study the static and the dynamic properties of the ADP-type AFE crystal with pseudo-spin-lattice-coupled Hamiltonian containing the tunneling term.

The recent theory of Havlin, Litov, and Sompolinsksy[7] (abbreviated as HLS) which explains the dielectric constants of the ADP-type crystals along the transverse (ϵ_a) and the longitudinal (ϵ_c) axes is definitely an oversimplified model for ADP, where both the proton tunneling effect and the proton-lattice coupling have been neglected. The theoretical approach of Broberg *et al.*[8] to fit the low-frequency Raman spectra of ADP and the B_2-mode character considering the model of two coupled harmonic oscillators seems to be overdetermined for obvious reasons (see Lines and Glass[9] for details). In the present paper the behavior of the B_2- and E-symmetry Raman-active modes (similar to those observed in KDP crys-

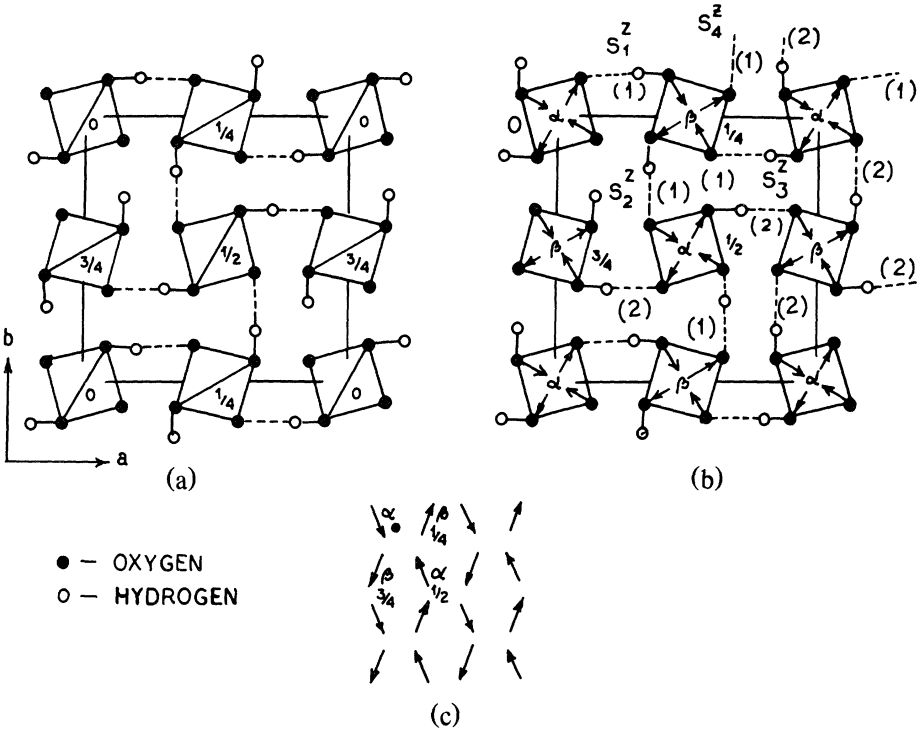

FIG. 1. Positions of the H atoms in the ferroelectric phase of KDP (a) and in the antiferroelectric phase of ADP (b). The four sublattice model of ADP is also indicated in (b). Here the H bonds along each transverse direction are divided into two sublattices, denoted by 1 and 2. α and β denote phosphorus atoms and the numbers near them indicate the heights along the c axis. (c) Dipole moments induced in PO_4 groups (Ref. 5).

tal[10–12]) has also been studied, at least qualitatively because of very complicated nature of these modes in ADP.

It is well known from the work of HLS and Ishibashi *et al.*[6] (abbreviated as IOT) that the dielectric constant data of the ADP-type AFE crystals can be fitted well both for the positive and negative values of ϵ_0 (the Slater configurational energy parameter). To avoid this sign ambiguity we have not directly included this energy parameter which is, however, invoked through the exchange integral in the usual way. This makes us convenient to elucidate the difference in the transition mechanisms of the antiferroelectric ADP and the ferroelectric KDP families and to show conclusively the unified behavior of these crystals starting with a pseudospin model of the Kobayashi type. From the calculations of the model parameters we find that the stronger proton-proton coupling in ADA along the c axis compared to that of ADP might make ϵ_0 positive for ADA while it is negative for ADP and DADP.

Another drawback of the assumption made by HLS arises in the following way: The previous model[13] used by HLS to explain the AFE character and the behavior of the E-symmetry mode in KDP along the a axis was later extended by them for showing the antiferroelectricity in the case of the ADP crystal. But it has been observed in recent theoretical[14,15] as well as experimental[16] studies that the previous model of HLS cannot adequately explain the low-temperature behavior of KDP. Thus their assumption of a unified model[7] for the transverse electrical susceptibilities in KDP and ADP needs further clarification. Our present calculations of the static and the dynamic properties of ADP crystal shows a complete uniqueness in the character of the transverse electrical susceptibilities of these two crystals.

To study the behavior of AFE phase transitions in the ADP-type crystals and to clarify the discrepancies mentioned above we have discussed the model used for our calculations in Sec. II. Sections III and IV deal with the theoretical calculation with Green's function wherein we have derived theoretical expressions for the static dielectric constants of the HLS type (Sec. III) and the dynamic properties, viz., the energy spectrum and the frequency-dependent transverse and longitudinal electrical susceptibilities (Sec. IV). In Sec. V the experimental values of ϵ_a and ϵ_c have been fitted with the corresponding theoretical expressions for ϵ_a and ϵ_c to find the model parameters for discussion comparing with the results of the KDP-type crystals. Finally, the paper ends with the conclusion (Sec. VI) on the unified behavior of KDP and ADP crystals.

