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Phenomenological explanation of the anomalous dielectric behavior of alums with pseudo-spin-lattice coupled-mode model

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With the use of the pseudo-spin-lattice coupled-mode (PLCM) model and the statistical Green's-function technique a phenomenological explanation of the hitherto unexplained ferroelectric phase transitions in $(CH_3NH_3)Al(SO_4)_2\cdot 12H_2O$ (MASD) and $(NH_4)Fe(SO_4)_2\cdot 12H_2O$ (AFeSD) alums has been given. The pseudospins assumed to be associated with the protons of the monovalent methylammonium group and the ammonium groups, respectively, in MASD and AFeSD alums undergo ordering at low temperatures. From our calculations the expression for the electrical susceptibility (χ) comes out to be of the form $\chi = A'_0 + B'_0 + C'_0 + \cdots$, where A'_0 is a temperature-independent term and B'_0 is a measure of the contribution from phonon-phonon interaction. The third term C'_0 arises from the rotation of the monovalent ions. For ferroelectric alums C'_0 is found to be highly temperature dependent, and for other nonferroelectric alums both B'_0 and C'_0 show negligibly small dependences on temperature. A single set of model parameters (Blinc—de Gennes parameters) has been calculated for AFeSD from fitting the experimental data of dielectric constant (ϵ), Curie-Weiss constant (C) and transition temperature (T_C) with the corresponding theoretical expressions. However, in the case of MASD alum, we must vary the renormalized phonon frequency $\bar{\omega}_0$ [$=\omega_0 + \bar{A}'(0,T)$] with temperature to fit the entire ϵ-T curve with a single set of model parameters. This is due to the presence of strong phonon-phonon interaction in MASD alum, causing the strongly temperature-dependent anharmonicity parameter $\bar{A}'(0,T)$. The present success of the PLCM model for explaining the phase transitions in alums definitely indicates the unified character of this model, which may also be applied to many other crystals.

I. INTRODUCTION

It is well known that some of the members of the alum family of double salts show very interesting phase transitions observed from magnetic,[1] dielectric,[2,3] and other studies.[4,5] Alums have the common chemical formula $M^{1+}M^{3+}(RO_4)_2\cdot 12H_2O$ with M^{1+}=K, Rb, Tl, NH_4, CH_3NH_3, NH_3NH_2, etc., M^{3+}=Al, Fe, Cr, V, In, etc., and R=S or Se. Though these alums are said to be isomorphous, Lipson[6] showed that there might be three different (α, β, and γ) types of alums depending on the radii of the monovalent ions. Griffith and Powell[7] first observed the anomalous dielectric constant of $(CH_3NH_3)Al(SO_4)_2\cdot 12H_2O$ (MASD) alum. No theoretical study explaining this anomalous dielectric behavior and other properties has yet been done. This is partly because of the peculiar nature of the ferroelectric transitions showing only in a few alums and partly due to the lack of our understanding about the mechanism of phase transitions in these alums.

Both MASD and $(NH_4)Fe(SO_4)_2\cdot 12H_2O$ (AFeSD) alums undergo structural phase transitions[8,9] (cubic to orthorhombic), respectively, at 177 and 88 K. This change of symmetry from the nonpolar class (space group *Pa*3) to the polar class (space group *Pca*21) occurs with the onset of ferroelectricity. Unlike the case of hydrogen-bonded ferroelectrics, very little or no isotope effect is observed on the transition temperatures[9] indicating that the H bonds are not primarily involved in the transition mechanisms of alums having a large number of H bonds as shown in Fig. 1. The dielectric constant (ϵ) in MASD follows the Curie-Weiss law in different temperature ranges[9] with different values of Curie-Weiss constants (C). On the other hand, AFeSD alum shows only one Curie-Weiss constant. Pepinsky *et al.*[2] showed, for the first time, the ferroelectric loop in MASD alum at the temperature range 177—154 K. The thermal variation of the dielectric constants of AFeSD has also been studied by Jona *et al.*[10,11]

