Indian Journal of Pure & Applied Physics
Vol. 47, January 2009, pp. 66-72

# Temperature dependence of microwave loss in ADP-type crystals

Trilok Chandra Upadhyay
Physics Department, H N B Garhwal University, Srinagar (Garhwal), Uttarakhand 246 174
E-mail: trilokphys@yahoo.co.in

*Received 1 April 2008; revised 22 July 2008; accepted 4 November 2008*

By using four sublattice pseudospin lattice coupled mode model along with third and fourth-order phonon anharmonic interaction terms for ADP-type crystals, expressions for shift, width, renormalized soft mode frequency, dielectric constant and loss have been evaluated. The method of double-time thermal Green's function has been used for calculation. Fitting the values of model parameters in expressions, the temperature dependences of soft mode frequency and loss have been calculated. In the microwave frequency range, an increase in frequency is followed by increase in loss. The loss decreases with increase in temperature for ADP crystal in its paraelectric phase. This shows Curie-Weiss behaviour of the dielectric tangent loss. Theoretical results are compared with experimental results of Nagamiya [*Progr Theor Phys,* 7 (1952) 275] and Busch, *Helv Phys Acta,* 11 (1938) 269]. A good agreement has been found.

**Keywords:** Antiferroelectrics, Anharmonic interactions, Dielectric, Loss tangent

## 1 Introduction

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$), ammonium dihydrogen arsenate and their deuterated forms, generally called ADP-type antiferroelectrics have been extensively studied due to their potential applications in electro-optic, opto-electronic and display devices. Very little theoretical work has been done on these antiferroelectrics as compared to KDP-type ferroelectrics. ADP crystal undergoes a first order transition at 148K, accompanied by tetragonal ($D_2$-42m) to orthorhombic ($D_2$-222) below $T_c$. The ($H_2PO_4$)-1 net work in which each phosphate group is linked by O-H...O bonds to a tetrahedral arrangement of phosphate group neighbours. A large isotope shift in transition temperature from 148 to 242K occurs in ADP when it is deuterated.

Earlier Ishibashi[1] and Havlin *et al.*[2] using mean field approximation and Banerjee *et al.*[3] using Green's function method have studied antiferroelectric transition and dielectric properties of ADP-type crystals. Many workers[4-12] have experimentally studied the dielectric properties of these crystals. Formulae were developed to explain ferroelectric transitions in displacive[13,14] and order-disorder[15,18] type crystals.

In the present study a four sublattice pseudospin lattice coupled mode model along with third and fourth order phonon anharmonic interactions[19] has been used to obtain expressions for shift, width, renormalized soft mode frequency, transition temperature, dielectric constant and loss. The method of double time thermal Green's function[20] has been used for the calculation. By fitting model values of various paramaters appearing in expressions obtained for ADP, temperature dependences of various quantities have been calculated. The frequency and temperature dependences of dielectric loss in the range (1-35 GHz) and in the temperature range 134-176K at 10 GHz for ADP crystal have been calculated and compared with experimental results of Busch[5] and Nagamiya[4].

## 2 Theory

### 2.1 Model Hamiltonian

For ADP-type antiferroelectric crystals, the four-sublattice pseudospin-lattice coupled mode model along with third and fourth order phonon anharmonic interaction terms is expressed as:

$$
\begin{aligned}
H = & -2\Omega\sum_i S_i^x - 2\Omega\sum_a \left( S_{i(1)}^{x(+a)} - S_{i(1)}^{x(-a)} \right) \\
& -2\Omega\sum_b \left( S_{i(2)}^{x(+a)} - S_{i(2)}^{x(-a)} \right) \\
& -\frac{1}{2}\sum_{ij} J_{ij} S_i^z S_j^z - \sum_{ij} \gamma S_i^z S_j^z \\
& +\frac{1}{2}\lambda\sum_a \left\langle S_{(2)}^{z(+a)} - S_{(2)}^{z(-a)} \right\rangle \left( S_{i(1)}^{z(+a)} - S_{i(1)}^{z(-a)} \right) \\
& +\frac{1}{2}\lambda\sum_a \left\langle S_{(1)}^{z(+a)} - S_{(1)}^{z(-a)} \right\rangle \left( S_{i(1)}^{z(+a)} - S_{i(1)}^{z(-a)} \right)
\end{aligned}
$$

