Dynamical Susceptibility in KH$_2$PO$_4$-type Crystals above and below $T_c$

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The time dependent cluster approximation called the path probability method (PPM) is applied to a pseudo-spin Ising Hamiltonian of the Slater-Takagi model for KH$_2$PO$_4$-type hydrogen-bonded ferroelectrics in order to calculate the homogeneous dynamical susceptibility $\chi(\omega)$ above and below the ferroelectric transition temperature $T_c$. Above the transition temperature all the calculations are carried out analytically in the cactus approximation of the PPM. Below the transition temperature the dynamical susceptibility is also calculated accurately since the analytical solution of spontaneous polarization in the ferroelectric phase can be utilized. When the temperature is approached from both sides of the transition temperature, only one of relaxation times shows a critical slowing down and makes a main contribution to the dynamical susceptibility. The discrepancy from Slater model (ice-rule limit) is discussed in comparison with some experimental data.

KEYWORDS: KDP(KH$_2$PO$_4$), phase transition, CVM (cluster variation method), PPM (path probability method), dynamical susceptibility

§1. Introduction

Recently, we successfully applied the cluster variation method (CVM) to the Slater-Takagi model for KH$_2$PO$_4$-type hydrogen-bonded ferroelectrics above and below the transition temperature to explain the anisotropy of the wave-number dependent susceptibility $\chi(q)$ observed in the neutron scattering experiment. On the other side, the path probability method (PPM) devised by Kikuchi is the time dependent cluster variation method and has been applied to various phase transitions and transport phenomena. Its characteristic is that the stationary solution of the kinetic equation given by the PPM yields the equilibrium solution obtained from the CVM in the corresponding approximation. Further, since the PPM provides a systematic approximation for the kinetic problem, it makes possible to calculate the dynamical susceptibility beyond the usual molecular field approximation.

A few years ago Matsuo et al. re-examined the excess entropy obtained from their own data and the other experimental data of heat capacity for KDP. They discussed about the discrepancy from the ice-rule of Slater model and emphasized the significance of excitation level in the Slater-Takagi model.

The present purpose is to calculate the dynamical susceptibility for KDP based on the Slater-Takagi model and to compare our results with experimental data of the dynamical susceptibility over all the temperature regime. Though Yoshimitu and Matubara have already calculated the dynamical susceptibility for the essentially same model for the KDP above the transition temperature, their calculation seems to be limited to the paraelectric phase. In the present paper, not only in the paraelectric phase but also in the ferroelectric phase we calculate accurately the dynamical susceptibility for KDP based on the above mentioned Slater-Takagi model by making use of an analytical expression for the spontaneous polarization.

§2. Formulation

There are $N$ PO$_4$ tetrahedra and $2N$ protons around PO$_4$ tetrahedra in the KDP-type crystal as shown in Fig. 1. The pseudo-spin Ising Hamiltonian $H$ for a configuration of $2N$ protons has a form

$$H = \sum_{ijkl} \left[ H_0(\sigma_i, \sigma_j, \sigma_k, \sigma_l) - \frac{\mu_4}{2} E(\sigma_i + \sigma_j + \sigma_k + \sigma_l) \right]$$

with

$$H_0(\sigma_i, \sigma_j, \sigma_k, \sigma_l) = -V_2(\sigma_i\sigma_j + \sigma_j\sigma_k + \sigma_k\sigma_l + \sigma_l\sigma_i) -V_4(\sigma_i\sigma_k + \sigma_j\sigma_l) -V_4\sigma_i\sigma_j\sigma_k\sigma_l + C$$

where the sum $\langle ijk l \rangle$ runs over four protons $ijk l$ around each PO$_4$ tetrahedron in the crystal, $\sigma_i = \pm 1$ stands for the site of the $i$-th proton in the double well potential along the O-O bond (hydrogen bond) between two nearest neighbor PO$_4$'s, $\mu_4$ is the magnitude of an electric dipole moment associated with a complex K-H$_2$PO$_4$ and $E$ is an external electric field. As is seen in Fig.1, we use a convention that when the $i$-th proton is located on the closer site to an O atom at the top (bottom) of the PO$_4$ tetrahedron along the easy z-axis, the $i$-th proton takes $\sigma_i = +1(-1)$. The energy parameters $V_2$, $V_4$, $V_5$ and $C$ are related to those of the Slater-Takagi model shown in Fig. 2 as

$$V_2 = \varepsilon_2/8, \quad V_4 = -\varepsilon_0/4 + \varepsilon_1/2 - \varepsilon_2/8,$$

