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Temperature dependence of soft mode frequency and loss tangent of ammonium iron alum

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The pseudo spin-lattice coupled mode model has been modified by adding third- and fourth-orders phonon anharmonic interactions terms, with the help of double-time temperature dependent Green's function method expressions. The values of ferroelectric mode frequency, dielectric constant and loss tangent have been derived. Model values of physical quantities in above expressions have been fitted. Temperature dependence of above quantities has been calculated numerically. Theoretical results have been compared with experimental results of others. A good agreement has been found.

Keywords: Pseudo spin-lattice coupled mode, Soft mode, Anharmonic interaction, Dielectric constant

1 Introduction

The ferroelectric substances have shown potential applications in production of small size capacitors of high capacitance, memory devices for computers, transducers, and infrared detectors. The alums are interesting materials. Some alums are ferroelectric. Ammonium iron alum, $(NH_4)Fe(SO_4)_2.12H_2O$ is ferroelectric below 88 K. Below 88 K, it is cubic while above 88 K it is paraelectric. In AFeSD alum NH_4^+ group gives rise to order-disorder type of mechanism in proton subsystem associated with these groups. This is assumed to be responsible for the ferroelectric phase transitions in several alums. Due to order-disorder character of the ammonium group in AFeSD, the H-bonds associated with these groups undergo some kind of ordering. It then becomes possible to apply pseudo spin model similar to the case of KDP system, after suitable modification. The proton motion is associated with the "active" ammonium ion. In this crystal there are very little isotope effect on T_c and C, the pseudo spin motion should be highly damped with strong anharmonic phonon interactions. There has been a considerable interest in the experimental study of AFeSD alum. Robert and Sambles[1] have carried out spin relaxation phenomena in ammonium ferric alum using Mossbauer spectroscopy. Weber[2] has carried out experimental study of dielectric properties of AFeSD alum. Compbell and Debenedetti[3] have carried out Mossbaur effect hyperfine structure of dilute ferric alum. Derby[4] has carried out crystal growth of AFeSD alums. Makoto and Kazuyuki[5] have carried out luminescence from alums. Boujelbene and Mihiri[6] have done Raman spectroscopic studies in AFeSD alum. Torgashev and Yuzyuk[7] have carried out Raman spectroscopy of alums. Sachdeva *et al.*[8] have done experimental crystal growth studies on AFeSD alum. Venkatesh and Narayanan[9] have carried out spectroscopy studies of ferroelectric alums. Petrusevki[10] has carried out vibrational spectra of AFeSD, alums. Frost and Kloprogge[11] have carried out Raman microscopy study of AFeSD alum and related alums. Gu and Li[12] have carried out spectral properties of AFeSD alum. Shaxin *et al.*[13] have studied application of AFeSD alum in inorganic synthesis. Gu and Ho[14] have done spectral properties studies on AFeSD alum. Bow *et al.*[15] have studied experimentally the adjuvant action of AFeSD alums. Earlier theoretical studies on AFeSD alum have been done by O' Reilly and Tsang[16]. Thereafter Chaudhury *et al.*[17] have done theoretical study of AFeSD and MASD alums. Chaudhury *et al.*[17] have applied pseudo spin-lattice coupled-mode model. These authors have not considered third order phonon anharmonic interaction term. Moreover, they have decoupled the correlations at an early stage. As a result some important interactions were disappeared from their calculations. In the present work, we shall modify pseudo spin-lattice coupled mode model by adding the third- and fourth-order phonon anharmonic interactions terms. By using double-time thermal Green's function method[18], expressions for ferroelectric mode frequency,

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dielectric constant and loss tangent will be obtained. Numerical calculations will be done to obtain thermal dependence of above quantities. Theoretical results will be compared with experimental results of others[19].

2 Theory

For AFeSD alum, Chaudhury *et al.*[17] have applied pseudo spin-lattice coupled mode model. We shall add third-and fourth-order phonon anharmonic interactions terms in to it. The modified model is then expressed as:

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

Following Zubarev[18], we consider the Green's function:

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

where

θ is unit step function, θ =1 for $t' > t$ and = 0 for $t' < t$, Ω is proton tunneling frequency, S_i^z is spin operator, ω_k is phonon frequency, A_k is position operator, B_k is momentum operator.