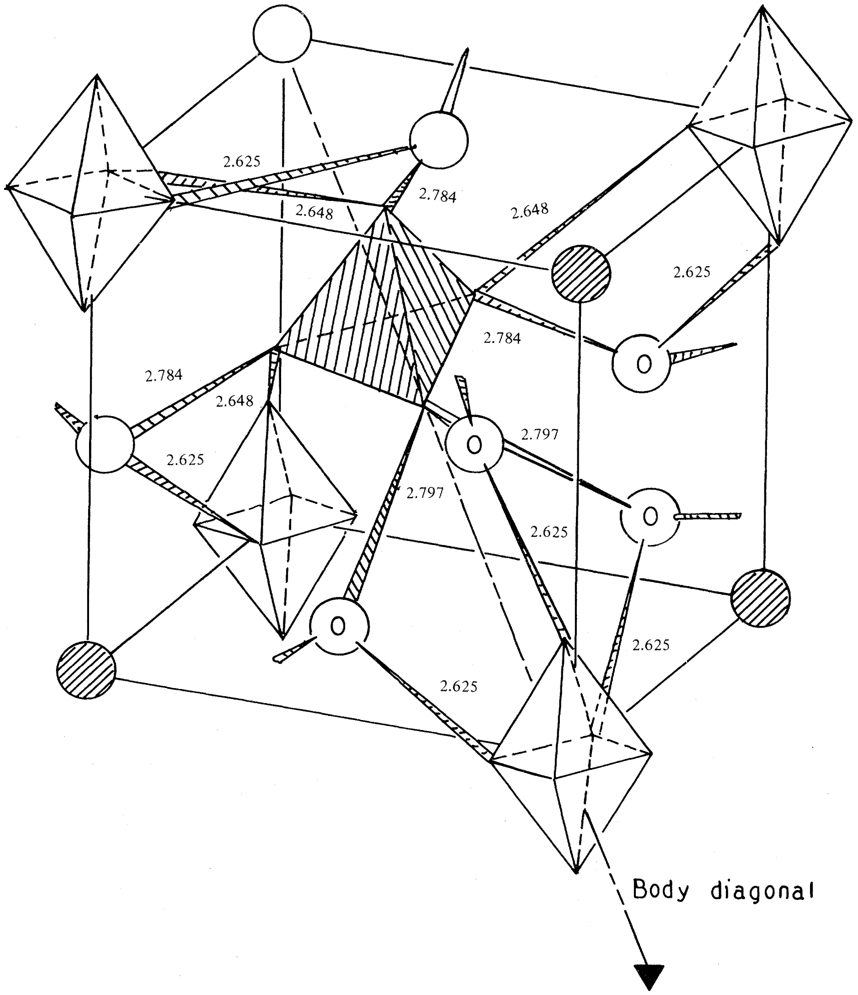

FIG. 1. Structure of MASD alum at room temperature (Ref. 9). Only one-quarter of the unit cell is shown. Hydrogen bonds are shown by shaded, directed lines; open circles—water of crystallization; tetrahedron—SO_4 group; CH_3NH_3 ions are tentatively placed at their centers of gravity and marked by shaded circles. The interatomic distances are in Å.

Recently Rao *et al.*[3] reported anomalous thermal variations of a large number of ferroelectric and nonferroelectric alums and concluded that the ferroelectric behavior is associated with the rotational motion of $NH_4{}^{1+}$, $CH_3NH_2{}^{1+}$, $CH_3NH_3{}^{1+}$, or NH_3OH^{1+} types of monovalent ions each containing a rotational group. That is, only β-type alums are found to be ferroelectric. Their results also indicate very small thermal variations of ϵ for other nonferroelectric alums with monovalent ions $M^{1+}=$Rb, Tl, K, etc. Thus it appears to be very interesting to develop a theoretical model for explaining the above facts related to the ferroelectric phase transitions in some alums for which the detailed high- (above T_C) and low- (below T_C) temperature crystal structures are available.[8]

From neutron-diffraction studies[12] it was concluded that the asymmetric distribution of the H bonds around the sulphate groups might be a cause of the ferroelectric transition in alums. Recent results from nuclear-magnetic-resonance[4] and low-temperature x-ray studies,[8] however, do not support this contention. But the instability arising due to the asymmetrical distribution of the bonding forces may give rise to a highly-temperature-dependent anharmonic contribution[13] depending on the size and kind of the monovalent ions. This will be shown later from the results of our calculations. Low-temperature structural analysis[8] of the MASD salt also indicates that the H-bonding arrangements in these alums are not disturbed in the low-temperature phase (below T_C). Thus the large number of H bonds shown in Fig. 1 are not very important for the ferroelectric phase transition in

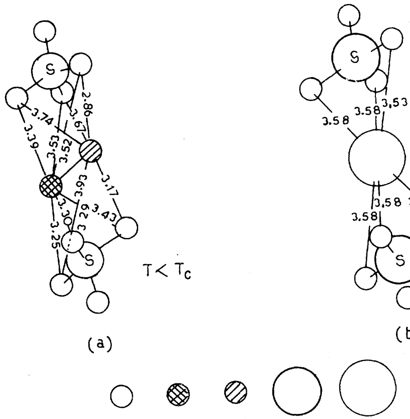

FIG. 2. Nature of contacts between the methylammonium ion and the sulphate ions. (a) At low temperature and (b) at room temperature (Ref. 8). The interatomic distances are in Å.

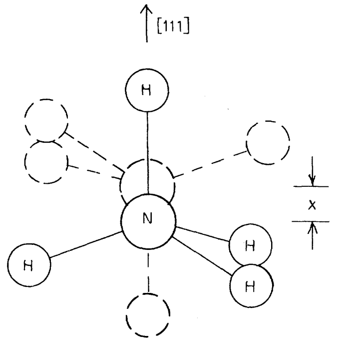

FIG. 3. Two equivalent orientations of NH_4^+ ion in $NH_4Al(SO_4)_2\cdot 12H_2O$ alum (Ref. 4).

