

Green's-function theory of ferroelectric phase transitions in hydrogen-bonded triglycine sulfate with the pseudospin-lattice coupled-mode model: A unified theory of structural phase transitions.

I. Static and dynamic properties

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A pseudospin-lattice coupled-mode (PLCM) model and the statistical Green's-function theory have been used to explain the static as well as the dynamic properties of ferroelectric phase transitions in triglycine sulfate (TGS) and in its deuterated and undeuterated families. An attempt to settle the long-standing controversy over the coexistence of both order-disorder and displacive phase transitions in TGS and in many other H-bonded crystals (as observed from the studies of different static and dynamic properties) has been made by expressing the transition mechanism in these crystals as a "mixed" type rather than a purely order-disorder or a purely displacive type. This mixed behavior is due to the importance of the pseudospin-phonon and the higher-order anharmonic phonon-phonon interaction terms. The pseudospins are considered to be associated with the local ordering (rotation, displacements, etc.) of some ions or groups in the lattice. This makes the mechanism of structural phase transitions, in general, very complicated. As a consequence, the calculated expression for the total phonon self-energy is found to contain an extra term in addition to that which appears in the existing theoretical calculations by Cowley and others describing purely displacive phase transitions with phonon-phonon interaction only. This additional self-energy term is found, in principle, to be responsible for the observed deviations of some thermal and dielectric properties of TGS from the Landau theory, the existence of the "double peak" in the NMR or NQR relaxation times in TGS and in other crystals, and the appearance of both order-disorder and the displacive type of behavior in many crystals. This additional part of the self-energy is also found to be related to the "central peak" phenomenon. Depending on the strengths of the pseudospin-phonon interaction terms, this part of the self-energy might also be responsible for the crossover from order-disorder to displacive behavior observed in some structural transitions. This is also supported by recent EPR and other experimental observations made by Müller. The theoretical expressions derived for the transition temperature (T_c), dielectric constant (ϵ'), spontaneous polarization (P_s), Curie-Weiss constant (C), renormalized phonon frequency, etc., have been fitted with the corresponding experimental data to find a single set of Blinc-de Gennes model parameters for the TGS family. Finally, the unified character of the PLCM model in explaining various salient features of structural phase transitions in crystals has been discussed, and supports the conclusion of our previous work.

I. INTRODUCTION

After the discovery of the ferroelectric phase transition in hydrogen-bonded triglycine sulfate, $(\text{CH}_2\text{NH}_2\text{COO})_3\text{H}_2\text{SO}_4$ by Matthias, Miller, and Remeika,¹ a great deal of experimental work² has been done with the aim of observing the critical phenomena very close to the transition temperature. But many peculiarities in the static as well as in the dynamic properties exhibited by this salt have not been clearly explained.²

This salt (TGS) undergoes a second-order order-disorder phase transition³ at $T_c = 49^\circ\text{C}$. Above this Curie point, TGS has monoclinic symmetry^{4,5} belonging to the centrosymmetric crystal class $2/m$, and after transition the mirror plane disappears and the crystal belongs to the isostructural phase transition as observed in the hydrogen-bonded $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ crystal.⁶ The TGS crystal and all its isomorphs are very similar in their essential character to the KH_2PO_4 (KDP) type of crystals. How-

ever, unlike KDP, the dielectric properties, transition temperature (T_c), and Curie-Weiss constant (C) of TGS are not greatly affected by deuteration,² indicating that the tunneling effect might not be very large in TGS. However, there is no clear evidence that tunneling is absent in TGS. This is yet to be clarified. Another interesting point is that unlike KDP, no soft mode has been observed in TGS from Raman and infrared studies.⁷ However, recent observation of the "central peak" from Brillouin scattering⁸ draws particular attention for understanding the mechanism of phase transition in these crystals. Theoretical investigation elucidating the origin of this "central peak" would be interesting.

Although TGS has a very complicated molecular and crystallographic structure (the H-bonded arrangements are shown in Figs. 1 and 2), the transition mechanism in this crystal was previously explained qualitatively with an Ising-type theoretical model.⁹ For qualitative understanding of the state dielectric properties,⁹ one can also

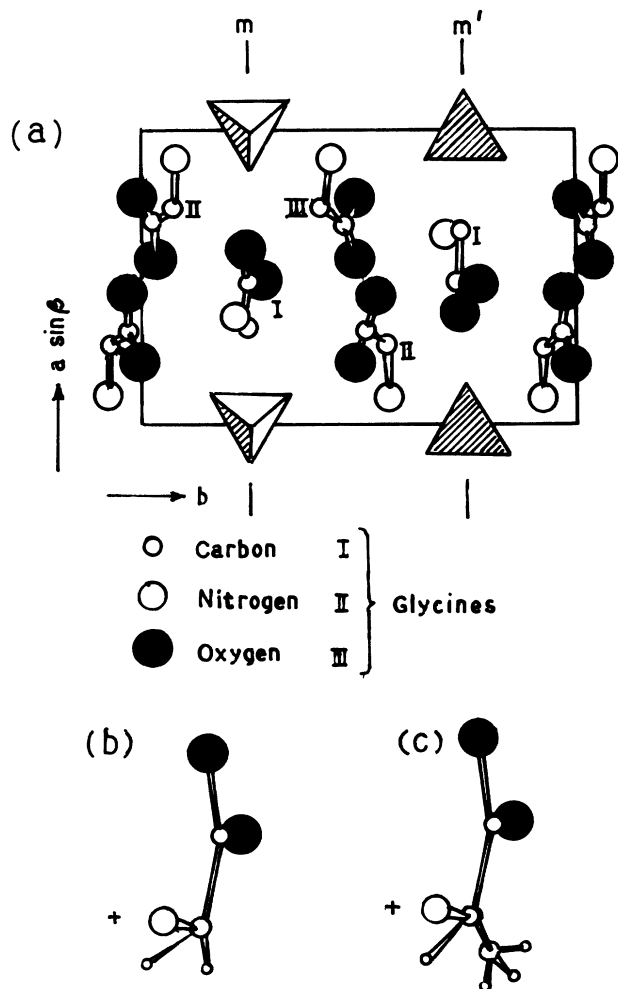


FIG. 1. (a) Crystal structure of TGS viewed along the c axis showing the three glycine groups I, II, and III. The sulfate ions are represented by tetrahedra and the oxygens have been omitted; m and m' are the sets of pseudomirror planes in which the glycine I molecules are inverted upon switching. (b) A glycine molecule, and (c) an L -alanine molecule shown for comparison. The smallest circles are hydrogen atoms (Ref. 2).

use a Devonshire- or Landau-type free-energy expansion with even powers of the spontaneous polarization. The theory of Gonzalo,⁹ which cannot explain the low-temperature flattening of polarization and the deviation of the Curie-Weiss law near the transition, was improved by Tello and Hernandez¹⁰ by allowing tunneling within the pure Ising model of Blinc and Svetina.¹¹ This theory cannot be fully supported as was also shown by Lines,¹² equivalent adjustments in polarization curves can be made by allowing the double-well local potential to deviate from the Ising δ -function form.

The deviations from the Landau-like behavior in the dielectric and thermal properties in the vicinity of T_c are also well recognized¹³⁻¹⁸ in TGS. Recent optical birefringence study¹⁸ also indicates slight deviation from the Landau-like behavior along the ferroelectric b axis.

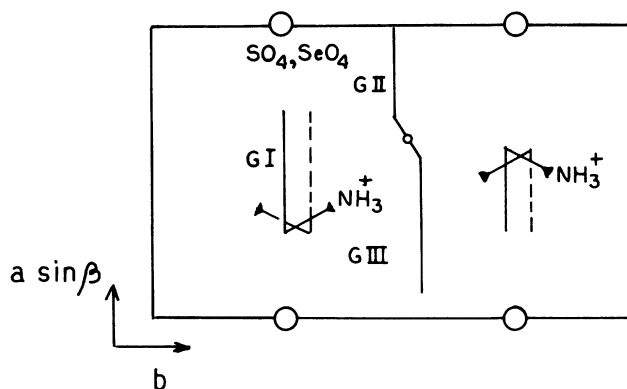


FIG. 2. Schematic (100) projection of the elementary cell of TGS or TGSe. Here G I, G II, and G III correspond to glycine, I, II, and III, respectively (Ref. 7).

However, the origin of these deviations is not clear because of marked discrepancies among the experimental results obtained by different authors.² The above-mentioned deviations might be due to various causes, like the presence of impurities, surface effects, and defects other than the critical fluctuation of polarization. Larkin and Khmel'nitskii¹⁹ (LK) predicted from their theory a Landau-like behavior modified by some correction terms with fractional powers of logarithms [$\ln t^{1/3}$, where $t = (T_c - T)/T_c$]. Recently similar results have also been derived²⁰ on the basis of the renormalization-group (RG) theory. Stauffer²¹ and Nattermann²² analyzed and estimated the LK parameters for the TGS.

However, it is observed from the heat-capacity data²³ of TGS that the height of the peak is low compared to many other H-bonded crystals, and in such a situation LK theory appears to be not strictly valid.²³ It should be mentioned here, that such a logarithmic correction has already been reported in the specific heats of the uniaxial dipolar ferromagnets like LiTbF_4 .^{24,25} In the case of ferroelectric phase transitions where the polarization is strongly coupled with the phonons (lattice deformations), the situation is different from the case of a ferromagnetic phase transition in which the coupling between the magnetization and the lattice deformation is, in general, very weak. Furthermore, the RG theory appears to be not strictly valid for molecular crystals²⁶ like TGS, where the critical region is quite narrow²⁷ similar to other H-bonded ferroelectric systems. Therefore, it seems to be not yet clear whether the nonclassical behavior predicted to exist in TGS is that of the LK type or not. Moreover, the LK theory was developed mainly for the purely displacive type of transitions. In TGS and in similar other crystals where the transitions appear to be neither purely order-disorder nor purely displacive type, applicability of the LK theory or any other similar theory for TGS is not beyond question.

From their magnetic resonance data, Bjorkstam,²⁸ and Kato and Abe²⁹ indicated the displacive nature of the transition, while the results of Blinc *et al.*,³⁰ and Nishimura and Hashimoto³¹ claim evidences for an

order-disorder character of the transition. More recently, Owens³² analyzed the linewidth effect in TGS and observed two distinct linewidths. One is assumed to be arising from the rotation of the NH_3 group (spin-like ordering), and other is considered to be associated with the fluctuation of the polarization which might be strongly coupled to the lattice. Thus two distinct mechanisms (order-disorder and displacive) might be responsible for the transition in TGS. More recent observation of the "central peak"⁸ in TGS also supports this view. Even in KDP, the transition is a "mixed" type where order-disorder and displacive character appear together.³³ Therefore it is necessary to develop a model to study the mixed behavior of phase transitions in TGS and in other similar crystals.

As mentioned in our earlier work,³⁴⁻³⁶ such a situation can be well described with an appropriate pseudospin-lattice coupled mode (PLCM) model, which has been applied for studying phase transitions in many H-bonded ferroelectric and antiferroelectric crystals. The principal advantage of using this model is that one can simultaneously consider the effect of spin-like ordering and the phonon-phonon interaction on the transition mechanism.³⁷ Furthermore, it has also been mentioned in our earlier work on KDP,³⁴ that the PLCM model is equivalent to the Jahn-Teller (JT) model as was also pointed out by Thomas³⁸ and others.^{39,40} Again the PLCM model and the so called vibronic model⁴¹ (where an extra term in the Hamiltonian describing the energy of the electrons in bare bands is included) appear to give identical results, after renormalization, elucidating the microscopic origin of ferroelectric phase transitions, in H-bonded crystals. Therefore, it is important to set up such a model for TGS explaining the dielectric and other properties in a unified way. From these studies it would also be possible to elucidate the origin of the deviation from the Landau behavior in TGS, the appearance of a "central peak" at the Brillouin scattering experiment along with other salient dynamic features.