II. MODEL

The model used in the present paper has already been described by IOT and developed by HLS as well as Vaks.[17] The four sublattice model of ADP is shown in Fig. 1(a). Unlike KDP, where two "upper" or two "lower" proton sites (with respect to the c axis) are filled for an arbitrary H_2PO_4 group in the ordered phase, ordered ADP has one upper and one lower site filled. For this configuration of the hydrogen bonds (Fig. 1), the pseudospin model in the cluster approximation can be written

$$\begin{aligned}\mathcal{H}_1=&-\tfrac{1}{2}\sum_{ij}J_{ij}S_i^zS_j^z-(\mu_cE_c+\gamma\langle S^z\rangle)\sum_i S_i^z-\sum_{\alpha=a,b}\left(\mu_\alpha E_\alpha-\tfrac{1}{2}\lambda\langle S_{(2)}^{z(+\alpha)}-S_{(2)}^{z(-\alpha)}\rangle\right)\left[\sum_i S_{i(1)}^{z(+\alpha))}-\sum_i S_{i(1)}^{z(-\alpha)}\right]\\&-\sum_{\alpha=a,b}\left(\mu_\alpha E_\alpha-\tfrac{1}{2}\lambda\langle S_{(1)}^{z(+\alpha)}-S_{(1)}^{z(-\alpha)}\rangle\right)\left[\sum_i S_{i(2)}^{z(+\alpha)}-\sum_i S_{i(2)}^{z(-\alpha)}\right]\ ,\end{aligned}\tag{1}$$

where $S_{i(\eta)}^{m(\pm\alpha)}$ are the mth component of the pseudospin for the sublattice η ($\eta=1,2$) associated with the direction $\pm\alpha$ ($\alpha=a,b$). γ represents the long-range dipole-dipole interaction, and λ is the long-range AFE interaction constant as defined by HLS.

To include the tunneling term we have to consider the additional Hamiltonian

$$\mathcal{H}_2=-2\Omega\left[\sum_i S_i^x+\sum_{\substack{\alpha=a,b\\ \eta=1,2}}\sum\left(S_{i(\eta)}^{x(+\alpha)}-S_{i(\eta)}^{x(-\alpha)}\right)\right]\ ,\tag{2}$$

where Ω is the effective tunneling frequency. Since strong evidence of proton-lattice coupling has been predicted for the arsenates KDA and ADA using electron-nuclear double resonance (ENDOR) and EPR techniques[18] one should also take into account the proton-lattice interaction Hamiltonian. The quasielastic scattering[19] near the z point, confirming the existence of a soft mode at that point, also indicates the importance of proton-lattice interaction in the ADP-type crystals. Following Kobayashi[20] very simplified form of the proton-lattice coupling Hamiltonian can be written

$$H_3=-N^{-1/2}\sum_{i,\vec{q}}V_{i\vec{q}}Q_{\vec{q}}S_i^z-N^{-1/2}\sum_{\substack{\alpha=a,b\\ i,\vec{q}\\ \eta=1,2}}\sum\sum V_{i\vec{q}}\left(S_{i(\eta)}^{z(+\alpha)}-S_{i(\eta)}^{z(-\alpha)}\right)Q_{\vec{q}}+\sum_{\vec{q}}\tfrac{1}{2}\left(P_{\vec{q}}P_{-\vec{q}}+\bar{\omega}_{\vec{q}}^2Q_{\vec{q}}Q_{-\vec{q}}\right)\ .\tag{3}$$

For a highly overdamped system like ADP we should replace the particularly simple form $H=\sum_{\vec{q}}\omega_{\vec{q}}^2Q_{\vec{q}}Q_{-\vec{q}}$ by the effective Hamiltonian with complex frequency $\bar{\omega}_{\vec{q}}=(\omega_{\vec{q}}+i/\tau_{\vec{q}})$ and relaxation time $\tau_{\vec{q}}$ so that $H=\sum_{\vec{q}}(\omega_{\vec{q}}-i/\tau_{\vec{q}})\times Q_{\vec{q}}Q_{-\vec{q}}$.

In Eq. (3) $V_{i\vec{q}}$ is the usual spin-phonon coupling term, $Q_{\vec{q}}$ and $P_{\vec{q}}$ are the normal coordinates and the conjugate momenta, respectively. To make our calculations simplified we assume $V_{i\vec{q}}^{\pm\alpha}=V_{i\vec{q}}$, $Q_{\vec{q}}^{\pm\alpha}=Q_{\vec{q}}$, and $P_{\vec{q}}^{\pm\alpha}=P_{\vec{q}}$ and hence the present model can be treated as a modified Kobayashi model. For the antiferroelectric case, where the stability occurs[19] at the zone boundary along c^* axis (called the z point and c^* is the reciprocal-lattice vector in the c direction) the order parameter $\langle Q_{\vec{q}_0}\rangle\neq 0$ and we have $\langle Q_{\vec{1}}\rangle=Q_{\vec{q}_0}\exp(i\vec{q}_0\cdot\vec{R}_l)\approx\pm Q_{\vec{q}_0}$. One may also write

$$Q_{\vec{q}}=Q_{\vec{q}_0}+\delta Q_{\vec{q}}\ .\tag{4}$$

In the paraelectric phase (PE) $Q_{\vec{q}_0}=0$ and in the FE phase $Q_{\vec{q}_0}\neq 0$; $\delta Q_{\vec{q}}=\bar{Q}_{\vec{q}}$ (say) denotes the fluctuations around the average value.

Here it should be noted that the Green's-function method and the procedure of our calculations used in this paper have already been discussed in our earlier papers.[21–24]

III. THEORY

A. Calculation of static susceptibility

The total Hamiltonian obtained from Eqs. (1)–(3) can be written

$$\bar{H}=H_1+H_2+H_3\ .\tag{5}$$

This is a generalized form of the pure pseudospin model originated from the Slater-Takagi[25] protonic configuration[26] around the PO_4 group with $U=-2\epsilon_1+2\epsilon_0$, $V=2\epsilon_1-\epsilon_0$ (where U and V are the short-range interaction energies; $J_{12}=J_{34}=U$, $J_{13}=J_{24}=J_{23}=J_{14}=V$ as in the KDP system. Following Zubarev,[27] the thermodynamic Green's function can be written (in units of $\hbar=1$)

$$G_{ij}^{mn}(t-t')=\langle\langle S_i^m(t);S_j^n(t')\rangle\rangle\ .\tag{6}$$

The Fourier transform of (6) has the form

$$E\langle\langle S_i^m;S_j^n\rangle\rangle=(2\pi)^{-1}\langle[S_i^m,S_j^n]\rangle+\langle\langle[S_i^m,H];S_j^n\rangle\rangle\ , \tag{6a}$$

where $\langle\cdots\rangle$ denotes the statistical average of the enclosed operators. The Bruevich-Tyablikov-type[28] decoupling used in the present calculations has already been discussed in our earlier papers.[21–24] To calculate the correlation functions we use the spectral theorem,[27] viz.,

