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Anisotropic dielectric properties of two-dimensional matrix in pseudo-spin ferroelectric system

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ABSTRACT

The anisotropic dielectric properties of a two-dimensional (2D) ferroelectric system were studied using the statistical calculation of the pseudo-spin Ising Hamiltonian model. It is necessary to delay the time for measurements of the observable and the independence of the new spin configuration under Monte Carlo sampling, in which the thermal equilibrium state depends on the temperature and size of the system. The autocorrelation time constants of the normalized relaxation function were determined by taking temperature and 2D lattice size into account. We discuss the dielectric constants of a two-dimensional ferroelectric system by using the Metropolis method in view of the Slater–Takagi defect energies.

1. Introduction

KH_2PO_4 (KDP) crystals have a tetragonal structure belonging to space group $I\bar{4}2d$ in the paraelectric phase [1]. In the ferroelectric phase, the crystal structure is orthorhombic with space group *Fdd*2 [2,3]. In the well-known structural phase transition of KDP at $T_c = 122$ K involving ferroelectricity, the hydrogen-bonded protons in the double-well potentials are displaced between the heavy atoms (K, P, O). The electric polarization mechanism occurs from the lattice in the displacive mode [4]. The hydrogen atoms have an intrinsic order-disorder feature, depending on the equilibrium position. Proton tunneling between these positions opposes localization [5]. Similarly, classical displacive perovskite ferroelectric materials such as $BaTiO_3$, which have been traditionally described by the condensation of the soft mode, contain an order-disorder component as the Ti ion is dynamically disordered between different off-center sites existing in the cubic phase [6]. The tunnel mode frequency decreases with decreasing temperature, and its softening induces a structural phase transition with a long-range order in the proton positions [7]. Within this model, the phase transition is driven by the direct proton–proton interaction coupled to the lattice [8]. A microscopic model for the ferroelectric phase transition in the KDP-type crystal was proposed by Slater, who investigated the order–disorder phase transition associated with different energy levels with proton configurations around PO_4 tetrahedra [9]. Fig. 1 shows the hydrogen-bond network on a two-dimensional plane. The Slater–Takagi model presents different proton configurations with their energy levels and polarization [10]. *Ab initio* electronic structure calculations are performed by considering the Slater and Takagi protonic defects in the ferroelectric phase of KH_2PO_4 [11]. While the *ab initio* energy estimation for the Takagi defect (54 meV) is in good agreement with previous calculations, the calculated Slater defect energy (17 meV) is greater than that from previous studies (5.2 meV), in accordance with the displacive phase-transition model [11–13]. The pseudo-spin model developed by Blinc, de-Gennes, Tokunanga and Matsubara, and Kobayashi takes into account the tunneling effect as well as the coupling between protons and the lattice [14–17]. By using this model, data on the thermodynamic properties, longitudinal polarization, and dielectric constant could be explained [18]. Later, the model was renamed “extended pseudo-spin model” under the assumption that the transverse polarization is due to the dipole moment associated with the equilibrium positions of the double-well potential in the hydrogen-bond networks [19,20]. We discuss the dielectric properties of a two-dimensional ferroelectric system by calculating the pseudo-spin Ising Hamiltonian with the Monte Carlo method while taking into account the dependence on the lattice size. In this work, the Monte Carlo simulation was employed by studying the size dependence of the dynamic transverse and longitudinal dielectric properties of the two-dimensional ferroelectric system.

2. Simulation and methods

Fig. 2 shows the projection of the KDP crystal onto the *x*–*y* plane on the basis of Fig. 1 for the 2D checkerboard lattice

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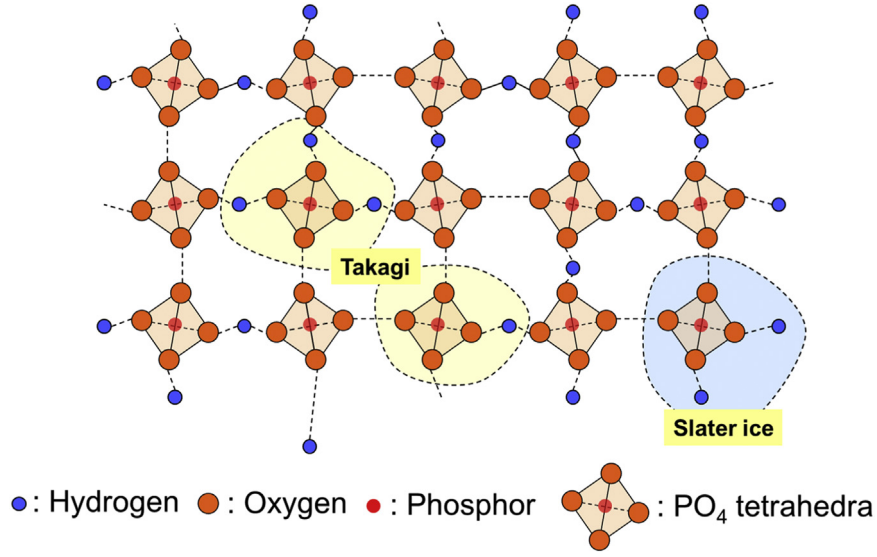

Fig. 1. (Color online) Schematic proton configurations for Takagi defects (H_3PO_4–HPO_4) and Slater defects with different internal-energy levels in the ferroelectric system.