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\( V_0 = \varepsilon_0/4 - \varepsilon_2/8, \quad C = \varepsilon_0/4 + \varepsilon_1/2 + \varepsilon_2 \)

where the pseudo-spin Hamiltonian (2.1) is a modified one used by Tokunaga et al.\(^{11}\) by allowing all the configurations of four protons around a PO\(_4\) tetrahedron. Here the ice-rule limit characteristic of the Slater model for KDP is realized when \((\varepsilon_1 - \varepsilon_0)/\varepsilon_0 \to \infty\) with \(\varepsilon_0 > \varepsilon_1\). The ice rule is described by proton configurations in which (A) only one proton exists on each hydrogen bond between two nearest neighbor PO\(_4\) tetrahedra and (B) all the PO\(_4\) tetrahedra have exactly two protons adjacent to them.

We now apply the path probability method (PPM) in the cactus approximation to the present system to find the kinetic equation for protons. The cactus approximation equivalent to Slater’s treatment\(^{8}\) takes account of the proton correlations around PO\(_4\) as well as the site of a proton in the double well potential on each hydrogen bond. However, since the derivation of the kinetic equation by the PPM is a little lengthy, though the final kinetic equation is relatively simple, here we only mention the idea of the PPM\(^{5,12}\). In equilibrium statistical mechanics, the realized state of a system in thermal contact with a heat reservoir is the minimum state of its free energy. When the system is not in equilibrium, we are interested in the time evolution of the system. The PPM is a method for determining the time evolution of the system. The idea of the PPM is to calculate a transition probability of the ensemble of equivalent systems in a short time interval \(\Delta t\) from time \(t\) to \(t + \Delta t\). This transition probability is called the path probability function. Then, we assume an extremum principle that the path maximizing this path probability function determines the time evolution of the system.

Now, in the cactus approximation of the PPM, the homogeneous state of the present system at time \(t\) is described by five state variables defined by

\[
m(t) = \langle \sigma_i \rangle_t, \quad s(t) = \langle \sigma_i \sigma_j \sigma_k \rangle_t, \quad q(t) = \langle \sigma_i \sigma_j \rangle_t,
\]

\[
q_0(t) = \langle \sigma_i \sigma_k \rangle_t, \quad q_4(t) = \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle_t \tag{2.4}
\]

where each state variable represents the correlation of protons \(ijkl\) around a PO\(_4\) cluster at time \(t\) (Fig.1) and \(\langle \cdots \rangle_t\) is an thermal average at time \(t\). After some manipulations of the PPM we obtain a generating function from which a set of kinetic equations are derived through differentiation of interaction parameters. The generating function is given by

\[
G(L) = \theta \text{Tr}_i p_1(\sigma_i, t) e^{-2L \cdot \sigma_i} \times \left[ \frac{\text{Tr}_{ijkl} p_4(\sigma_i, \sigma_j, \sigma_k, \sigma_l, t) e^{-\frac{2}{\beta} \Delta_i H_0(\sigma_i, \sigma_j, \sigma_k, \sigma_l)}}{p_i(\sigma_i, t)} \right]^2 \tag{2.5}
\]

\[
\Delta_i H_0(\sigma_i, \sigma_j, \sigma_k, \sigma_l) = H_0(-\sigma_i, \sigma_j, \sigma_k, \sigma_l) - H_0(\sigma_i, \sigma_j, \sigma_k, \sigma_l)
\]