$$\langle S_j^n S_i^m\rangle=\lim_{\delta\to 0+} i\int_{-\infty}^{+\infty}\frac{\langle\langle S_i^m,S_j^n\rangle\rangle_{E+i\delta}-\langle\langle S_i^m,S_j^n\rangle\rangle_{E-i\delta}}{\exp\beta E-1}\times\exp[-iE(t-t')]\,dE\ , \tag{7}$$

where $\beta=1/k_BT$ (k_B is the Boltzmann's constant and T is the absolute temperature). For different values of m and n ($m,n=x$, y, or z) and considering the total Hamiltonian (5), the equation of motion has the form

$$AG=B\ , \tag{8}$$

where

$$A=\begin{bmatrix} a & & \\ & a & \\ & & a\end{bmatrix}\ ,\qquad a=\begin{bmatrix} E & ia'' & 0\\ -ia'' & E & -i2\Omega\\ 0 & i2\Omega & E\end{bmatrix}\ ,$$

$$G=\begin{bmatrix} G_{xx}^{+a(1)}(E)\\ G_{yx}^{+a(1)}(E)\\ G_{zx}^{+a(1)}(E)\\ G_{xy}^{+a(1)}(E)\\ G_{yy}^{+a(1)}(E)\\ G_{zy}^{+a(1)}(E)\\ G_{xz}^{+a(1)}(E)\\ G_{yz}^{+a(1)}(E)\\ G_{zz}^{+a(1)}(E)\end{bmatrix}\ ,\qquad B=\frac{i}{2\pi}\begin{bmatrix} 0\\ -\langle S_{(1)}^{z(+a)}\rangle\\ \langle S_{(1)}^{y(+a)}\rangle\\ \langle S_{(1)}^{z(+a)}\rangle\\ 0\\ -\langle S_{(1)}^{x(+a)}\rangle\\ -\langle S_{(1)}^{y(+a)}\rangle\\ \langle S_{(1)}^{x(+a)}\rangle\\ 0\end{bmatrix}\ . \tag{9}$$

$G_{mn}^{+\alpha(\eta)}(E)$ is the Fourier transform of the Green's function $\langle\langle S_{(\eta)}^{m(+\alpha)}(t),\ S_{(\eta)}^{n(+\alpha)}(t')\rangle\rangle$ represented as

$$G_{mn}^{+\alpha(\eta)}(E)=\langle\langle S_{(\eta)}^{m(+\alpha)};S_{(\eta)}^{n(+\alpha)}\rangle\rangle_E\ , \tag{10}$$

$$a''=\lambda'-\mu_\alpha E_\alpha-\bar{V}_{\vec{q}}\langle Q_{\vec{q}}\rangle\ , \tag{10a}$$

$$\lambda'=\lambda(\langle S_{(2)}^{z(+a)}-S_{(2)}^{z(-a)}\rangle)\ . \tag{10b}$$

Now applying the procedure of our earlier work[21–24] one finds

$$\langle S_{(1)}^{z(\pm a)}\rangle=\mp\frac{a''}{[(a'')^2+4\Omega^2]^{1/2}}\tanh\tfrac{1}{2}\beta[(a'')^2+4\Omega^2]^{1/2}\ , \tag{11}$$

$$\langle S_{(2)}^{z(\pm a)}\rangle=\mp\frac{b''}{[(b'')^2+4\Omega^2]^{1/2}}\tanh\tfrac{1}{2}\beta[(b'')^2+4\Omega^2]^{1/2}\ , \tag{12}$$

where

$$b''=\lambda''-\mu_\alpha E_\alpha-\bar{V}_q\langle Q_q\rangle\ , \tag{12a}$$

$$\lambda''=\lambda(\langle S_{(1)}^{z(+a)}-S_{(1)}^{z(-a)}\rangle)\ . \tag{12b}$$

Defining the polarization along the a axis (transverse) as

$$P_a=N_a\mu_a(\langle S_{(1)}^{z(+a)}\rangle+\langle S_{(2)}^{z(+a)}\rangle-\langle S_{(1)}^{z(-a)}\rangle-\langle S_{(2)}^{z(-a)}\rangle)\ , \tag{13}$$

we calculate the corresponding susceptibility along the a axis from

$$\begin{aligned}\chi_a&=\left(\frac{\partial P_a}{\partial E_a}\right)_{E_a\to 0}\\ &=\frac{N\hat{a}\mu_a^2}{k_BT}\left[\frac{x^2}{(x^2+4\Omega^2)}+\frac{y^2}{(y^2+4\Omega^2)}+\frac{\tanh\frac{1}{2}\beta(x^2+4\Omega^2)^{1/2}}{(x^2+4\Omega^2)}\left(\frac{8\Omega^2k_BT}{(x^2+4\Omega^2)^{1/2}}-x^2\tanh\tfrac{1}{2}\beta(x^2+4\Omega^2)^{1/2}\right)\right.\\ &\qquad\left.+\frac{\tanh\frac{1}{2}\beta(y^2+4\Omega^2)^{1/2}}{(y^2+4\Omega^2)}\left(\frac{8\Omega^2k_BT}{(y^2+4\Omega^2)^{1/2}}-y^2\tanh\tfrac{1}{2}\beta(y^2+4\Omega^2)^{1/2}\right)\right]\ ,\end{aligned} \tag{14}$$

where

$$x=\lambda'-\bar{V}_0'\ ;\quad y=\lambda''-\bar{V}_0'\ ;\quad \bar{V}_0'=\bar{V}_{\vec{q}_0}\langle Q_{\vec{q}_0}\rangle\ . \tag{14a}$$

