RCBJSF-13 (2016 June, Matsue) proceedings
to be published in Ferroelectrics

Phase Transitions and the Quantum Effect in A_2BX_4-type Ferroelectric Crystals

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Abstract

Phase diagrams for modulated phases are constructed based on a competing interactive ISING model. Commensurate phases with the wave number q=0, 1/6, 1/3 and 1/2 are stable at zero temperature, if the model Hamiltonian is treated classically. On the other hand, the regions of incommensurate wave number as well as high-order commensurate ones extend down to 0 K, if the quantum statistical mechanics is employed. Based on the calculated phase diagram, phase transitions of K_2SeO_4, Rb_2MoO_4, Rb_2SeO_4, and Cs_2WO_4 are discussed.

Introduction

Forty years ago, an incommensurate phase in K_2SeO_4 was discovered by the neutron scattering experiment. The disordered (paraelectric) structure transforms to the incommensurate one with the modulation wave number q=1/3-δ. Further decreasing temperature, q locks-in 1/3, and the commensurate (ferroelectric) phase is stabilized down to low temperature [1]. Since then many isomorphous crystals were found to perform similar incommensurate-commensurate (lock-in) transitions.

Ising spin models with competing interactions were employed to describe the many kind of modulated structures. The ANNNI model [2, 3], the EXAFII model [4], the ERLI model [5], and others can demonstrate many modulated structures and the lock-in transition in A_2BX_4-type crystals.

All these models ensure that the incommensurate phase transforms to the commensurate one at low temperature; the ground state of the Ising system disfavors the incommensurate state thermodynamically. In nature, some A_2BX_4-type crystals do not perform the lock-in transition down to zero temperature [6-8].

Recently, we took into account the quantum effect on the free energy of modulated structures [9]. The quantum Ising model denominated QITNI was applied to the monoclinic A_2BX_4-type crystals to explain the incommensurate phase which is stable down to 0 K. It was demonstrated that quantum uncertainty makes commensurate phases rather unstable against the incommensurate state. So the crystal may retain the incommensurate phase down to 0 K, if interaction parameters are set properly.

In the case of the monoclinic system, it is shown that the neighboring interaction is ferroic for first and third neighbors, but antiferroic for second neighbors. If we apply the QITNI model to the modulated structures in the orthorhombic system, it seems that the

neighboring interactions are antiferroic for first and second neighbors, but weakly ferroic for third neighbors. Such situation is investigated in this paper, and the transition sequences of some A_2BX_4-type crystals are explained referring to the model.

Model and Formulation

The model Hamiltonian for one-dimensional modulated structures is written as,

$$H = \sum_j \left(\frac{1}{2}\dot{x}_j^{\,2} + V(x_j) - \frac{1}{2}\sum_l J_l x_j x_{j+l} \right) , \tag{1}$$

where a lattice variable x_j is a representative of a displacement pattern of atoms on the *j*-th lattice layer, belonging to a space-group representation relevant to the phase transition. The self-potential $V(x)$ is an even function as shown in Fig. 1, ensuring the disordered phase at high temperature. It may be quadratic or double Morse type function, however, our formalism does not matter the concrete functional form. The interaction J_l beyond the second neighbor one is necessary to realize the modulation structures with long period.

In order to analyze the system described by Eq. (1), we adopt the mean field approximation, and write the single particle Hamiltonian as

$$H_{\mathrm{MF}} = \frac{1}{2}\dot{x}_j^{\,2} + V(x_j) - h_j x_j \ , \tag{2}$$

where the mean field is the following:

$$h_j = \sum_{l=1}^{n} J_l \left(\langle x_{j+l} \rangle + \langle x_{j-l} \rangle \right). \tag{3}$$

