

# Temperature Dependence of Dielectric Constant and Loss Tangent in Methyl Ammonium Aluminium Alum

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**Abstract:** The ferroelectric phase transition of MASD alum was studied by model of pseudospin-lattice coupled mode which has been modified by including cubic and quartic phonon anharmonic interaction terms. With the help of double-time temperature dependent Green's function method and modified Hamiltonian, expressions for dielectric constant, soft mode frequency and loss tangent has been evaluated. By fitting model values of physical quantities in the theoretical expressions, temperature dependence of dielectric, soft mode frequency and loss tangent have been obtained and compared with literature values which shows a good agreement.

**Keywords:** Green's function, Dielectric constant, Anharmonic interactions, Loss tangent

## Introduction

It is well known that ferroelectric materials find potential applications in technology due to their peculiar properties. They are used in memory devices as like infrared detectors, optical modulators, large capacitors *etc*<sup>1</sup>. Methyl ammonium aluminium alum (MASD),  $(\text{CH}_3\text{NH}_3)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is ferroelectric below 177 K. In high temperature phase the  $\text{CH}_3\text{NH}_3$  groups are found to be symmetrically oriented so that they are indistinguishable from each other<sup>2</sup>. But in low-temperature phase  $\text{CH}_3\text{NH}_3$  groups are separately arranged which look like a dumbbell. In high temperature phase  $\text{CH}_3\text{NH}_3$  groups are oriented in a disordered fashion, as if their average orientation looks spherical, while below  $T_c$  in the ordered state, they take on a particular orientation and become distinguishable and symmetric. The ordering of methyl group in MASD gives rise to order-disorder type of phase transition. Singh *et al.*,<sup>3</sup> have done synthesis and characterization studies on alum. Derby<sup>4</sup> has carried out crystal growth studies of methyl ammonium aluminium alum. Ghanem *et al.*,<sup>5</sup> have studied experimentally the effect of doping different polymers on these alums. Sachdeva *et al.*,<sup>6</sup> have done crystal growth studies on methyl ammonium aluminium alum. Basra *et al.*,<sup>7</sup> have done electrical conductivity in methyl ammonium

aluminium alum. Sajan *et al.*,<sup>8</sup> have studied physical properties of polymer mixed alums. Previously Chaudhury *et al.*,<sup>9</sup> have studied ferroelectric transition in methyl ammonium aluminium alum using pseudospin-lattice coupled mode model with fourth order phonon anharmonic interaction term. They have not considered third-order phonon anharmonic interaction term. They have decoupled correlations at an early stage so that some important interactions disappeared from their results.

The present work include pseudospin-lattice coupled mode model along with third and fourth-order phonon anharmonic interactions terms. We shall decouple the correlations at proper stage. In MASD alum, since there is no isotope effect hence the term  $B_{ij}$  (which has been considered by earlier research<sup>2</sup>) makes almost no contribution to the system and so we have not included this term in our model of MASD (as suggested by Chunlei *et al.*,<sup>10</sup> also). By using double-time thermal Green's function method along with modified model Hamiltonian, expressions for renormalized soft mode frequency, dielectric constant and loss tangent, shift and width have been obtained. By fitting model values of various quantities in derived expressions, their thermal variations have been calculated. The theoretically calculated expressions for soft mode frequency have been compared with correlated values of soft mode frequency obtained from experimental results of dielectric constant for MASD crystal reported by Pepinsky *et al.*<sup>12</sup>.

Theoretical results for loss tangent and dielectric constant for MASD crystal have been compared with experimentally reported results of Pepinsky *et al.*<sup>12</sup>.

### Model Hamiltonian

In the case of methyl ammonium aluminium alum, it is concluded from neutron diffraction experiment that the asymmetric distribution of the H bonds around the sulphate groups might be a cause of the ferroelectric transition. Concentrating our attention on the proton subsystem associated with the active ions, the simplest form of modified model Hamiltonian is expressed as;

$$H = -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z + \frac{1}{4} \sum_k \omega_k (A_k A_k^+ + B_k B_k^+) - \sum_{ik} V_{ik} S_i^z A_k + \sum_{k_1 k_2 k_3} V^4(k_1, k_2, k_3) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1 k_2 k_3 k_4} V^4(k_1, k_2, k_3, k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4}. \quad (1)$$

In the above equation, last two terms have been added by us.  $S_i^a$  ( $a=x,y,z$ ) is the  $\alpha^{\text{th}}$  component of the pseudospin  $\vec{S}_i$ ,  $\Omega$  is proton tunneling frequency.  $J_{ij}$  is spin-spin interaction constant.  $A_k$  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.