where \(\text{Tr}_i\) and \(\text{Tr}_{ijkl}\) denote a trace operation \(\sum_{\sigma_i = \pm 1}^{\sum_{\sigma_j, \sigma_k, \sigma_l = \pm 1}}\) respectively, \(\beta = 1/k_B T\) is the inverse temperature, \(\theta^{-1}\) is a microscopic relaxation time of an isolated proton, \(L_i = \beta \mu_d E/2\) and \(\Delta_i\) defines an energy increase under an inversion of only \(\sigma_i\) variable into \(-\sigma_i\). Further, \(p_1(\sigma_i, t)\) and \(p_4(\sigma_i, \sigma_j, \sigma_k, \sigma_l, t)\) are, respectively, the probability of finding the site \(\sigma_i\) of a proton in the \(i\)-th bond and the probability of finding the sites \(\sigma_i, \sigma_j, \sigma_k, \sigma_l\) of protons \(i, j, k, l\) around a PO\(_4\) and are given in terms of above defined five state variables by

\[
p_1(\sigma_i, t) = \frac{1}{2} (1 + m(t) \sigma_i),
\]

\[\text{Fig. 1. } z\text{-axis projection of hydrogen bonds connecting PO}_4\text{ complexes and } \sigma_i, \sigma_j, \sigma_k, \sigma_l\text{ showing the four different pseudo-spins for protons around a PO}_4\text{ tetrahedron. The numeral in the center of each PO}_4\text{ tetrahedron shows relative heights of PO}_4\text{ along } z\text{-axis.}
\]

\[\text{Fig. 2. Energy levels, magnitude of dipole moments of a K-PO}_4\text{ complex and probability for proton configuration in Slater-Takagi model.}
\]
\[ p_4(\sigma_i, \sigma_j, \sigma_k, \sigma_l, t) = \frac{1}{24} \left( 1 + m(t)(\sigma_i + \sigma_j + \sigma_k + \sigma_l) + q(t)(\sigma_i \sigma_j + \sigma_j \sigma_k + \sigma_k \sigma_l + \sigma_l \sigma_i) + q_0(t)(\sigma_i \sigma_k + \sigma_j \sigma_l + \sigma_k \sigma_l + \sigma_l \sigma_i) + s(t)(\sigma_i \sigma_j \sigma_k + \sigma_j \sigma_k \sigma_l + \sigma_k \sigma_l \sigma_i + \sigma_l \sigma_i \sigma_j) + q_4(t)(\sigma_i \sigma_j \sigma_k \sigma_l) \right). \] 

(2.6)

Then a set of kinetic equations are given in a convenient form: \[ \frac{d m_i(t)}{dt} = 4 \lim_{L_i \to 0} \frac{\partial G(L)}{\partial L_i} \quad (i = 1 \sim 5) \] 

(2.7)

Here, it should be noted that in order to write the above expression an extra interaction term is virtually added to Hamiltonian (2.2) as

\[ \mathcal{H}_0(\sigma_i, \sigma_j, \sigma_k, \sigma_l) = -V_3(\sigma_i \sigma_j \sigma_k + \sigma_j \sigma_k \sigma_l + \sigma_k \sigma_l \sigma_i + \sigma_l \sigma_i \sigma_j) \]

\[ \rightarrow \mathcal{H}_0(\sigma_i, \sigma_j, \sigma_k, \sigma_l) \]

(2.8)

and \( V_3 \) is, however, put to zero just after differentiation with respect to \( L_3 = \beta V_3 \) in eq.(2.7). We also redefine order parameters as \( m_1(t) = 4m(t), m_3(t) = 4q(t), m_4(t) = 4s(t), m_5(t) = q_0(t) \) and \( L_5 = 2q_0(t) \) and the corresponding fields as \( L_1(t) = \beta \mu E(t)/2, L_2 = \beta V_2, L_3 = \beta V_3, L_4 = \beta V_4 \) and \( L_5 = \beta V_5 \), respectively.