For completeness sake, we should also mention the results of recent NMR relaxation measurements⁴² in TGS crystal showing the "double peaks" near the transition (yet unexplained). Whether this is connected to the frequency dependent damping factor (shown by Shirane and Axe⁴³ in the case of a purely displacive transition) or has some other origin needs further clarification. The "double-peak" behavior of TGS resembles that observed in many other crystals of displacive character like NaNbO_3 .⁴⁴ Of course, the frequency-dependent damping does not behave similarly in all systems and is also not equally sensitive to all dynamic effects. Though the recent observation with Brillouin scattering shows a central peak in TGS, it does not clearly indicate a second quasielastic response peak like NaNO_2 .⁴⁵ In support of the central-peak concept, one might also refer to the work of Fuji and Yamada⁴⁶ who found very anisotropic x-ray intensity distribution with scattering primarily in the plane normal to the polar b axis in TGS. Pura and Frzedmojski⁴⁷ also found a small increase in the scattering intensity close to the transition in TGS which resembles the appearance of a double peak (one peak extra) in the NMR relaxation

rate of TGS. No clear explanation of this behavior is yet to be found in the literature. In TGS, where no soft mode has so far been observed,⁷ appearance of these two peaks similar to those found in NaNbO_3 (Refs. 44 and 48) and NaTaO_3 (Ref. 48) [but not observed in SrTiO_3 (Ref. 49)] seems to be very interesting. In the perovskite, however, the cubic crystals in the high-temperature phase leads to soft-mode degeneracies and to a more complex diffuse scattering pattern than that for TGS. It is not yet clear why, in the case of TGS being an order-disorder system, such a complex behavior should also exist. For a clear understanding of all the characteristic features an intensive theoretical investigation would be interesting. This theory should simultaneously describe the characteristics of phase transitions of both the so-called order-disorder and the displacive behavior observed in TGS. This type of theory would be considered as the unified theory of phase transitions as also pointed out earlier by Aubry.⁵⁰

With the help of the PLCM model we have attempted, in this paper, a unique phenomenological explanation of all the above-mentioned controversial points associated with structural phase transitions in TGS and in other crystals. Here we consider all the transitions to be of mixed type rather than purely order-disorder or purely displacive type in nature. We have made elaborate calculations of the phonon self-energy and the damping constant from our PLCM model Hamiltonian and have tried to find the origin for various anomalous results in TGS and other crystals, indicated above, in a unified way (see Ref. 51, hereafter referred to as paper II).

The organization of this paper is as follows. In Sec. II we have described first the pure pseudospin model associated with the ordering of the glycine modes. The pseudospin-lattice (phonon) coupled mode (PLCM) model has also been written which might be valid for TGS and many other crystals.

Theoretical expressions for the transition temperature (T_0), spontaneous polarization (P_s), dielectric constant (ϵ'), Curie temperature (T_c), Curie-Weiss constant (C), and renormalized phonon energy have also been derived in this Sec. II. Statistical Green's-function technique has been used to calculate all the above-mentioned expressions.

To study the dynamical behavior we have calculated the renormalized phonon self-energy using higher-order pseudospin-phonon interaction terms. It has been shown in Sec. III that the phonon self-energy consists of two parts: one arising due to the phonon-phonon interaction (including higher-order anharmonic terms) and the other appears as a consequence of pseudospin-phonon interaction. Importance of these two parts of the self-energy as well as the damping constants (also having two parts from our calculations) have also been discussed. In Sec. IV the experimental data are fitted, similarly to our earlier work, with the derived expressions and the model parameters (also called the Blinc-de Gennes parameters) have been calculated. In this section, there is also a discussion of the validity of the PLCM model and its unified character. Finally the paper ends with the summary and conclusion in Sec. V, where we have pointed out the im-

portance of the two different parts of the phonon self-energy and damping constants.

The calculations and discussion made in this paper have been used in paper II for a critical analysis of the self energy and damping constants elucidating the origin of the central peak, central dip (observed in the temperature dependent NMR or NQR relaxation times in TGS), and other nonlinear behavior.

Here we should also mention that the discussion on the method of our calculations with statistical Green's-function technique and the random-phase (RPA) decoupling procedure used in this paper have already been made in our earlier papers.³⁴⁻³⁶

$$H_s = -2\Omega \sum_i (S_{iI}^x + S_{iII}^x) - \sum_{i,j} [J_{ij}(S_{iI}^z S_{iI}^z - S_{iII}^z S_{iII}^z) + K_{ij} S_{iI}^z S_{jII}^z] + \sum_{i,j} B_{ij}(S_{iI}^x S_{jII}^z + S_{iII}^x S_{jI}^z) - 2\mu E' \sum_j (S_{jI}^z + S_{jII}^z), \quad (1)$$

where S_α^m ($m = x, y$, or z) is the m th component of the pseudospin variables S_α .

Ω is the proton tunneling frequency, J_{ij} and K_{ij} are, respectively, the coupling within the same group (I or II) and that between the spins of different groups (I and II). The third term is the extra interaction term describing the influence of the transverse field of one proton to the transverse field of another; B_{ij} being the corresponding coupling constant. For TGS and many other H-bonded crystals like PbHPO_4 ,⁵⁴ alum,⁵⁵ squaric acid,⁵⁶ etc., having very small values of tunneling frequency, the third term of Eq. (1) is found to be important. This term has the effect of reducing⁵⁷ the value of Ω . However, this term cannot help in explaining the isotope effect without considering the higher-order phonon-phonon interaction already discussed in our earlier work.³⁴⁻³⁶ E' and μ are, respectively, the applied field and the resultant dipole moment along the direction of polarization.

The model (1) is simply the pure pseudospin Hamil-

II. THEORY

A. Model Hamiltonian

For studying the phase transition in TGS, the ordering of the H-bonds associated with the glycine I [see Figs. 1(a) and 1(b)] and glycine II (or glycine III) hydrogen bonds should be taken into consideration. The pseudospin variables S_α are associated with the ordering of the glycine molecules ($\alpha = \text{I and II}$).

The simplest way to describe the ordering of the pseudospin variables is to write the Ising-type Hamiltonian in the form^{27,52,53}

tonian describing purely order-disorder character of the pseudospin system,²⁷ viz.

$$H' = -2\Omega \sum_i S_i^x - \frac{1}{2} \sum_{i,j'} J_{ij'} S_i^x S_{j'}^x. \quad (2)$$

We have shown earlier (Refs. 34-36) that many of the salient features associated with the hydrogen-bonded systems, like isotope effect, phonon frequency shift, appearance of "central peak," damping character, etc., related to the static as well as to the dynamic properties of the structural transitions cannot be explained with this simple model alone. One has to consider the pseudospin-phonon coupled Hamiltonian containing higher-order anharmonic interaction term—similar to the case of the KDP crystal.^{7,34,58} Therefore, for the analysis of the static and dynamical properties of TGS, one has to consider the pseudospin-lattice (phonon) coupled-mode (PLCM) model of the form^{34,52,59}

$$H_{sp} = H_s + \frac{1}{2} \sum_{\mathbf{q}} P(\mathbf{q}) P^*(\mathbf{q}) + \omega^2(\mathbf{q}) Q(\mathbf{q}) Q^*(\mathbf{q}) + \sum_{i,\mathbf{q}} V_{i,\mathbf{q}}(\mathbf{q}) S_{i\alpha}^z(\mathbf{q}) Q(\mathbf{q}) + \frac{1}{3} \sum_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3} B'(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) Q(\mathbf{q}_1) Q(\mathbf{q}_2) Q(\mathbf{q}_3) + \frac{1}{4} \sum_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4} A(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) Q(\mathbf{q}_1) Q(\mathbf{q}_2) Q(\mathbf{q}_3) Q(\mathbf{q}_4), \quad (3)$$

where $V_{i,\mathbf{q}}(\mathbf{q})$ are the linear coupling constant⁵² governing the interaction between the pseudospin and the optic vibrations. $Q(\mathbf{q})$ and $P(\mathbf{q})$ are, respectively, the normal coordinates and conjugate momenta with wave vector \mathbf{q} , and the initial phonon frequency $\omega(\mathbf{q})$ (where $\mathbf{q} = \mathbf{q}_j$ for the j th mode). The transverse and longitudinal optic and acoustic branches may be numbered by the same index j . B' and A are, respectively, the third- and fourth-order anharmonicity constants. Following the procedure of our earlier work³⁴⁻³⁶ and that of Silverman⁶⁰ and Konsin and Kristofel,⁵⁹ the third- and fourth-order anharmonic contributions are taken into consideration in our calculations. For convenience we always use the notations of Refs. 34-36 and define the spin-wave transformation as

$$S_\alpha^m(\mathbf{q}) = \sum_{l,\alpha} S_\alpha^m \exp i \mathbf{q} \cdot \mathbf{R}_{\alpha,l}, \quad (4)$$

where \mathbf{R}_l denotes the Bravais lattice site of the l th bond. Equation (3) is the basic Hamiltonian which we shall use in the following section for investigating the static properties of the TGS crystal.

B. Static properties

Here we shall first study the behavior of the Hamiltonian H_s [Eq. (1)] and calculate spontaneous polarization p_s , and the transition temperature T_0 similar to our earlier work.³⁴⁻³⁶ We always follow the statistical Green's-function technique used by Ramkrishna and Tanaka⁶¹

who also pointed out the importance of this technique for studying the properties of H-bonded crystals compared to those of other techniques. We shall next use the total Hamiltonian Eq. (3) for calculating the electrical susceptibility (χ), Curie-Weiss constant (C), Curie temperature (T_c), and dielectric constant (ϵ').

The Green's function for our present calculations can be represented in the form^{61,62} (in units of $\hbar=1$, $c=1$)

$$G_{ij}^{mn}(t-t') = \langle\langle S_i^m(t), S_j^n(t') \rangle\rangle \\ = -i\theta(t-t') \langle [S_i^m(t), S_j^n(t')]_{\bar{\eta}} \rangle, \quad (5)$$

where

$$\bar{\eta} = \pm 1, [S_i^m, S_j^n]_{\bar{\eta}} = S_i^m S_j^n - \bar{\eta} S_j^n S_i^m$$

and

$$\theta = 1 \quad \text{for } t > 0 \\ = 0 \quad \text{for } t < 0.$$

The Green's functions (5) satisfy the equations of motion

$$E \langle\langle S_i^m, S_j^n \rangle\rangle_E = \frac{1}{2\pi} \langle [S_i^m, S_j^n]_{\bar{\eta}} \rangle \\ + \langle\langle [S_i^m, H_s]_{\bar{\eta}}, S_j^n \rangle\rangle_E. \quad (6)$$

It was shown by Zubarev⁶² that the poles of the Green's function correspond to the energies of the elementary excitations of the system. In Eq. (6) the notation $\langle \dots \rangle$ denotes the statistical average of the enclosed operators. Now applying RPA-type decoupling procedure used by Tyablikov,⁶³ viz.

$$\langle\langle AB, C \rangle\rangle \equiv \langle A \rangle \langle\langle B, C \rangle\rangle + \langle B \rangle \langle\langle A, C \rangle\rangle \quad (7)$$

we get from Eq. (6) nine coupled equations of motion. The pure pseudospin energy spectrum is obtained from the solution of these equations.³⁴⁻³⁶ The correlation functions like $\langle S_j^n S_i^m \rangle$ are obtained from the corresponding Green's function $\langle\langle S_i^m, S_j^n \rangle\rangle$ using the spectral theorem

$$\langle\langle S_j^n S_i^m \rangle\rangle = \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^{+\infty} \frac{i \langle\langle S_i^m, S_j^n \rangle\rangle_{E+i\epsilon} - \langle\langle S_i^m, S_j^n \rangle\rangle_{E-i\epsilon}}{E^2 - \bar{\eta}} dE, \quad (8)$$

where $\beta = 1/k_B T$ (k_B is the Boltzmann constant and T denotes the absolute temperature, $\bar{\eta} = +1$ for Bose operators, and -1 for Fermi operators). When all the correlation functions (with $m, n = x, y, z$) are calculated from Eq. (8) we find (see Refs. 34-36 for details)

$$\langle S_\alpha^z \rangle = \frac{\theta_\alpha}{(\theta_\alpha^2 + \Phi_\alpha^2)^{1/2}} \tanh \frac{\beta}{2} (\theta_\alpha^2 + \Phi_\alpha^2)^{1/2}, \quad (9)$$

and

$$\langle S_\alpha^x \rangle = \frac{\Phi_\alpha}{(\theta_\alpha^2 + \Phi_\alpha^2)^{1/2}} \tanh \frac{\beta}{2} (\theta_\alpha^2 + \Phi_\alpha^2)^{1/2}, \quad (10)$$

where

$$\Theta_I = 2\mu E' + 2J_0 \langle S_I^z \rangle + K_0 \langle S_{II}^z \rangle, \\ \Phi_I = 2\Omega + B \langle S_I^x \rangle, \quad \Phi_{II} = 2\Omega + B \langle S_{II}^x \rangle, \\ \Theta_{II} = 2\mu E' + 2J_0 S_{II}^z + K_0 S_I^z, \\ J_0 = \sum_{j'} J_{ij}; \quad K_0 = \sum_{j'} K_{ij}. \quad (11)$$

