PHYSICAL REVIEW B VOLUME 25, NUMBER 3 1 FEBRUARY 1982

Phenomenological theory of the isostructural phase transition in H-bonded $SnCl_2\cdot(H_2O)_2$ and $SnCl_2\cdot(H_2O)_x(D_2O)_{2-x}$ with a pseudospin model

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(Received 11 June 1981)

With the use of a statistical Green's-function technique and at the suggestion of Ishibashi [J. Phys. Soc. Jpn. 49, 613 (1980)] the two-sublattice pseudospin-phonon-coupled-mode (PLCM) model has been extended, for the first time, to explain the isostructural phase transitions in $SnCl_2\cdot 2H_2O$ and its partially deuterated forms. The expressions for the transition temperature (T_C), Curie-Weiss constant (C), dielectric constant (ϵ), and renormalized phonon spectrum have been derived and fitted with the available experimental data, and a single set of model parameters has been obtained. The experimental values of ϵ (for the pure salt) and the isotope dependences of T_C have been found to agree well with our calculated values. Using Ishibashi's formula and the calculated parameters of our model a symmetrical thermal behavior (around T_C) of heat capacity has also been predicted. Our present model can explain simultaneously the thermal behavior of both dielectric constant and heat capacity which is, however, not possible with the well-known dimer model. The exponents of the "staggered polarization" obtained from our calculations are found to be 0.41 for $T < T_0$ and 0.40 for $T > T_0$. These values agree well with those obtained from recent neutron-diffraction results by Youngblood and Kjems [Phys. Rev. B 20, 3792 (1979)]. The two-sublattice pseudospin model may, therefore, be considered as a unified model applicable for Rochelle salt, KH_2PO_4, $SnCl_2\cdot 2H_2O$, and similar other H-bonded salts with suitable modifications. This also suggests the unified character of the PLCM model.

I. INTRODUCTION

Stannous chloride dihydrate (or $SnCl_2\cdot 2H_2O$ hereafter abbreviated as SCD) undergoes a peculiar isostructural and order-disorder type of phase transition[1] at about −57 °C (from space group $P2_{1/c}$ to $P2_{1/c}$). This uncommon behavior has drawn particular attention for the study of static and dynamic properties of the phase transition in this crystal. The complete crystal structure of this salt was first determined by Kiriyama *et al.*[2] by x-ray structural analysis. Recently neutron-diffraction studies[3,4] have also been made and the existence of identical space group in both the phases has been confirmed. The cell parameters at room temperature are $a = 9.313$, $b = 7.250$, $c = 8.970$ Å, and $\beta = 114.91°$ with four formula units contained in the unit cell ($z = 4$) which does not change after transition.[2]

The anomalous heat capacity of this salt increases[5,6] symmetrically from both sides of the transition point indicating a two-dimensional (2D) character of the transition. The first-order and order-disorder nature of phase transition in this hydrogen-bonded crystal having alternating layers of $SnCl_2$ and H_2O molecules have also been pointed out from other experimental results like dielectric,[1,7] NMR,[1,7] neutron diffraction,[3,4] and Raman and Brillouin scattering measurements.[8,9] This order-disorder transition in SCD is associated with the ordering of the protonic positions in 2D layers of water molecules[1,2] (Fig. 1). The hydrogen atoms are disordered over nonequivalent sites (Fig. 1) as in the case[10] of

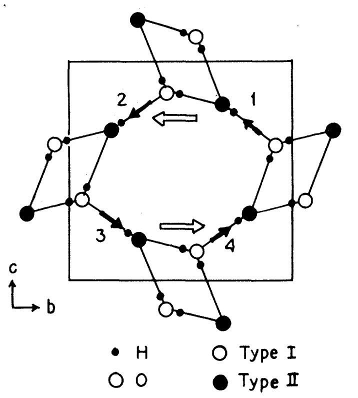

FIG. 1. The hydrogen-bond network (Refs. 1 and 2) in $SnCl_2\cdot 2H_2O$.

$(NH_4)_2CuCl_4 \cdot 2H_2O$. There are two types of water molecules in the layers. One of them is connected with Sn(II) ion and the other is a water of crystallization. Each of the water molecules is hydrogen bonded to three others of a different type in the same layer parallel to the (100) plane.[1,2] The isotope shift of T_C is, however, small in SCD compared to other H-bonded ferroelectrics and antiferroelectrics like KH_2PO_4, $NH_4H_2PO_4$, etc. But the ratio $T_C^D/T_C^H \simeq 1.076$ is of the same order of magnitude[11] as those of a group of H-bonded ferro- and antiferroelectrics such as $Cu(HCOO)_2 \cdot 4H_2O$, $K_4Fe(CN)_6 \cdot 3H_2O$, triglycinesulfate (TGS), triglycine selenate (TGSe), and Rochelle salt. It is interesting to note here that unlike KH_2PO_4 and many other similar crystals mentioned above, the transition is no longer first order in fully deuterated SCD (denoted hereafter by DSCD). This is another remarkable feature of the phase transition in SCD. However, the isotope shift of T_C (from −57 to −39 °C)[1,11] as well as the change of the behavior of phase transition on deuteration are definitely an indication of the importance of H bond in the transition mechanism.[12]