$$+\frac{1}{2}\lambda\sum_b\left\langle S_{(2)}^{z(+b)}-S_{(2)}^{z(-b)}\right\rangle\left(S_{i(1)}^{z(+b)}-S_{i(1)}^{z(-b)}\right)$$

$$+\frac{1}{2}\lambda\sum_b\left\langle S_{(1)}^{z(+b)}-S_{(1)}^{z(-b)}\right\rangle\left(S_{i(1)}^{z(+b)}-S_{i(1)}^{z(-b)}\right)$$

$$-\sum_{ik}V_{ik}S_i^zA_k-\sum_a V_{ik}\left(S_{i(1)}^{z(+a)}-S_{i(1)}^{z(-a)}\right)A_k$$

$$-\sum_b V_{ik}\left(S_{i(1)}^{z(+b)}-S_{i(1)}^{z(-b)}\right)A_k^+$$

$$+\frac{1}{4}\sum_k\omega_k\left(A_kA_k^++B_kB_k^+\right)$$

$$+\sum_{k_1k_2k_3}V^{(3)}\left(k_1,k_2,k_3\right)A_{k_1}A_{k_2}A_{k_3}$$

$$+\sum_{k_1k_2k_3k_4}V^{(4)}\left(k_1,k_2,k_3k_4\right)A_{k_1}A_{k_2}A_{k_3}A_{k_4} \quad \ldots (1)$$

where $\Omega$ is proton tunnelling frequency, $S^z$ and $S^x$ are components of pseudospin variable, $S$, $V_{ik}$ is spin-lattice interaction, $A_k$ and $B_k$ are position and momentum operators, $\omega_k$ is harmonic phonon frequency $V^{(3)}$ and $V^{(4)}$ are third-and fourth-order atomic force constants, $\lambda$ is antiferroelectric interaction constant, $J$ is exchange interaction constant and $\gamma$ is long range interaction constant.

**2.2 Green's functions, shifts, widths and soft mode frequency**

Green's function is evaluated following Zubarev[20] as follows:

$$G_{ij(1)}^{z(+a)}\left(t-t'\right)=\left\langle\left\langle S_{i(1)}^{z(+a)};S_{j(1)}^{z(+a)}\right\rangle\right\rangle$$

$$=-i\theta\left(t-t'\right)\left\langle\left[S_{i(1)}^{z(+a)},S_{j(1)}^{z(+a)}\right]\right\rangle \quad \ldots (2)$$

Differentiating Green's function [Eq. (2)] with respect to times $t$ and $t'$ respectively twice with the help of model Hamiltonian (1), Fourier transforming and putting in the Dyson's equation form, one obtains

$$\tilde{G}_{ij(1)}^{z(+a)}\left(\omega\right)=\frac{\Omega\left\langle S_i^x\right\rangle\delta_{ij}}{\pi\left[\omega^2-\tilde{\Omega}^2-P\left(\omega\right)\right]} \quad \ldots (3)$$

where

$$\tilde{\Omega}^2=4\Omega^2+\lambda^2\left(\left\langle S_{(2)}^{z(+a)}-S_{(2)}^{z(+a)}\right\rangle\right)^2 \quad \ldots (4)$$

and

$$P\left(\omega\right)=\frac{\pi}{\Omega\left\langle S_{(1)}^{z(+a)}\right\rangle}\left\langle\left\langle F\left(t\right);F'\left(t'\right)\right\rangle\right\rangle \quad \ldots (5)$$

$P\left(\omega\right)$ contains higher order Green's functions which are evaluated by decoupling them using scheme <abcd>= <ab> <cd> + <ac> <bd> + <ad> <bc>. The simpler Green's functions are then evaluated in zeroth order approximation.

Substituting values of various Green's functions in Eq. (5), $P\left(\omega\right)$ is resolved into its real and imaginary parts.

