Phase Transition Dielectric Properties in Order-disorder Antiferroelectric NH4(H2PO4) (ADP) Crystal

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Phase transition dielectric properties in order-disorder antiferroelectric $\text{NH}_4(\text{H}_2\text{PO}_4)$ (ADP) crystal

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ABSTRACT

A modified four sublattice pseudospin lattice coupled model Hamiltonian by adding extra spin-lattice interaction, direct spin-spin interaction has been used to study dielectric properties for ammonium dihydrogen phosphate (ADP) crystal. Using the double-time temperature-dependent Green's function method, the expressions for soft mode frequency, dielectric permittivity and loss tangent have been derived. By fitting the model values of various physical parameters, the thermal variations of the above quantities are calculated and compared with the experimental results. Our theoretical obtained results are in good agreement with experimental data.

Introduction

Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, abbreviated as ADP) crystal was first reported by Busch in 1937$^1$. Ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) crystal belongs to the family of isomorphous H-bonded ferroelectrics of the potassium dihydrogen phosphate (KDP)-type. Generally, ammonium dihydrogen phosphate (ADP), ammonium dihydrogen arsenate (ADA) and their deuterated forms belong to the ADP-type antiferroelectrics$^2$. ADP undergoes a phase transition from paraelectric (PE) to antiferroelectric phase (AFE) at Curie temperature ($T_c = 148K$). ADP has been extensively studied due to its potential applications in electro-optics, optoelectronics, transducers and display devices etc. Hydrogen bonds play a dominant role in determining the properties of these crystals. It is found that hydrogen bonds that are part of a three-dimensional network show enhanced dielectric properties and temperature dependence properties$^3$. The room temperature of $\text{NH}_4\text{H}_2\text{PO}_4$ is isomorphous with potassium dihydrogen phosphate. Above the Curie temperature ($T_c = 148K$) $\text{NH}_4\text{H}_2\text{PO}_4$ belongs to the tetragonal crystal structure in paraelectric phase (I) with space group $142d$ or $D_4d^2$. It lacks a centre of inversion and exhibits a linear electro-optic effect. Below the Curie temperature, $\text{NH}_4\text{H}_2\text{PO}_4$ belongs to the orthorhombic crystal structure in antiferroelectric phase (II) with space group $P2_12_12_1$ or $D_{2d}^5$. Ammonium dihydrogen phosphate undergoes a transition at 148K to an antiferroelectric state, the antiferroelectric axes being parallel to the a-axis of the room temperature tetragonal (paraelectric) phase. The $(\text{H}_2\text{PO}_4)^{-1}$ network in which each phosphate group is linked by O-H–O bonds to a tetrahedral arrangement of phosphate group neighbours. The lattice parameters in the antiferroelectric phase (II) are $a = b = 7.473 (1)\text{Å}$ and $c = 7.551 (2)\text{Å}$ at 152K$^6$. The lattice parameters in the paraelectric phase (I) are $a = 7.526 (1)\text{Å}$, $b = 7.551 (1)\text{Å}$ and $c = 7.464 (1)\text{Å}$.$^7$ A large isotope shift in transition temperature from 148K to 242K occurs in ammonium dihydrogen phosphate when deuterated. This indicates that the tunnelling effect as in the KDP crystal in ADP is important. In $\text{NH}_4\text{H}_2\text{PO}_4$, below Curie temperature ($T_c$) protons are ordered, which produce an antiparallel arrangement of electric dipoles in an a-axis direction. The ordered $\text{NH}_4\text{H}_2\text{PO}_4$ has one upper and one lower site for an arbitrary $\text{H}_2\text{PO}_4$ group filled. These positions are taken up to produce a perfectly ordered arrangement of bonds in an antiferroelectric pattern. Kasturi and Moran$^8$ have studied the antiferroelectric ammonium dihydrogen phosphate crystal by pulsed NMR over a temperature range from 315K to 74K. Havlin et al.$^9$ have investigated the dielectric properties of antiferroelectric ADP-type crystals by using an extended pseudospin model. Banerjee et al.$^{10}$ have studied Green’s function theory in antiferroelectric ADP-type crystals with a pseudospin model. Kim et al.$^{11}$ have studied the dielectric behaviour at various purity concentrations ADP and KDA of potassium dihydrogen phosphate crystals. Brehat et al.$^{12}$ have studied the far-infrared spectra of ammonium dihydrogen phosphate crystal in the paraelectric and antiferroelectric phases in the temperature range 7K to 300K. Kim and Sherman$^{13}$ have studied the Raman spectra on potassium- ammonium dihydrogen phosphate systems at room temperature and liquid-nitrogen temperature. Chandra
and Hashmi\textsuperscript{14} have carried out the proton transport mechanism in ammonium dihydrogen phosphate single crystal. Kader et al.\textsuperscript{15} have studied the thermal behaviour of ammonium dihydrogen phosphate single crystals in the temperature range of 298\textdegree{}K to 873\textdegree{}K. Ravi et al.\textsuperscript{16} have studied the growth and characterization of sulphated mixed L-arginine phosphate and ammonium/potassium dihydrogen phosphate crystals at room temperature. Kanesaka and Watanabe\textsuperscript{17} have studied the normal coordinate analysis and structure of ammonium dihydrogen phosphate crystal at room temperature. Peres et al.\textsuperscript{18} have studied the X-ray and neutron diffraction of ammonium dihydrogen phosphate single crystal. Gunming et al.\textsuperscript{19} have studied the magnitude and nature of the quadratic electro-optic effect in potassium dihydrogen and ammonium dihydrogen phosphate crystals. Moattar and Gasemi\textsuperscript{20} have determined the phase diagrams and liquid-liquid equilibrium of aqueous two-phase systems containing polyethylene glycol and ammonium dihydrogen phosphate. Chen et al.\textsuperscript{21} have studied the phase transition, electrical conductivity and dielectric relaxation in $NH_4(H_2PO_4)$ single crystal at a high-temperature range. Xue and Ratajczak\textsuperscript{22} have studied the effect of H-bonds on the physical properties of ammonium dihydrogen phosphate single crystals. Rajesh and Ramasamy\textsuperscript{23} have studied the effect of oxalic acid on the optical, thermal, dielectric and mechanical behaviour of $NH_4(H_2PO_4)$ single crystals. Upadhyay\textsuperscript{24} studied the thermal dependence of microwave loss in $NH_4(H_2PO_4)$ crystal.