MSAD. A very interesting change can, however, be noticed in the overall atomic arrangements of CH_3NH_3 groups as shown in Fig. 2. In the high-temperature phase (above T_C) the CH_3NH_3 groups are found to be symmetrically oriented so that they are indistinguishable from each other [Fig. 2(a)]. But in the low-temperature phase (below T_C) CH_3 and NH_3 groups separately arranged look like a dumbbell [Fig. 2(b)]. That is, in the high-temperature phase CH_3 and 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 asymmetric. It appears that this type of orientation which makes a minimum contribution to the potential energy of the system is responsible for the phase transition in MASD. The ordering of the methyl group in MASD and that of the ammonium group in AFeSD give rise to a order-disorder type of mechanism in the proton subsystem associated with these groups. This is assumed to be responsible for the ferroelectric phase transitions in several alums. The abrupt change of the flip motion of the CH_3NH_3 ion observed from magnetic resonance[14] also indicates the importance of the vibrational and/or rotational motion of the methyl group (for example). The nuclear relaxation time T_1 showing a single minimum is a characteristic of rotation of the CH_3 group about the triad axis. O'Reilly and Tsang[14] have also suggested that the ferroelectric transition in MASD results from a one-dimensional reorientation of the monovalent CH_3NH_3 ion. The situation will be further clarified by recent results of dielectric loss and spin-lattice relaxation measurements by Svare and Holt[4] who explained the dielectric losses and proton relaxation times T_1 and $T_{1\rho}$ of $NH_4A1(SO_4)\cdot 12H_2O$ alum considering hopping of NH_4^+ between two possible positions with two different orientations as shown in Fig. 3. Recent neutron diffraction[15] also shows that NH_4^+ ion is disordered in NH_4^+ alum with one H pointing in one of the two ways along the [111] axes (Fig. 3). The shifting of the NH_4^+ ion by about 0.1 Å from one to the other of these two positions due to the effect of the surroundings is responsible for giving the necessary dielectric losses with the same correlation times as the orientation motion observed[4] from NMR studies.

Owing to this order-disorder character of the methyl group (in MASD) and the ammonium group (in AFeSD) as mentioned above, the H bonds associated with these groups undergo some kind of ordering. It then becomes possible to apply the pseudospin model similar to the case of the KDP(KH_2PO_4) system[13,16] with suitable modification. Here the proton motion is associated with the "active" methyl or ammonium ion. Since there are very little isotope effects[9] on T_C and C, the pseudospin motion should be highly damped with strong anharmonic phonon interaction.[13] This is also acknowledged from the deviation of the Curie-Weiss behavior[9] of the electrical susceptibility of MASD. The proposed pseudospin model should, therefore, contain the pseudo-spin-phonon coupling term. Such a model has already been developed in our earlier work[13,16,17] and in the present work this model, called the pseudo-spin-lattice coupled-mode (PLCM) model, has been extended for explaining the anomalous thermal variations of the dielectric constants of MASD and AFeSD alums and to show the unified character of the model.

In Sec. II the usual pseudo-spin-lattice coupled

Hamiltonian containing an additional coupling term, viz. $\sum B_{ij} S_i^x S_j^x$, has been described in short. Section III deals with the theoretical calculations of electrical susceptibility (ϵ), transition temperature (T_C), and the Curie-Weiss constant (C). The results of our calculations have been discussed in Sec. IV. The paper ends with a conclusion in Sec. V.

It should be mentioned here that the detailed method of our calculations with a Green's-function technique has already been discussed in our earlier work[13,16,17] (hereafer referred to as paper I). Therefore, the theoretical calculations, in the present paper, will be described in brief.

II. THE MODEL

Concentrating our attention on the proton subsystem associated with the "active" ions as mentioned in Sec. I, the simplest form of the model Hamiltonian (H) for the coupled proton-phonon system can be written (paper I) as a sum of a pure protonic term (H_p), a lattice term (H_l), and a proton-lattice (H_{pl}) interaction term, viz.

$$H = H_p + H_l + H_{pl} \ , \tag{1}$$

H_p being the Hamiltonian of the "bare" proton system in a rigid lattice, which has the form[18]

$$H_p = -\Omega \sum_i S_i^x - \tfrac{1}{2} \sum_{ij} S_i^z S_j^z - \tfrac{1}{2} \sum_{ij} B_{ij} S_i^x S_j^x \ , \tag{2}$$

where S_i^α ($\alpha = x,y,z$) is the αth component of the pseudospin $\vec{S}_i$ and Ω is the proton tunneling frequency. Though the tunneling term is negligibly small for alums we have considered this term to find its magnitude as well as to make the model comparable with that of the potassium dihydrogen phosphate (KDP) problem. J_{ij} is the spin-spin interaction constant of the Ising type. When tunneling is not present the last term in (2) is more important[19] for describing a possible influence of the transverse field of one proton to the transverse field of another, whereas the second term in (2) takes account of the long-range dipole-dipole forces. H_l may also be written in the usual way including the anharmonic interaction as (in units of $\hbar = 1$, $M = 1$)

$$H_l = -\tfrac{1}{2} \sum_{\vec{q}} (P_{\vec{q}} P_{-\vec{q}} - \omega_{\vec{q}}^2 Q_{\vec{q}} Q_{-\vec{q}}) + \sum_{q_1,q_2,q_3,q_4} A(q_1,q_2,q_3,q_4) Q_{q_1}, Q_{q_2} Q_{q_3} Q_{q_4} \ , \tag{3}$$

where $Q_{\vec{q}}$, $P_{\vec{q}}$, and $\omega_{\vec{q}}$ are, respectively, the normal coordinate, conjugate momentum, and bare harmonic frequency of the phonons with wave vector $\vec{q}$. The last term is the fourth-order anharmonic part of the lattice vibrations. The contribution of the third-order anharmonic term is considered by means of normalization following the procedure of our earlier papers (paper I) and others.[20,21] The simplest form of the pseudo-spin-phonon interaction term can be written as

$$H_{pl} = -\sum_{i,\vec{q}} S_i^z V_{i,\vec{q}} Q_{\vec{q},i} \ . \tag{4}$$

This interaction of the pseudospin with polar optic phonons causes the two potential wells for proton motion associated with the methyl group to be unequivalent. The term like $\sum S_i^x V_{iq}^x Q_i$ indicating the coupling between the tunneling motion of one proton and the tunneling motion of another is not considered to be important for alums.