Similarly we get the longitudinal susceptibility along c axis having the form

$$\chi_c=\left(\frac{\partial P_c}{\partial E}\right)_{E\to 0}$$

$$=\frac{N_c\mu_c^2}{2k_BT}\left[\frac{x'^2}{(x'^2+4\Omega^2)}+\frac{\tanh\frac{1}{2}\beta(x'^2+4\Omega^2)^{1/2}}{(x'^2+4\Omega^2)}\left(\frac{8\Omega^2k_BT}{(x'^2+4\Omega^2)^{1/2}}-x'^2\tanh\tfrac{1}{2}\beta(x'^2+4\Omega^2)^{1/2}\right)\right] , \qquad (15)$$

where

$$x'=(J_0'+\gamma+\bar{V}_0')\langle S^z\rangle ,$$

$$J_0'=\sum_{j'}J_{ij} . \qquad (15a)$$

$\langle S^z\rangle$ is defined by $\langle S^z\rangle=(1/2N)\,(\sum_{i=1}^{2N}S_i^z)$. In the absence of tunneling and proton-lattice interaction terms, the above expressions for χ_a and χ_c reduce to those of our earlier calculations.[24] The longitudinal polarization has been defined as $P_c=N_c\mu_c\langle S^z\rangle$. Here we have for the ferroelectric phase $\langle S^z\rangle=1$ and for antiferroelectric phase

$$\langle S_{(1)}^{z(+\alpha)}-S_{(1)}^{z(-\alpha)}\rangle=-\langle S_{(2)}^{z(+\alpha)}-S_{(2)}^{z(-\alpha)}\rangle=2$$

similar to that considered by HLS. It is to be noticed that the expressions for χ_a and χ_c are quite different from those derived by HLS though we used a similar type of Hamiltonian for our calculations with Green's function. This is due to the fact that a different mathematical procedure was used by HLS. They (HLS) also modified the Hamiltonian into a more simplified form.

IV. DYNAMIC BEHAVIOR

A. Energy spectrum

It was pointed out by Cochran[29] that the antiferroelectric transition is due to a zone-boundary temperature-dependent mode which becomes unstable before the ferroelectric mode. We have observed this fact from our calculations as would be discussed below. The antiferroelectric mode should occur at the z point $[\vec{q}=(2\pi/c)c^*]$ in ADP, while in KDP it is at the zone center $(\vec{q}=0)$. To study the characteristic dynamic behavior we transform the pseudospin operator such that

$$S_{\vec{q}}^z=\sum_i S_i^z\exp(i\vec{q}\cdot\vec{r}_i) ,$$

$$J_{\vec{q}}=\sum_{ij}J_{ij}\exp[i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)] .$$

In the present case the required equations of motion can also be written by the matrix equation

$$MG=\bar{S} , \qquad (16)$$

where

$$M=\begin{bmatrix}
\omega & -iA_{\vec{q}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
iA_{\vec{q}} & \omega & -i2\Omega & 0 & 0 & 0 & 0 & 0 & 0 & iV'S' & 0\\
0 & i2\Omega & \omega & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & \omega & iA_{\vec{q}} & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & -iA_{\vec{q}} & \omega & i2\Omega & 0 & 0 & 0 & -iV'S'' & 0\\
0 & 0 & 0 & 0 & -i2\Omega & \omega & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & \omega & -iB_{\vec{q}} & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & iB_{\vec{q}} & \omega & -i2\overline{\Omega} & iV'S & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & i2\Omega & \omega & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \omega & -i\\
0 & 0 & -iV' & 0 & 0 & iV' & 0 & 0 & -iV' & i\omega_{\vec{q}}^2 & \omega
\end{bmatrix} , \qquad (16a)$$

$$G=\begin{bmatrix} G^{xQ(+\alpha)}_{\vec{q}(\eta)} \\ G^{yQ(+\alpha)}_{\vec{q}(\eta)} \\ G^{zQ(+\alpha)}_{\vec{q}(\eta)} \\ G^{xQ(-\alpha)}_{\vec{q}(\eta)} \\ G^{yQ(-\alpha)}_{\vec{q}(\eta)} \\ G^{zQ(-\alpha)}_{\vec{q}(\eta)} \\ G^{xQ}_{\vec{q}} \\ G^{yQ}_{\vec{q}} \\ G^{zQ}_{\vec{q}} \\ G^{QQ}_{\vec{q}} \\ G^{PQ}_{\vec{q}} \end{bmatrix} , \tag{16b}$$

$$\bar{S}=\frac{i}{2\pi}\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \end{bmatrix} . \tag{16c}$$

Similar matrix equation is obtained for the other set of equations of motion which can be written

$$MG'=S^* , \tag{17}$$

where

$$G'=\begin{bmatrix} G^{xz(+\alpha)}_{\vec{q}(\eta)} \\ G^{yz(+\alpha)}_{\vec{q}(\eta)} \\ G^{zz(+\alpha)}_{\vec{q}(\eta)} \\ G^{xz(-\alpha)}_{\vec{q}(\eta)} \\ G^{yz(-\alpha)}_{\vec{q}(\eta)} \\ G^{zz(-\alpha)}_{\vec{q}(\eta)} \\ G^{xz}_{\vec{q}} \\ G^{yz}_{\vec{q}} \\ G^{zz}_{\vec{q}} \\ G^{Qz}_{\vec{q}} \\ G^{Pz}_{\vec{q}} \end{bmatrix} , \tag{17a}$$

$$S^*=\frac{i}{2\pi}\begin{bmatrix} \langle S^{yQ(+\alpha)}_{\vec{q}(\eta)}\rangle \\ \langle S^{xQ(+\alpha)}_{\vec{q}(\eta)}\rangle \\ 0 \\ -\langle S^{yQ(-\alpha)}_{\vec{q}(\eta)}\rangle \\ \langle S^{xQ(-\alpha)}_{\vec{q}(\eta)}\rangle \\ 0 \\ -\langle S^{yQ}_{\vec{q}}\rangle \\ \langle S^{xQ}_{\vec{q}}\rangle \\ 0 \\ 0 \\ 0 \end{bmatrix} , \tag{17b}$$

$$\begin{aligned} A_{\vec{q}} &= \mu_\alpha E_\alpha-\lambda'+\bar{V}_{\vec{q}}\langle Q_{\vec{q}}\rangle , \\ B_{\vec{q}} &= (J_{\vec{q}}+\gamma_{\vec{q}})\langle S^{z}_{\vec{q}}\rangle+\mu_c E_c+\bar{V}_{\vec{q}}\langle Q_{\vec{q}}\rangle , \\ 2\bar{\Omega} &= 2\Omega-(J_{\vec{q}}+\gamma_{\vec{q}})\langle S^{x}_{\vec{q}}\rangle , \\ S' &= \langle S^{x(+\alpha)}_{\vec{q}(\eta)}\rangle ;\ \ S''=\langle S^{x(-\alpha)}_{\vec{q}(\eta)}\rangle ;\ \ S=\langle S^{x}_{\vec{q}}\rangle . \end{aligned} \tag{17c}$$

