Temperature dependence of dielectric constant and loss tangent in methyl ammonium aluminium alum

Arvind Kumar Rawat* & Trilok Chandra Upadhyay
Department of Physics, HNB Garhwal University, Srinagar 246 174, India

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A model of pseudospin-phonon coupled mode for methyl ammonium aluminium alum (MASD) has been modified to include cubic and quartic phonon anharmonic interactions. With the help of double-time temperature dependent Green’s function method and modified Hamiltonian, expressions for soft mode frequency, dielectric constant and loss tangent have been evaluated. By fitting model values of physical quantities in the theoretical expressions, temperature dependence of soft mode frequency, dielectric constant and loss tangent have been obtained and compared with experimental results of Pepinsky et al.15, which show a good agreement.

Keywords: Dielectric constant, Pseudospin-phonon interaction, Anharmonic interactions

1 Introduction
Ferroelectric materials find potential applications in technology due to their peculiar properties. They are used in memory devices, infrared detectors, optical modulators, large capacitors etc.1 Methyl ammonium aluminium alum (MASD), (CH$_3$NH$_3$)$_2$Al(SO$_4$)$_3$.12H$_2$O is ferroelectric below 177 K. In high temperature phase, the CH$_3$NH$_3$ groups are found to be symmetrically oriented so that they are indistinguishable from each other.2 But in low-temperature phase, CH$_3$NH$_3$ groups are separately arranged which look like a dumbbell. In high temperature phase, CH$_3$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. Derby3 has carried out crystal growth study of methyl ammonium aluminium alum. Weber4 has carried out studies of methyl ammonium aluminium alum. Boujelben and Mihiri5 have done Raman spectroscopic studies in methyl ammonium aluminium alum. Sachdeva et al.6 have done crystal growth studies on methyl ammonium aluminium alum. Zang et al.7 have carried out experimental determination of hysteresis curve for this alum. Basra et al.8 have studied electrical conductivity of alums. Singh et al.9 have done synthesis and characterization studies on alums. Sajan et al.10 have studied physical properties of polymer mixed alums. Ghanem et al.11 have studied experimentally the effect of doping different polymers on these alums. Previously Chaudhury et al.12 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 and some important interactions have disappeared from their results.

In the present work, the pseudospin-lattice coupled mode model along with third and fourth-order phonon anharmonic interactions terms, has been considered. 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 researchers5) 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.13 also). By using modified model and double-time thermal Green’s function method, expressions for width, shift, renormalized soft mode frequency, transition temperature, dielectric constant and loss tangent have been obtained. By fitting model values of various quantities in derived formulae, their thermal variations have been calculated. The theoretically calculated values for soft mode frequency have been compared with correlated values of soft mode frequency obtained from experimental

*Corresponding author (E-mail: arvindsgfi@gmail.com)
results of dielectric constant for MASD crystal reported by Pepinsky et al.\textsuperscript{15} Theoretical results for dielectric constant and loss tangent for MASD crystal have been compared with experimentally reported results of Pepinsky et al.\textsuperscript{15}

2 Model Hamiltonian

For methyl ammonium 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 sub-system groups might be a cause of the ferroelectric transition. 

\[ H = -2Ω \sum S_i^+ \sum_j S_j^- + \frac{1}{2} \sum_j J_j S_i^+ S_j^- + \frac{1}{4} \sum_j \omega_j (A_j^+ A_j^- + B_j^+ B_j^-) - \sum_{ij} V_{ij} S_i^+ A_j^- + \sum_{ijk} V^{ijk} (k_i k_j k_k) A_i A_j A_k \] 

(1)

In Eq. (1), the last two terms have been added by us. \( S_i^a (a=x, y, z) \) is the \( a \)th component of the pseudospin \( \vec{S} \), \( Ω \) is proton tunneling frequency, \( J_j \) 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.