Differentiating Eq. (2) with respect to time t using model Hamiltonian, Eq. (1) and multiplying both sides by i we obtains:

$$\frac{dG(t-t')}{dt} = \delta(t-t')\langle[S_i^z, S_j^z]\rangle + \langle\langle[S_i^z, H]; S_j^z(t')\rangle\rangle. \quad \ldots (3)$$

We again differentiate Eq. (4) with respect to time t and multiplying on both side by i and obtains:

$$i^2\frac{d^2G(t-t')}{dt^2} = \delta(t-t')\langle[-2\Omega i S_i^y, S_j^z]\rangle + \langle\langle[-2\Omega i S_i^y, H]; S_j^z\rangle\rangle \quad \ldots (4)$$

which gives:

$$[-2\Omega i S_{1i}^y, H] = 4\Omega^2 S_i^z + 2\Omega i J(S_i^x S_j^z + S_i^z S_i^x) + 2\Omega K_{ij} S_i^x S_j^x + 2\Omega V_{ik} A_k S_i^x + 2\Omega V_{ik} A_k^+ S_j^x. \quad \ldots (5)$$

Fourier transforming Eq. (4) we obtains:

$$\omega^2 G(\omega) = \frac{2\Omega\langle S_{1i}^x\rangle\delta_{ij}}{2\pi} + \langle\langle F_{1i}(t); S_{1j}^z(t')\rangle\rangle + 4\Omega^2 G(\omega). \quad \ldots (6)$$

Now if one considers Green's function:

$$\Gamma(t-t') = \langle\langle F_{1i}(t); S_{1j}^z(t')\rangle\rangle \quad \ldots (7)$$

and differentiates it with respect to time t' and preceding similar to that of above we obtains:

$$\omega^2\Gamma(\omega) = +4\Omega^2\Gamma(\omega) + \langle\langle F_{1i}(t); F_{1j}(t')\rangle\rangle. \quad \ldots (8)$$

Substitution of $\Gamma(\omega)$ from Eq. (8) in to Eq. (6), and writing the resulting equation in the form of Dyson's equation:

$$G(\omega) = G^0(\omega) + G^0(\omega)\,\tilde{P}\,(\omega)G^0(\omega) \quad \ldots (9)$$

We obtain Green's function Eq. (2) as:

$$G_{ij}(\omega) = \frac{\Omega\langle S_i^x\rangle\delta_{ij}}{\pi\left[\omega^2 - \hat{\Omega}^2 - 2i\Omega\Gamma(\omega)\right]}, \quad \ldots (10)$$

where

$$\hat{\Omega}^2 = \tilde{\Omega}^2 + \Delta(\omega), \quad \ldots (11)$$

$$\tilde{\Omega}^2 = a^2 + b^2 - bc, \quad \ldots (12)$$

$$a = J\langle S_i^z\rangle, = \quad \ldots (13)$$

$$b = 2\Omega, \quad \ldots (14)$$

$$c = J\langle S^x\rangle \quad \ldots (15)$$

and $\Delta(\omega)$ and $\Gamma(\omega)$ are obtained as:

$$\Delta(\omega) = \frac{a^4}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{b^2c^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{V_{ik}^2 N_K a^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{2V_{ik}^2\langle S_{1i}^x\rangle\omega_k\delta_{k-k'}(\omega^2 - \tilde{\tilde{\omega}}_k^2)}{(\omega^2 - \tilde{\tilde{\omega}}_k^2) + 4\omega_k^2\Gamma_k^2(\omega)}, \quad \ldots (16)$$

and

$$\Gamma(\omega)=\frac{\pi a^4}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega-\tilde{\Omega}\right)-\delta\left(\omega+\tilde{\Omega}\right)\right]+\frac{\pi V_{ik}^2 N_k a^2}{4\Omega\tilde{\Omega}}$$
$$\left[\delta\left(\omega-\tilde{\Omega}\right)-\delta\left(\omega+\tilde{\Omega}\right)\right]+\frac{2V_{ik}^2\langle S_{1i}^x\rangle\omega_k\delta_{k-k'}\left(\omega^2-\tilde{\tilde{\omega}}_k^2\right)}{\left(\omega^2-\tilde{\tilde{\omega}}_k^2\right)+4\omega_k^2\Gamma_k^2(\omega)}. \quad \ldots (17)$$