All the Green's functions and the corresponding correlation functions can be obtained from (16) and (17). The energy spectrum given by the solution of the secular determinant $|M|=0$ has the form

$$\omega_{\rm I}^3=0 , \tag{18a}$$

$$\omega_{\rm II}^2=B^2_{\vec{q}}+2\Omega[2\Omega-(J_{\vec{q}}+\gamma_{\vec{q}})\langle S^{x}_{\vec{q}}\rangle] , \tag{18b}$$

$$\omega_{\rm III}^2=\tfrac{1}{2}\{(\omega^2_{\vec{q}}+\bar{B}^2_{\vec{q}})\mp[(\omega^2_{\vec{q}}-\bar{B}^2_{\vec{q}})^2+\bar{y}^2]^{1/2}\} , \tag{18c}$$

where

$$\begin{aligned} \bar{y}^2 &= \frac{16\Omega^2\bar{V}^2_{\vec{q}}}{\alpha_{\vec{q}}}\left(\frac{\alpha_{\vec{q}}}{B'_{\vec{q}}}\tanh\tfrac{1}{2}\beta B'_{\vec{q}}+\frac{8}{\bar{A}_{\vec{q}}}\tanh\tfrac{1}{2}\beta\bar{A}_{\vec{q}}\right) , \\ \alpha_{\vec{q}} &= (\omega^2_{\rm III}-\bar{A}^2_{\vec{q}})/(\omega^2_{\rm III}-\bar{B}^2_{\vec{q}}) , \\ \bar{A}^2_{\vec{q}} &= A^2_{\vec{q}}+4\Omega^2 , \\ \bar{B}^2_{\vec{q}} &= B^2_{\vec{q}}+2\Omega[2\Omega-(J_{\vec{q}}+\gamma_{\vec{q}})\langle S^{x}_{\vec{q}}\rangle] , \\ B'^2_{\vec{q}} &= B^2_{\vec{q}}+4\Omega^2 . \end{aligned} \tag{18d}$$

The required expressions for the thermal averages $\langle S^{x(\pm\alpha)}_{\vec{q}(\eta)}\rangle$ and $\langle S^{x}_{\vec{q}}\rangle$ calculated have the following forms:

$$\langle S^{x(+a)}_{\vec{q}(1)} \rangle = \langle S^{x(+a)}_{\vec{q}(2)} \rangle = \langle S^{x(+b)}_{\vec{q}(1)} \rangle = \langle S^{x(+b)}_{\vec{q}(2)} \rangle = \frac{2\Omega}{\bar{A}_{\vec{q}}} \tanh\tfrac{1}{2}\beta \bar{A}_{\vec{q}} \ , \tag{18e}$$

$$\langle S^{x(-a)}_{\vec{q}(1)} \rangle = \langle S^{x(-a)}_{\vec{q}(2)} \rangle = \langle S^{x(-b)}_{\vec{q}(1)} \rangle = \langle S^{x(-b)}_{\vec{q}(2)} \rangle = -\frac{2\Omega}{\bar{A}_{\vec{q}}} \tanh\tfrac{1}{2}\beta \bar{A}_{\vec{q}} \ , \tag{18f}$$

$$\langle S^{x}_{\vec{q}} \rangle = \frac{2\Omega}{B'_{\vec{q}}} \tanh\tfrac{1}{2}\beta B'_{\vec{q}} \ . \tag{18g}$$

The existence of both the B_2- and E-symmetry Raman-active proton modes which interact with like symmetry lattice mode were reported by Ryan, Katiyar, and Taylor[30] and also by Broberg *et al.*[8] It is evident from (18b) that the behavior of even the B_2 mode in ADP (having soft-mode character[10,14] as in KDP) is much more complicated than that of the KDP system. It is also clear that the analysis due to Broberg *et al.*,[8] following the procedure of Ryan *et al.*[30] as mentioned earlier is nothing but an oversimplification for the case of the ADP crystal. Furthermore, the soft-mode behavior in ADP as reported by Meister *et al.*[19] has a very complicated behavior. The dispersion relation ω_{II}^2 in (18b) gives rise to the Tokunaga and Matsubara[31] frequency, namely,

$$\omega_{\mathrm{II}}^2 = 2\Omega[2\Omega - (J_{\vec{q}} + \gamma_{\vec{q}})\langle S^x \rangle] \ . \tag{19}$$

Expanding (19) around $(T - T_C)$ we have

$$\omega_{\mathrm{II}}^2(\vec{q}_0) = \lambda(\vec{q}_0)(T - T_C)/T_C \ , \tag{19a}$$

with

$$\lambda(\vec{q}_0) = \frac{\Omega^2}{4} \frac{J(\vec{q}_0)}{k_B T_C} \frac{1}{\cosh^2 \frac{1}{2}\beta_c \Omega} \tag{19b}$$

and $\beta_c = 1/k_B T_C$. For small values of $\vec{q}$ and $J_{\vec{q}}$, $\omega_{\mathrm{II}}^2(\vec{q})$ can also be expanded in the reciprocal-lattice space at the Brillouin zone boundary $(\vec{q} = \vec{q}_0 = \vec{q}_{\mathrm{BZB}})$, we find (for cubic lattice)

$$\omega_{\mathrm{II}}^2(\vec{q}) = \lambda(\vec{q}_0)\frac{T - T_C}{T_C} + P[(q_x - q_{x,0})^2 + (q_y - q_{y,0})^2 + (q_z - q_{z,0})^2] + \cdots \ . \tag{19c}$$

This shows an antiferroelectric soft-mode character at the low-temperature phase, which was also shown by Meister *et al.*[19] from inelastic neutron-diffraction studies. Following KDP, we may ascribe this mode ω_{II}^2 as the B_2 mode.