3 Green’s Function, Shift and Width

Following Zubarev\textsuperscript{14}, the Green’s function is considered as:

\[ G_{ij}(t-t') = \langle S_i(t) S_j(t') \rangle \]

(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 one obtains:

\[ G_{ij}(ω) = \frac{Ω}{π(ω^2 - \tilde{Ω}^2 - P(ω))} \delta_{ij} \]

(3)

where

\[ \tilde{Ω}^2 = 4Ω^2 + \frac{Ω^2}{Ω} \frac{\langle[S(t), S(t')] \rangle}{\langle S^+ \rangle} \]

(4)

and

\[ P(ω) = \frac{π}{Ω \langle S^+ \rangle} \langle [F(t), F(t')] \rangle \]

(5)

with

\[ \langle [F(t), F(t')] \rangle = Ω^2 J^2 \left[ \langle S_i^+ S_j^+ S_i^- S_j^- \rangle + \langle S_i^+ S_i^- S_j^+ S_j^- \rangle \right] \]

(6)

\[ + \langle S_i^+ S_j^+ S_i^- S_j^- \rangle + \langle S_i^+ S_i^- S_j^+ S_j^- \rangle + Ω^2 V_{ij} \left[ \langle A_i^+ A_j^- \rangle + \langle A_i^+ A_j^- \rangle \right] \]

(6)

\[ + Ω^2 V_{ij} \left[ \langle A_i^+ A_j^- \rangle + \langle A_i^+ A_j^- \rangle \right] \]

Eq. (6) contains 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, \( \langle [F(t), F(t')] \rangle \) is evaluated. Its real part is called shift \( ∆(ω) \) and imaginary part is called width \( Γ(ω) \)

Hence, Eq. (3) becomes

\[ G_{ij}(ω) = \frac{Ω}{π(ω^2 - \tilde{Ω}^2 - 2iΩΓ(ω))} \delta_{ij} \]

(7)

where

\[ \tilde{Ω}^2 = Ω^2 + Δ(ω) \]

(8)

\[ a = J \langle S_i^+ \rangle \]

(9)

\[ b = 2Ω \]

(10)

\[ c = J \langle S^+ \rangle \]

(11)

shift \( Δ(ω) \) and width \( Γ(ω) \) are obtained as:

\[ Δ(ω) = \frac{a^4}{8Ω} \left[ \delta(ω + Ω) - δ(ω - Ω) \right] + \frac{b^2 c^2}{2Ω} \left[ \delta(ω^2 - Ω^2) - \delta(ω^2 - Ω^2) \right] \]

(12)

\[ + \left( \omega^2 - \tilde{ω}_k^2 \right) + 4ω_k^2 Γ_k(ω) \]

(13)

and

\[ Γ(ω) = \frac{πa^4}{4ΩΩ} \left[ δ(ω - Ω) - δ(ω + Ω) \right] + \]

\[ \frac{b^2 c^2}{4ΩΩ} \left[ δ(ω - Ω) - δ(ω + Ω) \right] + \frac{2V_{ij}^2 \delta(ω - Ω) - \delta(ω + Ω)}{\left( ω^2 - \tilde{ω}_k^2 \right)} + 4ω_k^2 Γ_k(ω) \]

(14)

In Eqs (13) and (14), \( \tilde{ω}_k \) and \( Γ_k(ω) \) are modified phonon frequency and phonon width, respectively. These appear in the evaluation of phonon Green’s function \( \langle [A_i^+ A_j^-] \rangle \) which is obtained as:
\begin{align}
\left\langle A_k^* A_k \right\rangle &= \frac{\omega_k \delta_{kk}}{\omega^2 - \omega_k - 2i\omega \Gamma_k (\omega)} \quad \ldots (15)
\end{align}

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

\begin{align}
\tilde{\omega}_k^2 &= \omega_k^2 + 2\alpha \Delta_k (\omega) \quad \ldots (16)
\end{align}