The dimer model which has been proposed so far[13,14] explains the symmetrical increase of specific heat above and below the transition point, and the temperature dependence of proton site occupancy may not be perfect as also pointed out by Ishibashi,[15] Youngblood, and Kjems.[4] It is difficult with this model to explain the disappearance of the transition at a finite temperature and at a finite pressure as well as the existence of a gas-liquid-type critical point which has been suggested by Gesi and Ozawa.[16] Furthermore, the layered Ising model of Salinas and Nagle[14] is essentially a model for showing antiferroelectric transition accompanied by a change of symmetry which is in contrast of the case of SCD. The large protonic conductivity in the low-temperature phase of SCD is probably incompatible with ferro- or antiferroelectricity.[7] No theory has ever been developed to explain the thermal behavior of dielectric constants.[4] The isotope dependence of transition temperature has also not been predicted from any of the theoretical models considered so far.[13,14]

In the present paper, following Ishibashi[15] the lattice of the SCD crystal has been divided into two sublattices with polarizations carried by two sublattices as p_1 and p_2. Since in a unit cell belonging to the space group $P2_{1/c}$ the four molecules contained are arranged in such a way (Fig. 1) that the total dipole moment is zero in any direction, the polarizations p_1 and p_2 are considered to cancel out each other at all temperatures. This behavior is similar to that of Rochelle salt (RS)[17,18] where two paraelectric phases are separated by a ferroelectric phase. It has also been observed that under some special circumstances[19] (in presence of K, NH_4, etc., as impurities) the ferroelectric region disappears and RS shows only one transition. Therefore, in this case the situation becomes equivalent to that of SCD crystal. Thus the behavior of RS and SCD might have some common characteristics which was also pointed out by Ishibashi.[15] No evidence of antiferroelectricity in the low-temperature phase has been detected[20] in SCD.

The sublattice polarizations are, however, considered to have a nonzero value even in the high-temperature phase and to jump to another nonzero value at the transition point as in the case of RS. Therefore, it might be profitable to search for a unified model for studying phase transtions in both RS and SCD crystals. Using a two sublattice pseudospin Hamiltonian similar to that used in case of RS, the expressions for transition temperature T_C, Curie constant C, and dielectric constant ϵ have been derived and fitted with the respective experimental results of SCD. Since the lattice contribution to the heat capacity seems to be important[21] for SCD showing a Debye-type relaxation mode, we also consider the pseudospin-phonon interaction term along with the Hamiltonian. The above Hamiltonian has also been used for the mixed crystals, viz., $SnCl_2 \cdot (H_2O)_x(D_2O)_{2-x}$ and the numerical values of T_C, and C have been calculated for different values of deuteration concentration x which have finally been compared with the experimental data of T_C. The experimental values of C are not available for the deuterated system. Following the results of Ishibashi,[15] the symmetrical behavior of the heat-capacity curve around the transition point has also been indicated from our calculations.

The organization of the present paper is as follows: In Sec. II the two-sublattice pseudospin lattice coupled Hamiltonian suitable for the present system has been written. Expressions for the transition temperature, "staggered polarization" and the dielectric constant have been derived in Sec. III. Section IV deals with the results of our calculations and discussion wherein it has been shown that the two sublattice model suggested by Ishibashi[15] might be applicable for explaining the isostructural transition in SCD. Finally, the paper ends with a conclusion (Sec. V) showing a unified behavior of Rochelle salt and stannous chloride.

It should be pointed out here that the detailed method of our calculations with statistical Green's function theory has already been discussed in our earlier paper[18,22–24] (hereafter referred to as I).

II. MODEL HAMILTONIAN

For our analysis we shall first consider the Hamiltonian for the coupled proton-deuteron-lattice system which is written in the usual pseudospin formalism[25] as

$$H = H_s + H_{sp} \ , \tag{1}$$

where

$$\begin{aligned} H_s = & -\sum_{i,\alpha=1,2} 2\Omega S^x_{i\alpha} - 2\mu E \sum_{i,\alpha=1,2} (S^z_{i\alpha}) \\ & - \left(\sum_{\substack{ij \\ \alpha=1,2}} J_{ij} S^z_{i\alpha} S^z_{j\alpha} + K_{ij} S^z_{i1} S^z_{j2} \right) \ , \end{aligned} \tag{1a}$$

$$\begin{aligned} H_{sp} = & -\sum_{\substack{i\vec{q} \\ \alpha=1,2}} V_{i\vec{q}} S^z_{i\alpha} Q_{\vec{q}} + \frac{1}{2} \sum_{\vec{q}} (P_{\vec{q}} P_{-\vec{q}} + \omega^2_{\vec{q}} Q_{\vec{q}} Q_{-\vec{q}}) \\ & + \sum_{\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4} A(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) Q_{\vec{q}_1} Q_{\vec{q}_2} Q_{\vec{q}_3} Q_{\vec{q}_4} \ . \end{aligned} \tag{1b}$$