The brackets mean a statistical expectation value calculated by the following;

$$\langle O \rangle = \mathrm{Tr}\left[O \exp\left(-H_{\mathrm{MF}} / k_{\mathrm{B}} T \right) \right] / \mathrm{Tr}\left[\exp\left(-H_{\mathrm{MF}} / k_{\mathrm{B}} T \right) \right]. \tag{4}$$

The effect of anharmonicity of the self-potential is taken into account from the

quantum mechanical behavior of a particle;

$$\left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial x^2}+V(x)\right]\varphi_m=\varepsilon_m\varphi_m. \tag{5}$$

If the potential has deep double minima as shown in Fig. 1, then we may take only two energy levels ε_0 and ε_1 into account, and can obtain analytical expressions easily. The quantum effect emerges if the parameter

$$T_1 \equiv (\varepsilon_1 - \varepsilon_0)/k_B \tag{6}$$

is not vanishing; i.e. the energy gap between the ground and excited level is finite. The magnitude of the order parameter is scaled as

$$\xi_j \equiv \frac{\langle x_j \rangle}{x_0}, \qquad x_0 \equiv \left|\int x\varphi_0{}^*\varphi_1\, dx\right|.$$

It should also be understood that J_l is dimensionless hereafter;

$$J_l x_0{}^2/k_B \to J_l .$$

Using such scaled quantities, the free energy is given by [9]

$$\frac{F}{k_B}=\frac{1}{2}\sum_{j,l} J_l\xi_j\xi_{j+l} - T\sum_j \ln\left(2\cosh\frac{\Lambda_j}{T}\right), \tag{7}$$

where the quantum mean field Λ_j is related to the classical mean field h_j ;

$$\Lambda_j=\sqrt{\left(\frac{T_1}{2}\right)^2+h_j{}^2}\ . \tag{8}$$

Since the order parameter ξ_j is scaled, it takes ± 1 at 0 K, only if the system is classical (i.e. $T_1 = 0$). Otherwise, $|\xi_j| < 1$.

The free energy can be minimized with respect to the amplitudes of the order parameter expressed by Fourier components with the reduced wave number q;

$$\xi_j=\sum_n A_n \cos\left(2\pi q(2n-1)(j-\tau)\right)\ . \tag{9}$$

Generally, we can choose τ integer, but half integer in cases of $q = 1/4, 1/8, \cdots$ [5]. Numerical calculations were performed to minimize F iteratively, except for q=0, 1/2 and 1/4, for which the single amplitude A_1 is obtainable analytically. For an incommensurate phase, the sum in the last term of Eq. (2) is replaced by integration, as given in the previous report [9].

Phase Diagrams

In our previous paper explaining the monoclinic A_2BX_4 systems, we investigated the phase diagram for the interaction parameters in the range of $J_1>0$, $J_2<0$, and $J_3>0$ [9]. Here we are concerning the orthorhombic A_2BX_4 systems. The phase diagram for K_2SeO_4 and the similar crystals, which have the commensurate phase with q=1/3 if exists, can be reproduced for the effective interlayer interactions;

$$J_0 = 2, J_1 = -1, -1.5 < J_2 < 0, \text{ and } J_3 \geq 0 . \qquad (10)$$

Therefore, interaction parameters, temperature, and free energy are all scaled by $|J_1|$. We consider the commensurate phases which can be represented with up to 4 Fourier components in Eq. (9) as listed in Table 1. The number of Fourier Components is called rank. Other commensurate structure whose rank is higher than 4 are treated as the incommensurate state. The disordered phase $\xi_j = 0$ is stable

$$T > T_1 / \ln\{(2J(q_0) + T_1)/(2J(q_0) - T_1)\}, \qquad (11)$$

where $J(q) = J_0 + \sum_{l=1}^{3} 2J_l \cos 2\pi q l$ is the Fourier transform of the inter-layer interactions, and q_0 gives the maximum of $J(q)$ for the given J_l's.