The real part is called shift $\Delta\left(\omega\right)$ while imaginary part is known as width $\Gamma\left(\omega\right)$. The Green's function then finally becomes

$$G_{ij}^{z(+a)}\left(\omega+i\in\right)=\frac{\Omega\left\langle S_i^{x(+a)}\right\rangle}{\pi\left[\omega^2-\hat{\Omega}^2-2i\Omega\Gamma\left(\omega\right)\right]} \quad \ldots (6)$$

with

$$\hat{\Omega}^2=\tilde{\tilde{\Omega}}^2+\Delta'_{s-p}\left(\omega\right), \quad \ldots (7)$$

and

$$\tilde{\tilde{\Omega}}^2=\tilde{\Omega}^2+\Delta'_s\left(\omega\right), \quad \ldots (8)$$

shift $\Delta'_{s-p}\left(\omega\right)=\dfrac{2\bar{V}_{ik}^2b\left\langle S_{(1)}^{x(+a)}\right\rangle\omega_k}{\left[\omega^2+\tilde{\tilde{\Omega}}_k^2-2\omega_{ki}\Gamma_k\left(\omega\right)\right]}$ … (9)

and

shift $\Delta'_s\left(\omega\right)=\dfrac{a'^4+\bar{V}_{ik}^2a'^2N_k}{\left(\omega^2-\tilde{\Omega}^2\right)}$ … (10)

where $N_k=\coth\ \beta\tilde{\tilde{\omega}}_k$ .

width

$$\Gamma_1\left(\omega\right)=\Gamma'_{s,1}\left(\omega\right)+\Gamma'_{sp1}\left(\omega\right), \quad \ldots (11)$$

with

$$\Gamma'_{s,1}\left(\omega\right)=\frac{\pi\left(a'^4+V_{ik}^2a'^2N_k\right)}{\tilde{\Omega}}\left[\delta\left(\omega-\tilde{\Omega}\right)-\delta\left(\omega+\tilde{\Omega}\right)\right], \quad \ldots (12)$$

$$\Gamma'_{sp1}(\omega)=\frac{4\pi V_{ik}^2 b\left\langle S_{(1)}^{x(+a)}\right\rangle \omega_k \Gamma_k}{\left[\left(\omega^2-\tilde{\omega}_k^2\right)^2+4\omega_k^2\Gamma_k^2\right]}. \quad \ldots (13)$$

$$a'=\lambda\left\langle S_{(2)}^{z(+a)}-S_{(2)}^{z(-a)}\right\rangle,\ b=2\Omega \quad \ldots (14)$$

Similarly Green's function

$$G_{ij}^z(t-t')=\left\langle\left\langle S_i^z(t);S_j^z(t')\right\rangle\right\rangle$$
$$=-i\theta((t-t')\left\langle\left[S_i^z(t);S_j^z(t')\right]\right\rangle \quad \ldots (15)$$

can be evaluated with the help of Hamiltonian (1) and one obtains

$$G_{ij}^z(\omega)=\frac{\Omega\left\langle S_i^x\right\rangle}{\pi\left[\omega^2-\hat{\omega}_s^2-2\Omega i\Gamma(\omega)\right]}, \quad \ldots (16)$$

where

$$\hat{\omega}_s^2=\tilde{\tilde{\omega}}_s^2+\Delta_{sp}(\omega), \quad \ldots (17)$$

and

$$\tilde{\tilde{\omega}}_s^2=\tilde{\omega}_s^2+\Delta_s(\omega), \quad \ldots (18)$$

with shifts

$$\Delta_s(\omega)=\frac{a^4+V_{ik}^2a^2N_k^{\,2}}{\left(\omega^2-\tilde{\omega}_s^2\right)} \quad \ldots (19)$$

where

$$a=\left(J_{ij}+\gamma\left\langle S^z\right\rangle\right)\left\langle S^z\right\rangle.$$

$$\Delta_{sp}(\omega)=\frac{2\overline{V}_{ik}^2\left\langle S_k^x\right\rangle b\left(\omega^2-\hat{\omega}_k^2\right)}{\left[\left(\omega^2-\hat{\omega}_k^2\right)^2+4\omega_k^2\Gamma^2{}_k(\omega)\right]} \quad \ldots (20)$$

and width

$$\Gamma(\omega)=\Gamma_s(\omega)+\Gamma_{sp}(\omega), \quad \ldots (21)$$

$$\Gamma_s(\omega)=\frac{\pi a^4}{\tilde{\omega}_s}\left[\delta(\omega-\tilde{\omega}_s)-\delta(\omega+\tilde{\omega}_s)\right], \quad \ldots (22)$$

with

$$\Gamma_{s-p}(\omega)=\frac{4\pi V_{ik}^2\left\langle S_i^x\right\rangle b2\omega_k\Gamma(\omega)}{\left[\left(\omega^2-\hat{\omega}_k^2\right)^2+4\omega_k^2\Gamma^2(\omega)\right]} \quad \ldots (23)$$