Equation (1) represents the explicit form of the two-sublattice pseudospin lattice coupled Hamiltonian. The first term in (1a) describes the tunneling of protons and Ω is the tunneling frequency. The second term describes the interaction of the dipoles with the external electric field and μ is the magnitude of the dipole moment. The last term of (1a) describes the interaction between the dipoles belonging to the same ($\sim J_{ij}$) and to the different sublattices ($\sim K_{ij}$). The indices $\alpha(=1$ and $2)$ denote the two sublattices and the summation over i and j runs from 1 to $N/2$ (where N is the number of dipoles per unit volume of the crystal). It is assumed that $J_{ii} = 0$, $J_{ij} = J_{ji}$ and $K_{ii} = 0$, $K_{ij} = K_{ji}$. $V_{i\vec{q}}$ represents the spin-lattice interaction. Q_q and P_q are, respectively, the normal coordinates and conjugate momenta. $A(\vec{q})$ defines the fourth-order anharmonicity constant as defined earlier.[22] The third-order anharmonicity is considered by the renormalization[26] of $A(\vec{q})$ in the usual way (Ref. 1). Since a Debye-type relaxation[8] mode seems to be associated with H_2O molecule reorientation in SCD, the anharmonic effect should be important. Furthermore, it is also pointed out from Raman studies[8,9] that the anharmonic effect in SCD is likely to result in multipotential minima with different heights (similar to the case of Rochelle salt[17,18]). The small tunneling motion among these potential minima is assumed to give rise to a unique soft mode of a resonance type though the proton tunneling causes the lattice modes to be strongly damped. In such crystals, it is found to be a general behavior that the tunneling frequency, though not zero, is negligibly small which will be shown from our calculations (Sec. IV). For the mixed SCD-DSCD system we simply assume (as in the case of mixed[27] KDP-DKDP system) J_{ij}, K_{ij}, and $V_{i\vec{q}}$ to be proportional to the effective dipole moment (i.e., $\hat{J}_{ij} = \mu J_{ij}$, $\hat{K}_{ij} = \mu K_{ij}$, $\hat{V}_{i\vec{q}} = \mu V_{i\vec{q}}$; $\hat{J}_{ij}$, $\hat{K}_{ij}$, and $\hat{V}_{i\vec{q}}$ are the respective effective values). $\overline{\Omega}_i = n_i \Omega_i$ (n_i is the concentration of a particular type of ion H or D in the lattice).

III. CALCULATION OF TRANSITION TEMPERATURE AND DIELECTRIC CONSTANTS

We shall first consider the case of mixed SCD-DSCD system. Performing the thermodynamic average of the local field and also averaging over the chemical configurations of the crystal, H_s can be expressed for A-type particles[27] ($A =$ H or D) as

$$H_s = -2(S^z_{A\alpha} \overline{\Omega}_A) + S^z_{A\alpha} \hat{J}_A P_{A\alpha} + S^z_{A1} \hat{K}_A P_{B2} \ , \tag{2}$$

where

$$\begin{aligned} & \sum_{i\in A} J_{ij} = n_A \hat{J}_A = \overline{J}_A \ , \\ & \sum_{i\in A} K_{ij} = n_A \hat{K}_A = \overline{K}_A \ , \\ & P_{A\alpha} = 2 \sum_{\alpha} n_A \mu_A \langle S^z_{A\alpha} \rangle \ , \\ & P_{B2} = 2 n_A \mu_A \langle S^z_{A2} \rangle \ , \end{aligned} \tag{2a}$$

$\overline{\Omega}_A = n_H \Omega_H + n_D \Omega_D$ [Ω_H, Ω_D are the tunneling frequency of SCD and DSCD, respectively, and n_H and $n_D = (1 - n_H)$ denotes, respectively, the concentration of H and D ions], $\langle S^z_{A\alpha} \rangle$ is the statistical average of the enclosed operator. To calculate the averages $\langle S^x_{A\alpha} \rangle$, $\langle S^y_{A\alpha} \rangle$, and $\langle S^z_{A\alpha} \rangle$ for the pure tunneling Hamiltonian (2) we start with the double-time temperature dependent Green's-function (GF) technique of Zubarev.[28] For two operators S^m_i and S^n_j the GF can be written as (for details see I)

$$\begin{aligned} G^{mn}_{ij}(t - t') & \equiv \langle\langle S^m_i(t) | S^n_j(t') \rangle\rangle \\ & = -i\Theta(t - t') \langle [S^m_i(t), S^n_j(t')] \rangle \ , \end{aligned} \tag{3}$$

where m, $n = x$, y, and z. $\Theta(x)$ is the usual step function. The Fourier transform[28] of (3) has the form

$$2\pi\epsilon \langle\langle S^m_i | S^n_j \rangle\rangle = \langle [S^m_i, S^n_j] \rangle + 2\pi \langle\langle [S^m_i, H_s] | S^n_j \rangle\rangle_\epsilon \ . \tag{4}$$

Solving Eq. (4) for various Green's functions and using the spectral theorem[28] we obtain (for details see I)

$$\sigma^x_{A\alpha} = \langle S^x_{A\alpha} \rangle = \frac{\Phi_{A\alpha}}{F_{A\alpha}} \tanh \frac{\beta F_{A\alpha}}{2} \ , \tag{5}$$

$$\sigma^z_{A\alpha} = \langle S^z_{A\alpha} \rangle = \frac{\Theta_{A\alpha}}{F_{A\alpha}} \tanh \frac{\beta F_{A\alpha}}{2} \ , \tag{6}$$

where

$$\begin{aligned} & \Phi_{A\alpha} = \Phi_A = 2\overline{\Omega}_A \ , \\ & \Theta_{A1} = 2J_A \langle S^z_{A1} \rangle + K_A \langle S^z_{A2} \rangle \ , \\ & \Theta_{A2} = 2J_A \langle S^z_{A2} \rangle + K_A \langle S^z_{A1} \rangle \ , \\ & F^2_{A\alpha} = \Theta^2_{A\alpha} + \Phi^2_{A\alpha} \ , \end{aligned} \tag{6a}$$

$\beta = 1/k_B T$ (T is the absolute temperature and k_B is

Boltzmann's constant). To linearize the coupled Green's function, the simple RPA-like decoupling procedure of Tyablikov[29] was used (I).