If the third neighbor interaction J_3 is absent, which is the original ANNNI model, then only q=1/2 and 1/4 phases occupy finite regions at 0 K. As demonstrated in the

EXAFII model, J_3 makes the q=1/3 phase stable at 0 K in the range of $|2J_2+1|<3|J_3|$. To calculate concretely, we set J_3=0.1, hereafter. Figure 2 shows the phase diagram of the weak quantum case: T_1=2.5. The disordered phase transforms into a modulated state with the wave number q, if $|J_2|>0.025$. At low temperature, the commensurate phases with q=3/8, 5/14, 3/10 and 2/7 become stable in addition to q=1/2, 1/3, and 1/4 phases. The incommensurate state is depicted as gray domains.

The phase diagram for T_1=5 is shown in Fig. 3. The incommensurate state reaches down to 0 K, as demonstrated previously in other parameter set of J_1=1, J_2~−1, and J_3~1 [9].

Further increasing T_1, the phase transition disappears in a range of J_2 that satisfies $2J(q)<T_1$, as shown in Fig.4, where T_1=7.15. The commensurate phase of q=1/8 does not appear at all, but domains of commensurate phases of q=5/14, 2/5, and 3/7 are so narrow that they are omitted in Fig. 4.

Discussions

Our free energy Eq, (7) is equivalent to the ANNNI model and the EXAFII model so far as T_1=0 in Eq. (8). However, the order parameter ξ does not saturate unity at 0 K when T_1>0. This is a quantum effect that favors high rank of commensurate and incommensurate states. If T_1 is large enough, the disordered phase spreads down to 0 K, which is a well-known phenomenon as quantum paraelectricity [12, 13].

Among orthorhombic A_2BX_4-type crystals, K_2SeO_4 is a typical ferroelectric compound; the paraelectric (disordered) phase transforms to incommensurate phase with $q=1/3-\delta$, which is followed by the ferroelectric (commensurate) phase of $q=1/3$ [1]. Since there exist many type of transitions in A_2BX_4-type crystals, we

discuss only oxide components hereafter. The phase sequence of K_2SeO_4 can be represented by broken arrow in Fig. 3 (the right side arrow).

On the other hand, Rb_2MoO_4 transforms into the incommensurate phase from the paraelectric phase, however, it never transforms to commensurate phase of $q = 1/3$ [10]. Therefore, the transition sequence can be represented by the left side arrow in Fig. 3. Another type is Rb_2SeO_4 and Cs_2WO_4 which remain paraelectric phase down to 0 K [6, 11]. Such crystals may be represented by an arrow in Fig. 4. Here we fix J_0=2, however, J_0 may change with J_2, then the incommensurate state $0.5 < |J_2| < 1$ can be wiped.

In real A_2BX_4-type crystals, it has been recognized that the coupling between the order parameter and polarization (or stress) generate an additional lock-in energy to stabilize the commensurate phase of $q = 1/3$ or other commensurate phase [1]. Since our model does not consider such lock-in energy explicitly, it may sound crude to apply our model Hamiltonian to real A_2BX_4-type crystals. It should be noted that the microscopic mechanism to stabilize a commensurate state is reflected in the dispersion relation $\omega(q)$ of the normal coordinate $x(q)$, and can be taken into account as we want, if we consider a suitable set of J_l more than third neighbors. However, such complication is out of our present scope. The essential character that quantum effect weakens ordered phases and that the incommensurate phase may persist down to 0 K will not fail.

Acknowledgement

This work was partially supported by a research grant, category A1-2(2015) from the Yamaguchi University Foundation.

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Table 1. The wave number q and the modulation pattern at T=0. The number of Fourier components is called rank.