Rajesh et al.\textsuperscript{25} have studied the effect of $Ni^{2+}$ ion on the structural, optical, thermal and dielectric properties of ADP single crystals by a slow evaporation method. Chaki et al.\textsuperscript{26} studied the growth and characterization of ammonium dihydrogen phosphate single crystal grown by gel method. Jegatheesan et al.\textsuperscript{27} have studied the FTIR, XRD, SEM and TGA investigations of ADP single crystal. Upadhyay and Joshi\textsuperscript{28} have studied the thermal dependence of antiferroelectric ammonium dihydrogen phosphate crystal in the presence of electric field. Zion et al.\textsuperscript{29} have studied the dielectric and optical characterization of pure and boron-doped $NH_4(H_2PO_4)$ single crystals. Hasmuddin et al.\textsuperscript{30} have studied the structural, spectroscopic, optical, dielectric and mechanical properties of pure and L-proline doped ADP single crystals by slow evaporation solution method. Shaikh et al.\textsuperscript{31} have studied the optical properties of L-valine doped ammonium dihydrogen phosphate crystal by slow evaporation method at room temperature. Goel et al.\textsuperscript{32} have studied the effect of pure and crystal violet dye-doped on the structural, optical, mechanical and piezoelectric properties of ADP single crystal. Shaikh et al.\textsuperscript{33} have investigated the fluorescence, third-order non-linear optical and mechanical properties of glycine doped ADP single crystal by a slow solution evaporation method. Shetty et al.\textsuperscript{34} have studied the effect of gamma and neutron irradiation on structural and optical properties of ADP single crystals by slow evaporation growth method. Anis et al.\textsuperscript{35} have studied the pure and influence of $Ni^{2+}$ ion-doped on optical and dielectric properties of ADP single crystal. Joshi et al.\textsuperscript{36} have studied the growth and non-linear properties of pure and $Sr^{2+}$ ion-doped ammonium dihydrogen phosphate single crystal. Bharati et al.\textsuperscript{37} have studied the dielectric properties of ammonium dihydrogen phosphate single crystals. Baig et al.\textsuperscript{38} have studied the pure and $Zn^{2+}$ ion-doped on structural, optical and dielectric properties of ammonium dihydrogen phosphate single crystals. Fernandes et al.\textsuperscript{39} have studied the structural, optical, mechanical, electrical and non-linear properties of pure and doped ADP single crystals. Thejashwini et al.\textsuperscript{40} have studied the crystal growth and effect of defects on the dielectric properties of ADP single crystals by a slow evaporation method.

Earlier authors\textsuperscript{9} using mean-field approximation and some authors\textsuperscript{10,24,28} using Green’s function theory have studied the antiferroelectric transition and dielectric properties of $NH_4(H_2PO_4)$-type crystals. Many authors\textsuperscript{3,4} have experimentally investigated the dielectric properties of these crystals. The theory was developed to explain the ferroelectric transitions in displacive\textsuperscript{41} and order-disorder\textsuperscript{42} type crystals. In this paper, we have considered a four sublattice pseudospin lattice coupled-mode model Hamiltonian by adding anharmonic phonon interactions, extra spin-lattice interactions, and direct spin-spin interaction has been used to obtain the theoretical expressions for the shift, width, soft mode frequency, dielectric constant and loss tangent. The method of double-time temperature-dependent Green’s function\textsuperscript{43} has been used for the calculation. By fitting the model values of various physical parameters appearing in the theoretical expressions obtained for ammonium dihydrogen phosphate crystal, the thermal dependence of soft mode frequency, dielectric constant and loss tangent have been calculated. Our theoretical obtained results are well compared with experimental data reports by Kaminow\textsuperscript{3} for ammonium dihydrogen phosphate crystal.