III. THEORETICAL CALCULATIONS

A. Electrical susceptibility (χ)

As in the case of our earlier work (paper I) we start with the dynamical Green's functions like $G_{qq}^{QQ}(t-t') = \langle\langle Q_{\vec{q}}(t) \,|\, Q_{-\vec{q}}(t') \rangle\rangle$. The Fourier transform[22] of this Green's function can be written as

$$2\pi\omega \langle\langle Q_{\vec{q}} \,|\, Q_{-\vec{q}} \rangle\rangle_\omega = \langle [Q_{\vec{q}}, Q_{-\vec{q}}] \rangle + \langle\langle [Q_{\vec{q}}, H] \,|\, Q_{-\vec{q}} \rangle\rangle_\omega \ , \tag{5}$$

where the notation $\langle \ \rangle$ denotes the statistical average of the enclosed operator. The electrical susceptibility $\chi(\omega,\vec{q})$ is related to $\langle\langle Q_{\vec{q}} \,|\, Q_{-\vec{q}} \rangle\rangle_\omega$ as

$$\chi(\omega,\vec{q}) = \frac{n\mu^2}{v_0} (\langle\langle Q_{\vec{q}} \,|\, Q_{-\vec{q}} \rangle\rangle_\omega) \ , \tag{6}$$

where n is the number of pseudospins in the unit cell of volume v_0 (v_0 can be obtained from structural data[8]), μ is the average dipole moment along the polarization axis. Now using the decoupling scheme similar to our earlier work,[13] viz.

$$\langle\langle AB \,|\, C \rangle\rangle \equiv \langle A \rangle \langle\langle B \,|\, C \rangle\rangle + \langle B \rangle \langle\langle A \,|\, C \rangle\rangle \tag{7}$$

and the spin-wave transformation

$$S^{\alpha}_{\vec{q}}=\sum_{l} S^{\alpha}\exp i(\vec{q}\cdot\vec{R}_l) \tag{8}$$

(where $\vec{R}_l$ is the Bravais lattice vector), the required equations of motion can be written as [with help of Eqs. (5), (7), and (8)]

$$(M)(G)-(S)=0\ , \tag{9}$$

where

$$(M)=\begin{bmatrix} \omega & -J_0\sigma^z & 0 & -i\bar{V}_q\sigma^y & 0 \\ -iJ_0\sigma^z & \omega & iJ_{\vec{q}}\sigma^x-2i\bar{\Omega} & i\bar{V}_{\vec{q}}\sigma^x & 0 \\ 0 & 2i\bar{\Omega} & \omega & 0 & 0 \\ 0 & 0 & 0 & & -i \\ 0 & 0 & i\bar{V}_{\vec{q}} & \bar{\omega}_q & \omega \end{bmatrix}, \tag{10}$$

$$(G)=\begin{bmatrix} \langle\langle S^x_{i,\vec{q}} \mid Q_{-\vec{q}}\rangle\rangle_\omega \\ \langle\langle S^y_{i,\vec{q}} \mid Q_{-\vec{q}}\rangle\rangle_\omega \\ \langle\langle S^z_{i,\vec{q}} \mid Q_{-\vec{q}}\rangle\rangle_\omega \\ \langle\langle Q_{\vec{q}} \mid Q_{-\vec{q}}\rangle\rangle_\omega \\ \langle\langle P_{\vec{q}} \mid P_{-\vec{q}}\rangle\rangle_\omega \end{bmatrix}, \tag{11}$$

$$(S)=\frac{i}{2\pi}\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}, \tag{12}$$

$$\begin{aligned} &\bar{\omega}_{\vec{q}}=i\omega^2_{\vec{q}}+i\bar{A}'(\vec{q},T)\ , \\ &\bar{A}'(\vec{q},T)=\sum_{\vec{q}}\frac{6}{\omega_{\vec{q}\,'}}A(\vec{q},-\vec{q},\vec{q}\,',-\vec{q}\,')(2\eta_{\vec{q}}+\tfrac{1}{2})\ , \\ &\bar{V}_{\vec{q}}=\sum_{\vec{q}}V_{\vec{q}},\ \ J_{\vec{q}}=\sum_{j'}J_{ij}\exp i\vec{q}(\vec{R}_i-\vec{R}_j)\ , \\ &J_0=\sum_{j'}J_{ij},\ \ \bar{\Omega}=\Omega+B'_0\langle S^x\rangle\ , \\ &B_0=\tfrac{1}{2}\sum_{j'}B_{ij},\ \ \sigma^{\alpha}_i=\langle S^{\alpha}_i\rangle\equiv\langle S^{\alpha}_j\rangle\ , \\ &\alpha=x,\ y,\ \text{or}\ z\ . \end{aligned} \tag{13}$$