### Green's Function, Shift and Width

Following Zubarev<sup>13</sup>, we consider the Green's function

$$G_{ij}(t-t') = \langle \langle S_i^z(t); S_j^z(t') \rangle \rangle, = -i\theta(t-t') \langle [S_i^z(t); S_j^z(t')] \rangle \quad (2)$$

Differentiating Green's function Eq. (2) two times with respect to times  $t$  and  $t'$  respectively, Fourier transforming and writing in Dyson's equation form is obtained.

$$G_{ij}(\omega) = \frac{\Omega \langle S_i^x \rangle \delta_{ij}}{\pi [\omega^2 - \tilde{\Omega}^2 - P(\omega)]}, \text{ where} \quad (3)$$

$$\tilde{\Omega}^2 = 4\Omega^2 + \frac{i \langle [F(t)], S_j^y(t') \rangle}{\langle S_j^x \rangle}, \quad \text{and} \quad (4)$$

$$P(\omega) = \frac{\pi}{\Omega \langle S_i^x \rangle} \langle \langle F(t); F'(t') \rangle \rangle, \quad \text{with} \quad (5)$$

$$\begin{aligned} \langle \langle F_i(t); F_j'(t') \rangle \rangle = & \Omega^2 J_{ij}^2 \{ \langle \langle S_i^x S_j^z; S_i^x S_j^z \rangle \rangle + \langle \langle S_i^x S_j^z; S_i^z S_j^x \rangle \rangle + \langle \langle S_i^z S_j^x; S_i^x S_j^z \rangle \rangle + \langle \langle S_i^z S_j^x; S_i^z S_j^x \rangle \rangle \} \\ & + \Omega^2 V_{ik}^2 \{ \langle \langle A_k S_i^x; S_i^x A_k^+ \rangle \rangle \}. \end{aligned} \quad (6)$$

Above equation consist higher order Green's functions which are evaluated after decoupling them by using decoupling scheme  $\langle AB; CD \rangle = \langle AB \rangle \langle CD \rangle + \langle AC \rangle \langle BD \rangle + \langle AD \rangle \langle BC \rangle$ . Simpler Green's functions are evaluated using zeroth-order approximation: *i.e.* neglecting higher order Green's functions in them. In this way  $\langle \langle F(t); F(t') \rangle \rangle$  is evaluated. Its real part is called shift  $\Delta(\omega)$  and imaginary part is called width  $\Gamma(\omega)$ . Hence Eq. (3) becomes

$$G_{ij}(\omega) = \frac{\Omega \langle S_i^x \rangle \delta_{ij}}{\pi [\omega^2 - \tilde{\Omega}^2 - 2i\Omega\Gamma(\omega)]}. \quad (7)$$

$$\text{where,} \quad \hat{\Omega}^2 = \tilde{\Omega}^2 + \Delta(\omega), \quad (8)$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \quad (9)$$

$$a = J \langle S_i^z \rangle, \quad (10)$$

$$b = 2\Omega, \quad (11)$$

$$c = J \langle S^x \rangle, \quad (12)$$

shift  $\Delta(\omega)$  and width  $\Gamma(\omega)$  are obtained as

$$\Delta(\omega) = \frac{a^4}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{b^2 c^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{V_{ik}^2 N_K a^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{2V_{ik}^2 \langle S_{li}^x \rangle \omega_k \delta_{k-k'}}{(\omega^2 - \tilde{\omega}_k^2) + 4\omega_k^2 \Gamma_k^2(\omega)}, \quad (13)$$

and

$$\Gamma(\omega) = \frac{\pi a^4}{4\Omega\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{b^2 c^2}{4\Omega\tilde{\Omega}} [\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})] + \frac{2V_{ik}^2 \langle S_{li}^x \rangle \omega_k \delta_{k-k'}}{(\omega^2 - \tilde{\omega}_k^2) + 4\omega_k^2 \Gamma_k^2(\omega)}. \quad (14)$$

In Eqs. (13) and (14)  $\tilde{\omega}_k$  and  $\Gamma_k(\omega)$  are modified phonon frequency and phonon width respectively. These appear in the evaluation of phonon Green's function  $\langle \langle A_k; A_k^+ \rangle \rangle$  which is obtained as

$$\langle\langle A_k; A_k^+ \rangle\rangle = \frac{\omega_k \delta_{kk'}}{\omega^2 - \tilde{\omega}_k - 2i\omega_k \Gamma_k(\omega)} \quad (15)$$

In Eq. (15)  $\tilde{\omega}_k$  is obtained as

$$\tilde{\omega}^2 = \tilde{\omega}_k^2 + 2\omega_k \Delta_k(\omega). \quad (16)$$