1 Model Hamiltonian

The theoretical analysis of antiferroelectric ammonium dihydrogen phosphate crystal is based on a pseudospin model. This model incorporates both a transverse long-range dipole-dipole antiferroelectric interaction, an interaction between the transverse dipoles and an applied transverse field. Besides this we have added the phonon anharmonic interactions, extra spin-lattice interactions and direct spin-spin interaction into the model. The inclusion of a transverse long-range dipole-dipole interaction is
accomplished by introducing four sublattice pseudospin lattice coupled mode model Hamiltonian expressed as

\[
H_1 = -\frac{1}{2} \sum_{ij} J_{ij} S_i^j S_j^i - \mu_c E_c \sum_i S_i^c - \gamma Z \sum_i S_i^z - \sum_{ik} V_{ik} S_i^k A_k
\]

\[
- \sum_{\alpha = a, b} \sum_{\eta = 1, 2} \left( \mu_\alpha E_\alpha - \frac{1}{2} \lambda S_\alpha^{(\alpha)} - S_\alpha^{(-\alpha)} \right) \left[ \sum_i \left( S_\alpha^{(+\alpha)}(i) - S_\alpha^{(-\alpha)}(i) \right) \right]
\]

\[
- \sum_{\alpha = a, b} \sum_{\eta = 1, 2} \left( \mu_\alpha E_\alpha - \frac{1}{2} \lambda S_\alpha^{(\alpha)} - S_\alpha^{(-\alpha)} \right) \left[ \sum_i \left( S_\alpha^{(+\alpha)}(i) - S_\alpha^{(-\alpha)}(i) \right) \right]
\]

\[
- \sum_{\alpha = a, b} \sum_{\eta = 1, 2} \left( S_\alpha^{(+\alpha)}(\eta) - S_\alpha^{(-\alpha)}(\eta) \right) A_k
\]

(1)

where \( S_\alpha^{m(\pm\alpha)} \) are the \( m^{th} \) component of the pseudospin operator for the sublattice \( \eta \) \((\eta = 1, 2)\) associated with a plus or minus bond aligned in the direction \( \pm\alpha \) \((\alpha = a \text{ or } b)\). The quantity \( \gamma \) represents the long-range dipole interaction. The symbols \( Z^{\pm\alpha} \) \((1)\) and \( Z^{\pm\alpha} \) \((2)\) represents the pseudospins in sublattices \((1)\) and \((2)\) respectively associated with the direction \( \alpha \). \( J_{ij} \) is the exchange interaction constant. The first term of equation (1) describes the effective short-range proton interaction. The second term represents the interaction of the spins with an applied electric field along the c-direction. The third term represents their interaction with the average longitudinal polarization \( Z \) via the long-range dipole-dipole interaction \( \gamma \). Here the quantity \( Z \) is defined as \( Z = \frac{1}{2N} \sum_{i=1}^{2N} Z_{i} \), where \( N \) is the number of PO4 groups. In fourth term \( V_{ik} \) is the spin-lattice interaction constant. The fifth and sixth terms describes the interaction of the transverse polarization of the four sublattices with an applied transverse field and also the long-range transverse dipole-dipole antiferroelectric interaction between transverse dipole moments of different sublattices aligned in the same transverse direction. The last term describes the interaction of the pseudospins with polar optical phonons, which makes the two potential wells for proton motion non-equivalent.

\[
H_2 = -2\Omega \sum_i S_i^c - 2\Omega \sum_i \left( S_i^{(+\alpha)} - S_i^{(-\alpha)} \right) - 2\Omega \sum_{\eta} \left( S_\eta^{(+\alpha)} - S_\eta^{(-\alpha)} \right)
\]

(2)

where \( \Omega \) is the proton tunnelling frequency. The proton-lattice coupling has predicted for the potassium/ammonium dihydrogen phosphate crystals using electron-nuclear double resonance and EPR techniques. We have considered into account the proton-lattice interaction model. The quasi-elastic scattering near the z-point, confirming the existence of a soft-mode at the that point indicates the important of proton-lattice interaction in the ADP-type crystals. The proton-lattice coupling model Hamiltonian is expressed as

\[
H_3 = \sum_{k_1k_2k_3} V^{(3)}(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1k_2k_3k_4} V^{(4)}(k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4}
\]

\[
+ \frac{1}{4} \sum_k \left( A_k^\dagger A_k + B_k^\dagger B_k \right) - \sum_{ik} V_{ik} \left( S_i^c A_k \right) - \sum_{\alpha = a, b} \sum_{\eta = 1, 2} \left( S_\alpha^{(+\alpha)}(\eta) - S_\alpha^{(-\alpha)}(\eta) \right) A_k
\]

\[
+ \sum_{\alpha = a, b} \sum_{\eta = 1, 2} B_{\eta} \left( S_\alpha^{(+\alpha)}(\eta) - S_\alpha^{(-\alpha)}(\eta) \right)
\]

(3)

where the first two terms are the phonon anharmonic interactions, \( \omega_k \) is the phonon frequency. \( A_k = A_k^{(\pm\alpha)} \) and \( B_k = B_k^{(\pm\alpha)} \) are the normal coordinates and complex conjugate momenta respectively. For the antiferroelectric case, where the stability occurs at the Brillouin-zone boundary along \( c^*-\text{axis} \) (known the z-point and \( c^* \) is the reciprocal lattice vector in the c-direction), the order parameter \( A_{k_0} \neq 0 \) and we have \( A_1 = A_{k_0} e^{ik_0 \cdot \mathbf{R}_{\parallel}} \cong \pm A_{k_0} \). We may also define \( A_k = A_{k_0} + \delta A_k \). In the paraelectric phase \( A_{k_0} = 0 \) and in the ferroelectric phase \( A_{k_0} \neq 0 \), \( \delta A_k = A_k \) represents the fluctuations around the average value. The fourth terms in equation (3) describes the modulation distance between the two equilibrium sites in the O-H-O bonds, and the resulting
modulation of the tunnelling term \((\Omega)\) by nonpolar optic phonons. In last term \(B_{ij}\) describes the effect of the tunnelling motion of one proton on the tunnelling motion of another in a transverse field Hamiltonian. We shall consider the total Hamiltonian for ADP crystal expressed as

\[
H = H_1 + H_2 + H_3
\]