Defining the total polarization P_A for the pure system as

$$P_A = N\mu_A(\sigma_{A1}^z + \sigma_{A2}^z) \tag{7}$$

we have the expression for the dielectric constant ϵ_A as

$$\begin{aligned}\epsilon_A &= \left(\frac{\partial P_A}{\partial E}\right)_{E=0} \\ &= 2N\mu_H^2\left(\frac{C_{A1}\tau_{A2} + C_{A2}\tau_{A1}}{(2\bar{J}_A C_{A1} - 1)(2\bar{J}_A C_{A2} - 1) - \bar{K}_A^2 C_{A1} C_{A2}}\right) ,\end{aligned} \tag{8}$$

where

$$\begin{aligned}\tau_{A1} &= \bar{K}_A C_{A1} - (2\bar{J}_A C_{A1} - 1) , \\ \tau_{A2} &= \bar{K}_A C_{A2} - (2\bar{J}_A C_{A2} - 1) , \\ C_{A\alpha} &= \frac{\beta}{4}\frac{\theta_\alpha^2}{\theta_\alpha^2 + 4\Omega_A^2)}\operatorname{sech}^2\frac{\beta}{2}(\theta_\alpha^2 + 4\Omega_A^2) \\ &\quad + \frac{2\Omega_A^2}{(\theta_\alpha^2 + 4\Omega_A^2)}\tanh\frac{\beta}{2}(\theta_\alpha^2 + 4\Omega_A^2) .\end{aligned} \tag{9}$$

The system of Eqs. (5) and (6) might have various solutions.[18,23] But for the present SCD crystal, the system of Eqs. (5) and (6) must have solution $\sigma_{A1}^z = -\sigma_{A2}^z = \sigma_A$ (say) for all temperatures. Following the work of Youngblood and Kjems[4] we may consider σ_s as a "staggered polarization" the thermal variation of which is shown in Fig. 3. We shall compare this result with the neutron-diffraction results[4] in Sec. IV. Thus we have from (8)

$$\epsilon_A = \frac{4N\mu_A^2 C_A}{1 - (2\bar{J}_A + \bar{K}_A)C_A} , \tag{10}$$

where $C_{A1} = C_{A2} = C_A$ (where $\sigma_1^z = -\sigma_2^z = \sigma$). As in the case of Rochelle salt[18] the Curie temperature T_C is obtainable from the condition $\epsilon^{-1} = 0$, which gives [from (10)]

$$(2\bar{J}_A + \bar{K}_A)C_A = 1 . \tag{11}$$

It should be mentioned here that for the undeuterated and deuterated systems we replace $\bar{J}_A$ by $\bar{J}_{\mathrm{H}}$ and $\bar{J}_{\mathrm{D}}$, respectively. Again for the partially deuterated system we use simple linear variation[27] of the form

$$\bar{J}_A = n_{\mathrm{H}}\bar{J}_{\mathrm{H}} + (1 - n_{\mathrm{H}})\bar{J}_{\mathrm{D}} = n_{\mathrm{H}}\bar{J}_{\mathrm{H}} + n_{\mathrm{D}}\bar{J}_{\mathrm{D}}$$

and

$$\bar{K}_A = n_{\mathrm{H}}\bar{K}_{\mathrm{H}} + (1 - n_{\mathrm{H}})\bar{K}_{\mathrm{D}} = n_{\mathrm{H}}\bar{K}_{\mathrm{H}} + n_{\mathrm{D}}\bar{K}_{\mathrm{D}} . \tag{12}$$

To study the dynamic behavior, we calculate the Green's functions like $\langle\langle Q_{\vec{q}}(t) | Q_{-\vec{q}}(t')\rangle\rangle = G^{QQ}_{\vec{q},-\vec{q}}(t - t')$. The Fourier transform of this Green's function (in units of $\hbar = 1$) has the general form

$$\begin{aligned}2\pi\langle\langle Q_{\vec{q}} | Q_{-\vec{q}}\rangle\rangle_\omega &= \langle [Q_{\vec{q}}, Q_{-\vec{q}}]\rangle \\ &\quad + 2\pi\langle\langle [Q_{\vec{q}}, H] | Q_{-\vec{q}}\rangle\rangle_\omega .\end{aligned} \tag{13}$$

Fluctuation of the pseudospin operator around RPA is considered by making use of the following transformation:

$$S^m_{\vec{q}} = \sum_{\vec{l}} S^m_{\vec{l}} \exp i(\vec{q} \cdot \vec{R}_l) , \tag{14}$$

where $\vec{R}_l$ denotes the Bravais lattice site of the lth bond. The equations of motion connecting the required Green's function may be written as (see I for details)

$$\begin{bmatrix} \omega & -i\theta'_{A\alpha} & 0 & -i\bar{V}_{\vec{q}A}\langle S^y_{A\alpha}\rangle & 0 \\ i\theta'_{A\alpha} & \omega & -2i\Omega'_A & i\bar{V}_{\vec{q}A}\langle S^x_{A\alpha}\rangle & 0 \\ 0 & 2i\bar{\Omega}_A & \omega & 0 & 0 \\ 0 & 0 & 0 & \omega & -i \\ 0 & 0 & -2i\bar{V}_{\vec{q}A} & i\bar{\omega}^2_{\vec{q}} & \omega \end{bmatrix} \begin{bmatrix} \langle\langle S^x_{\alpha,\vec{q}} | Q_{-\vec{q}}\rangle\rangle \\ \langle\langle S^y_{\alpha,\vec{q}} | Q_{-\vec{q}}\rangle\rangle \\ \langle\langle S^z_{\alpha,\vec{q}} | Q_{-\vec{q}}\rangle\rangle \\ \langle\langle Q_{\vec{q}} | Q_{-\vec{q}}\rangle\rangle \\ \langle\langle P_{\vec{q}} | Q_{-\vec{q}}\rangle\rangle \end{bmatrix} - \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -i/2\pi \end{bmatrix} = 0 , \tag{15}$$