Solving Eq. (7) self-consistently one obtains antiferroelectric soft mode frequency $\hat{\Omega}_-$ and ferroelectric mode frequency $\hat{\omega}_s$ (In ADP-crystal it is $\hat{\Omega}$ which becomes soft before the ferroelectric mode frequency and hence antiferroelectric phase results below $T_c$).

$$\hat{\Omega}^2=\frac{1}{2}\left[\left(\hat{\omega}_k^2+\tilde{\tilde{\Omega}}^2\right)\pm\sqrt{\left(\hat{\omega}_k^2-\tilde{\tilde{\Omega}}^2\right)^2+8V_{ik}^2b\left\langle S_{(1)}^{x(+a)}\right\rangle}\right] \quad \ldots (24)$$

and

$$\hat{\omega}_s^2=\frac{1}{2}\left[\left(\hat{\omega}_k^2+\tilde{\omega}_s^2\right)\pm\sqrt{\left(\hat{\omega}_k^2-\tilde{\omega}_s^2\right)^2+2V_{ik}^2b\left\langle S_i^x\right\rangle}\right]. \quad \ldots (25)$$

**2.3 Dielectric constant and loss tangent**

Following Kubo[21] the electrical susceptibility $\chi$ is related to Green's function $G_{ij}(\omega+i\in)$ as

$$\chi=-2\pi N\mu^2 G_{ij}(\omega+i\in) \quad \ldots (26)$$

where $N$ is number of dipoles in sample with dipole moment $\mu$.

The dielectric constant $\in$ is related to $\chi$ as

$$\in=4\pi\chi \quad \ldots (27)$$

Using Eqs (27), (6) and (18) dielectric constants in $a$- and $c$-directions are obtained as (In ferro/antiferroelectrics $\in>>1$),

$$\in_a(\omega)=-8\pi N\mu_a^2\Omega\langle S_{i(1)}^{x(+a)}\rangle$$
$$\left[\omega^2-\hat{\Omega}^2-2\Omega i\Gamma_1(\omega)\right]^{-1} \quad \ldots (28)$$

and

$$\in_c(\omega)-1=-8\pi N\mu_c^2\Omega\langle S_i^x\rangle$$
$$\left[\omega^2-\hat{\omega}_s^2-2\Omega i\Gamma(\omega)\right]^{-1} \quad \ldots (29)$$

The dissipation of power when any dielectric, ferroelectric or antiferroelectric is exposed to electric

field is given by ratio of imaginary and real parts of dielectric constant, i.e.

$$\tan\delta_a = \frac{\text{Imaginary}\in}{\text{Real}\in} = -2\Omega\Gamma_1(\omega)\left(\omega^2 - \tilde{\tilde{\Omega}}^2\right)^{-1} \quad \ldots (30)$$

and

$$\tan\delta_c = -2\Omega\Gamma(\omega)\left(\omega^2 - \hat{\omega}_s^2\right)^{-1} \quad \ldots (31)$$

At microwave frequencies $\omega << \tilde{\tilde{\Omega}}$, $\omega << \hat{\omega}_s$.

**2.4 Numerical calculation of shift, width, soft mode frequency and dielectric constant**

By using model values of various quantities for ADP-crystal, $T_c$ = 148K, $\Omega$ = 45cm$^{-1}$, $\lambda$ = 90 cm$^{-1}$, $(J+\gamma)$ = 180 cm$^{-1}$, $V_0$ = 40 cm$^{-1}$, $\mu_a \times 10^{18}$ = 4.70 cgs, $\mu_c \times 10^{18}$ = 2.95 cgs, $\omega_k$ = 153 cm$^{-1}$, the temperature dependences of width, shift and soft mode frequency have been calculated. Pseudospins, soft mode frequency and antiferroelectric mode frequency have been shown in Figs 1-3, respectively. The dielectric constants $(\in_c)$ and $(\in_a)$ have been shown is Figs 4 and 5.