We obtain susceptibility χ from Green's function Eq. (2) as since:

$$\chi=-\lim_{x\to 0}2\pi\chi N\mu^2 G_{ij}(\omega) \quad \ldots (18)$$

N is number of dipoles per unit volume and μ is dipole moment associated with O-H……O bond. We know that dielectric constant ϵ is related to susceptibility χ as:

$$\in=\ 1+\ 4\pi\chi \quad \ldots (19)$$

or simply $\in=4\pi\chi$ as $\in>>1$ for ferroelectrics from Eqs (10), (18) and (19) we obtain:

$$\in=-\frac{8\pi N\mu^2\Omega\left\langle S_i^X\right\rangle\left\{(\omega^2-\hat{\Omega}^2)+2\Omega i\Gamma(\omega)\right\}}{\left[\left(\omega^2-\hat{\Omega}^2-2\Omega^2\Gamma^2(\omega)\right)\right]}. \quad \ldots (20)$$

The expression for tangent loss is obtained from Eq. (20):

$$\tan(\delta)=\frac{\in''}{\in'}=-\frac{2\Omega\Gamma(\omega)}{\left(\omega^2-\hat{\Omega}^2\right)}. \quad \ldots (21)$$

From Eqs (20) and (21) one observes that both dielectric constant and loss tangent depend on modified soft mode frequency. Hence these depend on tunneling frequency as well as on anharmonic interactions terms.

3 Numerical Calculation

By using model values[17] of various physical parameters (Table 1), temperature dependence of ferroelectric mode frequency, $\hat{\Omega}$, dielectric constant, $\in$, and loss tangent $\tan\delta$, using Eqs (11), (20) and (21) have been calculated as shown in Figs 1, 2 and 3.

4 Results and Discussion

In this paper, by modifying two sublattic pseudo spin coupled mode model for AFeSD ferroelectric crystal by, adding third and fourth order phonon anharmonic interaction terms theoretically expressions for shift, width, loss tangent, dielectric constant and soft mode frequency have been derived. With the help of model values given by Chaudhury *et al.*[17] and by using Eqs (16), (17), (11), (20) and (21) temperature dependence of width Δ, shift Γ, ferroelectric mode frequency, $\hat{\Omega}$, dielectric constant, $\in$ and loss tangent

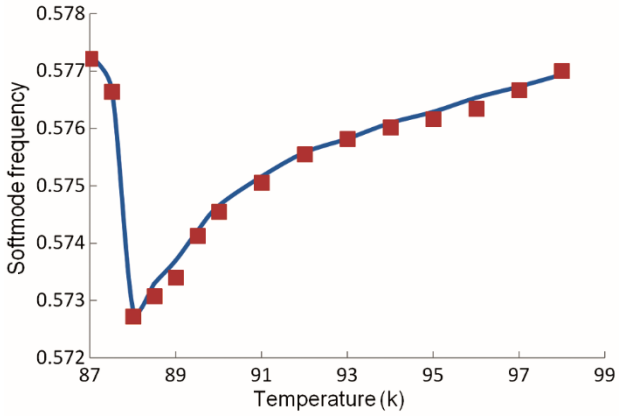

Fig. 1 — Temperature dependence of soft mode frequency $\hat{\Omega}$ (cm^{-1}) of AFeSD alum (— present results; ♦ experimentally correlated values of Pepinsky *et al.*[19] for dielectric data).