where

$$\begin{aligned}\theta'_{A\alpha} &= 2\hat{\bar{J}}_A\langle S^z_{A1}\rangle + \hat{\bar{K}}_A\langle S^z_{A2}\rangle , \\ 2\Omega'_A &= 2\bar{\Omega}_A - 2\bar{J}_{\vec{q}A}\langle S^x_{A1}\rangle - \bar{K}_{\vec{q}A}\langle S^x_{A2}\rangle , \\ \bar{\omega}^2_{\vec{q}A} &= \omega^2_{\vec{q}A} + \bar{A}'(\vec{q}, T) , \\ \bar{V}_{\vec{q},A} &= \sum \bar{V}_{\vec{q}A} = \hat{\bar{V}}_A , \\ \bar{A}'(\vec{q}, T) &= A(-\vec{q}, \vec{q}, -\vec{q}', \vec{q}')[n_{\vec{q}}(T) + \tfrac{1}{2})] , \\ J_{\vec{q}A} &= \sum J_{lk} \exp i[\vec{q} \cdot (\vec{R}_l - \vec{R}_k)] .\end{aligned} \tag{16}$$

$n_q(T)$ is the phonon number operator and $A'(\vec{q}, T)$ is the contribution from the anharmonic terms modifying the phonon frequency from $\omega_{\vec{q}}$ to $\bar{\omega}_{\vec{q}}$. The coupled proton-lattice spectrum obtained from the secular determinant [from (15)] has the form

$$\begin{aligned}2\omega^2_{1,2} &= (\omega^2_{\vec{q}A} + L^2_{\vec{q}A}) \mp [(\omega^2_{\vec{q}A} - L^2_{\vec{q}A})^2 \\ &\quad - 16\bar{\Omega}_A\bar{V}^2_{\vec{q}A}\langle S^x_{A\alpha}\rangle]^{1/2} ,\end{aligned} \tag{17}$$

where

$$L^2_{\vec{q}A} = 4\bar{\Omega}_A \Omega'_A + \theta'^2_{A\alpha} \ . \tag{18}$$

A pseudospin soft-mode theory for SCD has been proposed by Gordon.[30] Therefore the instability condition [viz., $\omega_1(\vec{q}=0, T=T_C)=0$] is assumed to be valid[31–34] for the H-bonded SCD crystal. Here the instability is associated with the orientations of H bonds. Thus from Eqs. (5) and (17) we have the critical temperature analogous to the Curie temperature

$$k_B T_C = \frac{\bar{\eta}_A}{2}\left(\tanh^{-1}\frac{\bar{\eta}_A^3}{4\bar{\Omega}_A^2 \bar{J}^*_{0A}}\right)^{-1} , \tag{19}$$

where we have used

$$\begin{aligned}
&\bar{\eta}_A^2 = (2\bar{J}_A - \bar{K}_A)^2\sigma^2 + 4\bar{\Omega}_A^2 \ ,\\
&\bar{J}^*_{0A} = (2\bar{J}_{0A} + \bar{K}_{0A}) + \frac{2\bar{V}_{0A}^2}{\bar{\omega}_{0A}^2} \ ,\\
&\bar{\omega}_{0A}^2 = \omega_{0A}^2 + \bar{A}'(\vec{q}=0, T=T_C) \ ,\\
&\bar{V}_{0A} = \bar{V}_{\vec{q}A}|_{\vec{q}=0} \ ,\\
&J^*_{0A} = J^*_{0H} n_H + J^*_{0D} n_D \ ,
\end{aligned} \tag{19a}$$

and

$$J^*_{0H} = (2\bar{J}_{0H} + \bar{K}_{0H}) + \frac{2\bar{V}_{0H}^2}{\bar{\omega}_{0H}^2} \ .$$

A similar expression holds for J^*_{0D}. $\bar{J}^*_{0A}$ and $\bar{\Omega}_A$ are, respectively, the effective interaction constant and effective tunneling frequency of the mixed system both depending on the hydrogen (n_H) and deuteration ($n_D = 1 - n_H$) concentrations in the lattice. It is to be noted here that the model parameters required to fit the experimental data should be such that the condition (11) and the Eq. (19) are simultaneously satisfied which has been discussed in Sec. IV.