Using (18b) and (19a)–(19c) the inelastic scattering cross section for the overdamped normal mode in the present case can be written

$$\frac{d^2\sigma}{d\Omega\, d\omega} \propto |F(\vec{Q})|^2 \frac{k_B T}{(T - T_0) + f(\Delta\vec{q})^2} \frac{\frac{1}{2}\gamma}{\omega^2 + (\frac{1}{2}\gamma)^2} \ , \tag{20}$$

which is identical to that derived by Meister *et al.*[19] $|F(\vec{Q})|$ is the inelastic scattering factor and Γ is the damping constant with the quasielastic energy broadening $\gamma = 2\omega_{\mathrm{II}}^2/\Gamma$. The temperature dependence of $f(\Delta\vec{q})$ has the form

$$f(\Delta\vec{q})^2 \approx (T - T_0)G(\Delta\vec{q})^2 \ .$$

Since the curvature of the ω_{II}-dispersion curve at the z point decreases as the transition temperature is approached, $G(\Delta\vec{q})$ should be independent of temperature. To fit the intensity profile, Meister *et al.*[19] showed that

$$f(\Delta\vec{q})^2 = (T - T_0)(\Delta\vec{q}\cdot\bar{\mathrm{A}}\cdot\Delta\vec{q} + \cdots)$$

having $A_{xx} \approx 16 A_{zz}$ and $A_{zz} = 0$. This characteristic of the AFE mode indicates that the polarization fluctuations are strong within the ab plane in contrast to the critical scattering due to the ferroelectric mode in KDP where the polarization fluctuation[32] is parallel to the c axis.

It also appears from (18c) that ω_{III}^2 should vanish at $\vec{q} \approx \vec{q}_0$ (say) when

$$\bar{B}^2_{\vec{q}}\,\omega^2_{\vec{q}_0} = \frac{4\bar{V}^2_{\vec{q}}\,\Omega^2}{\alpha_{\vec{q}_0}} \left(\frac{\alpha_{\vec{q}_0}}{B'_{\vec{q}_0}} \tanh\tfrac{1}{2}\beta_c B'_{\vec{q}_0} + \frac{8}{\bar{A}_{\vec{q}_0}} \tanh\tfrac{1}{2}\beta_c \bar{A}_{\vec{q}_0} \right) \ . \tag{21}$$

But due to the presence of $\alpha_{\vec{q}}$ as defined in (18d) the condition (21) should not be strictly satisfied for showing a proper soft-mode character. This mode is a hard antiferroelectric mode. However, it might be pseudosoft as it is coupled with the soft B_2 mode. We call this ω_{III} mode pseudosoft since this mode does not vanish at T_C but may show a minimum around T_C as in the case of the E mode observed in the KDP crystal. The "cusp"-like singularity of the transverse susceptibility[14] versus temperature curves in both KDP and probably in ADP (not yet observed) are due to this pseudosoft nature of the E mode associated with ω_{III}^2. Detailed Raman spectroscopic studies in the low-frequency range might be very interesting to elucidate this behavior of ADP crystal.

B. Calculation of susceptibility from dynamic Green's functions

Similar to the case studied[21] in KDP one may find the expression for the longitudinal susceptibility along the c axis calculated from the Green's function $\langle\langle Q_{\vec{q}} | Q_{-\vec{q}} \rangle\rangle$ having the form

$$\chi_c(\omega=0, \vec{q}=\vec{q}_0) = \frac{n\mu_c^2}{v_0} \left(\omega^2_{\vec{q}_0} - \frac{2\bar{V}^2_{\vec{q}_0}\Omega y}{\bar{B}^2_{\vec{q}_0}\alpha'_{\vec{q}_0}} \right)^{-1} , \qquad (22)$$

where

$$\alpha'_{\vec{q}_0} = \bar{A}^2_{\vec{q}_0} / \bar{B}^2_{\vec{q}_0} ,$$

$$\bar{A}^2_{\vec{q}_0} = A^2_{\vec{q}_0} + 4\Omega^2; \quad A_{\vec{q}_0} = (A_{\vec{q}})_{\vec{q}=\vec{q}_0} ,$$

$$B_{\vec{q}_0} = (B_{\vec{q}})_{\vec{q}=\vec{q}_0} ,$$

$$\bar{B}^2_{\vec{q}_0} = B^2_{\vec{q}_0} + 2\Omega[2\Omega - (J_{\vec{q}_0} + \gamma_{\vec{q}_0})\langle S^x_{\vec{q}_0} \rangle] ,$$

$$y = \sum_{\alpha,y} (\alpha_{\vec{q}_0} \langle S^x_{\vec{q}_0} \rangle + \langle S^{x(+\alpha)}_{\vec{q}_0(\delta)} \rangle - \langle S^{x(-\alpha)}_{\vec{q}_0(\delta)} \rangle) ,$$

and

$$\mu_c = \epsilon_0^* l_c .$$

(ϵ_0^* is the effective charge, l_c being the distance between the double-well potential minima at the H bond.) n is the number of pseudospins per unit volume and v_0 is the volume of the unit cell. In the above expressions for $A_{\vec{q}_0}$ and $B_{\vec{q}_0}$ we have put the fields $E_a = E_c = 0$. Following the procedure of our earlier paper for the calculation of transverse susceptibility of KDP crystal,[14] the corresponding expressions for ADP crystals can be derived. The final result[33] comes out to be of the form

$$\chi_a(\omega=0, q=q_0) = \frac{n\mu_a^2}{v_0} \left(\frac{2\Omega\langle S^x_{\vec{q}_0} \rangle y_a}{\bar{B}^2_{\vec{q}_0}(\alpha_{\vec{q}_0}\omega^2_{\vec{q}_0}\bar{B}^2_{\vec{q}_0} - 2\Omega\bar{V}^2_{\vec{q}_0} y)} \right) , \qquad (23)$$

where

$$y_a = \alpha_{\vec{q}_0}\omega^2_{\vec{q}_0}\bar{B}^2_{\vec{q}_0} + 4\Omega\bar{V}^2_{\vec{q}_0}\langle S^{x(-\alpha)}_{\vec{q}_0(\delta)} \rangle . \qquad (23a)$$

It is observed from (23) that the expression for χ_a in ADP is very complicated compared to that of KDP [see Eq. (9b) of Ref. 14]. But the interesting point is that both the equations give identical results to be discussed in Sec. V. The lattice-coupling term in (23) having the form [using (3)]

$$\sum_{\vec{q}} \bar{V}_{\vec{q}} \langle Q_{\vec{q}} \rangle = \frac{1}{N} \bar{V}^2_{\vec{q}=0} \langle Q_{\vec{q}_0} \rangle^2 + \frac{1}{N} \sum_{\vec{q}} \bar{V}_{\vec{q}} \langle \bar{Q}_{\vec{q}} \rangle \qquad (24)$$

has a very important role on the behavior of χ_a. The first term on the right-hand side of (24) might be considered to be arising from the proton-lattice interaction of spontaneous distortion (or polarization). Thus if polarization appears abruptly, as occurs in KDP[34] as well as in ADP[35] (reported recently) the reduction in the susceptibility $\chi_a(0,T)$ at T_C should also occur abruptly. The second term of (24), on the other hand, is a consequence of the softening of the lattice due to the presence of soft mode. This term is very important around T_C to reduce the value of $\chi_a(0,T)$ as observed experimentally[36,37] in KDP or in similar other crystal systems.