The pure pseudospin energy spectrum as mentioned above has the form

$$\epsilon_{0,\alpha}^2 = 0 \quad \text{and} \quad \epsilon_{\pm\alpha}^2 = (\Theta_\alpha^2 + \Phi_\alpha^2). \quad (12)$$

The polarization for the ferroelectric phase is

$$P = N\mu [\langle S_I^z \rangle + \langle S_{II}^z \rangle], \quad (13)$$

and the corresponding dielectric constant ϵ' is obtained from

$$(\epsilon' - 1) = \left[\frac{\partial P}{\partial \epsilon} \right]_{E'=0}. \quad (14)$$

For the paraelectric phase we put, as usual, $\langle S_I^z \rangle = -\langle S_{II}^z \rangle = \sigma$ (say) and hence

$$(\epsilon' - 1) = \frac{4N\mu^2 F}{1 - (2J_0 + K_0)F}, \quad (15)$$

where

$$F = \frac{\beta\Theta^2}{2(\Theta^2 + \bar{\Omega}^2)} \operatorname{sech}^2 \beta' + \frac{\bar{\Omega}^2}{(\Theta^2 + \bar{\Omega}^2)^{3/2}} \tanh \beta', \quad (16)$$

$$\Theta = \Theta_{II} = -\Theta_{II}, \quad 2\beta' = \beta(\Theta^2 + \bar{\Omega}^2)^{1/2}, \quad \bar{\Omega} = 2\Omega + B_0 \langle S^x \rangle. \quad (17)$$

Here we should mention that the system of Eqs. (9) and (10) may also have other solutions showing antiferroelectric character of the transition valid for the case of squaric acid⁶⁴ and copper formate.⁶⁵ This theory can also be extended for the study of phase transitions in NH_4Cl and NH_4Br (Ref. 66), where the orientations of the NH_4^+ tetrahedra are parallel oriented in NH_4Cl , while in NH_4Br they are antiparallel ordered in the ab plane and parallel ordered along the c axis. In TGS we consider the case of the paraelectric-ferroelectric transition.

Equation (15) is similar to that derived for the case of ferroelectric PbHPO_4 (Ref. 35) studied earlier. From Eq. (17) one finds that the tunneling frequency is modified by the presence of extra coupling term $B_{ij} S_i^x S_j^x$ which has also been explained by Blinc *et al.*⁵⁷ Although this term is important to modify Ω , it cannot adequately and consistently explain the isotope shifts of T_c and C in H-bonded systems. Since T_{cD} [= 230 K, transition temperature for deuterated KDP (Refs. 2 and 3)] is very large compared to the corresponding undeuterated value [T_{cH} = 123 K (Refs. 2 and 3)], one must make the deuterated value of exchange constant J_D very large compared to that of the undeuterated value J_H to fit the experimental data of T_c (transition temperature), ϵ' , and C consistently with a single set of model parameters. On

the other hand, the transition temperature in some other hydrogen bonded crystals like the lower transition point of Rochelle salt³ and anilinium halides (Ref. 67) like $(C_6H_4NH_3)Br$ (Ref. 68) are found to decrease on deuteration, which demands decrease of the exchange constant in the deuterated salt. This appears to be contradictory, and the lowering or increase of transition temperatures in the deuterated salts cannot be solely related to the length and dynamics of the H bonds. In KDP, undeuterated tunneling frequency Ω_H is also very large (82 cm^{-1}) (Ref. 69) compared to the corresponding deuterated value Ω_D (0.486 cm^{-1}) (Ref. 69). Furthermore, the trend of variations of T_c and C (in deuterated samples) are not the same for all hydrogen bonded ferroelectrics and antiferroelectrics. All these are due to different strengths of the anharmonic phonon-phonon interactions in different H-bonded systems.³⁵ The higher-order phonon-phonon interaction seems to be always important for explaining the isotope effect.³⁴⁻³⁶

Now putting $\epsilon'^{-1} \rightarrow 0$ in Eq. (15), one finds the transition temperature T_c from the relation

$$1 = F_0(2J_0 + K_0), \quad (18)$$

where F_0 is the value of F at $T = T_0$. Equation (18) is satisfied for ferroelectric transition at T_0 . The importance of tunneling is also indicated by Eq. (18), but its magnitude depends on the sign and magnitude of the coupling parameter P_0 [see Eq. (17)]. The parameter B_0 which appears to be important for all hydrogen bonded ferroelectric and antiferroelectrics is related to the coupling of the phonons with the transverse component of the pseudospin variables.

C. Electrical susceptibility

Here we start with the pseudospin-lattice coupled Hamiltonian Eq. (3) and calculate all the Green's functions of the form

$$\langle\langle Q(q, t), Q^*(q, t') \rangle\rangle = G_q^{QQ}(t - t'),$$

$$\langle\langle S_\alpha^z(q, t), S_\alpha^z(q, t') \rangle\rangle = G_{qq}^{SS}(t - t'),$$

etc. Again following Refs. 34-36 all the required equations of motion are written which can be expressed in the matrix form

$$\begin{pmatrix} \omega & -a & 0 & b & 0 \\ a & \omega & -c & d & 0 \\ 0 & 2i & \omega & 0 & 0 \\ 0 & 0 & -2i\bar{V}_q & 0 & i\bar{\omega}_q^2 \end{pmatrix} \begin{pmatrix} \langle\langle S_\alpha^x(q), Q^*(q) \rangle\rangle \\ \langle\langle S_\alpha^y(q), Q^*(q) \rangle\rangle \\ \langle\langle S_\alpha^z(q), Q^*(q) \rangle\rangle \\ \langle\langle Q(q), Q^*(q) \rangle\rangle \\ \langle\langle P(q), Q^*(q) \rangle\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -i/2\pi \end{pmatrix}, \quad (19)$$

where

$$a = i\theta'_\alpha, \quad b = i\bar{V}_q \langle S_\alpha^z(q) \rangle, \quad c = 2i\bar{\Omega}, \quad d = i\bar{V}_q \langle S_\alpha^x(q) \rangle; \quad 2\bar{\Omega} = 2\Omega - J_q \langle S_I^x(q) \rangle - K_q \langle S_{II}^x(q) \rangle$$

$$\Theta'_\alpha = 2J_0 \langle S_I^x \rangle + K_0 \langle S_{II}^x \rangle, \quad \bar{V}_q = N^{-1/2} \sum_q V_q, \quad \bar{\omega}_q^2 = \omega_q^2 + 2N^{-1/2} \bar{V}_q \langle S_\alpha^z \rangle + A'(q), \quad (20)$$

$$A'(q) = \sum_q \frac{12\hbar^3}{M^2 \omega_q'} A(q, -q, q', -q') (n_{q'}(T) + \frac{1}{2}). \quad (21)$$

In deriving the above Eqs. (19)-(21) we used $\langle S_i^x \rangle = \langle S_j^x \rangle$, $\langle S_i^z \rangle = \langle S_j^z \rangle$, and $\langle S_i^y \rangle = \langle S_j^y \rangle = 0$. $n_q(T)$ are the phonon occupation numbers and $A'(q)$ is the contribution from the fourth-order anharmonic term in Eq. (3). The contribution from the third-order term is also taken into consideration following the procedure of Silverman⁶⁰ (see also Refs. 34-36). M is the effective mass of the "active ions" in TGS.

From Eq. (19) one can calculate all the Green's functions and the energy spectrum of the pseudospin-phonon coupled system (see Refs. 34-36). These Green's functions also give (using RPA type decoupling) the corre-

sponding correlation functions like $\langle Q^*(q)Q(q) \rangle$, $\langle S_\alpha^z(-q)S_\alpha^z(q) \rangle$, $\langle P^x(q)P(q) \rangle$, etc. The electrical susceptibility is related to the Green's function

$$G_q^{QQ}(\omega) = \frac{\omega^2 - L_q^2}{2\pi\Delta_q^2}, \quad (22)$$

where

$$L_q^2 = \bar{\Omega}^2 - \bar{\Omega} \langle S^x \rangle J_q + (J_0 \langle S_\alpha^z \rangle)^2$$

and

$$\Delta_{\mathbf{q}} = (\omega^2 - \omega_1^2)(\omega^2 - \omega_2^2),$$

$$\omega_{1,2}^2(\mathbf{q}, T) = \frac{1}{2} \left[\omega_{\mathbf{q}}^2 + 2\bar{\Omega} \left[2\bar{\Omega} - J_0 \tanh \frac{2\bar{\Omega}}{k_B T} \right] + A'(\mathbf{q}, T) \mp \left[\omega_{\mathbf{q}}^2 + A'(\mathbf{q}, T) - 2\bar{\Omega}(2\bar{\Omega} - J_0 \tanh \frac{2\bar{\Omega}}{k_B T}) \right]^2 + \bar{V}_{\mathbf{q}}^2 \bar{\Omega} \tanh \frac{2\bar{\Omega}}{k_B T} \right]^{1/2}. \quad (23)$$

Now using the Kubo equation we obtain the expression for the susceptibility $\chi(q=0, \omega=0)$

$$\chi(0,0) = \frac{n\mu^2}{v_0} \left[\omega_{\mathbf{q}}^2 + A'(0, T) - \frac{8\bar{\Omega}^2 \bar{V}_0^2 \tanh \frac{\eta}{2k_B T}}{\eta^3 - \eta' \tanh(\eta/k_B T)} \right]^{-1}, \quad (24)$$

where

$$\eta' = 4\bar{\Omega}(2J_0 + K_0) = 4\bar{\Omega}\bar{J}_0, \quad \bar{J}_0 = 2J_0 + K_0 \quad (25)$$

and v_0 is the volume of the unit cell with number of pseudospin values n in TGS.

Since Eq. (23) indicates ferroelectric instability, "soft-mode"-like behavior may also be predicted in TGS. This has recently been observed from the Brillouin scattering⁸ experiment. Actually, with a PLCM model, a soft-mode-like behavior is always possible. But the anharmonic phonon coupling might be strong enough⁵⁹ in some samples to destroy this possibility (sometimes showing only a minimum in the energy spectrum). As soft mode has not been observed from the Raman studies,⁷ we believe the $\omega_{1,2}$ mode does not describe the in-phase motion of the pseudospin system and the lattice system, but both of them behave independently. It has, however, been shown earlier that for the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$,³⁶ and for the transition-metal ferroelectric alums,⁵⁵ the lattice instability condition could be applied even if these salts do not show true soft-mode behavior. Therefore, considering this assumption is also valid for TGS, we get the Curie temperature T_c from Eq. (23) in the usual way ($T \rightarrow T_c$ as $\omega \rightarrow 0$) as

$$k_B T_c = 2\bar{\Omega} [\text{arc tanh} \tau(T_c)]^{-1}, \quad (26)$$

where

$$\tau(T_c) = \frac{8\bar{J}_0 \bar{\omega}_0^2(T_c) + \bar{V}_0^2}{16\bar{\Omega} \omega_0^2(T_c)}, \quad (27)$$

$$\bar{\omega}_0^2(T_c) = \omega^2(q=0) + A'(q=0, T=T_c). \quad (28)$$

A phase transition with the PLCM model is possible if $\tau(T_c) > 1$. Now expanding Eq. (24) around T_c we have³⁴⁻³⁶ the Curie-Weiss constant

$$C = \frac{n\mu^2}{v_0} \left[\left[\frac{A'(0, T)}{T} \right]_{T=T_c} - \frac{4\bar{\Omega}^2 \bar{V}_0^2 \eta^2 (1 - \tanh^2 \eta / 2k_B T_c)}{k_B T_c^2 (\eta^3 - \eta \tanh \eta / 2k_B T)^2} \right]. \quad (29)$$

Since exact calculation of $(\partial A / \partial T)$ is difficult, we approximate as before³⁴⁻³⁶ $A'(T) \approx A'_0 k_B T$ and fit the experimental data of T_c , C , and $\epsilon' (= 1 + 4\pi\chi)$ to find the value of A'_0 (see Sec. IV). The sign as well as the magnitude of the anharmonicity parameters $A'(\mathbf{q}, T)$ have great influence on the transition mechanism, isotope effect on T_c , etc. These parameters are also related to the Landau free energy⁶⁷ \bar{F} which can be expressed as a power series in the order parameter (discussed in paper II).