### 2 Green’s function theory

Following the Zubarev\(^{3,4}\) the thermodynamic Green’s function (in units of \(\hbar\)) can be expressed as

\[
\begin{align*}
G_{ij}^{(+a)}(t-t') &= \langle \langle S_{ij}^{(+a)}(t) ; S_{ij}^{(+a)}(t') \rangle \rangle = -i\Theta(t-t') \left[ S_{ij}^{(+a)}(t) , S_{ij}^{(+a)}(t') \right] \\
\end{align*}
\]

where \(\Theta(t-t')\) is the Heaviside step unit function which is for \(t < t'\) and 0 for \(t < t'\). Differentiating equation (5) twice with respect to time \(t\) and \(t'\) respectively with the help of model Hamiltonian and taking the Fourier transform we obtained

\[
\begin{align*}
G(\langle \langle S_{ij}^{(+a)}(t) ; S_{ij}^{(+a)}(t') \rangle \rangle) &= \frac{1}{2\pi} \left\langle \left[ S_{ij}^{(+a)}(t) , S_{ij}^{(+a)}(t') \right] \right\rangle \\
&+ \langle \langle \left[ S_{ij}^{(+a)}(t) , H \right] ; S_{ij}^{(+a)}(t') \rangle \rangle
\end{align*}
\]

where the angular brackets \(\langle \langle \cdots \rangle \rangle\) denotes the notation for corresponding Green’s function and \(\langle \cdots \rangle\) represents the statistical average of the enclosed operators. With the help of Fourier transform and Dyson’s equation treatment, we obtained the Green’s function in the form of Dyson’s equation as

\[
G_{ij}^{(+a)}(\omega) = G_{ij}^{(0,+a)}(\omega) + G_{ij}^{(0,+a)}(\omega) P(\omega) G_{ij}^{(+a)}(\omega)
\]

where \(G_{ij}^{(0,+a)}(\omega)\) represents unperturbed Green’s function given by

\[
G_{ij}^{(0,+a)}(\omega) = \frac{\Omega S_{ij}^{(+a)} \delta_{ij}}{\pi \left[ \omega^2 + \Omega^2 \right]}
\]

and \(P(\omega)\) is the response function obtained as

\[
P(\omega) = \frac{\pi \langle \langle F_i(t) ; F_i^+(t') \rangle \rangle}{\Omega \langle \langle S_{ij}^{(+a)} \rangle \rangle}
\]

where

\[
\begin{align*}
F_i(t) &= 2\Omega V_{ik}A_k S_{ik}^{(+a)} + 2\Omega V_{ik} A^2_k S_{ik}^{(+a)} \\
&- V_{ik} A_j \left( S_{ij}^{(+a)} S_{jk}^{(+a)} + S_{ij}^{(a)} S_{jk}^{(+a)} \delta_{ij} \right) \\
&- 2\Omega V_{ik} A_j S_{ik}^{(+a)} - V_{ik} A^2_j S_{ij}^{(a)} S_{jk}^{(+a)} + S_{ij}^{(a)} S_{jk}^{(+a)} \delta_{ij} \\
&- 2\Omega I_{ij} \left( S_{ij}^{(+a)} S_{ik}^{(+a)} + S_{ij}^{(a)} S_{ik}^{(+a)} \delta_{ij} \right) - 2\Omega I_{ij} S_{ik}^{(+a)} + I_{ik} S_{ij}^{(+a)} \delta_{ij} \\
&- V_{ik} A_k K_{ij} S_{ik}^{(+a)} S_{jk}^{(+a)} \delta_{ij} - V_{ik} A_k K_{ij} S_{ik}^{(+a)} S_{jk}^{(+a)} \delta_{ij} - V_{ik} A_k^2 S_{ij}^{(+a)} \\
&+ 2\Omega V_{ik} A_k S_{ik}^{(+a)} + V_{ik} A^2_k S_{ij}^{(+a)} + 2\Omega V_{ik} A^2_k S_{ij}^{(+a)} \\
&+ 2\Omega B_{ij} \left( S_{ij}^{(+a)} S_{ik}^{(+a)} \delta_{ij} + S_{ij}^{(a)} S_{ik}^{(+a)} \delta_{ij} \right) - 4\Omega \mu_c E_S S_{ik}^{(+a)} \\
&+ V_{ik} A_k B_{ij} \left( S_{ij}^{(+a)} S_{ik}^{(+a)} \delta_{ij} + S_{ij}^{(a)} S_{ik}^{(+a)} \delta_{ij} \right) - 2\mu_c E_v V_{ik} A_k S_{ik}^{(+a)}
\end{align*}
\]
and \( F_i (t') \) is the complex conjugate of \( F_i (t) \). With the help of Dyson’s equation treatment and after simplification, we obtained the Green’s function in the form

\[
G_{ij}^{(a)} (\omega) = \frac{\Omega S_{i (1)}^{(a)} \delta_{ij}}{\pi \left[ \omega^2 - \tilde{\Omega}^2 - P(\omega) \right]}
\]

where the pseudospin frequency is given by

\[
\tilde{\Omega}^2 = 4\Omega^2 + \frac{1}{2\Omega \langle S_{j (1)}^{(+a)} \rangle} \left[ F_i (t), B'^{+a}_j \right]
\]

where \( B' = \left[ S_{j (1)}^{(+a)} , H \right] \). In evaluating \( \langle [F_i (t), B'] \rangle \), the assumption that the correlation functions are finite for average values of pseudospins i.e.