In what follows we shall calculate the Curie constant C for the partially deuterated crystals. The electrical susceptibility $\bar{\chi}_A$ (and hence the dielectric constant) is calculated from the Green's function (see I) $G^{QQ}_{\vec{q},-\vec{q}}(\omega)$

$$G^{QQ}_{\vec{q},-\vec{q}}(\omega) = \frac{1}{2\omega}\left[(\omega^2 - \bar{\omega}^2_{\vec{q}A}) - \frac{4\bar{\Omega}_A \bar{V}^2_{\vec{q}A}\langle S^x_{A\alpha}\rangle}{(\omega^2 - L^2_{\vec{q}A})}\right]^{-1} , \tag{20}$$

which is derived from (15). If v_0 is the volume of the unit cell and n is the number of pseudospins in the unit cell, the expression for $\bar{\chi}_A(\omega, \vec{q}) = -(n\bar{\mu}_A^2/v_0)G^{QQ}_{\vec{q},-\vec{q}}(\omega)$, which gives

$$\bar{\chi}_A(0) = \frac{n\bar{\mu}_A^2}{v_0}\left(\omega^2_{\vec{q}A} + \bar{A}'(0,T) - \frac{8\bar{\Omega}_A^2 \bar{V}_{0A}^2 \tanh(\bar{\eta}_A/2k_B T)}{\bar{\eta}_A^3 - 4\bar{\Omega}_A^2(2\bar{J}_{0A} + \bar{K}_{0A})\tanh(\bar{\eta}_A/2k_B T)}\right)^{-1} . \tag{21}$$

Expanding (21) around T_C we have the Curie constant

$$\bar{C}_A = \frac{n\bar{\mu}_A^2}{v_0}\left[\left(\frac{\partial \bar{A}'}{\partial T}\right)_{T=T_C} + B\right]^{-1} , \tag{22}$$

where

$$B = \frac{4\bar{\Omega}_A^2 \bar{V}_{0A}^2 \bar{\eta}_A^4 (1 - \tanh^2\bar{\eta}_A/2k_B T_C)}{k_B T_C^2[\eta_A^3 - 4\bar{\Omega}_A^2(2\bar{J}_{0A} + \bar{K}_{0A})\tanh(\bar{\eta}_A/2k_B T_C]^2} \ . \tag{23}$$

To calculate $\partial\bar{A}'/\partial T$ we approximately write $\bar{A}' = \bar{A}_0 k_B T$ as in the case of KH_2PO_4-type H-bonded ferroelectrics.[27] The above expressions for T_C, $\chi(0,0)$ and C are then fitted with the experimental results for finding the model parameters shown in Sec. IV.

IV. RESULTS AND DISCUSSION

Recent experimental data of Curie temperatures[11] and dielectric constants[7] for the mixed $SnCl_2\cdot(H_2O)_x(D_2O)_{2-x}$ crystals were fitted with (11), (19), and (21) by varying the parameters $\bar{J}^*_{0H}/\bar{J}^*_{0D}$ and Ω_H/Ω_D. The values of the parameters obtained for the best fit are shown in Table I. For determining the anharmonic contribution which is highly temperature dependent for the present salt, we have made the following assumption. Since the second part of (22) is very small for DSCD, the contribution from the first part, i.e., the anharmonic contribution is found from (22) by equating it to the value of Curie constant[35] $C_D = 1800$ K for the fully deuterated system (DSCD). This gives $\bar{A}_0 k_B \simeq 3.60\times 10^{-18}$ erg/K. Assuming this value of $\bar{A}_0 k_B$ the concentration-dependent Curie constants are calculated as shown in Table I. However, the frequency $\bar{\omega}^2_{\vec{q}=0}[=\omega^2_{\vec{q}=0} + \bar{A}_0(0,T)]$ of the active branch, renormalized by the phonon-phonon interaction should be varied with temperature as shown in

TABLE I. Model parameters for undeuterated ($SnCl_2 \cdot 2H_2O$) and deuterated ($SnCl_2 \cdot 2D_2O$) salts.

$J_{0H}^* = 8369.40$ cm^{-1}
$\Omega_H = 5.00$ cm^{-1}
$\bar{V}_{0H} = 24.44$ cm^{-1}
$\eta_H = 11.00$ cm^{-1}
$\mu_H = 2.66 \times 10^{-18}$ esu cm
$v_0 = 549.28 \times 10^{-24}$ cm^3

$J_{0D}^* = 470.40$ cm^{-1}
$\Omega_D = 0.50$ cm^{-1}
$\bar{V}_{0D} = 2.19$ cm^{-1}
$\eta_D = 1.20$ cm^{-1}
$\bar{A}_0 k_B = 3.60 \times 10^{-18}$ erg/K

n_D	0	0.125	0.250	0.520	0.750	0.875	0.985	1.00
T_C (K) (theor)	219.53	219.94	221.88	225.92	229.14	230.86	234.59	235.00
(Expt.) (Ref. 11)	219.53	219.96	221.88	225.92	229.15	230.92	234.64	235.00
C (K) (theor)	126.77	130.32	133.57	138.90	141.69	142.58	143.07	143.24

Fig. 2 for exact fitting of the experimental values of ϵ as discussed below. The high-temperature dependence of $\bar{\omega}_0$ is also resembled from the thermal variation[8,9] of the peak frequency and spectral linewidth discussed in terms of anharmonicity in the hydrogen bond potential. The calculated and the experimentally[1,11] observed values of T_C [from (19)] for the mixed system are also shown in the same table. No experimental data for the Curie constant are available for the partially deuterated compounds. However, very good agreement between the calculated and the experimental values of T_C for different deuteration concentration are obtained as observed from Table I. Both T_C and C are also found to vary almost linearly with deuteration concentration similar to the case of mixed KDP-DKDP system.[27]

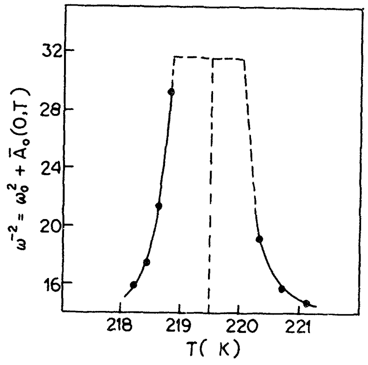

FIG. 2. Thermal variation of the renormalized phonon frequency of the "active" branch around the transition temperature. ●—calculated points only.