III. DYNAMICAL BEHAVIOR

In order to investigate the dynamical properties of phonons on the basis of the pseudospin lattice coupled Hamiltonian H_{sp} in Eq. (3) it is convenient to calculate the phonon and the pseudospin Green's functions in the form^{63,70}

$$G^Q(\mathbf{q}, t) \equiv -i \langle T_t \{ Q(\mathbf{q}, t) Q^*(\mathbf{q}, 0) \} \rangle \quad (30a)$$

and

$$G^S(\mathbf{q}', t) \equiv -i \langle T_t \{ S_{\alpha}^z(\mathbf{q}, t) S_{\alpha}^z(-\mathbf{q}', t) \} \rangle. \quad (30b)$$

Here the Green's functions are to be defined on the imaginary axis ($-\beta \leq it \leq \beta$). T_t is the Wick's time ordering operator for real time it . For the interval $0 \leq it \leq \beta$, it is well known that the Green's functions $G(t)$ satisfy a periodic boundary condition in the time variable.^{63,70}

Here we like to mention that in Eq. (3) we have considered only the first linear term⁷¹⁻⁷³ of an expansion of the interaction energy in powers of the pseudospin and normal coordinates. One may also consider like Winterfeldt and Schaack⁷ two important additional higher-order terms along with Eq. (3) to calculate the dynamical properties of TGS and similar other crystals. However, in our RPA-type calculations with statistical Green's functions, an average contribution of these pseudospin-phonon (normal coordinate) interaction terms will appear (discussed below). Considering these two terms our total Hamiltonian written in a renormalized form is

$$H'_{sp} = \frac{1}{2} \sum_{\mathbf{q}} \{P^*(\mathbf{q})P(\mathbf{q}) + \omega^2(\mathbf{q})Q^*(\mathbf{q})Q(\mathbf{q})\} - \frac{1}{2} \sum_{\mathbf{q}} J_{\text{eff}}(\mathbf{q})S_{\alpha}^z(-\mathbf{q})S_{\alpha}^z(\mathbf{q}) - \sum_{\mathbf{q}, \mathbf{q}'} V_{\text{eff}}^{(1)}(\mathbf{q}, \mathbf{q}')S_{\alpha}^z(\mathbf{q})Q^*(\mathbf{q})Q(\mathbf{q}-\mathbf{q}') \\ + \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} V_{\text{eff}}^{(2)}(\mathbf{q}, \mathbf{q}', \mathbf{q}'')S_{\alpha}^z(\mathbf{q})S_{\alpha}^z(\mathbf{q}')Q^*(\mathbf{q})Q(\mathbf{q}-\mathbf{q}'-\mathbf{q}'') + H_{\text{anh}}, \quad (31)$$

where

$$J_{\text{eff}}(\mathbf{q}) = J(\mathbf{q}) + \sum_{\mathbf{q}} |V(\mathbf{q})|^2$$

is the effective exchange energy of the pseudospins. H_{anh} is the anharmonic terms of Eq. (3) including the normal coordinates of phonons. $V_{\text{eff}}^{(1)}$, $V_{\text{eff}}^{(2)}$, etc. terms contain the geometrical coordinates, and coordinate derivatives of the potential evaluated at the equilibrium position of the ions appropriate for the TGS type crystals (obtained by using the procedure of Nagamiya,⁷² Yamada *et al.*,^{53,73} and also by following the lattice dynamical method⁷⁴).

Equation (31) is the effective Hamiltonian of our calculations in this section. The Green's functions [Eqs. (30)] possess a Fourier series expansion and spectral function $F(\omega)$ defined as

$$G(t) = \frac{i}{\beta} \sum_n \exp(-i\omega_n t) G(\omega_n) \quad (32a)$$

and

$$G(\omega_n) = \int \frac{d\omega}{2\pi} \frac{F(\omega)}{\omega_n - \omega}, \quad (32b)$$

where $\omega_n = 3\pi n' / \beta$ and n' is an integer. To calculate, as usual, the phonon self-energy, we use the second derivative of the phonon Green's function $G^Q(\mathbf{q}, t)$ which has the form

$$-\frac{d^2}{dt^2} G^Q(\mathbf{q}, t) = \delta(t) \langle [Q(\mathbf{q}), H'_{sp}], Q^*(\mathbf{q}) \rangle \\ - iT_i \{ [[Q(\mathbf{q}, t)], H'_{sp}] Q^*(\mathbf{q}, 0) \}. \quad (33)$$

From Eqs. (31) and (33) we have

$$\left[- \left[\frac{d^2}{dt^2} \right] - \omega^2(\mathbf{q}) \right] G^Q(\mathbf{q}, t) \equiv \delta(t) + \langle T_t \{ [P^*(\mathbf{q}, t), H_{\text{anh}}] Q^*(\mathbf{q}, 0) \} \rangle - i \sum_{\mathbf{q}'} \bar{V}^{(1)}(\mathbf{q}, \mathbf{q}') \langle T_t \{ Q(\mathbf{q}-\mathbf{q}', t) S_{\alpha}^z(\mathbf{q}, t) Q^*(\mathbf{q}, 0) \} \rangle \\ - i \sum_{\mathbf{q}', \mathbf{q}''} \bar{V}^{(2)}(\mathbf{q}, \mathbf{q}', \mathbf{q}'') \langle T_t \{ Q(\mathbf{q}-\mathbf{q}'-\mathbf{q}'', t) S_{\alpha}^z(\mathbf{q}, t) S_{\alpha}^z(\mathbf{q}'', t) Q^*(\mathbf{q}, 0) \} \rangle, \quad (34)$$

where

$$\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}') = V_{\text{eff}}^{(1)}(\mathbf{q}, \mathbf{q}') + V_{\text{eff}}^{(1)}(-\mathbf{q} + \mathbf{q}', \mathbf{q}') \quad (35a)$$

and

$$\bar{V}^{(2)}(\mathbf{q}, \mathbf{q}', \mathbf{q}'') = V_{\text{eff}}^{(2)}(\mathbf{q}, \mathbf{q}', \mathbf{q}'') + V_{\text{eff}}^{(2)}(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'', \mathbf{q}, \mathbf{q}''). \quad (35b)$$

We considered in deriving Eq. (34) the second-order approximation for the pseudospin variables. Carrying out a perturbation calculation for the Green's function in the fourth term of Eq. (34) and using RPA for the fifth term we can write [using Eq. (32)]

$$[\omega_n^2 - \{\omega^2(\mathbf{q}) + V^{(1)}(\mathbf{q}, \mathbf{q}'=0) \langle S_{\alpha}^z(q=0) \rangle + \bar{V}^{(2)}(\mathbf{q}, \mathbf{q}', -\mathbf{q}') \langle |S_{\alpha}^z(\mathbf{q})|^2 \rangle + \pi_{\text{pp}}(\mathbf{q}, \omega_n) + \pi_{\text{sp}}(\mathbf{q}, \omega_n) \}] G^Q(\mathbf{q}, \omega_n) = 1, \quad (36)$$

where the terms π_{sp} and π_{pp} are the two parts of the phonon self-energy. The first part π_{pp} arises due to the interaction between phonons and agrees (to be discussed below) with that derived by Cowley⁷⁵ and also by Feder^{76,77} for the purely displacive (or phonon mechanism of the transition). The second part of the self-energy π_{sp} arises, on the other hand, from the interaction between the phonons and the pseudospins (or with the spin-like ordering and/or displacements of some ions or groups in the lattice).

For explaining various salient features associated, in particular, with the dynamic behavior of the crystal, one has to make critical analysis of both π_{sp} and π_{pp} terms (as discussed in paper II).

The strength of the pseudospin-phonon coupling contribution would actually decide which mechanism (order-disorder or displacive type) would predominate over the other. The additional self-energy term π_{sp} obtained from our calculation does not appear in the calculations of Cowley⁷⁵ and others⁷⁶⁻⁷⁹ obtained by considering the pure phonon-phonon interaction Hamiltonian, where the pseudospin part was neglected.

Both $\pi_{\text{pp}}(\mathbf{q}, z)$ and $\pi_{\text{sp}}(\mathbf{q}, t)$ are analytic functions of the complex variables z except on the real axis. Approaching the real axis from above, one can define the real and imaginary parts of π_{pp} (say) in the following manner:

$$\lim_{\delta \rightarrow 0} \pi_{\text{pp}}(\mathbf{q}, \omega + i\delta) = \text{Re} \pi_{\text{pp}}(\mathbf{q}, \omega) - i \text{Im} \pi_{\text{pp}}(\mathbf{q}, \omega). \quad (37)$$

The real part in Eq. (37) denoted by Δ_{pp} (say) measures the anharmonic frequency shift, and the imaginary part of π_{pp} is the reciprocal of the phonon relaxation time (τ_{pp}) and hence proportional to the phonon damping constant (Γ_{pp}). This shift is observable, for instance, from the Raman spectroscopic studies.⁷ The real part of Eq. (37) may again be split into two parts like

$$\Delta_{pp} = \Delta_{pp}^T + \Delta_{pp}^A, \quad (38)$$

where Δ_{pp}^T is associated with the thermal strain $U_{\alpha\beta}^T$ and represents the anharmonic frequency shift due to thermal expansion and can also be expressed as

$$\Delta_{pp}^T = \sum \hat{V}_{\alpha\beta}(\mathbf{q}-\mathbf{q}') U_{\alpha\beta}^T, \quad (39)$$

where Δ_{pp}^A is the contribution from the higher-order anharmonic terms. In the present paper we have considered only the third and the fourth-order terms similar to that used by Cowley⁷⁵ and others⁷⁶⁻⁷⁸ and, therefore, we have

$$\Delta_{pp}^A = A_{pp}^{(3)} + A_{pp}^{(4)}, \quad (40)$$

where $A_{pp}^{(3)}$ and $A_{pp}^{(4)}$ are, respectively, the self-energies arising from the cubic and quartic terms which contribute in the same order in perturbation theory. Following the calculations of Cowley,⁷⁵ Maradudin *et al.*,⁷⁴ and Califano *et al.*,⁷⁹ the leading terms for the cubic anharmonicity that appears from our calculations (up to second order) have the usual form

$$A_{pp}^{(3)} = -\frac{18}{\hbar^2} \sum_{\mathbf{q}, \mathbf{q}'} |\bar{B}(\mathbf{q}, \mathbf{q}', \mathbf{q}'')|^2 \left[\frac{n(\mathbf{q}') + n(\mathbf{q}'') + 1}{\{\omega(\mathbf{q}') + \omega(\mathbf{q}'') + \omega\}_P} + \frac{n(\mathbf{q}') - n(\mathbf{q}'')}{\{\omega(\mathbf{q}') - \omega(\mathbf{q}'') + \omega\}_P} \right. \\ \left. + \frac{n(\mathbf{q}'') - n(\mathbf{q}')}{\{\omega(\mathbf{q}') - \omega(\mathbf{q}'') + \omega\}_P} + \frac{n(\mathbf{q}') + n(\mathbf{q}'') + 1}{\{\omega(\mathbf{q}') + \omega(\mathbf{q}'') - \omega\}_P} + \frac{2[2n(\mathbf{q}'') + 1]}{\{\omega(\mathbf{q}')\}_P} \right], \quad (41)$$

where P denotes the principal part. Similarly, the corresponding leading term in quartic interaction has been found to have the form

$$A_{pp}^{(4)} = \frac{12}{\hbar} \sum_{\mathbf{q}'} \bar{A}(\mathbf{q}, -\mathbf{q}, \mathbf{q}', -\mathbf{q}') [4n(\mathbf{q}') + 1] \quad (42)$$

which is independent of the applied frequency ω unlike the $A_{pp}^{(3)}$ term. In Eqs. (41) and (42)

$$n(\mathbf{q}) = n(\mathbf{q}, j) = [\exp(\hbar\omega(\mathbf{q}_j)/k_B T) - 1]^{-1}. \quad (43)$$

Now we calculate the imaginary part of π_{pp} from [Eq. (37)] which is denoted by π'_{pp} and can be expressed as

$$\pi'_{pp} = \frac{18}{\hbar^2} \sum_{\mathbf{q}, \mathbf{q}'} [\bar{B}(\mathbf{q}, -\mathbf{q}', -\mathbf{q}') \bar{B}(-\mathbf{q}, \mathbf{q}', \mathbf{q}')] \\ \times \{ [n(\mathbf{q}') + n(\mathbf{q}'') + 1] \delta[\omega(\mathbf{q}') + \omega(\mathbf{q}'') + \omega] - \delta[\omega(\mathbf{q}') + \omega(\mathbf{q}'') + \omega] \\ + [n(\mathbf{q}'') - n(\mathbf{q}')] \delta[\omega(\mathbf{q}') - \omega(\mathbf{q}'') - \omega] - \delta[\omega(\mathbf{q}') - \omega(\mathbf{q}'') + \omega] \}, \quad (44)$$

where δ is the Dirac δ function having its usual meaning.