\[
\frac{\langle S_{i (1)}^{(+a)} \rangle}{\rho} = \frac{\langle S_{i (1)}^{(+a)} \rangle}{\sigma} = \frac{1}{2\Omega \eta} \text{tanh} \left( \frac{\Omega \eta}{2k_B T} \right)
\]

where \( \eta = 1, 2 \) and \( k_B \) is the Boltzmann’s constant and \( T \) is the absolute temperature. Using the mean field approximation, we obtained the pseudospin frequency \( \tilde{\Omega} \) in the lowest approximation as

\[
\tilde{\Omega}^2 = \rho^2 + \sigma^2 - \sigma \tau
\]

where

\[
\rho = 2J_{ij} \left( \langle S_{i (1)}^{(+a)} \rangle - \langle S_{i (1)}^{(-a)} \rangle \right) + \lambda \left( \langle S_{i (1)}^{(+a)} \rangle - \langle S_{i (1)}^{(-a)} \rangle \right)
\]

\[
- 2B_{ij} \left( \langle S_{i (1)}^{(+a)} \rangle - \langle S_{i (1)}^{(-a)} \rangle \right) + 2\mu_c E_c
\]

\[
\sigma = 2 \Omega
\]

and

\[
\tau = 2J_{ij} \left( \langle S_{i (2)}^{(+a)} \rangle - \langle S_{i (2)}^{(-a)} \rangle \right) + \lambda \left( \langle S_{i (2)}^{(+a)} \rangle - \langle S_{i (2)}^{(-a)} \rangle \right)
\]

\[
- 2B_{ij} \left( \langle S_{i (2)}^{(+a)} \rangle - \langle S_{i (2)}^{(-a)} \rangle \right)
\]

In equation (9), \( P (\omega) \) contains higher-order Green’s functions which are evaluated by using symmetric decoupling scheme defined as, \( \langle [AB : CD] \rangle = AB\langle C : D \rangle + AC\langle B : D \rangle + AD\langle B : C \rangle + BC\langle A : C \rangle + CD\langle A : B \rangle \). We thus obtained the simpler Green’s functions which are then evaluated in zeroth-order approximation. The response function \( P (\omega) \), for a vanishingly small quantity \( \varepsilon \) breaks into two parts: \( P (\omega) = \Delta (\omega) + i\Gamma (\omega) \) with the help of formula (Dirac delta function property) \( \lim_{\varepsilon \to 0} \frac{1}{\varepsilon \pi \alpha} = \frac{1}{2} \rho \pm i\pi \delta (Z) \). The real part of response function is called shift \( \Delta (\omega) \) and the imaginary part of response function is called width \( \Gamma (\omega) \) at half maximum (called line width or damping constant arises from phonon anharmonic
interactions). The shift $\Delta(\omega)$ is obtained as:

\[
\Delta(\omega) = \frac{\rho^4}{(\omega^2 - \Omega^2)} + \frac{\sigma^2 \tau^2}{(\omega^2 - \Omega^2)} + 16\Omega^2 V_{ik}^2 N_k + 16\Omega V_{ik}^2 \rho \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right) + \frac{2\Omega V_{ik}^2 \rho^2}{(\omega^2 - \Omega^2)} \sigma
\]

\[
+ \frac{4\Omega V_{ik}^2 \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{\left(\omega^2 - \omega_k^2\right)^2 + 4\omega_k^2 \Gamma_k(\omega)} + \frac{4\Omega V_{ik}^2 j_{ij} \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{(\omega^2 - \Omega^2)^2} + \frac{4\Omega V_{ik}^2 \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{(\omega^2 - \Omega^2)^2} \sigma^2
\]

\[
+ \frac{4\Omega V_{ik}^2 \rho \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{\Omega \left(\omega^2 - \omega_k^2\right)^2 + 4\omega_k^2 \Gamma_k(\omega)} + \frac{V_{ik}^2 K_{ij} \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{(\omega^2 - \Omega^2)^2} + \frac{V_{ik}^2 K_{ij} a \langle S_{1i}^{(a)} \rangle a^2 \sigma^2}{(\omega^2 - \Omega^2)^2} \sigma
\]

\[
+ \frac{2\Omega V_{ik}^2 N_k \langle S_{1i}^{(a)} \rangle}{(\omega^2 - \Omega^2)^2} + \frac{4\Omega V_{ik}^2 B_{ij}^2 \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{(\omega^2 - \Omega^2)^2} \sigma^2 + \frac{8\Omega V_{ik}^2 B_{ij}^2 \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{\left(\omega^2 - \omega_k^2\right)^2 + 4\omega_k^2 \Gamma_k(\omega)} \sigma
\]

\[
+ \frac{4\mu^2 E^2 V_{ij}^2 N_k a^2}{(\omega^2 - \Omega^2)^2} \sigma^2 + \frac{8\mu^2 E^2 \rho \langle S_{1i}^{(a)} \rangle \omega_k \left(\omega^2 - \omega_k^2\right)}{\sigma \left(\omega^2 - \omega_k^2\right)^2 + 4\omega_k^2 \Gamma_k(\omega)}
\]
and the width $\Gamma(\omega)$ is obtained as