$\Gamma_k(\omega)$  is obtained as

$$\begin{aligned} \Gamma_k(\omega) = & 9\pi \sum_{k_1 k_2} \left| V^{(3)}(k_1, k_2, -k) \right|^2 \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \left\{ (n_{k_2} + n_{k_1}) [\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2})] \right. \\ & + (n_{k_2} - n_{k_1}) [\delta(\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta(\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2})] \left. \right\} \\ & + 48\pi \sum_{k_1 k_2} \left| V(k_1, k_2, k_3, -k_4) \right|^2 \left\{ 1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_4} \right\} \\ & \left[ \delta(\tilde{\omega} + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}) - \delta(\tilde{\omega} - \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2} - \tilde{\omega}_{k_3}) \right] \end{aligned} \quad (17)$$

In Eq. (16)  $\Delta_k(\omega)$  appears which is obtained as

$$\begin{aligned} \Delta_k(\omega) = & 18P \sum_{k_1 k_2} \left| V^3(k_1, k_2, -k) \right|^2 \frac{\omega_{k_1} \omega_{k_2}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2}} \left\{ (n_{k_1} + n_{k_2}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_2} + \tilde{\omega}_{k_2})^2} + (n_{k_2} + n_{k_1}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2})^2} \right\} + 48P \\ & \sum_{k_1 k} \left| V^{(4)}(k_1, k_2, k_3, -k) \right|^2 \frac{\omega_{k_1} \omega_{k_2} \omega_{k_3}}{\tilde{\omega}_{k_1} \tilde{\omega}_{k_2} \tilde{\omega}_{k_3}} \left\{ (1 + n_{k_1} n_{k_2} + n_{k_2} n_{k_3} + n_{k_3} n_{k_1}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} \right. \\ & \left. + 3(1 - n_{k_2} n_{k_1} + n_{k_2} n_{k_3} - n_{k_3} n_{k_1}) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3}}{\omega^2 - (\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2} + \tilde{\omega}_{k_3})^2} + \text{higher terms.} \right\} \end{aligned} \quad (18)$$

In Eq. (18) P stands for principal part.

### Modified soft mode frequency

According to Cochran the ferroelectric transition in certain crystals results from freezing of normal mode frequency at transition temperature. The expression for this frequency can be easily obtained from Eq. (8). Putting value of  $\Delta(\omega)$  in Eq. (8) and simplifying Eq. (19) obtained as follows.

$$\hat{\Omega}^2 = \frac{1}{2} \left[ (\tilde{\Omega}^2 + \tilde{\omega}_k^2) \pm \left\{ (\tilde{\omega}_k^2 - \tilde{\Omega}^2)^2 + 8V_{ik}^2 \langle S_i^x \rangle \Omega \right\}^{\frac{1}{2}} \right]. \quad (19)$$

The transition temperature  $T_C$  can be evaluated by putting the condition that phase transition occurs when T approaches  $T_C$ , i.e. when  $\tilde{\Omega}$  becomes zero. From Eq. (9) we get  $\sqrt{a^2 + b^2 - bc} = 0$ ,  $a = J \langle S^Z \rangle$  and  $\langle S^Z \rangle = 0$  at  $T_C$  so  $b^2 - bc = 0$ , where  $c = J' \langle S^X \rangle$  and  $\langle S^X \rangle = \tanh(\frac{\Omega}{2k_B T_C})$  at  $T_C$ . Hence we obtain  $\tanh(\frac{\Omega}{2k_B T_C}) = \frac{4\Omega}{J'}$  which gives transition temperature  $T_C$  as

$$T_c = \frac{\Omega}{2k_B \tanh^{-1}\left(\frac{4\Omega}{J'}\right)}, \quad (20)$$

Where

$$J' = J + \frac{2V_{ik}^2 \omega_k^2}{\tilde{\omega}_k^2}. \quad (21)$$

Above equations show that modified soft mode frequency  $\hat{\Omega}_-$  is function of tunneling frequency  $\Omega$  as well as modified phonon anharmonic frequency  $\tilde{\omega}_k$ . The transition temperature  $T_c$  is function of tunneling frequency  $\Omega$ , spin-lattice interaction constant  $V_{ik}$  as well as modified phonon frequency  $\tilde{\omega}_k$ . The phonon frequency depends upon phonon anharmonic interactions terms.