The solution of det $|M|=0$ gives the energy spectrum, viz.

$$\begin{aligned} 2\omega^2_{1,2}=(&[L^2+\omega^2_{\vec{q}}+A(\vec{q},T)] \\ &\pm\{[L^2-\omega^2_{\vec{q}}-A(\vec{q},T)]^2 \\ &-8\bar{\Omega}\bar{V}_{\vec{q}}\sigma^x\}^{1/2})\ , \end{aligned} \tag{14}$$

where

$$L=4\bar{\Omega}^2+J_0(\sigma^z)^2-2\bar{\Omega}J_{\vec{q}}\sigma^x\ . \tag{15}$$

The thermal average σ^x and σ^z can be obtained from the pure tunneling model (H_p) which can be written as (paper I)

$$\sigma^x=\frac{B_0}{\Gamma}\tanh\frac{\beta\Gamma}{2} \tag{16}$$

and

$$\sigma^z=\frac{\gamma}{\Gamma}\tanh\frac{\beta\Gamma}{2}\ , \tag{17}$$

where

$$\Gamma^2=\gamma^2+\bar{\Omega}^2,\ \ \gamma=J_0\sigma^z\ , \tag{18}$$

and $\beta=1/k_BT$ (k_B is the Boltzmann constant and T is the absolute temperature). Since $\sigma^z\rightarrow 0$, $\sigma^x\rightarrow\sigma^x_0$ as $T\rightarrow T_0$ (T_0 being the transition temperature) we have in the mean-field approximation,

$$(B_0\sigma^x_0+\Omega)/J_0=\tanh\tfrac{1}{2}(\Omega+\sigma^xB_0)\beta\ . \tag{19}$$

The effect of the new coupling term S^xS^x in the pure pseudospin Hamiltonian (2) is to renormalize the pure tunneling frequency Ω to $\bar{\Omega}=(\Omega+B_0\sigma^x)$. σ^xB_0 acts as the correction term. σ^x_0 in (12) is the value of at $T=T_0$. For $T\leq T_0$ one finds

$$\bar{\Omega}=\Omega(J_0/J_0-B_0)\ . \tag{20}$$

For positive B_0 and close to J_0 there may be large shift of T_0 for small $\bar{\Omega}$ similar to the case of $PbHPO_4$ (Ref. 13) and squaric acid[23] in particular. Following Kubo's theory[24] the Green's function $\langle\langle Q_{\vec{q}}\mid Q_{-\vec{q}}\rangle\rangle_\omega$ gives the static susceptibility ($\omega=0,q=0$) from

$$\chi(0,0)=\frac{n\mu^2}{v_0}\left[\omega^2_0+\bar{A}'(0,T)+\frac{\bar{V}^2_0\tanh\bar{\Omega}/k_BT}{(4\bar{\Omega}-J_0\tanh\bar{\Omega}/k_BT)}\right]^{-1}, \tag{21}$$

which may be written as

$$\chi(0,0)=A'_0+B'_0+C'_0+\cdots\ , \tag{22}$$

where

$$A'_0=n\mu^2/\omega^2_0v_0\ , \tag{23}$$

$$B'_0=A'_0B''_0(B''_0-1)\ , \tag{24}$$

$$C'_0=A'_0C''_0(C''_0+1)\ , \tag{25}$$

$$B''_0=\frac{A'_0(T)}{\omega_0^2}\ ,$$

$$C''_0=\frac{\bar{V}_0^2\tanh\bar{\Omega}/k_BT}{(4\bar{\Omega}-J_0\tanh\bar{\Omega}/k_Bt)}\ .$$

Equation (22) has the same form of the susceptibility expression derived by Bosman and Havinga,[25] viz.

$$\begin{aligned}\frac{1}{(\epsilon-1)(\epsilon+2)}\left[\frac{\partial\epsilon}{\partial T}\right]_p &=\frac{1}{3V}+\frac{V}{\alpha_m}\left[\frac{\partial\alpha_m}{\partial V}\right]_T\frac{1}{3V}\left[\frac{\partial V}{\partial T}\right]_p\\ &\quad+\frac{1}{3\alpha_m}\left[\frac{\partial\alpha_m}{\partial T}\right]\\ &=P''+Q''+R''\ ,\end{aligned} \tag{26}$$

where α_m is the polarizability of a macroscopic small sphere of volume V. In case of alum α_m consists of three parts.[3,25] Besides α^{op} and α^{ir} (α^{op} is the optical polarizability and α^{ir} is the infrared polarizability; see Ref. 25 for details), there is another contribution arising from the reorientation and ordering of the "active" ions or group (α^d). In (26), $(P''+Q'')$ represents simply the volume effect and the temperature-dependent dielectric constant appears only from the last term (R''). In our case the first and the second terms $(A'_0+B'_0)$ mainly depend on the volume v_0 if the anharmonic contribution $A'(0,T)$ is assumed to be temperature independent. But this is not true for all the alums. This will be made clear from our subsequent discussion.