\section{3. Thermal equilibrium}

In order to obtain the dynamical susceptibility \( \chi(\omega) \) as the linear response to the external field, equilibrium values of the order parameters are required. Since the equilibrium state is more easily obtained from the CVM than from the stationary solution of the kinetic equation (2.7), we apply the cactus approximation of the CVM to the present system. \(^3\) \(^10\) The variational free energy \( F \) is obtained by

\[ F = U - TS \]

where the internal energy \( U \) is given by

\[ U/N = -4V_2q - 2V_3q_0 - V_4q_4 - 2\mu_mE \]

(3.2)

and the entropy \( S \) is given by

\[ S/Nk_B = 2 \text{Tr} \left[ p_1(\sigma_i) \ln p_1(\sigma_i) \right] - \text{Tr} \left[ p_4(\sigma_i, \sigma_j, \sigma_k, \sigma_l) \ln p_4(\sigma_i, \sigma_j, \sigma_k, \sigma_l) \right]. \]

(3.3)

The minimum condition of the variational free energy with respect to \( m, s, q, q_0, q_4 \) yields equilibrium relations with a definition \( h_e = \exp(\beta \mu E) \)

\[ \frac{c_+}{c_-} = \left( \frac{1 + m}{1 - m} \right)^2 h_e^4, \quad \frac{d_+}{d_-} = \left( \frac{1 + m}{1 - m} \right) h_e^2, \]

(3.4)

\[ \frac{c_2}{c_0} = \frac{\eta_2}{\eta_0}, \quad \frac{c_+ c_-}{c_0^2} = \frac{1}{\eta_0^2}, \quad \frac{d_+ d_-}{c_0^2} = \left( \frac{\eta_1}{\eta_0} \right)^2 \]

where \( c_+, c_-, d_+, d_-, c_2, c_0 \) shown in fig.2 are defined by \( p_4(\sigma_i, \sigma_j, \sigma_k, \sigma_l) \) by

\[ c_+ = \frac{1}{24} \left( 1 + 4m + 4q + 2q_0 + 4s + q_4 \right), \]

\[ c_- = \frac{1}{24} \left( 1 - 4m + 4q + 2q_0 - 4s + q_4 \right), \]

\[ d_+ = \frac{1}{24} \left( 1 + 2m - 2s - q_4 \right), \]

\[ d_- = \frac{1}{24} \left( 1 - 2m + 2s - q_4 \right), \]

\[ c_2 = \frac{1}{24} \left( 4 - 4q + 2q_0 + q_4 \right), \]

\[ c_0 = \frac{1}{24} \left( 1 - 2q_0 + q_4 \right) \]

(3.5)

with a normalization condition

\[ c_+ + c_- + 4c_0 + 4d_+ + d_- + 2c_2 = 1. \] (3.6)

From eq.(3.4) and eq.(3.6) it is easy to solve \( c_+, c_-, d_+, d_-, c_2, c_0 \) in terms of the polarization \( m \) and field variable \( h_e \):

The spontaneous polarization \( m_0 \) \(^10\) is determined by the relation

\[ m = \frac{1}{2} \left( 4m + 4q + 2q_0 - 4s + q_4 \right) \]

(3.8)

as

\[ m_0 = \left\{ \begin{array}{ll} 
\sqrt{1 - \frac{4\eta_1^2}{(1 - 2\eta_0 - \eta_2)^2}} & \text{for } T < T_C \\
0 & \text{for } T > T_C 
\end{array} \right. \] (3.9)

and the electric susceptibility is given by \(^3\)

\[ \chi_{\text{stat}} = \frac{\mu_0^2}{k_B T} \left( 1 + \eta_1^2 \left( 1 - 2\eta_0 + 2\eta_2 \right) \right)^{\frac{1}{2}} \] (3.10)

The other equilibrium order parameters in eq.(3.7) without electric field are found from eq.(3.9). Further, utilizing eq.(3.3) the entropy versus temperature are shown in Fig.3, in order to compare our result with experimental data of Matsuo et al.\(^7\) In the following figures energy parameters such as \( \varepsilon_1 \) are measured in the units of Boltzmann factor \( k_B \).