\[ \Gamma(\omega) = \frac{\rho^4}{2\Omega} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{\sigma^2 \omega^2}{2\Omega} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{16\Omega^2 V_{ik}^2 N_k}{2\Omega} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{32\Omega V_{ik}^2 \rho (S_{ij}^{(+a)}) \omega_k^2 \Gamma_k(\omega)}{\left( \omega^2 - \tilde{\omega}_k^2 \right)^2 + 4\omega_k^2 \Gamma_k(\omega)} \sigma \]

\[ + \frac{2\Omega V_{ik}^2 N_k \rho^2}{2\Omega \sigma} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{8\Omega V_{ik}^2 (S_{ij}^{(+a)}) \omega_k^2 \Gamma_k(\omega)}{\sigma} \left[ \omega^2 - \tilde{\omega}_k^2 \right]^2 + 4\omega_k^2 \Gamma_k(\omega) \]

\[ + \frac{8V_{ik}^2 J_{ij}^2 N_k (S_{ij}^{(+a)})^2 \omega_k^2 \Gamma_k(\omega)}{2\Omega \sigma^2} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{4V_{ik}^2 J_{ij}^2 (S_{ij}^{(+a)}) (S_{ij}^{(+a)})^2 \omega_k^2 \Gamma_k(\omega)}{\sigma} \left[ \omega^2 - \tilde{\omega}_k^2 \right]^2 + 4\omega_k^2 \Gamma_k(\omega) \]

\[ + \frac{V_{ik}^2 K_{ij}^2 N_k (S_{ij}^{(+a)})^2 \omega_k^2 \Gamma_k(\omega)}{2\Omega \sigma^2} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{4V_{ik}^2 K_{ij}^2 (S_{ij}^{(+a)}) (S_{ij}^{(+a)})^2 \omega_k^2 \Gamma_k(\omega)}{\sigma} \left[ \omega^2 - \tilde{\omega}_k^2 \right]^2 + 4\omega_k^2 \Gamma_k(\omega) \]

\[ + \frac{16V_{ik}^2 J_{ij} N_k (S_{ij}^{(+a)}) \omega_k^2 \Gamma_k(\omega)}{2\Omega} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{2\Omega V_{ik}^2 N_k (S_{ij}^{(+a)})}{2\Omega} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{16V_{ik}^2 B_{ij}^2 (S_{ij}^{(+a)})^2 \omega_k^2 \Gamma_k(\omega)}{\left( \omega^2 - \tilde{\omega}_k^2 \right)^2 + 4\omega_k^2 \Gamma_k(\omega)} \sigma \]

\[ + \frac{4V_{ik}^2 C_{ij}^2 V_{ik}^2 N_k (S_{ij}^{(+a)})}{2\Omega \sigma^2} \left[ \delta(\omega - \Omega) - \delta(\omega + \Omega) \right] + \frac{16\mu^2 E_{ik}^2 V_{ik}^2 N_k (S_{ij}^{(+a)}) \omega_k^2 \Gamma_k(\omega)}{\sigma} \left[ \omega^2 - \tilde{\omega}_k^2 \right]^2 + 4\omega_k^2 \Gamma_k(\omega) \]

In the above equations (18) and (19), $\Gamma_k(\omega)$ is the phonon width arises due to the phonon anharmonic interactions, $\tilde{\omega}_k = \omega_k + A(k, T)$ is the renormalized phonon frequency ($A(k, T)$ is the anharmonic parameter). The phonon shift for phonon
Green’s function is obtained as

\[
\Delta_k (\omega) = 18 \sum_{k_1, k_2} \left| V^{(3)} (k_1, k_2, -k) \right|^2 \left( \frac{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \right)
\]

\[
\times \left\{ \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2})^2} + \frac{\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2})^2} \right\}
\]

\[
+ 48 \sum_{k_1, k_2, k_3} \left| V^{(4)} (k_1, k_2, k_3, -k) \right|^2 \left( \frac{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}} \right)
\]

\[
\times \left\{ \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} \right\}
\]

\[
+ 3 \left( \frac{\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3})^2} \right)
\]

\[
+ \text{higher order terms}
\]

(20)

And the phonon width \( \Gamma_k (\omega) \) for phonon Green’s function obtained as

\[
\Gamma_k (\omega) = 18\pi \sum_{k_1, k_2} \left| V^{(3)} (k_1, k_2, -k) \right|^2 \left( \frac{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \right)
\]

\[
\times \left\{ \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2})^2} + \frac{\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2})^2} \right\}
\]

\[
+ 48\pi \sum_{k_1, k_2, k_3} \left| V^{(4)} (k_1, k_2, k_3, -k) \right|^2 \left( \frac{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}} \right)
\]

\[
\times \left\{ \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} \right\}
\]

\[
+ 3 \left( \frac{\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3})^2} \right)
\]

\[
+ \text{higher order terms}
\]

(21)

where \( \bar{n}_k \) is the phonon occupation number given by

\[
\bar{n}_k = \frac{\omega_k}{\tilde{\omega}_k} \coth \left( \frac{h \tilde{\omega}_k}{4\pi k_B T} \right)
\]

(22)