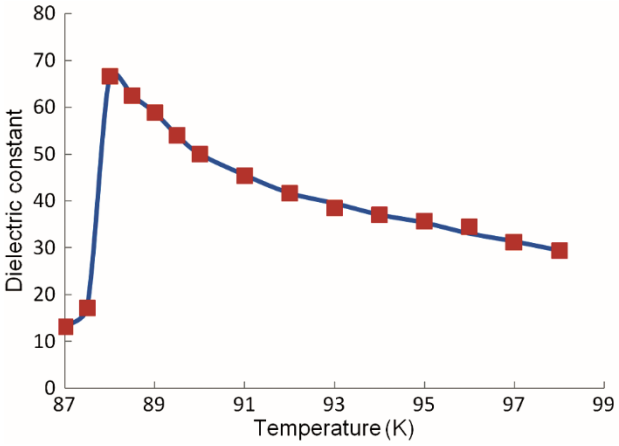

Fig. 2 — Temperature dependence of dielectric constant ϵ of AFeSD alum (—present results; ♦ experimental results of Pepinsky *et al.*[19]).

Table 1 — Model values of physical quantities for ammonium iron alum crystal[17]

T_C	Ω	J	K	V_{ik}	$\frac{1}{\omega^2}$	C	μ	A_k
(K)	(cm^{-1})	(cm^{-1})	(cm^{-1})	($cm^{-3/2}$)	(cm^{-1})	(K)	(esu)	($ergK^{-1}$)
88	0.25	183.49	125	6.49	5	425	1.405×10^{-18}	0.05×10^{-17}

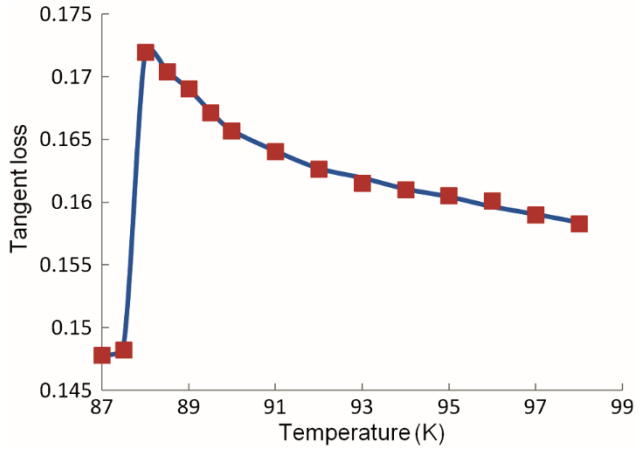

Fig. 3 — Temperature dependence of tangent loss (tanδ) of AFeSD alum (—present results; ♦ experiment results of Pepensky *et al.*[19]).

tanδ, have been obtained. The results for soft mode frequency, dielectric constant and loss tangent have been shown in Figs 1, 2 and 3, respectively. Theoretical results have been compared with experimental results of Pepinsky *et al.*[19] for dielectric constant and tangent loss and correlated results for ferroelectric mode frequency for AFeSD crystal. Our theoretical results agree with experimental results of Pepinsky *et al.*[19]. From Fig. 1 and Eq. (11), it is observed that ferroelectric mode frequency decreases as we approach from low temperature side towards Curie temperature. At Curie temperature ferroelectric frequency becomes infinitesimally small, and increases above it. Our results are in agreement with experimental observations. From Fig. 2 and Eq. (20) it is shown that dielectric constant first increases as we increase temperature from low temperature side becoming anomalously large at transition temperature. Above T_c, the dielectric constant values decrease with the increase of temperature. Our findings agree with experimental results of Pepinsky *et al.*[19] and similar behavior for AFeSD alum was predicted by Fig. 3.

5 Conclusions

From the above discussion it can be understood well that with the help of double time temperature dependent Green's function method along with pseudo spin-lattice coupled mode model and by adding third- and fourth-orders phonon anharmonic interactions terms explains the dielectric properties and ferroelectric behaviour of AFeSD alum clearly. The phonon anharmonic interactions terms significantly affect the temperature dependence of soft mode frequency, dielectric constant and loss tangent in AFeSD alum. As earlier authors[17] used different approach and decoupled correlations at an early stage due to which some important interaction disappeared from their expressions. Shift and width are the result of present work. This ultimately gives modified soft mode frequency. Our results are better than the results of earlier authors[17], quantitatively.

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