V. RESULTS AND DISCUSSION

Equations (14) and (15) are used to fit the experimental[1,36] values of transverse (χ_a) and longitudinal (χ_c) susceptibilities of ADP, DADP, and ADA crystals. The single set of model parameters, being different for the respective salts, are shown in Table I. For all the three crystals we find a very good fit of the experimental data[1,36] (within 1%) with the respective theoretical expressions for χ_a and χ_c as shown in Fig. 2. The fits of the experimental data[1,36] with $\Omega \neq 0$ and $\bar{V}_{\vec{q}_0} \neq 0$ seems to be better than those obtained[24] with $\Omega = 0$ and $\bar{V}_{\vec{q}_0} = 0$, which points out the importance of tunneling as well as proton-lattice interaction. From Fig. 2 we also find that in case of transverse susceptibility (χ_a) of ADA only, the fit is not good in the high-temperature region though very good fittings are obtained in other salts. This might be due to the inaccuracy of the experimental data which was also pointed out by HLS. Another interesting characteristic we notice from the data of Table I is that the value of λ in ADA is much larger than that of ADP and DADP. That is, the transverse long-range interaction is very strong in ADA compared to other salts of its group. This resembles to the behavior of KDP. The value of direct exchange J' in ADA also seems to be larger than the corresponding values of ADP and DADP (if we put $\gamma = 0$, since γ cannot be obtained separately from our calculations). However, the value of J' is about two times larger than λ for all the three salts. In other words, the short-range interaction associated with J' (since J' is related to the short-range energy ϵ_0) is found to be larger than the transverse long-range interaction λ. Here we should note that in KDP the long-range ordering interaction is small compared to the short-range energy. The value of proton-lattice interaction $\bar{V}_{\vec{q}}$ is also large in ADA though it is comparable to the values of ADP anad DADP. Ω is larger in ADP (≈ 20 cm^{-1}) but comparable to that of ADA (≈ 15 cm^{-1}). This value of Ω is much smaller than that of KDP (≈ 80 cm^{-1}).[38] Thus the behavior of ADP is more contradictory to that of the KDP crystal than that of the ADA crystal. This difference in the characteristics of ADP and ADA might also be responsible for the positive value of ϵ_0 in ADA with

TABLE I. Pseudo-spin-model parameters for ADP, DADP, and ADA crystals calculated from our theory.

Crystal	T_C (K)	$N_a/k_B(10^{-36})$ (cm K)	λ/k_B (K)	Ω/k_B (K)	$\bar{V}'/k_B$ (K)	$N_c/k_B(10^{-36})$ (cm K)	$(J'+\gamma)/k_B$ (K)	$(10^{18})\mu_a$	$(10^{18})\mu_c$
$NH_4H_2PO_4$ (ADP)	148	78.33	70.00	20.00	20.00	31.26	140.00	2.95	4.70
$ND_4D_2PO_4$ (DADP)	242	78.00	73.00	5.00	25.00	31.26	155.66	3.40	5.90
$NH_4H_2AsO_4$ (ADA)	216	77.61	100.60	15.00	30.00	39.71	205.50	4.50	3.70

the corresponding negative values in the cases of ADP and DADP. This finding is also in agreement with the observation of Ishibashi *et al.*[39] who showed that a strong dipolar interaction along the *a* or *b* axis can make an energetically stable AFE configuration as long as a critical positive ϵ_1 is not exceeded.

To show the analogy between the transverse dielectric behavior of both ADP and KDP, we have also fitted the experimental values of the transverse susceptibilities of the two undeuterated salts ADP and ADA with expression (23) calculated from dynamic Green's functions. Here also very good fits of the experimental data (χ_a) of ADA and ADP are obtained with the sets of parameters shown in Table II. The values of $\omega_{\vec{q}_0}$ calculated are 153 and 110 cm^{-1}, respectively, for ADP and ADA. Compared to KDP (where $\omega_{\vec{q}_0}$ was found to be ≈ 150 cm^{-1}) the corresponding values of $\omega_{\vec{q}_0}$ for ADP and ADA are of equal magnitudes but it is slightly smaller in case of ADA. Here also we find that the value of $J'+\gamma$ is much larger in ADA compared to that of ADP (Table II). However, owing to lack of experimental data (particularly Raman spectroscopic data) we cannot compare our calculated results. It is interesting to note that the transverse susceptibility data[36] of KDP are also found to be fitted well with (23) (see Table III). The experimental and the theoretically calculated values of transverse susceptibilities of KDP with a single set of parameters are shown in Fig. 3.

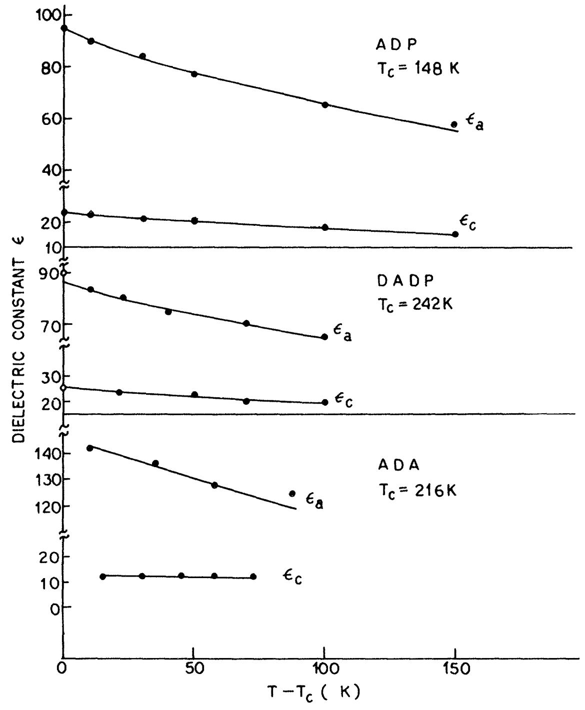

FIG. 2. Thermal variations of transverse (ϵ_a) and longitudinal (ϵ_c) dielectric constants of ADP, DADP, and ADA. ● — experimental (Refs. 1 and 36), continuous line — theoretical.