Substituting the value of \( P (\omega) \) after simplification into equation (11), we obtained the Green’s function in the form

\[
G_{ij}^{(+a)} (\omega + i\epsilon) = \frac{\Omega! (\Omega^{(a)})^2}{\pi} \delta_{ij}
\]

\[
\frac{\Omega! (\Omega^{(a)})^2}{\pi} \delta_{ij}
\]

(23)

where \( \tilde{\Omega} \) is the soft (normal) soft mode frequency and can be written in terms renormalized pseudospin frequency \( \tilde{\Omega} \) given by

\[
\tilde{\Omega} = \tilde{\Omega}^2 + 2\Omega \Delta (\omega)
\]

(24)

and

\[
\tilde{\Omega} = \tilde{\Omega}^2 + 2\Omega \Delta (\omega)
\]

(25)
On solving equation (24) self-consistently we obtained the antiferroelectric soft mode frequency \( \tilde{\Omega} \) at low temperature phase for antiferroelectric ADP crystal

\[
\tilde{\Omega}^2 = \left( \frac{\omega_k^2 + \Omega^2}{2} \right)^{\frac{1}{2}} + \frac{1}{2} \left\{ \left( \omega_k^2 + \Omega^2 \right)^{\frac{1}{2}} + 4 \left\{ 8V_{ik}^2 \left( \frac{\delta_{ii}^{(\alpha)}}{\delta_{ik}} \right) \omega_k + 4\Omega V_{ik}^2 \left( \frac{\delta_{ii}^{(\alpha)}}{\delta_{ik}} \right) \omega_k \right\} \right\} \quad (26)
\]

According to Cochran\(^{46}\) that in the antiferroelectric crystal transition is due a zone-boundary mode which becomes unstable before the ferroelectric mode. In the antiferroelectric crystals, some of the normal mode of vibration of crystal becomes unstable (i.e., its frequency becomes zero) when Curie transition temperature approached. This mode called soft mode is held responsible for the phase transition from antipolar to non-polar phase and anomalous behaviour of dielectric properties of crystal near transition temperature. The antiferroelectric mode should occur at the \( z \)-point \( ( \tilde{k} = \frac{2\pi}{\pi} ) \) in ADP crystal while in ferroelectric mode \( ( \tilde{k} = 0 ) \).

### 3 Dielectric permittivity and loss tangent

Following the Zubarev \([43]\) and Kubo \([47]\), the general expression for the complex dielectric susceptibility \( \chi(\omega) \) is related to the Green’s function \( G_{ij}^{(\alpha \alpha)}(\omega + i\epsilon) \) as

\[
\chi(\omega) = -\lim_{\epsilon \to 0} \frac{2\pi N \mu^2 G_{ij}^{(\alpha \alpha)}(\omega + i\epsilon)}{\omega}
\]

where \( N \) is the number of dipoles in a unit cell and \( \mu \) is the effect dipole moment per unit cell. The dielectric permittivity and electrical susceptibility are related by the relation

\[
\varepsilon(\omega) = (1 + 4\pi \chi)
\]

By using the equations (23), (27) and (28), we obtained the dielectric permittivity in \( a \)- and \( c \)-directions \( (\varepsilon_a \gg 1, \varepsilon_c \gg 1) \).

\[
\varepsilon_a(\omega) = -\frac{8\pi N_c \mu_a^2 \Omega \delta_{ii}^{(+\alpha)} \left( \omega^2 - \tilde{\Omega}^2 \right)}{\left[ \left( \omega^2 - \tilde{\Omega}^2 \right)^2 + 4\Omega^2 \right] \Gamma^2(\omega)}
\]

(29)

and

\[
\varepsilon_c(\omega) = -\frac{8\pi N_a \mu_c^2 \Omega \delta_{ii}^{(+\alpha)} \left( \omega^2 - \tilde{\Omega}^2 \right)}{\left[ \left( \omega^2 - \tilde{\Omega}^2 \right)^2 + 4\Omega^2 \right] \Gamma^2(\omega)}
\]

(30)

In the dielectric material there will be some power loss in the form of heat (electromagnetic energy) because of the work done to overcome the frictional damping forces encountered by the dipoles during their rotation. This loss is in dielectric material is known as dielectric loss or loss tangent. It is denoted by \( \tan \delta \). The two components of \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) of the complex dielectric permittivity are given by

\[
\varepsilon'(\omega) = \left( \frac{D_0}{E_0} \right) \cos \delta
\]

(31)

\[
\varepsilon''(\omega) = \left( \frac{D_0}{E_0} \right) \sin \delta
\]

(32)
Since the displacement vector in a time varying field will not be in phase with electric field vector and difference ∆ between them. Dividing equations (32) and (31) we get

\[
\tan \delta_{\omega} = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = -\frac{2N_\gamma \mu_s \Omega(\omega)}{\omega^2 - \Omega^2}
\]

(33)

and

\[
\tan \delta_{\omega} = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = -\frac{2N_\gamma \mu_c \Omega(\omega)}{\omega^2 - \Omega^2}
\]

(34)

The polarization along the a-axis (transverse) obtained as

\[
P_a = N_\gamma \mu_a \left[ \langle S^{(+)}_{(1)} \rangle + \langle S^{(+)}_{(2)} \rangle - \langle S^{(-)}_{(1)} \rangle - \langle S^{(-)}_{(2)} \rangle \right]
\]

(35)

The longitudinal polarization has been obtained as

\[
P_c = N_\gamma \mu_c \langle S^c \rangle
\]

(36)

Here we have \langle S^c \rangle = 1 for ferroelectric phase and \langle S^{(+)}_{(1)} \rangle - \langle S^{(-)}_{(1)} \rangle = \langle S^{(+)}_{(2)} \rangle - \langle S^{(-)}_{(2)} \rangle = 2 for antiferroelectric phase.