To fit the experimental dielectric constant $\epsilon_A (\simeq 1 + 4\pi \bar{\chi}_A)$ data we put $\langle \sigma_1^z \rangle = -\langle \sigma_2^z \rangle = \sigma = c\,\mathrm{sgn}(T - T_C) | (T - T_C)/T |^{\gamma}$ and γ was found to be 0.59 for both the phases (above and below T_C). We may define σ as a "pseudo-order parameter" which remains nonzero even above the transition temperature (Fig. 3). The values of the exponent γ required to fit the thermal variation of dielectric constant data agree very well with those obtained from neutron-diffraction data[4] to calculate the "staggered polarization." From neutron diffraction[4] $(1-\gamma)$ was found to be (0.41 ± 0.03) for $T < T_0$ and (0.41 ± 0.1) for $T > T_0$. The symmetric values of γ thus obtained definitely indicate the symmetric behavior of heat capacity.[10,11] Following the work of Youngblood and Kjems[4] we find that the significance of σ in our calculation is the same as that of "staggered polarization." They also showed that the Bragg reflection intensity depends in a very simple way on σ and hence σ is a very important parameter for SCD. The same set of parameters as shown in Table I (viz., J_{0H}^*, Ω_H, $\bar{V}_{0H}$, η_H, μ_H, and v_0) are used to fit the experimental (ϵ-T) curve of pure (undeuterated) SCD crystal. The very good agreement between the theoretical and experimental[7] dielectric constant versus temperature curve is shown in Fig. 4. This also points out the validity of the two sublattice picture proposed by Ishibashi[15] for the SCD crystal. The interlayer interactions ($\bar{K}_{0A}$) are found to be much weaker than the intralayer interaction ($\bar{J}_{0A}$)($\bar{K}_{0A} \simeq \frac{1}{3}\bar{J}_{0A}$) between the H bonds. As expected the value of $\bar{\Omega}_A$ is extremely small (Table I) both for the undeuterated (≈ 5 cm^{-1}) and deuterated (≈ 0.5 cm^{-1}) crystals compared to those of the KDP type crystals (for KDP $\Omega \approx 85$ cm^{-1}).[22] This means that the tunneling effect is negligibly small in the SCD crystal which was

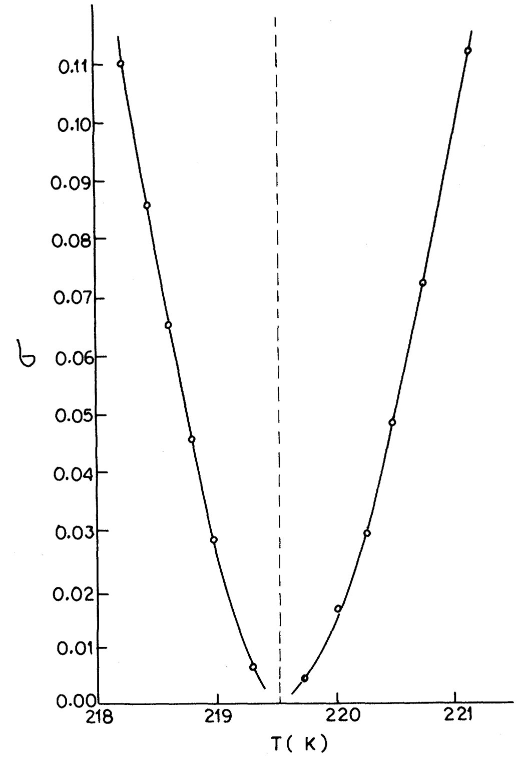

FIG. 3. Thermal variation of staggered polarization σ around the transition point calculated from our model.

also pointed out from heat-capacity measurement by Tatsumi *et al.*[11] However, the value of Ω for the SCD crystal is comparable with those of quasi-one-dimensional $PbHPO_4$ crystal where a similar type of the two-sublattice model may be used[23] and in both cases the interchain coupling is much weaker than the intrachain coupling. Squaric acid,[36,37] $(NH_4)_2CuCl_4 \cdot 2H_2O$,[10] $Cu(COOH)_2 \cdot 4H_2O$,[38] and other hydrogen-bonded-layer structural compounds, also seem to have very small Ω and a similar model might also be valid for this crystal with suitable modifications.

The parameters of Table I are then used to calculate the approximate thermal behavior of heat capacity in SCD crystal. It was shown by Ishibashi[15] that for the SCD crystal the approximately symmetrical nature of heat capacity C_v can be obtained from the relation

$$C_v - C_{v_0} = \frac{r^2 t}{(t-t_0)+3(r-1)^2-K'} , \tag{24}$$

where $r=\sigma/\sigma_0$ (σ_0 is the value of σ corresponding to the isomorphous transition at temperature T_0 $K'=\Delta/\sigma^2$, $t=t'+\alpha'/\gamma'\sigma_0$, and Δ, α', γ' are constants). Using the calculated values of σ as shown in Fig. 3, the values of $(C_v - C_{v_0})/t$ are calculated from (24) and plotted in Fig. 5 as a function of $(t-t_0)$ for $K'=0$. An interesting first-order symmetrical peak around T_C is observed (Fig. 5). This definitely shows the validity of our model along with that of Ishibashi[15] and hence the suitability of the calculated