\section{4. Dynamical response in paraelectric phase}

In the paraelectric phase we can carry out all the calculations analytically. In thermodynamic equilibrium of the paraelectric phase, under the inversion of external field \( E \), the order parameters \( m \) and \( s \) are changed into \( -m \) and \( -s \), respectively, while \( q, q_0 \) and \( q_4 \) are invar-
Now we assume five equations is reduced to two closed equations for long to the external field by

\begin{align*}
    c_0 &= \frac{\eta_0}{4\eta_0 + 2\eta_2 + \left(h_e \frac{1 + m}{1 - m} + h_e^{-2} \frac{-1}{1 + m}\right) + 4\eta_1 \left(h_e \sqrt{\frac{1 + m}{1 - m}} + h_e^{-1} \sqrt{\frac{1 - m}{1 + m}}\right)}, \\
    c_+ &= h_e \frac{1 + m}{1 - m} c_0, \\
    c_- &= h_e^{-1} \frac{1 - m}{1 - m} c_0, \\
    d_+ &= h_e \sqrt{\frac{1 + m}{1 - m} \eta_0} c_0, \\
    d_- &= h_e^{-1} \sqrt{\frac{1 - m}{1 + m} \eta_0} c_0.
\end{align*}

(3.7)

Especially the static susceptibility \( \chi_{stat} \) is obtained by putting \( \omega = 0 \) in eq.(4.4) as

\[ \chi_{stat} = \chi(\omega = 0) = \frac{\mu_4^2}{k_B T} \frac{2(1 + \eta_1)}{-1 + 2\eta_0 + 2\eta_1 + \eta_2} \] (4.6)

The transition temperature \( T_c \) to the ferroelectric phase is determined as a divergent point of the static susceptibility as

\[ 2 e^{-\varepsilon_0/k_B T_c} + 2 e^{-\varepsilon_1/k_B T_c} + e^{-\varepsilon_2/k_B T_c} = 1 \] (4.7)

This expression is the one obtained by Ishibashi. When the transition temperature is approached, the first term of eq.(4.4) shows a critical slowing down and contributes mainly to the dynamical susceptibility.

\section{5. Dynamical response in ferroelectric phase}

In the ferroelectric phase a finite spontaneous polarization \( m_0 \) occurs as given in eq.(3.9). When the external electric field \( E(t) \) is applied, the short range order parameters \( q(t), q_0(t), q_1(t) \) have also components proportional to \( E(t) \) indirectly through the spontaneous polarization \( m_0 \). Thus we assume that

\begin{align*}
    m_1(t) &= 4m(t) = 4m_0 + \chi_1(\omega) E \exp i \omega t, \\
    m_2(t) &= 4q(t) = 4q_0 + \chi_2(\omega) E \exp i \omega t, \\
    m_3(t) &= 4s(t) = 4s_0 + \chi_3(\omega) E \exp i \omega t, \\
    m_4(t) &= q_4(t) = q_0^4 + \chi_4(\omega) E \exp i \omega t, \\
    m_5(t) &= 2q_5(t) = 2q_0^5 + \chi_5(\omega) E \exp i \omega t
\end{align*}

(5.1)

where the required dynamical susceptibility is \( \chi(\omega) = \mu_4 \chi_{1}(\omega)/4 \) and \( m_0, s_0, q_0, q_0^4 \) and \( q_0^5 \) are equilibrium order parameters in the absence of external electric field. Then, substituting eq.(5.1) into eq.(2.7), we finally obtain a set of algebraic equations for five \( \chi_i(\omega) \) \((i = 1 \sim 5)\) which is read in a matrix form as

\[ \left( \frac{i \omega}{\theta} I + M \right) \chi(\omega) = b \]

(5.2)

where \( A_{\pm}, D \) are given as

\begin{align*}
    c_+ &= h_e \frac{1 + m}{1 - m} c_0, \\
    c_- &= h_e^{-1} \frac{1 - m}{1 - m} c_0, \\
    d_+ &= h_e \sqrt{\frac{1 + m}{1 - m} \eta_0} c_0, \\
    d_- &= h_e^{-1} \sqrt{\frac{1 - m}{1 + m} \eta_0} c_0.
\end{align*}

(3.7)

Since the explicit forms of a matrix \( M \) and a column vector \( b \) are complicated and lengthy compared with the paraelectric phase, they are given in Appendix. Referring to Appendix, the elements of the matrix \( M \) and the column vector \( b \) can be expressed in terms of only \( \eta_0, \eta_1 \) and \( \eta_2 \) without unknown state variables since order parameters at equilibrium are obtained analytically. Then the algebraic equation can be easily calculated numerically for fixed \( \omega \) using the Gaussian elimination method for linear algebraic equation. With the relaxation time \( \tau_i \) \((i = 1 \sim 5)\), the dynamical susceptibility per proton

\[ \chi(\omega) = \frac{i \omega}{\theta} \left( \frac{1}{\tau_1} I + \sum_{i=1}^{5} \frac{1}{\tau_i} \chi_i(\omega) \right) \]