B. Transition temperature (T_C)

It is evident from (14) that the energy ω_1 gives the soft-mode-like behavior (see paper I for details), and the transition temperature, using the ferroelectric instability condition, is given by

$$\bar{\Omega}\beta_C=\tanh4\bar{\Omega}/J_0^*\ , \tag{27}$$

where

$$J_0^*=J_0+\bar{V}_0^2/[\omega_{q=0}^2+\bar{A}'_{q=0}(T)]\ .$$

Here it should be mentioned that the phase transitions in solids are now believed to be associated with instability of one of the vibration modes. In particular, ferroelectric phase transition in alums can also be assumed to be associated with the unstable optical mode. Soft-mode behavior has been observed[17,26,27] in many other crystals where there are temperature-dependent dielectric constants even though the crystals do not undergo ferroelectric transitions.[17] To verify this conjecture experimentally, particularly in the case of alums, would be a highly interesting observation.

C. Curie-Weiss constant (C)

Since the first part of the right-hand side of (22) is temperature independent, the contribution to the Curie-Weiss constant must be derived from the second and the third terms. Expanding (22) around T_C (by Taylor's series) we have

$$C=\frac{n\mu^2}{v_0}\left[\left[\frac{\partial A'(0,T)}{\partial T}\right]_{T=T_C}+\frac{8\bar{\Omega}^2\bar{V}_0^2(1-\tanh\bar{\Omega}/k_BT_C)}{T_C^2k_B(4\bar{\Omega}-J_0\tanh\bar{\Omega}/k_BT_C)^2}\right]^{-1}\ . \tag{28}$$

For our present purpose we assume similar to (paper I)

$$A'(0,T)=A'_0(T)=\bar{A}'_0(0)k_BT\ ,$$

where $\bar{A}'_0(0)$ is the anharmonicity parameter. Using (22) the dielectric constant (ϵ) can be calculated from the usual relation $\epsilon=(1+4\pi x)$.

IV. RESULTS AND DISCUSSION

It has already been mentioned that our derived theoretical expression for electrical susceptibility (22) consists of two temperature-dependent terms B'_0 and C'_0. The nature of thermal variation of B'_0 and C'_0 are quite different in contrast to the expression (26) derived by Bosman and Havinga.[25] The Bosman-Havinga relation (referred to as the BH relation) with one temperature dependent term cannot be used to fit the complete ($\epsilon-T$) curve of MASD. This relation is valid when the thermal variation of the anharmonic contribution is not important as in the case of a few H-bonded ferroelectric crystals. However, the BH relation is applicable for AFeSD where the contributions from A'_0 and B'_0 are almost constant for all temperatures; the temperature-dependent contribution comes mainly from the third term C'_0. For other alums with $M^{1+}=$K, Rb, Tl, and $M^{3+}=$Al, Fe, Cr, V, In, Ga, etc., very slow thermal variations of dielectric constants arising only from B'_0 (since C'_0 is absent) are expected, and these alums may not even show any ferroelectric behavior. If at all ferroelectric, they should be improper ferroelectrics with

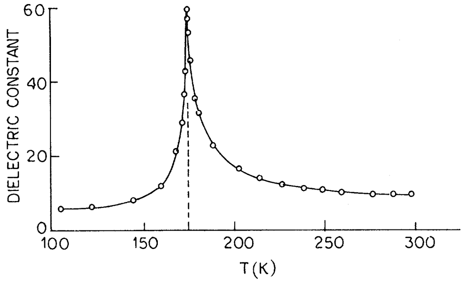

FIG. 4. Thermal variations of the dielectric constants of MASD alum [circles—experimental (Ref. 2); continuous line—theoretical].

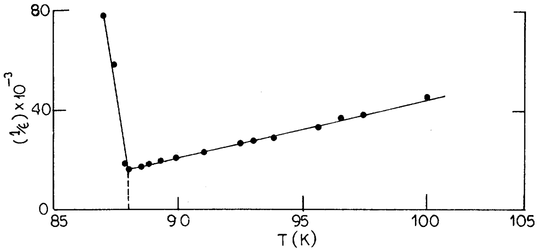

FIG. 5. Thermal variations of inverse dielectric constants of AFeSD alum [circles—experimental (Ref. 10); continuous line—theoretical].

strong anharmonic interactions and temperature dependence like the K_2SeO_4-type crystals. This was also pointed out by Rao *et al.*[3] from their recent dielectric measurement of a large number of alums.