**2.5 Temperature dependence of dielectric loss**

Using Eq. (31) and the calculated values dielectric loss has been calculated in the temperature range (134-176K) at 10 GHz for ADP crystal. The theoretical results are in fair agreement with experimental results of Busch[5] and Nagamiya[4]. The temperature variation of loss have also been shown in Figs 6-8. The dielectric loss versus $(T-T_c)^{-1}$ for ADP crystal is shown in Fig. 8.

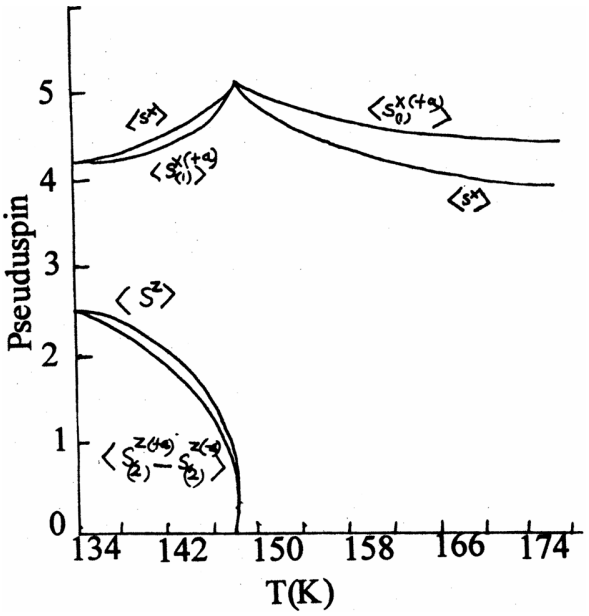


Fig. 1 — Temperature dependence of psuedospin in ADP crystal. (Present calculation)

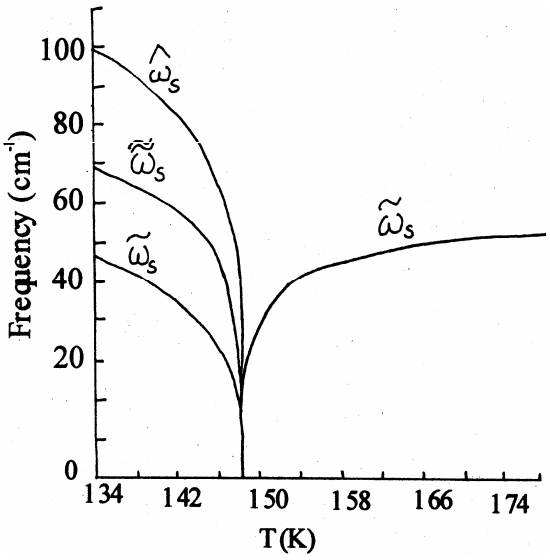


Fig. 2 — Temperature dependence of ferroelectric mode frequency in ADP crystal. (Present calculation – Exp.●)

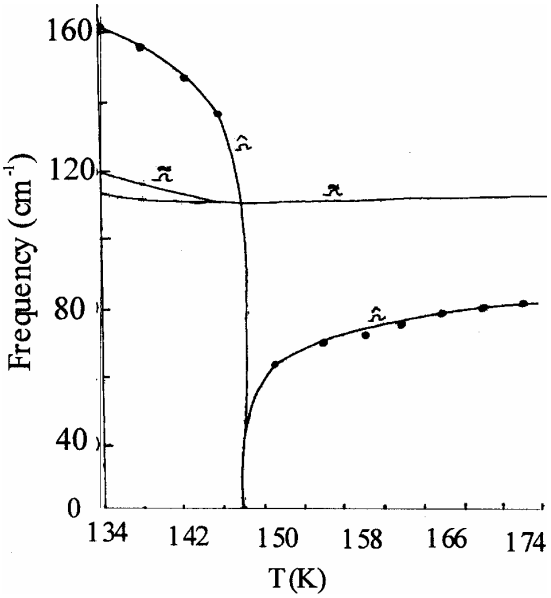


Fig. 3 — Temperature dependence of antiferroelectric soft mode frequency in ADP crystal. (Present calculation – Exp.[7]●)