4 Numerical analysis and results

Using the model values of different physical parameters shown in table (1), the temperature dependence of antiferroelectric soft (normal) mode frequency, dielectric constant and loss tangent have been calculated for antiferroelectric ADP crystal. The theoretical obtained for these quantities are shown in figures (1-3). We have used the values of \(N_\gamma = 78.33 \times 10^{20} \text{cm}^{-3}\), \(\mu_a = 2.95 \times 10^{-18} \text{esu}\), \(N_c = 31.26 \times 10^{20} \text{cm}^{-3}\), \(\mu_c = 4.70 \times 10^{-18} \text{esu}\), \(E_a = E_c = 0\) and \(\gamma = 0\) throughout numerical analysis for antiferroelectric ADP crystal. By fitting the model values of different physical parameters in the theoretical obtained expressions, the thermal dependence of antiferroelectric soft mode frequency, dielectric constant and loss tangent have been calculated and shown in figures (1-3). Our theoretical obtained results are well compared with experimental data.

5 Discussion

In the present paper, we have modified the four-sublattice pseudospin lattice coupled mode model Hamiltonian for antiferroelectric ADP crystal. The model Hamiltonian is modified by adding phonon anharmonic interactions, extra spin-lattice interactions and direct spin-spin interaction to explain the phase transition mechanism for ADP crystal. with the help of modified model and Green’s function theory, the theoretical expressions for antiferroelectric soft mode frequency, dielectric constant and loss tangent have been derived. By fitted the model values of various physical parameters given in table (1), the thermal dependence of antiferroelectric soft mode frequency, dielectric permittivity and dielectric loss were calculated. Earlier authors\(^{10,24,28}\) have not considered the phonon anharmonic interactions, extra spin-lattice interactions and direct spin-spin interaction. They have decoupled the correlation functions at an early stage by using simple decoupling scheme. Due to the lack...
Figure 1. Thermal dependence of soft mode frequency for antiferroelectric ADP crystal (symbols: values extracted from correlating with dielectric data\textsuperscript{3}, solid line: present calculation)

Figure 2. Thermal dependence of dielectric constant for antiferroelectric ADP crystal (symbols: experimental data\textsuperscript{3}, solid lines: present calculation)
of these interactions, some significant results are disappeared. In the present work we have considered the all above interactions and decoupled the correlation functions of Green’s function at a proper stage. We evaluated the correlation functions by using the symmetric decoupling scheme. The equation (29) for dielectric permittivity is proportional to the tunnelling integral ($\Omega$) and inversely proportional to the antiferroelectric soft mode frequency. From equation (33) we obtained that the dielectric loss varies linearly proportional to the tunnelling frequency, which is in good agreement with earlier studies\textsuperscript{1,3} shown in figures (3). A transverse radiation field derives the low-lying transverse mode in a force vibration of material. Energy is transferred from the electromagnetic field to this lattice mode and is then degraded into other vibrational modes of the material. Due to third- and fourth-order phonon anharmonic interactions, decay process take place such as third-order coupling leads to the decay of a virtual phonon into two real phonons or the virtual phonon may be destroyed by scattering, a thermally excited phonon. Similar processes are occurred for higher-order coupling. From the figures (2,3) we obtained that the dielectric permittivity and loss tangent obeys the Curie-Weiss behaviour in the vicinity of Curie temperature ($T_c$). The phonon anharmonic interactions, extra spin-lattice interactions and direct spin-spin interaction significantly contribute to the thermal dependence of antiferroelectric soft mode, dielectric permittivity and dielectric loss at and above the Curie temperature.

6 Conclusion

In the present paper, we have considered the modified four sublattice pseudospin lattice coupled mode model Hamiltonian by adding phonon anharmonic interactions, extra spin-lattice interactions, direct spin-spin interaction to explain the phase transition dielectric properties of antiferroelectric ADP crystal. The soft mode theory successfully explains the dynamics of antiferroelectric transition in ADP crystal in a similar way as the ferroelectric KDP crystal, which explains the possibility of a unified theory of ferroelectric and antiferroelectric transitions. The theoretical obtained results of present model theory may also applicable to similar antiferroelectric crystals such as $\text{Cu(CHO)}_2\cdot4\text{H}_2\text{O}$, $\text{NH}_3\text{H}_4\text{AsO}_4$, $\text{AgH}_3\text{IO}_3$ and $\text{(NH}_4)_2\text{H}_3\text{IO}_6$ etc to explain the phase transition mechanism.

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Conflict of interest
The authors declare that they have no conflict of interest.

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Figure 1

Thermal dependence of soft mode frequency for antiferroelectric ADP crystal (symbols: values extracted from correlating with dielectric data, solid line: present calculation)
Figure 2

Thermal dependence of dielectric constant for antiferroelectric ADP crystal (symbols: experimental data, solid lines: present calculation)
Figure 3

Thermal dependence of loss tangent for antiferroelectric ADP crystal (symbols: experimental data, solid lines: present calculation)