Rank	Wave Number q	Modulation Pattern at T=0
1	1/2	↑↓
	1/4	↑↑↓↓
2	1/3	↑↓↓
	3/8	↑↓↑↓↓↑↓↑
3	2/5	↑↓↑↓↑
	3/10	↑↓↑↑↓↓↑↓↓↑
4	2/7	↑↓↓↑↑↓↓
	3/7	↑↓↑↓↑↓↑
	5/14	↑↓↑↓↓↑↓↓↑↓↑↑↓↑

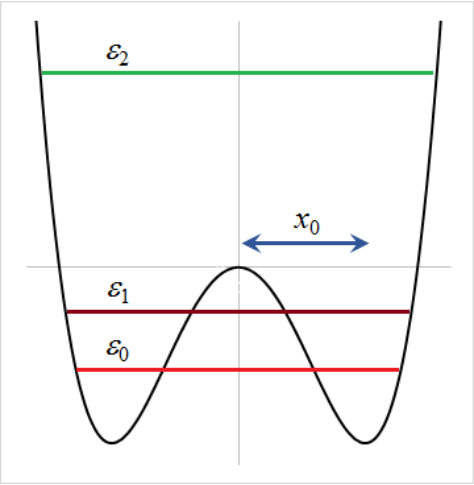
Figure captions

Fig. 1 Schematic picture of a self-potential $V(x)$ and the quantum energy levels. The energy gap $\varepsilon_1-\varepsilon_0=k_BT_1$ is the quantum parameter.

Fig. 2 Phase diagram for T_1=2.5. The fractional number indicates the modulation wave number q. The incommensurate q is shown by filled regions. The commensurate phases with q=3/8, 5/14, 3/10 and 2/7 reach down to 0 K.

Fig. 3 Phase diagram for T_1=5. The incommensurate state reaches down to 0 K.

Fig. 4 Phase diagram for T_1=7.15. The disordered phase reaches down to 0 K around $|J_2|$=0.2~0.3. Commensurate phases q=5/14, 2/5, and 3/7 are omitted, because their regions are so narrow.



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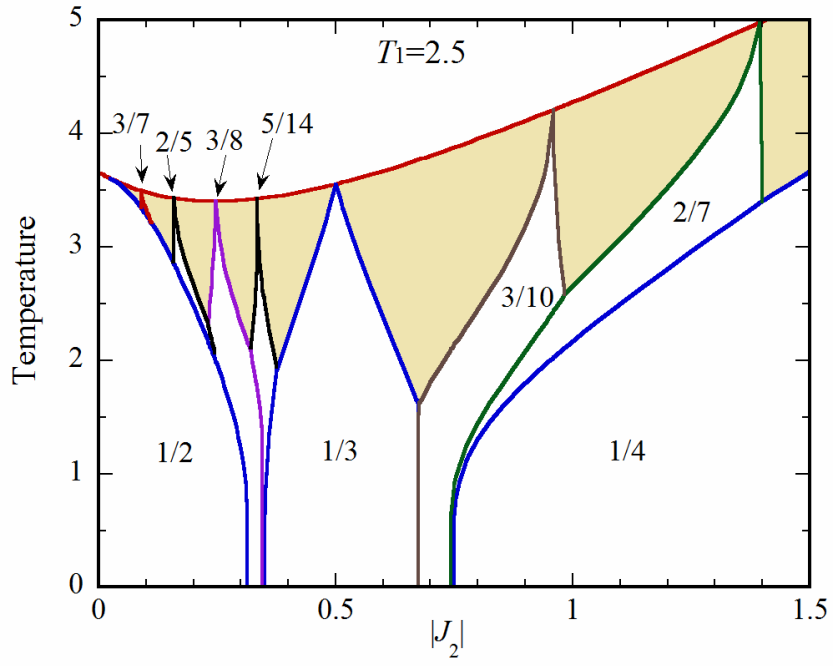

Fig. 2 Phase diagram for T_1=2.5. The fractional number indicates the modulation wave number q. The incommensurate state is shown by filled domain. The commensurate phases with q=3/8, 5/14, 3/10 and 2/7 reach down to 0 K.