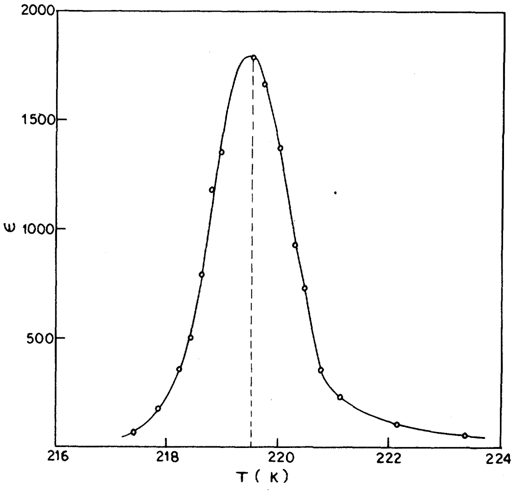

FIG. 4. Thermal variation of the dielectric constant of $SnCl_2 \cdot 2H_2O$. Circles denote experimental (Ref. 7) points; continuous line indicates present theoretical curve.

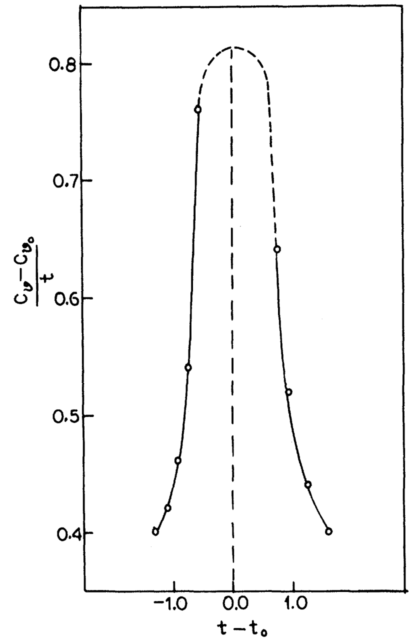

FIG. 5. Symmetrical thermal variation (qualitative) of heat capacity using Ishibashi's (Ref. 15) formula and putting the values of the model parameters of our calculations (Table I). ○—calculated points.

model parameters. Here we should mention that the thermal behavior of heat capacity is dependent on many of the adjustable parameters, viz., J, K, Ω, V, A, etc., and most of them are temperature and pressure dependent. Proper account of these variables (supported by the results of different experiments like low-frequency Raman and far infrared) might give the correct critical behavior of SCD. But the main interest as well as the success of our model is that it has been possible to get the correct thermal behavior of dielectric constant and heat capacity from the two sublattice pseudospin Hamiltonian formally suggested by Ishibashi.[15] But Ishibashi's Landau expansion of free energy may not be very persuasive for two reasons: (i) the two-dimensional system is difficult to describe by the molecular-field theory, and (ii) the Landau theory does not take into account the strong correlation in the H-bonded system that must obey the ice rule.

V. CONCLUSION

In the present paper we have successfully applied the two sublattice pseudospin model to explain the isomorphous phase transition in $SnCl_2 \cdot 2H_2O$ and $SnCl_2 \cdot (H_2O)_x(D_2O)_{2-x}$. This success also points out the unified character of the pseudospin model. We have found negligibly small values of the tunneling frequency Ω and the renormalized phonon frequency $\bar{\omega}_{0A}$ for this compound. Though we have considered tunneling, fitting of all the experimental data done in this paper could also be carried out without considering the tunneling term at all. However, to make our calculations more general and to draw the analogy between the behavior of SCD and Rochelle salt, both the tunneling and the proton-lattice interaction terms have been taken into account in our Hamiltonian. Furthermore, since the anharmonic term $\bar{A}_0'$ and the renormalized phonon frequency $\bar{\omega}_{0A}$ of the "active branch" are temperature dependent for the present crystal the behavior of the phase transition is also highly sensitive to these parameters. Very good agreement between the calculated and experimental values of T_C and ϵ definitely justify the validity of our phenomenological model and the values of the parameters obtained. The temperature dependence of each sublattice polarization σ_1 and σ_2 may give rise to discontinuous isomorphous transition for a particular choice of the model parameters. The change of first-order nature of the transition in the heavily deuterated crystals[11] might also be accounted for considering the fact that the model parameters are quite different in the deuterated system along with the renormalized phonon frequency. It is observed from our calculations that though there is small isotope shift in T_C for SCD, the tunneling frequency Ω and renormalized phonon frequency $\bar{\omega}_0$ are very small in contrast to the case of $PbHPO_4$ (Ref. 23) and squaric acid[36] where one finds very large isotope shifts in T_C with very small values of both Ω and ω_0. In all the salts, however, the intrachain couplings are much stronger than the interchain couplings.

Finally, it may be concluded that very good fitting of the experimental data of ϵ and T_C for SCD and partially deuterated crystals (T_C vlaues only) as well as the correct prediction of the exponent α obtained from "staggered polarization" indicate the validity of a unified theory for SCD and Rochelle salt, where the same two sublattice model is applicable with suitable modification and both the salts behave in a similar manner before and after the transition. We would also like to point out here that our calculations with the pseudospin-lattice coupled model and the use of a simple Green's-function technique (I) are applicable only to give a qualitative behavior of phase transitions in the $SnCl_2 \cdot 2H_2O$-type crystals. A more sophisticated theory for understanding the critical behavior of this salt sould be highly interesting.

ACKNOWLEDGMENTS

One of the authors (B.K.C.) is deeply grateful to Professor H. Suga and Dr. T. Matsuo for valuable discussions.

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