\( \Gamma_k (\omega) \) is obtained as:

\begin{align}
\Gamma_k (\omega) &= 9\pi \sum_{k'k_2} \left| V^{(1)} (k, k_2, -k) \right|^2 \frac{\omega_{k_2} \omega_{k_2}}{\omega_{k_1} \omega_{k_1}} \\
&\times \left[ n_{k_2} + n_{k_1} \right] \left\{ \delta (\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta (\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}) \right\} \\
&+ \left( n_{k_2} - n_{k_1} \right) \times \\
&\times \left\{ \delta (\omega + \tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}) - \delta (\omega + \tilde{\omega}_{k_1} - \tilde{\omega}_{k_2}) \right\} \\
&+ 48\pi \sum_{k_2} \left| V^{(4)} (k, k_2, k_2, -k) \right|^2 \\
&\times \left[ n_{k_2} + n_{k_1} \right] \left\{ \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} + \omega_{k_2}} + \left( n_{k_2} + n_{k_1} \right) \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} - \omega_{k_2}} \right\} \\
&\times \left\{ \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} + \omega_{k_2}} + \left( n_{k_2} + n_{k_1} \right) \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} - \omega_{k_2}} \right\} \\
&+ 48P \\
&\times \sum_k \left| V^{(4)} (k, k_2, k_2, -k) \right|^2 \\
&\times \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} + \omega_{k_2}} \left\{ \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} + \omega_{k_2}} + \left( n_{k_2} + n_{k_1} \right) \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} - \omega_{k_2}} \right\} \\
&\times \left\{ \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} + \omega_{k_2}} + \left( n_{k_2} + n_{k_1} \right) \frac{\omega_{k_2}}{\omega^2 - \omega_{k_1} - \omega_{k_2}} \right\} \\
&+ 3 \\
&\times \left( 1 - n_{k_2} n_{k_1} + n_{k_2} n_{k_1} - n_{k_2} n_{k_1} \right) \frac{\tilde{\omega}_{k_2}^4 + \tilde{\omega}_{k_2}^4 + \tilde{\omega}_{k_2}^4}{\omega^2 - \tilde{\omega}_{k_1}^2 + \tilde{\omega}_{k_2}^2 + \tilde{\omega}_{k_3}^2} + \\
&\text{higher terms.} \quad \ldots (17)
\end{align}

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

\begin{align}
A_k (\omega) &= 188 \sum_{k,k_2} \left| V^{(1)} (k, k_2, -k) \right|^2 \frac{\omega_{k_2} \omega_{k_2}}{\omega_{k_1} \omega_{k_1}} \\
&\times \left( n_{k_2} + n_{k_1} \right) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - \omega_{k_1} + \omega_{k_2}} \left( n_{k_2} + n_{k_1} \right) \frac{\tilde{\omega}_{k_1} + \tilde{\omega}_{k_2}}{\omega^2 - \omega_{k_1} - \omega_{k_2}} \\
&+ 3 \\
&\text{higher terms.} \quad \ldots (18)
\end{align}

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

4 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, one obtains:

\[ \hat{\Delta}^2 = \frac{1}{2} \left[ \tilde{\Omega}^2 + \tilde{\omega}_i^2 \right] \left\{ \frac{\tilde{\omega}_i^2 - \tilde{\Omega}^2}{\tilde{\omega}_i^2 - 2\Omega i T(\omega)} \right\} \quad \ldots (19) \]

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), one obtains \( \sqrt{a^2 + b^2 - bc} = 0, a = J \langle S^z \rangle \) and \( \langle S^z \rangle = 0 \) at \( T_C \) so \( b^2 - bc = 0 \), where \( c = J' \langle S^z \rangle \) and \( \langle S^x \rangle = \tanh \left( \frac{\Omega}{2k_B T_C} \right) \) at \( T_C \). Hence, we obtain

\[ \tan \left( \frac{\Omega}{2k_B T_C} \right) = \frac{4\Omega}{J'} \] which gives transition temperature \( T_C \) as:

\[ T_C = \frac{\Omega}{2k_B \tanh^{-1} \left( \frac{4\Omega}{J'} \right)} \quad \ldots (20) \]

where

\[ J' = J + \frac{2V_ik^2 \omega_k^2}{\omega_k^2} \quad \ldots (21) \]

Equations (19-21) show that modified soft mode frequency \( \tilde{\Omega}_- \) is a 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.