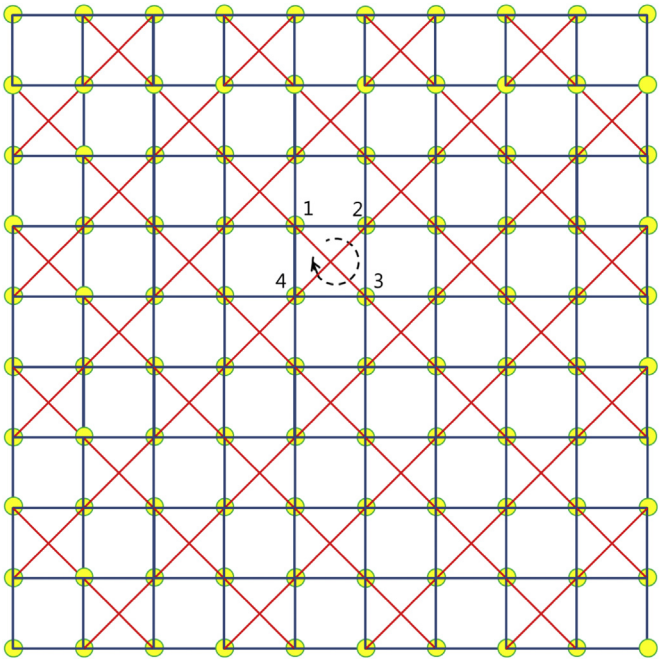

Fig. 2. (Color online) Schematic configuration of the 2D checkerboard lattice structure. The pseudo-spins labeled 1, 2, 3, and 4 on the square lattice are aligned in the clockwise direction. The pseudo-spins are randomly initialized in the "up" (↑) or "down" (↓) states. The red cross line "X" of the squares in the checkerboard indicates the PO_4 tetrahedra.

structure. The "X" in the square box denotes PO_4 tetrahedra. The four circles around PO_4 denote the hydrogen atoms linked to other phosphates. Taking into account the different Slater–Takagi configurational energies of the PO_4 groups, two different interaction constants U and V are considered. The parameter U represents the interaction between protons belonging to the PO_4 tetrahedra groups in the next-nearest-neighboring horizontal plane, and the parameter V represents the interaction between two protons in the nearest-neighboring plane. The four-cluster Hamiltonian H_4 for the interaction energy of four protons around a PO_4 sublattice is given by

$$H_4 = -V(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1) - U(S_1S_3 + S_2S_4), \tag{1}$$

where U and V are related to the Slater–Takagi defect energies ϵ_0 and ϵ_1 by $V = (2\varepsilon_1 - \epsilon_0)/4$ and $U = -(2\epsilon_1 - 2\epsilon_0)/4$ [21].

The Hamiltonian corresponding to the longitudinal susceptibility χ_c with an external electric field along the c-axis is given by

$$H_c = -\mu_c E_c \sum_i S_i. \tag{2}$$

According to Fig. 2, the longitudinal and transverse polarizations of the ferroelectric 2D plane are as follows:

$$P_c = 2N\mu_c\langle S\rangle = N\mu_c\big(\langle S_+\rangle + \langle S_-\rangle\big), \tag{3}$$

and

$$P_a = \tfrac{1}{2}N\mu_a\big(\langle S_+\rangle - \langle S_-\rangle\big)$$
$$P_b = \tfrac{1}{2}N\mu_b\big(\langle S_+\rangle - \langle S_-\rangle\big), \tag{4}$$

where N is the number of H_2PO_4 groups in the crystal and $\langle S\rangle$ are the averages of the pseudo-spins in the system indicating the up-spin (↑) positive (+) and down-spin (↓) negative (−) dipole moment in the hydrogen-bond networks. The factor $\frac{1}{2}$ is multiplied to consider the polarization along the a-axis and b-axis dipole moments of the protons in the lattice.

The Hamiltonian of a pseudo-spin dielectric system with a 2D lattice can be considered in terms of the four-cluster Hamiltonian and the longitudinal and transverse dielectric Hamiltonian in the presence of a general field through the following equation:

$$H = -V\sum_{i,j} S_iS_j - U\sum_{i,j} S_iS_j - \mu_c E_c \sum_i S_i$$
$$-\mu_a E_a\left(\sum_{i\in a} S_{i+} - \sum_{i\in a} S_{i-}\right) - \mu_b E_b\left(\sum_{i\in b} S_{i+} - \sum_{i\in b} S_{i-}\right), \tag{5}$$

where the transverse dielectric Hamiltonian term is the summation of the pseudo-spins with positive (+) and negative (−) dipole moments along the a- and b-axes [4]. The initial values of the pseudo-spin lattice are randomly assigned the up-state (+1) or down-state (−1) in the Monte Carlo (MC) simulation. Since a finite-sized system is simulated, appropriate boundary conditions are required to measure the critical phenomena. The correlation length is infinite at the critical point; however, we only choose the finite size. Periodic boundary conditions, which identify boundary sites with initial sites, were used. When the system moves to an