Taking both B_0' and C_0' temperature dependent, the entire range of the dielectric constant versus temperature curve of the MASD alum is fitted (Fig. 4) with a single set of Bline—de Gennes parameters, viz. J, $\bar{V}_0$, and $\bar{\Omega}$ as shown in Table I. The procedure used for this fitting has already been discussed elsewhere (paper I). The experimental values of P_s, μ, v_0, C and T_C as shown in Table I are obtained from the experimental work of Mitsui *et al.*,[11] Pepinsky *et al.*,[2] Jona and Shirane,[9] and from the x-ray structural data.[8] For the AFeSD alum, the anharmonicity parameter $\bar{A}_0'$ is found to be almost constant and the entire $(\epsilon-T)$ curve (Fig. 5) can be fitted with a single value of $\bar{A}_0'$. This behavior is similar to the case of the H-bonded KH_2PO_4 crystal[13] studied earlier. In case of MASD, on the other hand, we have to vary $\bar{A}_0'(0)$ to fit the $(\epsilon-T)$ curve above the transition point. There are three distinct values of $\bar{A}_0'$ $(37.88\times10^{-17}$, 39.5×10^{-17}, and 45.8×10^{-17} erg/K) for three different ranges of temperature (viz. 177→183→203→255 K) giving rise to three different values of the Curie-Weiss constants. However, for $T<T_C$ the $(\epsilon-T)$ curve can be fitted with a single value of $\bar{A}_0'$ $(37.66\times10^{-17}$ erg/K) as in the case of the AFeSD alum mentioned above. This difference in the behavior of MASD above the transition point might be due to the fact that above T_C, various other vibrational modes are coupled to the active modes which freeze at lower temperatures. It might also be possible that the rotation of the active ion (say the methyl group) in MASD occurs in a slow process with long relaxation time. At T_C this rotation is complete and comes to an equilibrium phase. In such a case the MASD alum might have a common and very interesting property of showing "glassy" state (somewhere above T_C) as in the case of $SnCl_2\cdot2H_2O$ observed by Suga *et al.*[28] Accurate heat-capacity measurement of this alum might be very interesting in elucidating this behavior.

The Curie-Weiss constant calculated from the experimental[11] inverse dielectric constant versus temperature curve of AFeSD is found to be 425 K. In the case of MASD we calculated three different values of Curie-Weiss constants, viz. $C=540$, 700, and 1100 K, for three different ranges of temperatures, viz. 177—183 K, 183—203 K, and 203—255

TABLE I. Pseudospin (Blinc—de Gennes) model parameters for MASD and AFeSD alums. The values within the parameters correspond to those of AFeSD. The first part of the table contains the experimental values (Refs. 2 and 8—10) of T_C, C, P_s, Ω, and μ used to fit the experimental values of C and the $(\epsilon-T)$ curves with the corresponding theoretical expressions using a single set of parameters, viz. J_0^*, J_0, V_0 and $\bar{A}_0'$.

$P_s=0.6$ C/cm^2	$v_0=1953.125\times10^{-24}$ cm^3	$\mu=3.513\times10^{-18}$ esu cm
(0.4 C/cm^2)	$(1869.049\times10^{-24}$ cm$^3)$	$(1.405\times10^{-18}$ esu cm)
$N=2.5\times10^{22}$	$T_C=177$ K (88 K)	$C=500$ K, 700 K, 1200 K (425 K)

Ω (cm^{-1})	J_0^* (cm^{-1})	J_0 (cm^{-1})	B_0 (cm^{-1})	$\bar{V}_0$ (cm^{-1})	ω_0 (cm^{-1})	$\bar{A}_0'\times10^{-17}$ (erg/K)
0.11	488.99	366.75	60.52	65.56	5.00	37.66
(0.15)	(244.64)	(183.49)	(38.76)	(6.49)	(5.00)	(0.05)

K. These values of C obtained from our calculations agree very well with those obtained experimentally,[9] viz. 500, 700, and 1200 K for the respective three ranges of temperatures. For the AFeSD alum, on the other hand, we require only one value of $C=540$ K to fit the $(\epsilon-T)$ curve for this salt. This value of C agrees very well with that calculated from experimental $(1/\epsilon-T)$ curve (Table I). The different values of the model parameters for the AFeSD alum are also shown in Table I for comparison with those obtained for the MASD alum. To fit the $(\epsilon-T)$ curve below T_C we calculated σ^z from the spontaneous polarization $P_s=2N\mu\sigma^z$.

Both the tunneling frequency Ω and the phonon frequency ω_0 calculated from fitting the experimental data are extremely small ($\Omega=0.1$ cm^{-1} and $\omega_0=5$ cm^{-1}) compared to those of the KDP-type crystal ($\Omega=85$ cm^{-1} and $\omega_0=153$ cm^{-1} for KDP crystal).[29] Very small values of Ω and ω_0 have also been observed in many H-bond crystals like $PbHPO_4$,[13,23] $SnCl_2 \cdot 2H_2O$,[17] and squaric acid,[23] indicating the presence of very strong phonon-phonon interaction in these crystals.[13]

The alum family, therefore, forms a special class of ferroelectric crystal where only few hydrogen bonds coupled to the methyl ammonium group, for example, are involved in the dynamics of phase transitions keeping the rest of the lattice as a "heat bath." However, the collective motion stimulated by the reorientation of SO_4^{-2} of SeO_4^{-2} around the symmetry axis is also possible. X-ray crystallographic examinations showing a considerable thermic motion of oxygen atoms[30] seems to confirm this. The collective motion is in turn responsible for the strong phonon-phonon interaction in alums.