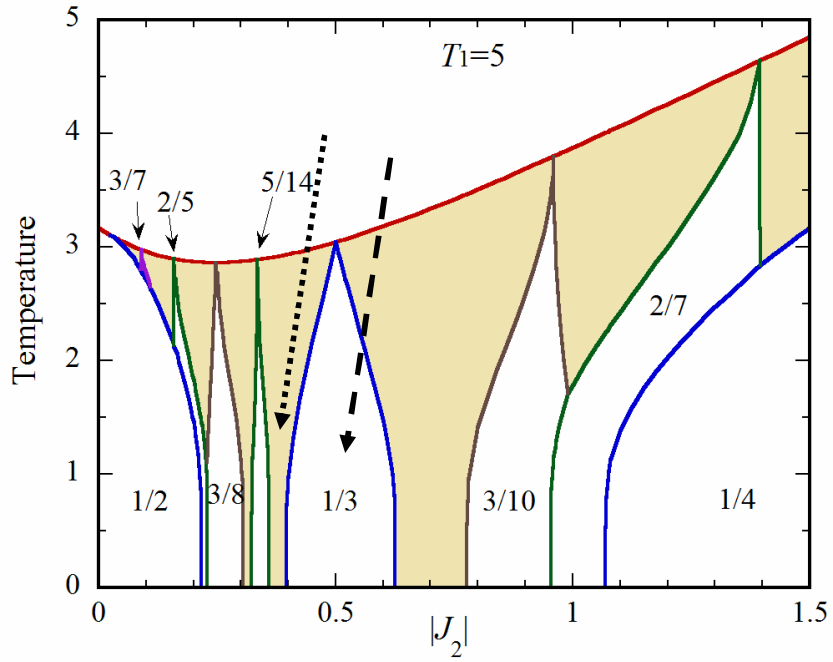

Fig. 3 Phase diagram for T_1=5. The incommensurate state reaches down to 0 K.

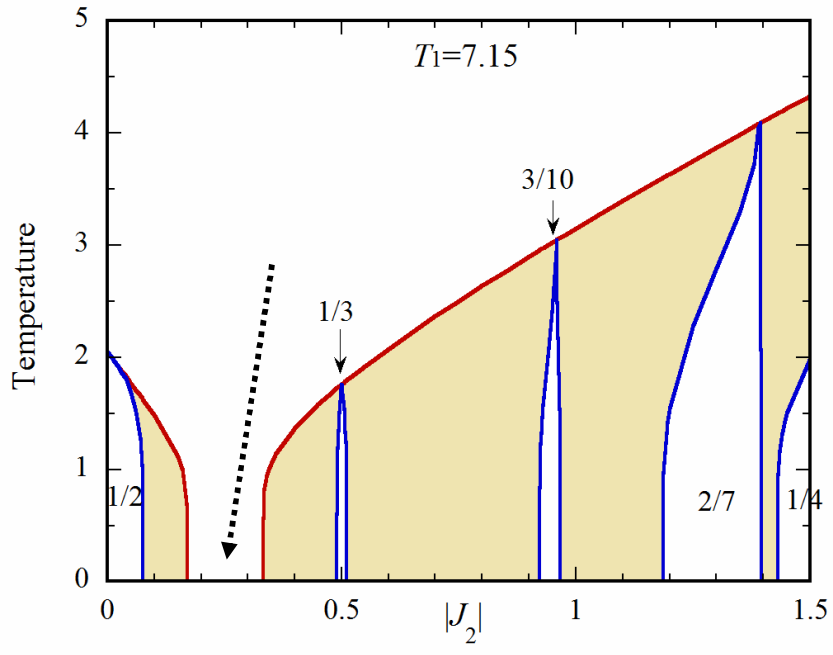

Fig. 4 Phase diagram for T_1=7.15. The disordered phase reaches down to 0 K around $|J_2|$=0.2~0.3. Commensurate phases q=5/14, 2/5, and 3/7 are omitted, because their domains are so narrow.