(5.2)

Now we assume \( \mu_4 m(t) = \chi(\omega) E \exp i \omega t \) and \( \mu_4 s(t) = \chi_4(\omega) E \exp i \omega t \). Substituting these relations into this set of kinetic equations, we finally obtain the dynamical susceptibility \( \chi(\omega) \) by

\[ \chi(\omega) = \frac{i \omega}{\theta} \left( \frac{1}{\tau_1} I + \sum_{i=1}^{5} \frac{1}{\tau_i} \chi_i(\omega) \right) \]

(5.2)
\[
\frac{dn(t)}{dt} = 8\theta \lambda^2 \left[ L_1 + \left( 1 - \frac{2\eta_1 + 2\sqrt{\eta_1 \eta_2 - 1}}{4\sqrt{\eta_1 \lambda}} \right) m(t) - \frac{2\eta_1 - 2\sqrt{\eta_0 - \sqrt{\eta_2} + 1}}{4\sqrt{\eta_1 \lambda}} s(t) \right]
\]
\[
\frac{ds(t)}{dt} = 8\theta \mu \left[ L_1 + \left( 1 - \frac{2\eta_1 + 2\sqrt{\eta_0 \eta_2 - 1}}{8\sqrt{\eta_1 \lambda}} + \frac{-6\eta_1 + 2\sqrt{\eta_0 + \eta_2 + 3}}{8\sqrt{\eta_1 \mu}} \right) m(t) - \left( \frac{2\eta_1 - 2\sqrt{\eta_0 - \sqrt{\eta_2} + 1}}{8\sqrt{\eta_1 \lambda}} + \frac{6\eta_1 + 2\sqrt{\eta_0 + \eta_2 + 3}}{8\sqrt{\eta_1 \mu}} \right) s(t) \right]
\] (4.1)

\[
\chi(\omega) = \frac{\mu d}{k_B T} \frac{\theta \lambda}{A_+ + A_-} \left( \frac{D - 8A_+ \lambda}{i\omega + \theta A_- \lambda} + \frac{D - 8A_+ \lambda}{i\omega + \theta A_+ \lambda} \right)
\] (4.4)

\(\chi(\omega)\) can be written for \(T < T_c\) as

\[
\chi(\omega) = \frac{\mu d}{4} \chi(\omega) = \sum_{i=1}^{5} \frac{\chi_i}{1 + i\omega \tau_i}\n\] (5.3)

where the relaxation times \(\tau_i\) are obtained by a diagonalization of \(M\) in terms of a matrix \(U\) as

\[
(U M U^{-1})_{ij} = \frac{1}{\theta \tau_i} \delta_{ij}\n\] (5.4)

and the intensity coefficients \(\chi_i\) are given by

\[
\chi_i = \frac{\theta \mu d \tau_i}{4} \sum_{j=1}^{5} (U^{-1})_{1i} U_{ij} b_j.
\]

Especially for \(T > T_c\), \(\chi_3, \chi_4\) and \(\chi_5\) representing the intensity from each relaxation mode reduce to zero and in consistency to eq.(4.4) we obtain

\[
\chi(\omega) = \sum_{i=1}^{2} \frac{\chi_i}{1 + i\omega \tau_i}.
\] (5.5)

Though there appear five relaxation times in the ferroelectric phase, only one of them shows the critical slowing down and contributes mainly to the dynamical susceptibility when the transition temperature is approached (Fig.4). The real \(\chi'(\omega)\) and imaginary \(\chi''(\omega)\) part of the dynamical susceptibility are defined as \(\chi(\omega) = \chi'(\omega) - i\chi''(\omega)\). The results for \(\chi'(\omega)\) and \(\chi''(\omega)\) versus \(\omega\) and temperature \((T - T_c)/T_c\) in the para- and ferro-electric phases are shown in Fig.5.