#### Dielectric constant and loss tangent

The dielectric constant  $\epsilon$  is related to susceptibility

$$\chi \text{ as } \epsilon = 1 + 4\pi\chi. \quad (23)$$

$$\text{In ferroelectric crystals, always, } \epsilon \gg 1 \text{ therefore } \epsilon = 4\pi\chi \quad (24)$$

Hence one obtains using Eqs. (24), (22) and Green's function (7) the expression for dielectric constant  $\epsilon$  as

$$\epsilon = - \frac{8\pi N \mu^2 \Omega \langle S_i^x \rangle}{\left[ \omega^2 - \hat{\Omega}^2 - 2\Omega i \Gamma(\omega) \right]} \quad (25)$$

The ferroelectric and dielectric material loses energy in the form of heat, called dielectric tangent loss. This is ratio of real and imaginary parts of dielectric constant. From Eq. (25) we get the following:

$$\tan \delta = - \frac{2\Omega \Gamma(\omega)}{(\omega^2 - \hat{\Omega}^2)} \quad (26)$$

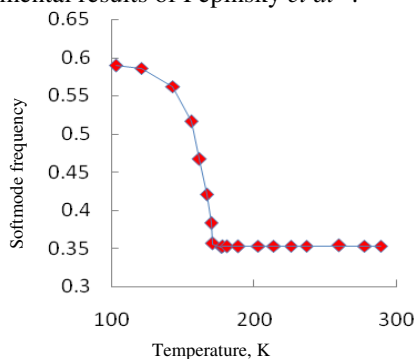
From Eqs. (25) and (26) we observe that dielectric constant and loss tangent depend on modified soft mode frequency. Hence these depend upon tunneling frequency as well as anharmonic interactions terms.

#### Numerical calculation and Discussion

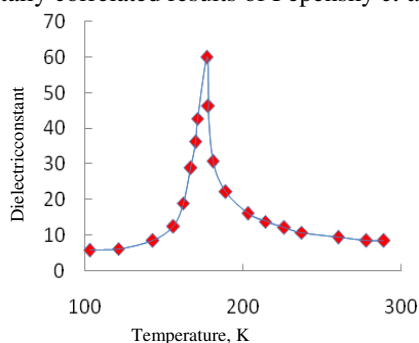
Numerical calculations have been carried out with the help of model values of the physical quantities appearing in expressions, derived for methyl ammonium aluminium alum, *i.e.*  $\Omega = 0.7$ ,  $T_c = 177$  K,  $J = 488.99$  cm<sup>-1</sup>,  $V_{ik} = 65.56$  cm<sup>-1</sup>,  $N = 0.512 \times 10^{21}$ ,  $\mu \times 10^{18}$  cgs = 3.513,  $\omega_k = 5$  cm<sup>-1</sup>,  $C = 540$  K,  $J = 366.75$  cm<sup>-1</sup>,  $A_k \times 10^{17}$  (erg K<sup>-1</sup>) = 37.66. Their temperature variations of shift, width, soft mode frequency, dielectric constant and loss tangent have been calculated. The theoretical variation of soft mode frequency with temperature are compared with values obtained by correlating the experimental data on dielectric constant measurements reported by Pepinsky *et al.*,<sup>11</sup> for MASD crystal. The variations of dielectric constant and loss tangent have been compared with experimental results of others<sup>13</sup>. Our results agree with experimental results of these researchers [Figures (1, 2 and 3)].

## Conclusion

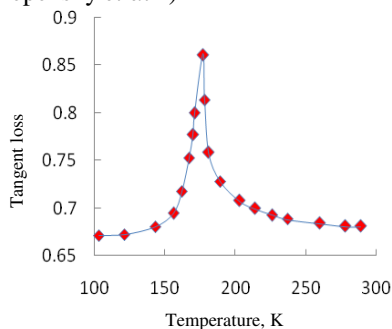
Our study shows that the pseudospin-lattice coupled mode model along with third-and fourth-order phonon anharmonic interaction terms explains well the temperature dependences of ferroelectric properties of methyl ammonium aluminium alum. The soft mode frequency is renormalized by phonon anharmonic interaction terms. The modified soft mode frequency clearly explains the nature of phase transition at 177 K in MASD alum, which agrees with experimental results of Pepinsky *et al*<sup>12</sup>.



**Figure 1.** Temperature dependence of soft mode frequency  $\hat{\Omega}(\text{cm}^{-1})$  of MASD alum (— Our results;  $\blacklozenge$  experimentally correlated results of Pepinsky *et al*<sup>12</sup>)



**Figure 2.** Temperature dependence of dielectric constant  $\epsilon$  of MASD alum (— Our results;  $\blacklozenge$  Experimental results of Pepinsky *et al*<sup>12</sup>)



**Figure 3.** Temperature dependence of tangent loss ( $\delta$ ) of MASD alum (— Our results;  $\blacklozenge$  Experimental results of Pepinsky *et al*<sup>12</sup>)

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