**2.6 Frequency dependence of dielectric loss**

Putting calculated values of $\Gamma(\omega)$ and $\tilde{\tilde{\Omega}}$ for different temperatures into Eq. (31) dielectric loss is

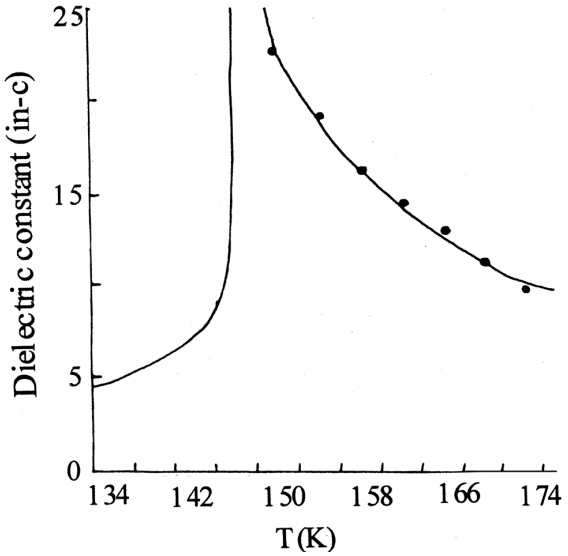


Fig. 4 — Temperature dependence of dielectric constant in ADP crystal. Present calculation – Exp.[6]●

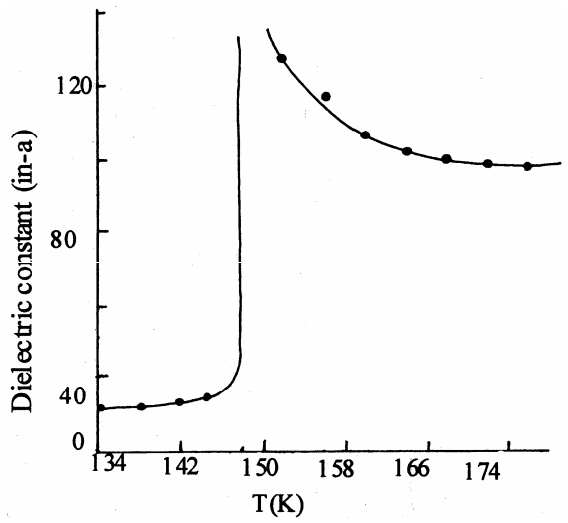


Fig. 5 — Temperature dependence of dielectric constant in ADP crystal. Present calculation – Exp.[6]●

obtained for ADP crystals in 1-35 GHz range at 134K. The variations are shown in Fig. 9. The increase in loss is followed by an increase in frequency in ADP crystal.

## 3 Results and Discussion

In this paper, by modifying four-sublattice pseudospin lattice coupled mode (PLCM) model for ADP-type antiferroelectric crystals by adding the third and fourth order phonon anharmonic interaction terms, the expressions for the soft mode frequency, dielectric constant and dielectric tangent loss are

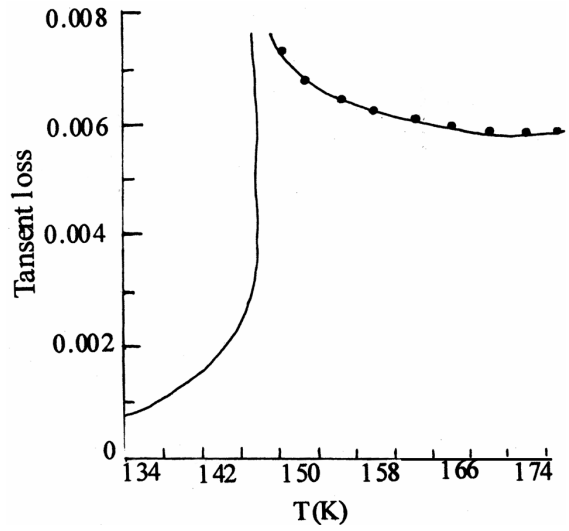


Fig. 6 — Temperature dependence of dielectric loss in ADP crystal. Present calculation – Exp.[6]●