V. CONCLUSION

In this paper the pseudo-spin-lattice coupled-mode model has been applied to explain phenomenologically the mechanism of phase transitions in MASD and AFeSD alums. It has been shown that the strength of anharmonic phonon-phonon interaction in the AFeSD alum is much smaller than that of the MASD alum. This might cause the observed difference in the dielectric behavior of these two alums. This difference is also indicated by the different values of the model parameters obtained for these two alums shown in Table I. It is observed that the PLCM model used in this paper is applicable for both of the alums. But the classical Bosman-Havinga[25] relation is strictly valid only for the AFeSD alum where the anharmonicity parameter is extremely small; that is, the one type of molecular motion in this salt is almost uniform. On the other hand, in the cases of the $NH_4Al(SO_4)_2 \cdot 12H_2O$ and MASD alums, there are actually three types of molecular motion with different activation energies E_a. This was also observed[4] from the measurements of dielectric losses and proton spin-lattice relaxation times T_1 and $T_{1\rho}$. These three types of molecular motions are responsible for the three different values of the Curie-Weiss constant C. This would be highly interesting to find out both theoretically and experimentally the actual reason for such difference in the molecular motion of the magnetic AFeSD alum compared to that of the nonmagnetic $NH_4Al(SO_4)_2 \cdot 12H_2O$ alum. The magnetic chrome alum[1,26] showing anomalies both in the magnetic susceptibility and dielectric constant also appears to show identical behavior with that of the magnetic AFeSD alum.

Thus the study of phase transitions in alums, which is in no way complete, might be a very interesting field for both theoretical and various experimental investigations. However, the PLCM model is found to be successful for the phenomenological explanations of the anomalous dielectric and other related behavior of the alums. Furthermore, the anomalies simultaneously apearing in the electrical as well in the magnetic susceptibilities of some of these alums mentioned above might be explained considering the coupling between the pseudospins and the magnetic moments through phonons. The fact that this type of coupling is different for different alums might also be responsible for the differences in the dielectric behavior of the magnetic and nonmagnetic alums. However, the present success of the PLCM model for explaining the temperature-dependent anomalous dielectric behavior of alums as in the cases of many other H-bonded systems (paper I) definitely indicates the universal character of this model.

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[1] S. Mitra and S. K. Dutta Ray, Physica 30, 1557 (1964).
[2] R. Pepinsky, F. Jona, and G. Shirane, Phys. Rev. 102, 1181 (1956).
[3] A. H. Rama Rao, M. R. Srinivasan, H. L. Bhat, and P. S. Narayanan, Ferroelectrics 21, 433 (1978).
[4] I. Svare and R. M. Holt, Solid State Commun. 29, 851 (1979).
[5] S. Grande, Z. Wiss, Karl-Marx-Univ. Leipzig, Mat-Nat-Reihe 14, 843 (1965).
[6] H. Lipson, Proc. R. Soc. London Ser. A 151, 347 (1935).
[7] J. H. E. Griffiths and J. A. Powell, Proc. Phys. Soc. London Sect. A 65, 289 (1952).
[8] R. O. W. Fletcher and H. Steeple, Acta Crystallogr. 14, 891 (1961); 17, 291 (1964).
[9] F. Jonaand and G. Shirane, *Ferroelectric Crystals* (Macmillan, New York, 1962).
[10] T. Mitsui, *An Introduction to the Physics of Ferroelectrics* (Gordon and Breach, New York, 1976), p. 158.
[11] F. Jona, K. Vedam, T. Mitsui, and R. Pepinsky (unpublished).
[12] G. E. Bacon and W. E. Gardner, Proc. R. Soc. London Ser. A 246, 78 (1958).
[13] B. K. Chaudhuri, S. Ganguli, and D. Nath, Phys. Rev. B 23, 2308 (1981).
[14] D. E. O'Reilly and T. Tsang, Phys. Rev. 157, 417 (1967).
[15] D. T. Cromer and M. I. Kay, Acta Crystallogr. 22, 600 (1967).
[16] S. Ganguli, D. Nath, and B. K. Chaudhuri, Phys. Rev. B 21, 2937 (1980).
[17] S. Banerjee, D. Nath, and B. K. Chaudhuri, Phys. Rev. B 24, 6469 (1981).
[18] See, for example, L. Novakovic, *The Pseudo-spin Method in Magnetism and Ferroelectricity* (Pergamon, Oxford, 1975).
[19] R. J. Nelmes, Ferroelectrics 24, 237 (1980).
[20] B. D. Silverman, Phys. Rev. 135, A1596 (1964); Phys. Rev. Lett. 25, 107 (1970).
[21] P. I. Konsin and N. N. Kristoffel, Fiz. Tverd. Tela (Leningrad) 14, 2873 (1972).
[22] D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys.-Usp. 3, 320 (1960)].
[23] A. Volkov, paper presented at the IVth International Meeting on Ferroelectricity, Leningrad, 1977 (unpublished); R. Blinc, B. Zeks, J. F. Sampaio, A. S. T. Pires, and F. C. Sa Barreto, Phys. Rev. B 20, 1991 (1979).
[24] R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957); see also the appendix in M. Suzuki and R. Kubo, *ibid.* 24, 51 (1968).
[25] A. J. Bosman and E. E. Havinga, J. Phys. Chem. Solids 18, 253 (1961); Phys. Rev. 129, 1593 (1963).
[26] R. Rai, Physica 57, 152 (1972).
[27] P. Konsin, Phys. Status Solidi B 70, 451 (1975).
[28] H. Suga and S. Seki, Faraday Discuss. R. Soc. Chem. 69, 221 (1980).
[29] G. A. Samara, Ferroelectrics 5, 25 (1973).
[30] H. A. C. Ledsham and H. Steeple, Acta Crystallogr. Sect. B 24, 1287 (1968).