So far, in this section, we have tried to establish the similarity in the behavior of the phonon self-energy (when the phonon is coupled with the pseudospin subsystem) with that observed from the calculation of Cowley,⁷⁵ where only pure phonon-phonon interaction is considered. Further analysis of the above theoretical results could also be made following the procedure of Cowley and others.⁷⁶⁻⁷⁸ It is found that the cubic anharmonic term (second order in the interaction representation) contributes both to the real and imaginary parts of π_{pp} , while the quartic term contributes only to the real part Δ_{pp} , and hence does not contribute to damping Γ_{pp} related to the imaginary part of the π_{pp} .

The imaginary part ($\text{Im}\pi_{pp}$) of Eq. (44) can be written in the form

$$\text{Im}\pi_{pp} = \pi'_{pp} = 2\omega\Gamma_{pp}(\mathbf{q}, \omega), \quad (45)$$

where $\Gamma_{pp}(\mathbf{q}, \omega)$ is the damping constant. Now one can

write^{77,80} the spectral function F_{ppj} , which is basically the imaginary part of the dynamic phonon susceptibility χ_{ppj} , as

$$F_{ppj}(\mathbf{q}, \omega) = [1 - \exp(\hbar\omega/k_B T)]^{-1} \\ \times \text{Im}\{[\omega_j^2(T) + \pi_{ppj}(\mathbf{q}, \omega) - \omega^2]^{-1}\} \quad (46)$$

and

$$\chi_{ppj}[\omega_j(q=0), \omega, T] = [\omega_j^2(T) + \Gamma_{ppj}(\mathbf{q}, \omega, T) - \omega^2]^{-1}, \quad (47)$$

where

$$\omega_j(T) = |\omega_j^2(q=0) + \Delta_{ppj}(T)|^{1/2}$$

is the renormalized quasi-harmonic frequency and $\omega_j(q=0)$ is the harmonic frequency of phonon mode j (say). The static mode susceptibility is proportional to $\bar{\omega}_j^2$, which in turn is proportional to the integrated inten-

sity of the mode j (for $k_B T \gg \hbar\omega$). For a damped harmonic oscillator with self-energy π_{pp} [Eq. (37)] one finds from Eq. (46)

$$F_{ppj} = \frac{\omega}{1 - \exp(-\hbar\omega/k_B T)} \frac{\Gamma_{ppj}(T)}{[\omega_j^2(T) - \omega^2]^2 - \omega^2 \Gamma_{ppj}(T)}. \quad (48)$$

Equation (48) is identical with that derived by Cowley^{75,77} and Maradudin and Fein,⁷⁸ which is appropriate for the purely displacive mechanism of the transition. However, the effect of pseudospin phonon coupling which is found (from our calculation) to largely modify the phonon ener-

gy does not appear in their calculations. It can be shown from our subsequent discussion that the additional phonon self-energy term introduced in the theory of Cowley⁷⁵ [see Eq. (65)] to account for the central peak behavior in some crystals, should actually originate from the π_{sp} part of the self-energy obtained in our calculations with PLCM model. We have shown below that this additional self-energy term π_{sp} is also very important for the studies of the dynamical behavior of phase transitions in TGS and many other crystals.

This additional self-energy π_{sp} arising from the phonon-pseudospin interaction comes out to be [from Eq. (36)] of the form

$$\pi_{sp}(\mathbf{q}, \omega_n) = -\frac{1}{k_B T} \sum_{\mathbf{q}'} |\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}')|^2 \sum_{n'} G_{\mathbf{q}}^Q(\mathbf{q} - \mathbf{q}', \omega_n - \omega_{n'}) G_{\mathbf{q}}^S(\mathbf{q}, \omega_{n'}). \quad (49)$$

Using Eq. (49) and the spectral Green's function [Eq. (32)] we have

$$\pi_{sp}(\mathbf{q}, \omega_n) = -\frac{1}{k_B T} \sum_{\mathbf{q}'} |\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}')|^2 \sum_{n'} \int \int \frac{d\omega d\omega'}{(2\pi)^2} \frac{F_{pp}(\mathbf{q} - \mathbf{q}', \omega) F_{sp}(\mathbf{q}, \omega')}{(\omega_n - \omega_{n'} - \omega)(\omega_n - \omega')}, \quad (50)$$

where F_{pp} and F_{sp} are, respectively, the spectral functions for the phonon and the pseudospin Green's functions [Eq. (30)]. The Fourier transform of the correlation function (dynamic scattering function) of the pseudospin variable is

$$S_{sp}(\mathbf{q}, \omega) = \int dt \exp(i\omega t) \langle S_{\alpha}^z(\mathbf{q}, t) S_{\alpha}^z(-\mathbf{q}, 0) \rangle \quad (51)$$

which is related to F_{sp} as

$$F_{sp}(\mathbf{q}, \omega) = [n(\omega + 1)] F_{sp}(\mathbf{q}, \omega). \quad (52)$$

Now using the summation rule

$$\frac{1}{k_B T} \sum_n \frac{1}{\omega_n - \omega} = -\frac{1}{2} [2n(\omega) + 1] \quad (53)$$

and the Bose occupation number $n(\omega) = [\exp\omega/k_B T - 1]^{-1}$, we obtain from Eq. (50)

$$\pi_{sp}(\mathbf{q}, \omega_n) = \sum_{\mathbf{q}'} |\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}')|^2 \int \frac{d\omega d\omega'}{(2\pi)^2} [n(\omega) + n(\omega') + 1] \frac{F_{pp}(\mathbf{q} - \mathbf{q}', \omega) F_{sp}(\mathbf{q}, \omega')}{\omega_n - \omega' - \omega}. \quad (54)$$

Since $\pi_{sp}(\mathbf{q}, \omega_n)$ is also an analytic function of the complex variable like π_{pp} [Eq. (37)], as mentioned above, we may define the real and the imaginary parts of π_{sp} as

$$\pi_{sp}(\mathbf{q}, \omega) = \Delta_{sp}(\mathbf{q}, \omega) - i \text{Im} \pi_{sp}(\mathbf{q}, \omega). \quad (55)$$

The real part denoted by Δ_{sp} (say) will also contribute like Δ_{pp} [Eq. (37)] a shift in the phonon frequency $\omega(\mathbf{q})$, while the imaginary part denoted by π'_{sp} (say) will contribute to the damping. This contribution arising from the pseudospin-phonon interaction has not so far been considered in the literature while describing the quasielastic neutron scattering or other experimental data of crystals undergoing structural or other transitions.

Using, for convenience, the spectral function $F_{pp}(\mathbf{q}, \omega)$ of noninteracting phonons [in Eq. (54)] viz,

$$F_{pp}(\mathbf{q}, \omega) = \frac{\pi}{\omega} [\delta(\omega - \omega(\mathbf{q})) - \delta(\omega + \omega(\mathbf{q}))], \quad (56)$$

one might calculate the real (Δ_{sp}) and the imaginary (π'_{sp}) parts of π_{sp} (similar to that made for the π_{sp}) which can be written as

$$\Delta_{sp}(\mathbf{q}, \omega) = \sum_{\mathbf{q}'} \frac{|\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}')|^2}{2\omega(\mathbf{q} - \mathbf{q}')} \text{P} \int \left[\frac{d\omega'}{d\pi} F_{sp}(\mathbf{q}, \omega') \left(\frac{n\omega(\mathbf{q} - \mathbf{q}') + n(\omega') + 1}{\omega - \omega(\mathbf{q} - \mathbf{q}') - \omega'} + \frac{n\omega(\mathbf{q} - \mathbf{q}') - n(\omega')}{\omega + \omega(\mathbf{q} - \mathbf{q}') - \omega} \right) \right], \quad (57)$$

where P again denotes the principal part of the integral. Similarly, for the imaginary part we have

$$\pi'_{sp}(\mathbf{q}, \omega) = \sum_{\mathbf{q}'} \frac{|\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}')|^2}{4\omega(\mathbf{q}-\mathbf{q}')} \{ [n(\omega(\mathbf{q}-\mathbf{q}')) + n(\omega - \omega(\mathbf{q}-\mathbf{q}')) + 1] F_{sp}(\mathbf{q}', \omega - \omega(\mathbf{q}-\mathbf{q}')) + [n(\omega(\mathbf{q}-\mathbf{q}')) - n(\omega + \omega(\mathbf{q}-\mathbf{q}'))] F_{sp}(\mathbf{q}', \omega + \omega(\mathbf{q}-\mathbf{q}')) \} . \quad (58)$$

Now the damping constant related to π_{sp} may be obtained from

$$\text{Im}\pi_{sp}(\mathbf{q}, \omega) = 2\omega\Gamma_{sp}(\mathbf{q}, \omega) , \quad (59)$$

where Γ_{sp} denotes the damping constant due to the pseudospin-phonon interaction. Similarly, earlier we have obtained Γ_{pp} for the phonon-phonon interaction from the imaginary part of π_{pp} [Eq. (37)]. Using Eqs. (52), (58), and (59) we get

$$\Gamma_{sp}(\mathbf{q}, \omega) = \sum_{\mathbf{q}'} \frac{|\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}')|^2}{8\omega\omega(\mathbf{q}-\mathbf{q}')} \left[\left[\frac{n(\omega(\mathbf{q}-\mathbf{q}'))}{n(\omega - \omega(\mathbf{q}-\mathbf{q}')) + 1} + 1 \right] S_{sp}(\mathbf{q}, \omega - \omega(\mathbf{q}-\mathbf{q}')) + \frac{n(\omega(\mathbf{q}-\mathbf{q}')) + 1}{n(\omega + \omega(\mathbf{q}-\mathbf{q}')) + 1} + 1 \right] . \quad (60)$$

It is observed from Eq. (60) that the temperature dependence of the damping constant for the phonon frequency $\omega_j(\mathbf{q})$ is modulated by the presence of scattering function $S_{sp}(\mathbf{q}, \omega)$. The dynamic scattering function $S_{sp}(\mathbf{q}, \omega)$, is known^{81,82} to undergo a sharp increase near a phase transition. Therefore, Eq. (60) arising from the pseudospin-phonon interaction will give rise to an anomaly and increase in its value around the transition point. This contribution is in addition to that arising from pure-phonon interaction.⁷⁵ Consequently, both the damping constants Γ_{sp} and Γ_{pp} would show anomalies around the transition. Temperature dependences of both Γ_{sp} and Γ_{pp} is shown in Fig. 3. Now similar to Eq. (47) we can also write the spectral function F_{spj} (related to dynamic "pseudospin susceptibility," χ_{sp}) as

$$F_{spj}(\mathbf{q}, \omega) = [1 - \exp(\omega'\hbar/k_B T)]^{-1} \times \text{Im}[\omega_j^2(\mathbf{q}=0) + \pi_{spj}(\mathbf{q}, \omega') - \omega^2]^{-1} \quad (61)$$

and

$$\chi_{sp}(\omega_j, T, \omega) = [\omega_j^2(\mathbf{q}=0) + \Gamma_{spj}(\mathbf{q}, \omega', T) - \omega^2]^{-1} . \quad (62)$$

Equation (61) can also be written in the form of Eq. (48) as

$$F_{spj}(\mathbf{q}, \omega) = \frac{\omega'}{1 - \exp(\omega'\hbar/k_B T)} \frac{\Gamma_{spj}(T)}{[\omega_j^2(T) - \omega'^2]^2 - \omega'^2\Gamma_{spj}^2(T)} . \quad (63)$$

The importance of Eq. (63) and other additional contributions arising from π_{sp} would be visualized if one makes a critical analysis of the experimental neutron scattering, Brillouin scattering, or Raman scattering data. These results would actually illuminate the salient features of the dynamical properties of TGS or other crystals as discussed in Paper II.