5 Dielectric Constant and Loss tangent

Following Zubarev, the electrical susceptibility \( \chi \) is expressed as:

\[ \chi = -\lim_{\omega \to 0} 2\pi N\mu^2 G_{ij} (\omega + i\pi \chi) \quad \ldots (22) \]

The dielectric constant \( \varepsilon \) is related to susceptibility \( \chi \) as \( \varepsilon = 1 + 4\pi \chi \). \ldots (23)

In ferroelectric crystals, always, \( \varepsilon >> 1 \) therefore \( \varepsilon = 4\pi \chi \) \ldots (24)

Hence, one obtains using Eqs. (24), (22) and Green’s function in Eq. (7), the expression for dielectric constant \( \varepsilon \) as:

\[ \varepsilon = -\frac{8\pi N\mu^2 \Omega \langle S^x \rangle}{\left[ \omega^2 - \tilde{\Omega}^2 - 2\Omega i T(\omega) \right]} \quad \ldots (25) \]
In dielectric and ferroelectric materials, some power is lost in the form of heat, called dielectric tangent loss. This is ratio of real and imaginary parts of dielectric constant. From Eq. (25), one obtains

\[
\tan\delta = \frac{2\Omega\hat{H}(\omega)}{\Omega^2 - \hat{Q}^2} \quad \ldots (26)
\]

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

6. Results and Discussion

For calculation of the model values, the physical quantities appearing in expressions, derived for methyl ammonium aluminium alum, i.e., \( \Omega = 0.7, T_c = 177 \text{ K}, J = 488.99 \text{ cm}^{-1}, V_{k} = 65.56 \text{ cm}^{-1}, N = 0.512 \times 10^{21}, \mu \times 10^{18} \text{ cgs} = 3.513, \omega_k = 5 \text{ cm}^{-1}, C = 540 \text{ K}, J = 366.75 \text{ cm}^{-1}, A_k \times 10^{17} (\text{erg.K}^{-1}) = 37.66, \) have been used. Temperature variations of shift, width, soft mode frequency, dielectric constant and loss tangent have been calculated. The theoretical variations of soft mode frequency with temperature are compared with values obtained by correlating the experimental data on dielectric constant measurements reported by Pepinsky \textit{et al.}\textsuperscript{15} for MASD crystal. The variations of dielectric constant and loss tangent have been compared with experimental results of Pepinsky \textit{et al.}\textsuperscript{15} Present results agree with experimental results of these researchers (Figs. 1-3).

7. Conclusions

Present study shows that the pseudospin-lattice coupled mode model along with third-and fourth-order phonon anharmonic interaction terms explains well the temperature dependence of dielectric and ferroelectric properties of methyl ammonium aluminium alum. The phonon anharmonic terms renormalize the soft mode frequency. The modified soft mode frequency clearly explains the nature of phase transition at 177 K in MASD alum.

If shift, width, and third order anharmonic interaction terms are neglected from present calculations, present results at once reduce to results of Chaudhury \textit{et al.}\textsuperscript{12} These researchers have decoupled the correlations in the early stage and have
not considered the third-order phonon anharmonic terms. Therefore, they could not obtain better and convincing results to explain ferroelectric transition in MASD alum. In the present work, the correlations have been solved by decoupling them at proper stage. Hence, all the important interactions could be contained in the expressions. Therefore, present results are much better and convincing, which agree with experimental results of Pepinsky et al\textsuperscript{15}.

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References