\section{Results and discussions}

The result shows that, though there are, respectively, two and five relaxation times in para- and ferro-electric phase according to a set of independent kinetic equations, only one of the relaxation times shows a critical slowing down when the temperature \(T\) approaches the transition temperature \(T_c\) from above and below the transition temperature and makes a main contribution to the dynamical susceptibility.

In order to compare the experimental data with our results we present the temperature dependence of the real part \(\chi'(\omega)\) and imaginary part \(\chi''(\omega)\) for constant \(\omega\) for various values \(\varepsilon_1\) (Fig.6). The hilly behaviors appear not only above the transition temperature \(T_c\) but also below \(T_c\) for the finite \(\varepsilon_1\) whereas in the ice-rule limit \(\chi(\omega)\) vanishes completely below \(T_c\). The dip of \(\chi'(\omega)\) at \(T = T_c\) is caused by the vanishing of the numerator due to the contribution from the relaxation mode showing a critical slowing down. The experimental data\(^{14}\) show the hilly behavior below the transition temperature and the dip structure at the transition temperature. In our calculation the contribution from the relaxation mode showing a critical slowing down overwhelms contributions from other modes and the dip goes to almost zero contrary to the experimental data. Recently, Matsuoo \textit{et al.}\(^{7}\) re-examined experiments of the heat capacity and estimated the transition entropy \(\Delta S\) due to proton ordering from the experimental data. They discussed the discrepancy from the Slater theory and estimated the contribution from the excitation level of the Slater-Takagi model. We presented the entropy curve versus temperature from our calculation for various parameters in Fig.3. These results reveal that the ice-rule in the Slater model is not completely satisfied in the KDP crystal.

The dynamical susceptibility has been calculated not only above the transition temperature but also below it in the cactus approximation of the Slater-Takagi model.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{Relaxation times versus temperature for \(\varepsilon_1 = 813\,K\). For \(T > T_c\), only \(\tau_1\) and \(\tau_2\) take part in \(\chi(\omega)\).}
\end{figure}
\[ A_\pm = B \pm \sqrt{B^2 - C}, \quad B = 2 \left( \frac{1 + 4\eta_0 + 4\eta_1 + 4\eta_2 + 4\eta_1\sqrt{\eta_0} + 4\sqrt{\eta_0\eta_2} + 2\eta_1\sqrt{\eta_2}}{\sqrt{\eta_1(1 + 2\sqrt{\eta_0} + \sqrt{\eta_2})}} - 2\lambda \right), \]

\[ C = \frac{32(2\sqrt{\eta_0} + \sqrt{\eta_2})(-1 + 2\eta_0 + 2\eta_1 + \eta_2)}{1 + 2\eta_0 + 4\eta_1 + \eta_2}, \quad D = \frac{64(1 + \eta_1)(2\sqrt{\eta_0} + \sqrt{\eta_2})}{1 + 2\eta_0 + 4\eta_1 + \eta_2}. \] (4.5)

utilizing an analytical solution for the spontaneous polarization. The results based on the Slater-Takagi model are in good agreement with the experiments on dynamical susceptibility and excess entropy.

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**Appendix: Derivation of eq. (5.2)**

The generating function (2.5) is conveniently written as

\[ G(L) = \theta \text{Tr} \frac{2}{1 + m(t)\sigma_i} \left( \text{Tr} \rho_4(\{\sigma\}_{ijkl})e^{L\Delta,\sigma/2} \right)^2 \]

(A-1)
where $L$ is the energy parameter vector defined as

$$L = \beta(C \cdot \mu \cdot E/2 \ V_2 \ V_3 \ V_4 \ V_5)$$

(A-2)

and the Ising spin vector $\sigma$ is defined as

$$\sigma = \begin{pmatrix}
1 \\
\sigma_i + \sigma_j + \sigma_k + \sigma_l \\
\sigma_i \sigma_j + \sigma_j \sigma_k + \sigma_k \sigma_l + \sigma_l \sigma_i \\
\sigma_i \sigma_j \sigma_k + \sigma_j \sigma_k \sigma_l + \sigma_k \sigma_l \sigma_i + \sigma_l \sigma_i \sigma_j \\
\sigma_i \sigma_j \sigma_k \sigma_l \\
\sigma_i \sigma_k + \sigma_j \sigma_l
\end{pmatrix}.$$  (A-3)