A. Total damping constant

From the above calculations it is, therefore, evident that there are two parts of the damping constant, viz. Γ_{pp} and Γ_{sp} , arising from the phonon-phonon and the pseudospin-phonon interactions, respectively. That is, the total damping constant is

$$\Gamma(\mathbf{q}, \omega) = \Gamma_{pp}(\mathbf{q}, \omega) + \Gamma_{sp}(\mathbf{q}, \omega) . \quad (64)$$

The Γ_{sp} part has not previously been considered while explaining various anomalous (nonlinear) behavior⁷⁵⁻⁷⁷ in H bonded and other crystals as observed from NMR (or NQR) relaxation, Brillouin, or Raman scattering experiments. For example, neutron scattering experimental results^{75,80} indicate that at low frequencies there is an addi-

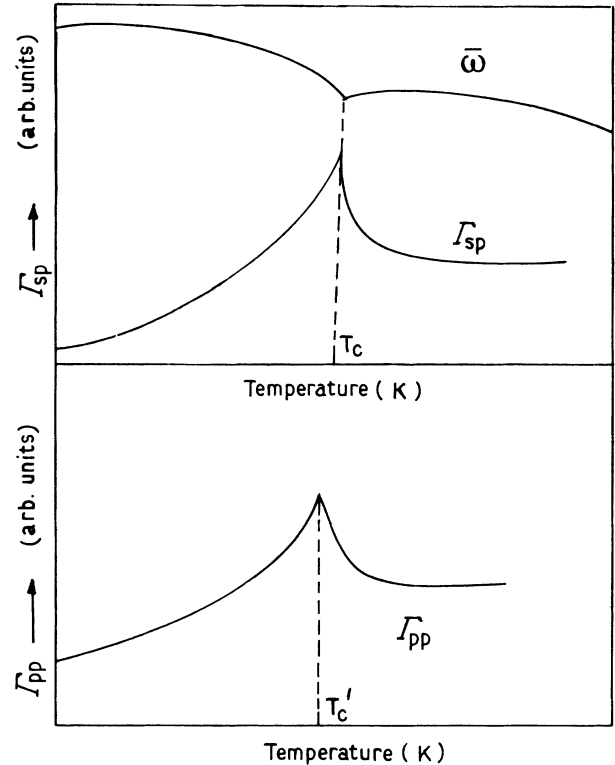


FIG. 3. Anomalous temperature dependences of the renormalized phonon frequency (energy), and the damping constants (Γ_{pp} and Γ_{sp}) are shown schematically. The total damping constant $\Gamma = \Gamma_{pp} + \Gamma_{sp}$ might, however, show a smaller or larger anomaly at the transition point. It is also, unnecessary that both Γ_{pp} and Γ_{sp} and, hence, the total damping constant, as well as the energy should show the anomaly at the same temperature T_c (say). All these depend on the various interaction strengths already mentioned in the text.

tional response not described by the “soft mode” formula [Eq. (48)] where damping is proportional to ω . To describe this additional response the self-energy expression [Eq. (37)] was modified^{75,77,80} in the form

$$\pi_{pp}(\mathbf{q}, \omega) = \Delta_{pp}(\mathbf{q}, \omega) - i\Gamma_{pp}(\mathbf{q}, \omega) - i\omega \frac{\delta^2(T)}{\gamma - i\omega}. \quad (65)$$

To write this additional term, it was assumed earlier^{75–77} that the “soft mode” decays into some other mode or combination of modes, and then this further mode decays exponentially with a long characteristic time $1/\gamma$. The coupling constant δ^2 has not yet been possible to specify. We have shown in paper II that this term could be explained by considering the π_{sp} part of the self-energy. It has also been shown in paper II that the origin of the hitherto unexplained “double peaks” observed from the NMR relaxation rate measurement in TGS, is associated with the π_{sp} part of the self-energy.

It should also be mentioned that Eq. (64) bears considerable significance indicating the presence of two subsystems (phonons and pseudospins) contributing to the dynamic behavior of crystals. The transition mechanism in TGS or in other crystals would be mainly of the displacive (or order-disorder) type depending on the importance attributed to π_{pp} or π_{sp} . That is, the contribution from the π_{pp} part of the phonon self-energy would be greater for the displacive behavior, while that from the π_{sp} part would be greater for the order-disorder behavior of the transition. The weaker part of the self-energy, in this competition (say π_{sp} in case of displacive behavior), usually becomes more important near the transition point (i.e., the fluctuating region). During the ferroelectric transition in TGS or in other crystals, both the π_{pp} and π_{sp} parts of the self-energy contributed, respectively, by the lattice vibrations and the molecular ordering (pseudospin ordering) become important. Therefore, the deviation of the Landau behavior in TGS, as mentioned in Sec. I, might also be due to the importance of the π_{sp} term rather than that due to other causes. Since it appears from our calculations and also from other facts (discussed in Sec. I) that the transition mechanism in TGS is a “mixed” type (both order-disorder and displacive behavior of transition coexist), one cannot directly apply the LK theory or similar other theories for TGS. This picture would be more vivid from our subsequent discussion (see also paper II). Here we should therefore mention that the transition mechanism in TGS is also more complicated than the usual magnetic spin-ordering transition, where the lattice has very little part to play. These two situations should not be mingled together. However, the magnon-phonon coupled system could be described by the PLCM model with suitable modifications.

B. Phonon frequency

If we assume that the real and the imaginary parts of π_{sp} are very small compared to $\omega^2(\mathbf{q})$, the mean frequency ω obtained from Eq. (36) is given by the expression

$$\omega^2 = \bar{\omega}^2(\mathbf{q}, \omega) + \bar{V}^{(1)}(\mathbf{q}, \mathbf{q}'=0) \langle S_\alpha^z(\mathbf{q}=0) \rangle + \sum_{\mathbf{q}'} \bar{V}^{(2)}(\mathbf{q}, \mathbf{q}', -\mathbf{q}') \langle |S_\alpha^z(\mathbf{q}')|^2 \rangle + \pi_{sp}(\mathbf{q}, \omega), \quad (66)$$

where $\omega(\mathbf{q}, \omega)$ is the renormalized phonon frequency

$$\bar{\omega}(\mathbf{q}, \omega) \equiv \omega^2(\mathbf{q}) + \text{Re}\pi_{pp}(\mathbf{q}, \omega)$$

which might be calculated for TGS from the fitting of various experimental results following the procedure of our earlier work.^{34–36} The second term in Eq. (66) is the first-order correction of the frequency shift with respect to the pseudospin variable (associated with the microscopic rotation or ordering of some ions or groups in the lattice, say the glycine molecules in TGS). The corresponding order parameter, $\langle S_\alpha^z(q_0) \rangle$, can be obtained from the mean-field-type calculation shown in Sec. II, and its temperature dependence has been well discussed by Bront.⁸¹ Here q_0 is the specific wave vector with which the pseudospins are macroscopically ordered. The third and fourth terms in Eq. (66) denote the second-order correction of the frequency shifts caused by the pseudospin correlation. To study the salient features of the transition in TGS and other H-bonded crystals one can write Eq. (66) using Eq. (41) as

$$\omega^2 = \bar{\omega}^2(\mathbf{q}, \omega) + \bar{V}^{(1)}(\mathbf{q}, \mathbf{q}'=0) \langle S_\alpha^z(\mathbf{q}=0) \rangle + \sum_{\mathbf{q}'} \bar{V}^{(2)}(\mathbf{q}, \mathbf{q}', -\mathbf{q}') \int \frac{d\omega'}{2\pi} S_{sp}(\mathbf{q}', \omega') + \sum_{\mathbf{q}'} \frac{|\bar{V}^{(1)}(\mathbf{q}, \mathbf{q}')|^2}{2\omega(\mathbf{q}-\mathbf{q}')} \int \frac{d\omega'}{2\pi} \left[\frac{n\omega(\mathbf{q}-\mathbf{q}') + n(\omega') + 1}{\omega - \omega(\mathbf{q}-\mathbf{q}') - \omega'} + \frac{n\omega(\mathbf{q}-\mathbf{q}') - n(\omega')}{\omega + \omega(\mathbf{q}-\mathbf{q}') - \omega'} \right] \frac{S_{sp}(\mathbf{q}', \omega')}{n(\omega') + 1}. \quad (67)$$

The dynamic scattering function $S_{sp}(\mathbf{q}, \omega)$ in Eq. (67) being related to the dynamic susceptibility (by fluctuation dissipation theorem) is known^{81,82} to undergo a sharp increase near the transition. This is also exhibited by the damping constants discussed above. The temperature variation of ω^2 is shown schematically in Fig. 3. Thus it is evident from Eq. (67) that the pseudospin ordering should also give rise to an additional temperature-dependent anomaly to the phonon frequency. Conse-

quently, the anomalous temperature dependence of the phonon frequency due to the pseudospin ordering and correlation is given by $\langle S^z(q_0) \rangle$ and Eq. (67), respectively. A question may arise as to whether the temperature at which the pseudospin ordering (with the specified wave vector q_0) takes place would also coincide with the soft-mode (phonon) transition. To answer this question one has to find the pseudospin-phonon coupling strength and the higher-order phonon anharmonicity parameters. An

estimate of these parameters can be obtained from the spectroscopic studies, and also from fitting the experimental values of T_c , C , χ , P_s , renormalized phonon frequency, etc. with the corresponding theoretically derived expressions. The latter procedure has been adopted in this paper. As the sign and magnitudes of these coupling parameters are different in different crystals, several peculiarities near the transition region might appear. These are actually observed from various experimental results on TGS and other crystals (see also paper II).

In Sec. IV we have tried to fit the experimental results of T_c , χ , P_s , C , etc. for the TGS and its isomorphs (both deuterated and undeuterated) with the corresponding theoretically derived expressions to find the Blinc-de Gennes model parameters for these crystals.

IV. RESULTS AND DISCUSSION

The experimental values of T_c , dielectric constant (ϵ'), spontaneous polarization (P_s), and the Curie-Weiss constant (C) of the TGS, deuterated triglycine sulfate (DGS), triglycine selenate (TGSe), and deuterated triglycine selenate (DTGSe) crystals are fitted with the respective expressions [Eqs. (26), (24), (13), and (29)] derived theoretically in Sec. II. It was attempted in our earlier work³⁴⁻³⁶ and also in this paper for the present TGS crystal to fit all these theoretical expressions with a single set of model parameters, being different for different crystals. The model parameters \bar{J}_0 , $\bar{\Omega}$, $\omega(q=0)$, μ , $A'_0(q=0,0)$, etc. thus obtained for the above-mentioned deuterated and undeuterated TGS family are shown in Table I. The experimental and the theoretical ($\epsilon'-T$), and (P_s-T) curves for these crystals are shown in Figs. 4-6. It is observed from these figures that the agreement between the theoretical and the experimental curves for all of the above four crystals studied, are very good except for the regions very close to the transition point—the fluctuating region, where this deviation is obvious. However, if these model parameters are varied from these derived values by about 10%, on the average, similar to that done by Samara Samuelsen⁶⁴ for KDP and squaric acid, the ($\epsilon'-T$) and (P_s-T) curves can be fitted even very close to the transition region. This agreement between the theoretical and the experimental results definitely indicates the validity of the PLCM model for explaining, at least within the RPA limit, the ferroelectric phase transi-

tion of the TGS family similar to other H-bonded ferroelectrics studied earlier.³⁴⁻³⁶ This also indicates the unified character of the PLCM model. Of course, proper generalization of the model is necessary for every crystal system. Furthermore, our calculations also point out that the RPA-type calculation with the statistical Green's-function technique is good for TGS similar to other H-bonded ferroelectric crystals, in particular.