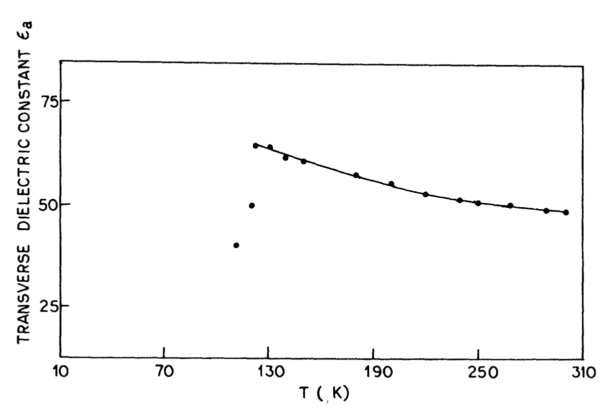

FIG. 3. Thermal variations of transverse dielectric constants (ϵ_a) of KDP, ● — experimental (Ref. 36), continuous line — theoretical, calculated with Eq. (23).

TABLE II. The pseudo-spin-lattice-coupled mode model parameters obtained from fitting of the transverse susceptibility data of ADP and ADA with Eq. (23). The experimental (Refs. 1 and 36) and theoretically calculated values of $(\chi_a)_T/(\chi_a)_{T_c}$ are also shown.

ADP			ADA		
$(J'+\gamma)/k_B=258.99$ K, $\Omega/k_B=20.00$ K $\lambda/k_B=70.00$ K; $\bar{V}/k_B=20.00$ K $\omega^2_{\vec{q}_0}=153.00\ \mathrm{cm}^{-1}$			$(J'+\gamma)/k_B=431.64$ K; $\Omega/k_B=15.00$ K $\lambda/k_B=100.72$ K; $\bar{V}/k_B=28.78$ K $\omega^2_{\vec{q}_0}=110.00\ \mathrm{cm}^{-1}$		
Temperature T (K)	$(\chi_a)_T/(\chi_a)_{T_C}$ Calc.	$(\chi_a)_T/(\chi_a)_{T_C}$ Expt.	Temperature T (K)	$(\chi_a)_T/(\chi_a)_{T_C}$ Calc.	$(\chi_a)_T/(\chi_a)_{T_C}$ Expt.
158	0.96	0.95	303.5	0.83	0.87
178	0.88	0.88	273.5	0.88	0.89
198	0.81	0.81	251.0	0.94	0.95
248	0.68	0.68			
298	0.58	0.60			

Thus the ADP model is also equally suitable for describing the transverse susceptibility of the KDP crystal. In the PE phase, according to (23), $\chi_a(0,T)$ increases as temperature decreases. Experimental values[1,36] of $\chi_a(0,T)$ both for KDP and ADP also behave in this way. At the transition point $\chi_a(0,T)$ begins to fall sharply (not observed in the case of ADP; but sublattice polarization is found to fall sharply[35]) caused by the first term on the right-hand side of (24). This term does not vanish as the phase transition takes place in the phonon sublattice.

TABLE III. Pseudospin model parameters obtained from fitting of the experimental transverse susceptibility (χ_a) data (Ref. 36) of KDP with Eq. (23) derived from the ADP model.

$(J'+\gamma)/k_B$ (K)	Ω/k_B (K)	λ/k_B (K)	$\bar{V}/k_B$ (K)	$\omega^2_{\vec{q}_0}$ (cm^{-1})
489.19	115.11	244.60	36.83	150.00

VI. CONCLUSION

We have shown using a statistical Green's-function technique with a four-sublattice cluster model that very good fits of the experimental dielectric constant data of ADP, DADP, and ADA crystals are possible with a single set of Blinc–de Gennes model parameters. Calculations of the dynamic correlation functions and renormalized energy spectrum indicate that the energy spectrum is more complicated than those derived by Broberg *et al.*[8] In the phonon subsystem two complex proton-phonon vibrational branches appear in both the systems (KDP and ADP), one of which is the usual soft mode (B_2 mode like) and the other is the pseudosoft mode (E mode like) which is hard. The latter mode is primarily responsible for the thermal dependences of χ_a in both types of crystals. The analysis of the E mode (18c) is found to be extremely difficult in the case of ADP. This mode is strongly coupled to the B_2 mode. This strong coupling might also be responsible for the pseudosoft character of the E mode. Again, since the phase transition produced probably by softness of the prominent phonon-proton mode at the zone boundary (in the case of ADP) occurs earlier, the pseudosoft mode is not allowed to reduce to zero value. The dispersion energy $\omega^2_{\rm III}$ decreases slowly as $T \rightarrow T_C$ from above and then it increases (without going to zero) similar to the behavior observed in case of KDP.[14]

In the case of KDP the minimum value of this mode was observed[10] to be $\approx 80\ \mathrm{cm}^{-1}$. It has not been possible to calculate this value for ADP because of very complicated nature of ω_{III}^2. The behavior of the transverse susceptibility should reflect that of ω_{III}^2. This has already been verified in the case of the KDP crystal.[14] It has also been shown that the ADP model described in Sec. I can also be used satisfactorily for the study of the transverse dielectric behavior of the KDP crystal. Thus one can fervently recommend a unified model for studying the static as well as the dynamic behavior of the transverse dielectric constants of the KDP- and the ADP-type crystals.

Finally, we would like to conclude that our present Green's-function theory with four sublattice pseudospin model might also be extended with a little modification to enlighten the phase-transition mechanism in layer structural compounds like squaric acid, tin chloride dihydrate, copper formate tetrahydrate, and other similar crystals.

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[33] Here it is to be remembered that the dielectric susceptibility measured along the *a* axis corresponds to the dielectric susceptibility of proton subsystem and hence the transverse susceptibility $\chi_a(\omega_{\vec{q}}, \vec{q})$ is related to the Green's function (Refs. 14 and 15) $\langle\langle S^z_{\vec{q},\sigma} | S^z_{-\vec{q},\sigma} \rangle\rangle$ which is obtained from (17) in the usual way (Refs. 21–24).

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