The thermal average of the Ising spin vector is the order parameter vector defined by

$$m(t) = \begin{pmatrix}
1 \\
4m(t) \\
4q(t) \\
4s(t) \\
q_1(t) \\
2q_0(t)
\end{pmatrix}.$$  (A-4)

The probability $p_4(\{\sigma\}_{ijkl}) \equiv p_4(\sigma_i, \sigma_j, \sigma_k, \sigma_l)$ can also be written by using $\sigma$ and $m(t)$ as eq.(2.6). Then a set of kinetic equation (2.7) is written in a vector form by

$$\frac{d\Delta m(t)}{dt} = 4\frac{\partial G(L)}{\partial L}$$

(A-5)

and is further rewritten to a linear order of the external electric field $E$ as

$$\frac{d\sigma}{dt} = \frac{1}{2} \frac{\partial^2 G}{\partial \sigma^2} \sigma + \frac{1}{2} \frac{\partial^2 G}{\partial \sigma^2} \sigma$$

where $p_4^L(\sigma) = (1 + m_0 \sigma)/2$ and $p_4^L(\{\sigma\}_{ijkl}) = p_4^L(\sigma_i, \sigma_j, \sigma_k, \sigma_l)$ are thermal equilibrium probabilities without external field $E = 0$ and $\Delta m(t)$ is a linear difference from equilibrium value of order parameter vector $m(t)$. The variable $\Delta$ and the vector $h'$ are further defined as

$$h(\{\sigma\}_{ijkl}) = h(\sigma_i, \sigma_j, \sigma_k, \sigma_l) = e^{L_0 \cdot \Delta \sigma / 2},$$

$$h'(\{\sigma\}_{ijkl}) = h'(\sigma_i, \sigma_j, \sigma_k, \sigma_l) = e^{L_0 \cdot \Delta \sigma / 2 \Delta L}$$

where $L_0$ is an interaction parameter vector $L$ with $E = 0$. In order to obtain the dynamical susceptibility $\chi(\omega)$, $\Delta m(t) = \chi(\omega) E \exp(\text{i} \omega t)$ is assumed and then eq.(A-6) can be easily rewritten into a form (5.2) in the main text:

$$\left(\frac{i \omega}{\theta} I + M\right) \chi(\omega) = b.$$  (A-7)
\[
\frac{d\Delta m(t)}{dt} = -4\mu_\alpha E \beta \frac{\sigma_i}{p^2_1(\sigma_i)} \left( \text{Tr} \ p^\gamma_4(\{\sigma\}_{ijkl}) h(\{\sigma\}_{ijkl}) \right) \left( \text{Tr} \ p^\gamma_4(\{\sigma\}_{ijkl}) h'(\{\sigma\}_{ijkl}) \right)
\]
\[-2\Delta m(t) \frac{\sigma_i}{p^2_1(\sigma_i)} \left( \text{Tr} \ p^\gamma_4(\{\sigma\}_{ijkl}) h(\{\sigma\}_{ijkl}) \right) \left( \text{Tr} \ p^\gamma_4(\{\sigma\}_{ijkl}) h'(\{\sigma\}_{ijkl}) \right)
\]
\[+4 \text{Tr} \frac{1}{p^2_1(\sigma_i)} \left( \text{Tr} \ p^\gamma_4(\{\sigma\}_{ijkl}) h'(\{\sigma\}_{ijkl}) \right) \left( \text{Tr} \ p^\gamma_4(\{\sigma\}_{ijkl}) h(\{\sigma\}_{ijkl}) \right)
\]
\[+4 \text{Tr} \frac{1}{p^2_1(\sigma_i)} \left( \text{Tr} \ p^\gamma_4(\{\sigma\}_{ijkl}) h(\{\sigma\}_{ijkl}) \right) \left( \text{Tr} p^\gamma_4(\{\sigma\}_{ijkl}) h'(\{\sigma\}_{ijkl}) \right)
\] (A.6)