Since experimental values of $\bar{\Omega}_H$ (undeuterated value of $\bar{\Omega}$), $\bar{\Omega}_D$ (deuterate value of $\bar{\Omega}$), $\bar{J}(q=0)$, $\bar{V}(q=0)$, and $A'_0(q=0)$ are not available for the TGS salt, we could not directly compare the calculated values of these parameters with experimental ones. However, the values of $N\mu$ for all the salts studied are found to be very close to the experimentally⁸² observed ones (Table I). It is observed from Table I that the tunneling contribution is not zero in TGS. Therefore, it appears that the tunneling contribution is never zero in H-bonded crystals.

Neglecting higher-order $\bar{V}(q=0)$ terms in Eq. (61), and also if we assume that the anharmonic contribution is very small, we have

$$[\omega_q^2(T) - \omega^2(q=0)] \propto P_s(T). \quad (68)$$

(It is clear from the subsequent discussion that this assumption is not strictly valid for the TGS crystal.) If the mean-field approximation (MFA) is assumed to be valid⁸⁴ for TGS (or TGSe) down to $|T - T_c| \gg (5 \times 10^{-3})^\circ\text{C}$ [i.e., $P_s \propto (T_c - T)^{1/2}$], Eq. (68) would also be equivalent to

$$[(\bar{\omega}_q^2(T) - \omega^2(q=0))] = \lambda'(T_c - T), \quad (69)$$

where λ' is a constant. Equation (69) is, however, valid up to the straight part of the P_s^2 versus $(T_c - T)$ curve (for the C -type modes⁷) as shown in Fig. 6(a). Similar linear temperature dependence of the frequency shift, proportional to the order parameter (up to the linear portion of P_s), was also observed^{28,85} in the NMR and ESR experimental results of TGS and DTGS [Fig. 6(b)]. We believe that this linear variation is possible, while the anharmonic contribution to the EFG remains small or if this contribution is neglected. Although this behavior might also indicate that the origin of the temperature-dependent coupling constant is essentially due to Coulomb interaction, the frequency shift as observed from the Raman or other spectroscopic techniques in

TABLE I. Pseudospin-lattice coupled mode (PLCM) model parameters obtained for TGS, TGSe, DTGS, and DTGSe from the best fitting of the experimental data (Ref. 83) of T_c , C , P_s , and ϵ' . (These data are fitted with parameters $K_0 = B_0 = 0$ and taking $1 \text{ eV} = 8056.80 \text{ cm}^{-1}$.) T_c and C are the experimental values (Ref. 83) used to fit the dielectric constant (ϵ') curves of the TGS family as a function of temperatures as shown in Figs. 4 and 5. The model parameters $\bar{\Omega}$ and $\bar{\omega}(q=0)$ are found to be very small compared to those of other H-bonded ferroelectric and antiferroelectric crystals (Refs. 34-36). However, relatively higher values of the anharmonicity parameters A'_0 are obtained from the theoretical fitting of the above-mentioned experimental data for the TGS family.

Samples	T_c ($^\circ\text{C}$)	C ($^\circ\text{C}$)	$\bar{\Omega}$ (cm^{-1})	\bar{J}_0 (cm^{-1})	\bar{V}_0 (cm^{-1})	$\hbar\bar{\omega}_{q=0}$ (cm^{-1})	A'_0 (cm^{-1})	$N\mu$ ($\mu\text{C}/\text{cm}^2$)
TGS	49.10	3007	0.10	340	10	0.59	10.20	2.22 (at 50°C)
TGSe	22.50	4727	0.40	320	12	0.61	11.15	3.70 (at 12.50°C)
DTGS	60.70	4600	0.01	470	15	1.92	14.22	2.30 (at 30.70°C)
DTGSe	34.00	4507	0.05	430	20	1.99	15.25	2.70 (at 24°C)

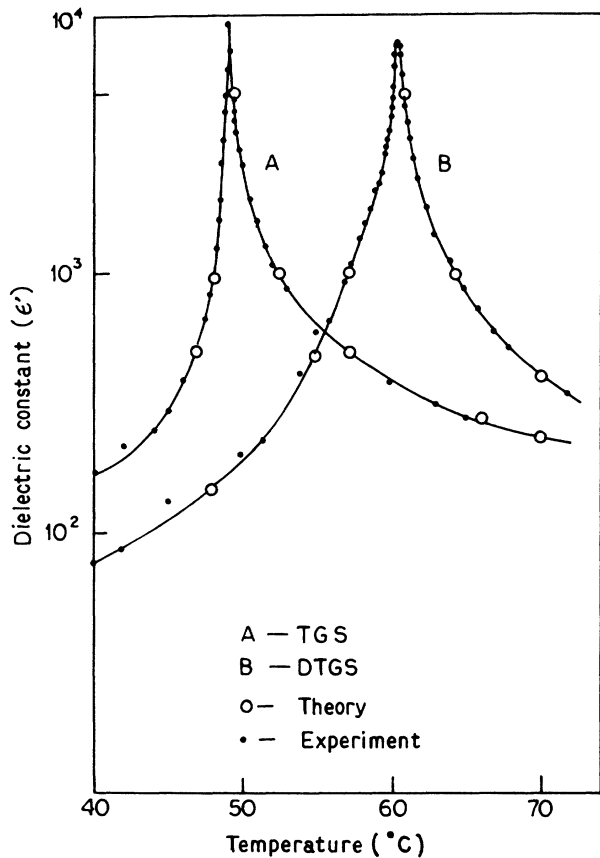


FIG. 4. Thermal variation of dielectric constants of TGS and DTGS. Solid circles, experimental points (Ref. 83); large open circles, present theory.

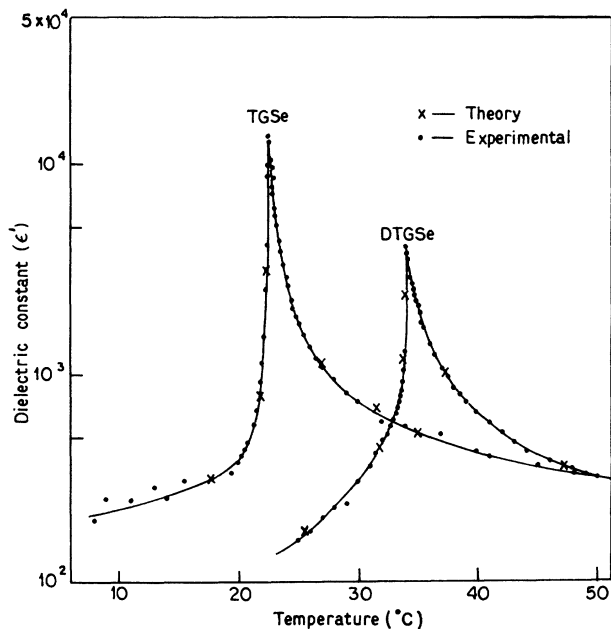


FIG. 5. Thermal variation of dielectric constants of TGSe and DTGSe. Small circles, experimental points (Ref. 83); \times , present theory.

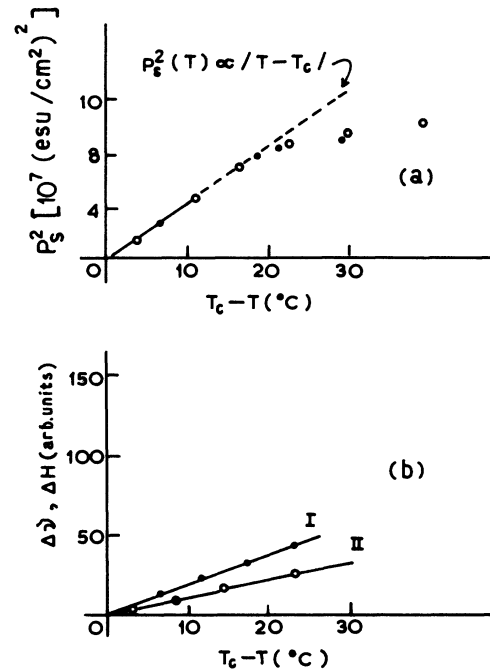


FIG. 6. (a) Linear temperature-dependent part of spontaneous polarization (P_s) (Ref. 83), (b) thermal variation of NQR splitting (denoted by I) (Ref. 28), and resonance field shift (denoted by II) (Ref. 85) obtained from the ESR spectra of Cu^{2+} in TGS.

TGS (or in other crystals) could not be explained without considering the higher-order pseudospin-phonon interaction terms.

The order-disorder model^{4,86} of the ferroelectric phase transition was used by Bjorkstam²⁸ to explain the NQR data of TGS, considering that the transition is triggered by the proton in a double-well potential between the glycine molecules (Fig. 1). This model, however, describes only the qualitative behavior of the complicated phase transition in TGS. Proper care has not been taken in this work²⁸ to elucidate the importance of the higher-order phonon-phonon interaction terms for the interpretation of the NQR results. Not only in NQR,⁸⁷ these higher-order interaction terms were also considered to be important to explain the ultrasonic velocity and attenuation⁸⁸ in TGS [where a model similar to that given by Eq. (3) is valid]. More about the importance of the higher-order phonon-phonon and the pseudospin-phonon interaction terms will be discussed in Paper II.

It has already been shown in Sec. III that the expressions for Γ_{pp} , Γ_{sp} , and the renormalized phonon frequency $\bar{\omega}(\mathbf{q})$ contain the scattering function $S_{sp}(\mathbf{q}, \omega)$. Thus both Γ_{pp} and Γ_{sp} are expected to exhibit anomalous behavior, i.e., anomalously large values near T_c as shown in Fig. 3. However, these anomalies associated with Γ_{pp} and Γ_{sp} may not appear at the same temperature (i.e., the same T_c). There may be two (say T_{c1} and T_{c2}) or one (either T_{c1} or T_{c2} , if the two anomalies appear simultaneously) T_c values. One may consider T_{c1} (say) associated with Γ_{sp} or π_{sp} and T_{c2} associated with Γ_{pp} or π_{pp} . These features of the damping constants and the renormalized

phonon frequency must also be reflected in the dynamic properties of the crystals undergoing structural phase transitions. This behavior would again vary from crystal to crystal depending on the coupling strengths between the pseudospin [local potential^{37,89} $\psi(r)$] and the phonons (including higher-order anharmonic interaction terms).

Under some special circumstances, depending on the above-mentioned coupling strengths and also on the resolution function of the experimental technique used for measuring the response, the anomalies at or around T_c (or at T_{c1} and T_{c2} as shown by Γ_{sp} and Γ_{pp} in Fig. 3) might be observed. The two anomalies, if at all possible, might also appear separately (when $T_{c1} \neq T_{c2}$) or as a single anomaly ($T_{c1} \approx T_{c2} = T_c$). The latter situation will occur due to the importance of either Γ_{pp} (or Γ_{sp}), when one part π_{pp} (or π_{sp}) would predominate over the other, and the crystal would behave either as the order-disorder or as the displacive system (depending on whether π_{sp} or π_{pp} predominates).