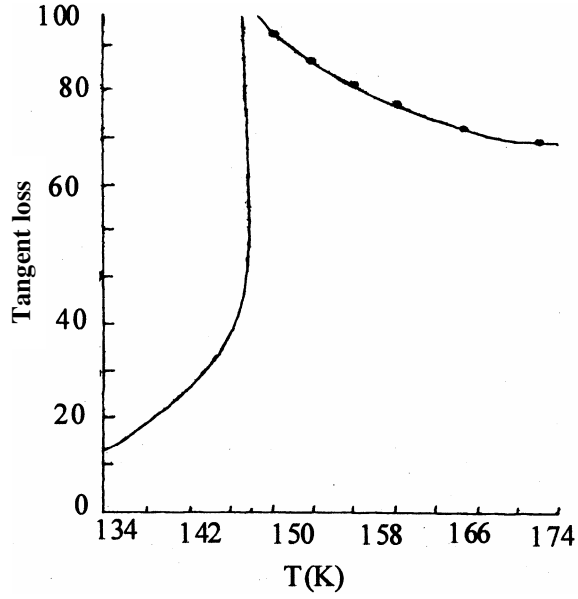


Fig. 7 — Temperature dependence of dielectric constant in ADP crystal. Present calculation – Exp.[6]●

evaluated theoretically. Using model values as given by Banerjee *et al.*[3]. , temperature variations of these quantities for ADP crystal were calculated. The present work differs with the earlier works in the sense that phonon anharmonic terms are not considered in this work. Only Benerjee *et al.* have considered but they truncated the correlations at an early stage and so could not obtain width and shift. In this way they could not explain dielectric loss and also could not obtain better results as reported in this

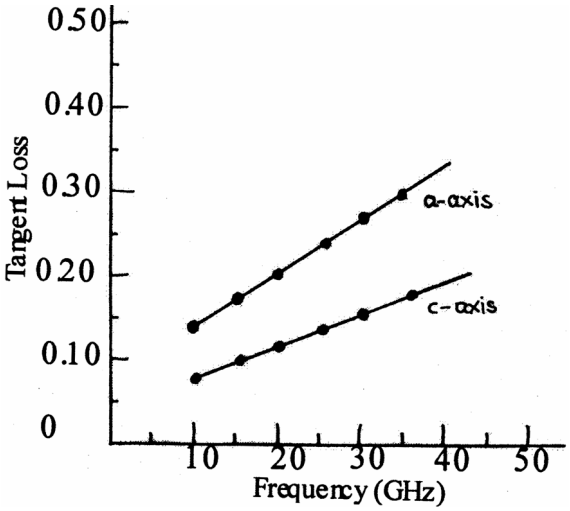


Fig. 8 — Temperature dependence of dielectric loss in ADP crystal. Present calculation – Exp.[5,6]●

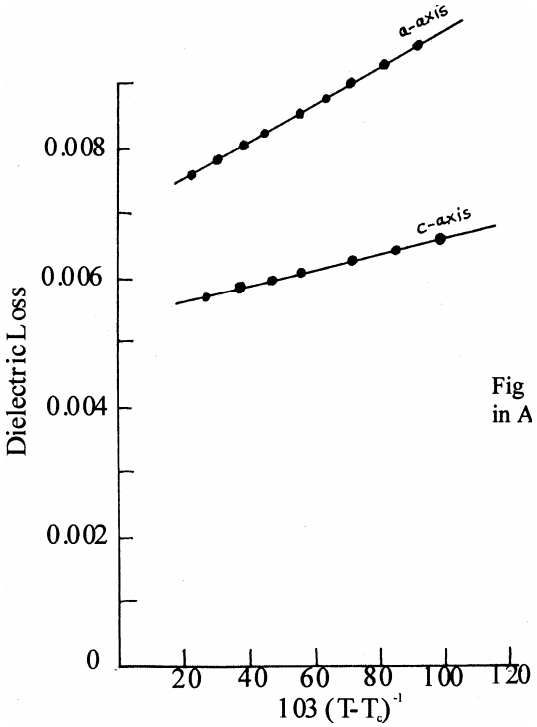


Fig. 9 — Frequency dependence of dielectric loss in ADP crystal. Present calculation – Exp.[5,6]●

paper. The Eq. (31) of this paper along with Figs 8 and 9 show that the values of dielectric loss vary linearly with frequency, which is in agreement with earlier experiments[5,6]. A transverse radiation field derives the low lying transverse mode of material in a forced vibration. Energy is transferred from the electromagnetic field to this lattice mode and is then degraded into other vibrational modes of the material. Due to anharmonic phonon interactions, decay processes take place. For example, third-order interaction 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 occur for fourth-and higher order interactions. In Figs 6-8, the loss shows Curie-Weiss behaviour i.e. losses are proportional to $(T\text{-}T_c)^{-1}$ in the vicinity of $T_c$ which is in agreement with earlier experiments[5,6]. The phonon anharmonic interactions significantly contribute to temperature dependences of soft mode, dielectric constant and loss at and above $T_c$.