It can be shown that the order-disorder character corresponds to $E_m \gg k_B T_c$ and the displacive behavior appears when $E_m \ll k_B T_c$ [where E_m corresponds to the minimum in the local potential $\psi(r)$ described in Fig. 7]. If the two anomalies due to Γ_{pp} and Γ_{sp} (or, in other words, due to π_{pp} and π_{sp}) appear simultaneously, it

mean that the pseudospin mode and the phonon mode are equally important and simultaneously trigger the transition. Otherwise, the transitions might appear separately at different temperatures (both with equal intensity or one with very small intensity compared to the other). One anomaly might also be associated with the structural transition, while the other might appear showing only little anomalous behavior in the physical properties. In this way several peculiarities might be observed in the system.

As mentioned above, the transition appears to be mostly displacive (or mostly order-disorder) type, when the π_{pp} (or the π_{sp}) term becomes important. That is, for a displacive transition the characteristic features of the transition might be qualitatively explained with a purely phonon-phonon interaction Hamiltonian⁷⁵⁻⁸⁰ studied by Cowley⁷⁵ and others,⁷⁷ while the so-called order-disorder transition might be qualitatively explained with a purely pseudospin-like model^{9,52} studied by Blinc and others. Since it appears from our calculations that no such transition is purely order-disorder or purely displacive type, both the π_{sp} and π_{pp} terms are important for a critical understanding of the dynamic behavior of any crystal undergoing a phase transition. The mathematical picture for such a transition mechanism could only be properly represented with a pseudospin-lattice coupled Hamiltonian (PLCM model).

The peak height, position, and width, as shown in Fig. 3, all depend on the strengths of the pseudospin-phonon, and the phonon-phonon interaction parameters. Actually, these coupling constants decide the order-disorder or the displacive character of the structural transitions. Therefore, depending on these parameters, it appears quite plausible that interesting "crossover" phenomenon (order-disorder to displacive or vice versa) would be observed in some crystals. This would, of course, occur under certain special circumstances. For example, in a perovskite structure like BaTiO_3 showing displacive behavior, the local mode character (pseudospin⁸⁹) is associated with the displacement of Ti atoms with respect to the O_6 oxygen case (illustrated by the rotation of TiO_6 octahedra). This incipient pseudospin character^{11,12} becomes modulated (pseudospin-phonon coupling constant changes) when BaTiO_3 (say) is doped⁸⁹ with Fe^{3+} or other suitable ions. Consequently, one might observe "crossover" behavior in this doped system.⁸⁹ This behavior is also observed in H-bonded squaric acid.⁹⁰ In Fig. 7 we have also represented schematically the probable "crossover" behavior in H-bonded or nonhydrogen-bonded crystals, where both π_{sp} and π_{pp} terms are equally sensitive. Here the transition mechanism should be called a mixed type since both π_{pp} and π_{sp} terms characterize the transition mechanism. To be specific, the observed crossover phenomenon arises due to the failure of the strong competition between the order-disorder and the displacive mechanism or, in other words, due to the break of coupling between the short-range (H bonds, covalent bonds, Pauli repulsive forces, etc.) and long-range (Coulombic) forces in such a mixed system, and are subject to considerable change when some ions or groups in the lattice get reoriented (for example, in TGS the glycine-I ion reorients). As a result, one mechanism,

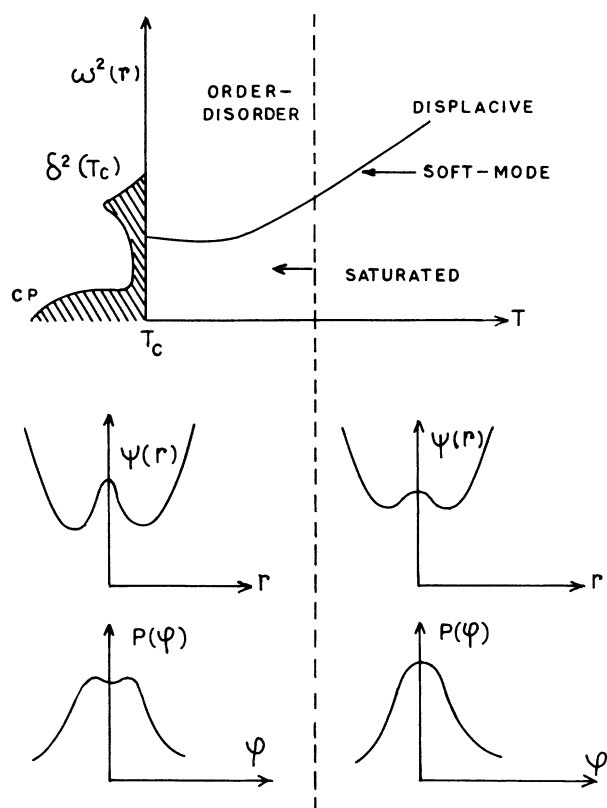


FIG. 7. (a) Schematic "crossover" (displacive to order-disorder) (Ref. 89) behavior observable in a structural phase transition. (b) Average local potential $\psi(r)$ associated with the pseudospin variable. (c) Single-peak and double-peaked order parameter (ϕ) distribution $P(\phi)$.

order-disorder or displacive, wins over the other, and the crystal under consideration behave accordingly.

Not only crossover phenomenon in perovskite but also some other interesting change in the physical property might be expected with the addition of foreign ions. For instance, addition of Nb in SrTiO₃ gives rise to a superconducting transition.⁹¹ Here also both the π_{pp} and π_{sp} part of the self-energy are involved.⁹² This part π_{sp} would also effect the superconducting energy gap in the case of superconducting transition.⁹² The π_{sp} part of the self-energy associated with the local ordering motion is actually involved in all kinds of transition mechanism and should be properly taken care of.

It should be noted that approaching towards T_c , short-range order might also exist due to correlated order-parameter fluctuations giving rise to a saturated soft mode (Fig. 7). This is an intrinsic characteristic property of the central peak phenomenon about which we shall deal with in paper II. Upon cooling towards T_c , the short-range order implies a displacive to order-disorder crossover.

We also believe that the origin of the "double peaks" as observed in the relaxation rate versus temperature curve of the H-bonded TGS crystal,⁹ is due to the appearance of two separate anomalies related to the two different contributions from the damping constants Γ_{sp} and Γ_{pp} and hence to the two relaxation times which might also have different frequency responses (for details see Paper II).

V. SUMMARY AND CONCLUSION

In this paper we have first developed the PLCM model appropriate for describing the transition mechanism in TGS and its family (deuterated and undeuterated). Our calculations with statistical Green's function technique and with RPA-type decoupling procedure indicate that the PLCM model is sufficient to explain the various salient features of the structural phase transitions in TGS and similar other crystals in a unified way. A single set of the model parameters (Blinç-de Gennes) have also been obtained from fitting simultaneously the experimental values of T_c , C , ϵ' , and P_s .

We believe, as also observed from our calculations (see also paper II), that the exciting nonlinear behavior (appearance of the central peak, central dip, etc.) and the deviation from the Landau theory observed from some of the physical properties of TGS are due to the importance of the second part π_{sp} of the phonon self-energy. This part arises due to the importance of the pseudospin-phonon interaction and higher-order phonon anharmonic interaction. The large values of the anharmonicity parameter as shown by TGS (Table I) and also by other crystals (Refs. 34-36) give rise to a small anomaly in the thermal variation of specific heat.^{23,28} This is also true for the case of Rochelle salt.⁹³⁻⁹⁵ A comparatively small anomaly in the specific heat curve of the TGS (Refs. 23 and 28) also indicates the importance of the anharmonic phonon-phonon interaction in this crystal. The small values of the transition entropy $\Delta S = R \ln 2$ observed in Rochelle salt,⁹⁴ squaric acid,⁹⁰ PbHPO₄,³⁵ and also in

TGS,²³ support the important role of the higher-order anharmonic interaction terms in these crystals. For all the above-mentioned crystals, the properly generalized PLCM model might be the unique model to elucidate the mechanism of phase transitions in them.

Our calculations also indicate that the pseudospin phonon coupled system behave like two subsystems (the local pseudospin subsystem and the usual phonon subsystem) and they are active to trigger the transition in TGS or in other H-bonded crystals. The first one described by the pseudospin variables, tries to stimulate the order-disorder behavior while the second one (described by the phonons) tries to give rise to the displacive character of the transition. As a consequence, a competition starts. At which temperature, field or frequency this competition will terminate or one mechanism will predominate, is decided by the coupling strengths as well as by the sign and magnitudes of the higher-order phonon-phonon and the pseudospin-phonon interaction terms. The transition is characterized by which mechanism predominates. In this way one might get order-disorder and the displacive mechanism when the π_{sp} and π_{pp} parts of the self-energy become important.

It should be noted here and also pointed out in Refs. 34-36, that the above-mentioned competition between the order-disorder and the displacive mechanisms (or between π_{pp} and π_{sp}) might even be responsible for the appearance of the incommensurate phase in many H-bonded systems like SC(NH₂)₂,⁹⁶ (NH₄)₂BF₄,⁹⁷ ammonium Rochelle salt,⁹⁸ etc. One might also expect this competition to exist even in non-hydrogen-bonded crystals like K₂SeO₄, BaTiO₃ doped with other ions, Nb, Sn, etc., where the pseudospin concept^{11,91,92} appears in a broadened sense and it is associated with the rotations and/or displacements of some ions or groups in the crystal lattice.

Again, it might also be concluded that if at low temperature the contribution from the phonon-phonon interaction (vis. Γ_{pp}) becomes very weak, the "frozen-in" disorder of the local modes (associated with the pseudospin variables and hence with Γ_{sp}) would be responsible for the glasslike behavior observed in some single crystals like SnCl₂(H₂O)₂,⁶ ferroelectric alums⁵⁵ (hydrogen-bonded crystals) and K₂SeO₄,⁹⁹ Sr_{1-x}Ba_xNb₂O₃ (non-hydrogen-bonded crystals),¹⁰⁰ etc. In support of this assumption we might mention that the transverse Ising model which is actually the pure pseudospin model [Eq. (2)] has already been found theoretically to show the glassy behavior.¹⁰¹

The π_{sp} part of the self-energy also appears to be responsible for the observed maximum in the \bar{C}^2/T versus T curve,^{99,100} a characteristic feature of glassy samples (\bar{C} being the specific heat). Calculation of the specific heat with the PLCM model following the procedure of our earlier work³⁴⁻³⁶ and finding out of the specific heat contributed by the pseudospin-phonon part, will give important clues to this glassy behavior in crystals.

It is interesting to note that this glassy behavior has so far been observed only in the ferroelectric type single crystals, where the contributions of both the phonons and pseudospins (hence π_{sp} and π_{pp}) are found to be impor-

tant. That is, the transition mechanism should be characterized by the mixed mechanism. This is probably because of the fact that the π_{pp} and also the π_{sp} parts of the self-energy are not equally important in the magnetic systems where the mechanism of real spin ordering is quite different.

We have discussed earlier³⁵ that depending on the strength of the anharmonicity parameters, the H-bonded crystals, in which we are interested in this paper, might also be classified into four groups: group I having very small or zero values of A'_0 shows large isotope effects on both T_c and C (i.e.; PbHPO_4 , RbHSO_4 , squaric acid, etc.); group II having A'_0 very small but not zero shows large isotope effects on T_c but relatively small (compared to group III cited below) isotope dependence on C (i.e.; $\text{LiH}_3(\text{SeO}_3)_2$, Rochelle salt, TGS, etc.); group III having comparatively large values of A'_0 shows very large isotope effects on T_c but small isotope effects on C (i.e.; all KDP family), and the crystals belonging to group IV have large values of A'_0 and are non-hydrogen-bonded (i.e.; BaTiO_3 , K_2SeO_4 , etc.). Here large or small values of A'_0 correspond to the relative values in comparison to that of the KDP crystal. Comparing the values of A'_0

(from Table I) with those of other H-bonded crystals (Refs. 34–36) we find that the TGS family belongs to group II.

Finally, we would like to point out that the calculations made in this paper may also be extended to the cases of other H-bonded or non-H-bonded crystals with suitable generalization of the model. The spin-phonon, or magnon-phonon coupled system could also be well treated following the procedure of this paper.

In paper II we will try to show, using the calculations made in this paper, the origin of the central peak, central dip; etc. which, we believe, are also associated with the pseudospin-phonon part of the derived self-energy. All of these will ultimately support the unified character of the PLCM model.

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