## 4 Conclusions

Present study shows that soft mode theory successfully explains the dynamics of antiferroelectric transition in ADP in a quite similar way as the ferroelectric transition in KDP, which shows the possibility of a unified theory of ferroelectric and antiferroelectric transitions. It reveals that four sublattice lattice coupled mode model alongwith third and fourth order anharmonic interactions explains phase transition and the dielectric properties of ADP-type antiferroelectric crystals. The results of present calculation can also be extended to explain phase transition and the dielectric properties of other antiferroelctric crystals $Cu(HCOO)_2.\ 4H_2O$, $AgH_3IO_6$ and $(NH_4)_2H_3IO_6$.

## Acknowledgements

The author is indebted to Prof B S Semwal, Ex-Head, Physics Department, HNB Garhwal University, Srinagar for his valuable suggestions. He is also thankful to Prof RP Gairola (HNBGU, Srinagar), Prof U C Naithani (HNBGU, Pauri), Prof T C Goel (Director, BITS, Goa), Prof KPR Nair (CUSAT), Prof DC Dube (IIT, Delhi), Prof Ratnamala Chatterjee (IIT, Delhi), Prof RP Tandon (Delhi Univ), Prof Kamal Singh (VC Amrawati Univ), Prof VK Rastogi (Meerut University) and Dr Vinay Gupta (Delhi University) for their kind encouragements.

## References

1 Ishibashi S Ohya & Takagi Y, *J Phys Soc Jpn,* 37 (1974) 1035.
2 Havlin S, Litov E & Sompolinsky H, *Phy Lett* A, 51 (1975) 33.
3 Banerjee S, Nath D & Chaudhuri, B K, *Phys Rev* B, 24 (1981) 6469.
4 Nagamiya T, *Progr Theor Phys,* 7 (1952) 275.

5 Busch G, *Helv Phys Acta,* 11 (1938) 269.
6 Kaminow I P, *Phys Rev,* 138 A (1965) 1539.
7 Broberg T W, C Y She, Wall L S & Edwards D F, *Phys Rev B,* 6 (1972) 3332.
8 Sengupta S & Sengupta S P, *Bull Mat Sc,* 15 (1992) 333.
9 Khan H & Khan A H, *Indian J Pure & Appl Phys,* 33 (1995) 333.
10 Wada K, Yoshida S & Ihara N *J Phys Soc Jpn,* 70 (2001) 1019.
11 Stasyuk I V, Levitskii R R & Moina A P, *Phys Rev* B, 59 (1999-I) 8530.
12 Van S J, Reeuwijk, Moina A P & Graafsma H, *Phys Rev* B, 62 (2000-II) 6192.
13 Panwar N S, Upadhyay T C & Semwal B S *Pramana,* 33 (1989) 603.
14 Panwar N S, Upadhyay T C & Semwal B S, *Indian J Pure & Appl Phys*, 27 (1989) 765.
15 Upadhyay T C, Panwar N S & Semwal B S*, Int J Mod Phys,* 9 (1995) 45.
16 Upadhyay T C & Semwal B S, *Ind J Theor Phys,* 49 (2001) 53.
17 Upadhyay T C & Semwal B S, *Ind J Pure & Appl Phys,* 40 (2002) 615.
18 Upadhyay T C & Semwal B S, *Pramana,* 60 (2003) 525.
19 Semwal B S & Sharma P K, *Prog Theor Phys Jpn,* 51 (1974) 639.
20 Zubarev D N*, Sov Phys Usp,* 3 (1960) 320.
21 Kubo R, *J Phys Soc Jpn,* 12 (1957) 570; Suzuki M & Kubo R, *J Phys Soc Jpn* (Appendix), 24 (1968) 51.