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Proton induced ferroelastic-superprotonic phase transition in $M_3H(XO_4)_2$

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Abstract

A mechanism of the strain transition in $M_3H(XO_4)_2$, especially in $Rb_3H(SeO_4)_2$, involved in the ferroelastic-superprotonic phase transition is proposed where a coupling between strain and mobile protons plays a crucial role. The two dimensional Kagome lattice on the ab-plane is extracted for proton's pathway, and the pair approximation of the cluster variation method and path probability method is applied to evaluate thermodynamics and proton dynamics: the first-order long-range strain transition and the strain-involved dc-conductivity are qualitatively discussed. Both behaviors suggest the present proposed mechanism of the ferroelatic-superprotonic phase transition.

Keywords: Strain transition of $Rb_3H(SeO_4)_2$; Proton-strain coupling; Proton hopping; CVM; PPM

1. Introduction

So far, different types of ionic conductivity mechanisms have been reported. One is the conventional ion hopping where mobile ions distributed on a sublattice move due to an excitation by thermal phonons as typically seen in α-AgI. The paddle-wheel (cogwheel) mechanism found in the high temperature rotor phase of, for example, fcc Li_2SO_4, is of another type such that cation mobility is enhanced by a strong coupling of cations to the thermally excited rotational motion of translationally immobile sulphate ions [1,2].

It has been reported that $Rb_3H(SeO_4)_2$ crystals exhibit a transition from ferroelastic to superprotonic (paraelastic) phase [3]. The conduction mechanism in the high temperature phase is considered to be associated with the rotation of selenates [4]. Ito and Kamimura [5] proposed a mechanism of proton conduction in the hydrogen-bonded crystals $M_3H(XO_4)_2$ [M=Rb, Cs, X=S, Se] in the high temperature paraelastic phase such that two kinds of defect states $H_2XO_4^{(+e)}$ and $XO_4^{(-e)}$ are formed thermally by breaking of a hydrogen-bond at around 0.26[eV], and the two defect states independently move via a successive proton tunneling among hydrogen bonds. Recently the relaxation of spontaneous strain has been explicitly and quantitatively reported in crystalline $Rb_3H(SeO_4)_2$ [6,7] as well as Tl_2SeO_4 [8], which is related to the ferroelastic and superionic transition. Also it has been confirmed even in the low temperature ferroelastic phase that proton conduction exists [4,7].

On the other hand, the local (short-range) distortion has experimentally been found in the superionic transition process, for example, in CuBr, AgI and PbF_2 materials [9,10]. The mechanism was proposed as that pairs of mobile ions induce a local distortion [11–13]. Quite recently we have preliminary discussed a release of the long-range strain by means of mobile ions in ferroelastic materials and proposed a mechanism of the strain transition [14].

The mobile ions involved in the ferroelastic-superionic phase transitions are H^+ in $Rb_3H(SeO_4)_2$ and Tl^+ ions in Tl_2SeO_4. Thus in this paper, a mechanism of the long-range strain transition and the associated conductivity behavior will be discussed based on the classical hopping, specifically by paying attention to $Rb_3H(SeO_4)_2$.

2. Models and free energy

2.1. Model

Since the electrical conductivities along the a- and b-axes in $Rb_3H(SeO_4)_2$ are about 10^2 times larger than that along the c^*-axis[15], one may consider a two-dimensional model system. Now let us deal with the Kagome lattice on the ab-plane [14], which forms a pathway of protons in hexagonal

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systems of $M_3H(XO_4)_2$ [5]. On this Kagome lattice consisting of three sublattices A, B and C, interacting lattice gas ions (lattice liquid) classically hop, where at ground state the A sublattice is fully occupied and the other two sublattices are empty (Fig. 1). In the model system concerned, we consider a coupling between the order parameter and displacement, and apply the pair approximation of the cluster variation method (CVM) [16,17]. We assume here that the probability of finding protons both on B sublattice and C sublattice is equal.

2.2. Free energy

Now let us introduce a proton-strain coupling. The force exerted on a selenate by protons is given by

$$F_{x(y)} = \sum_{\alpha=A,B,C} K^{\alpha}_{x(y)} x^{\alpha}_1 \tag{1}$$

where $K^{\alpha}_{x(y)}$ is a proportionality constant (Kanzaki force [18,19]) in the $x(y)$-direction, taken parallel to $a_m(b_m)$ axis, respectively, and the superscript α means the sublattice A, B or C shown in Fig. 1. The quantity x^{α}_1 is the probability of finding a proton ($i=1$) on α-site. Then we approximate a triangle by the equilateral triangle to obtain

$$F_x = -\frac{3c}{2}K\xi\ ,\ F_y = \frac{3\sqrt{3}c}{2}K\xi\ ,\ K = K^{\alpha}_{x(y)} \tag{2}$$

in terms of the order parameter

$$\xi = x^A_1 - x^C_1\ ,\ x^C_1 = x^B_1 \tag{3}$$

where $K^{\alpha}_{x(y)}$ is isotropically taken as in Eq. (2) and $c=1/3$ is the proton density per site. In the superprotonic phase at $T>T_c$ in which $\xi=0$, it is naturally assumed that $\boldsymbol{F}=0$. Utilizing Eq. (2), we have the strain energy per unit cell composed of three sites A, B and C:

$$H = 2\left\{\frac{1}{2}\mu(\Delta\boldsymbol{R})^2 - \Delta\boldsymbol{R}\cdot\boldsymbol{F}\right\} \tag{4}$$

where μ is the force constant between a selenate and protons and $\Delta\boldsymbol{R}$ is the associated displacement vector. By minimizing H with respect to $\Delta\boldsymbol{R}$, one has $\Delta\boldsymbol{R}=\boldsymbol{F}/\mu$ and then obtains the equilibrium energy

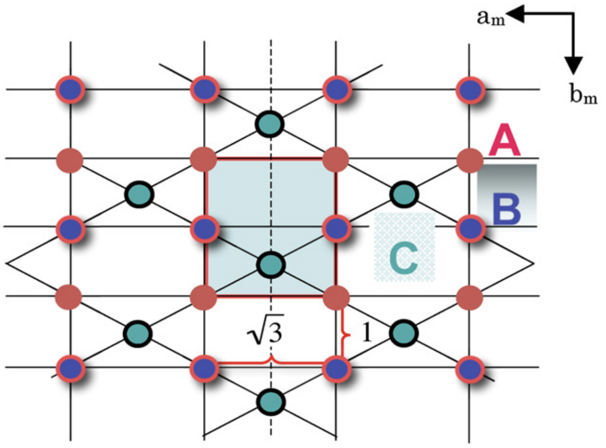

Fig. 1. Kagome lattice in the paraelastic phase.

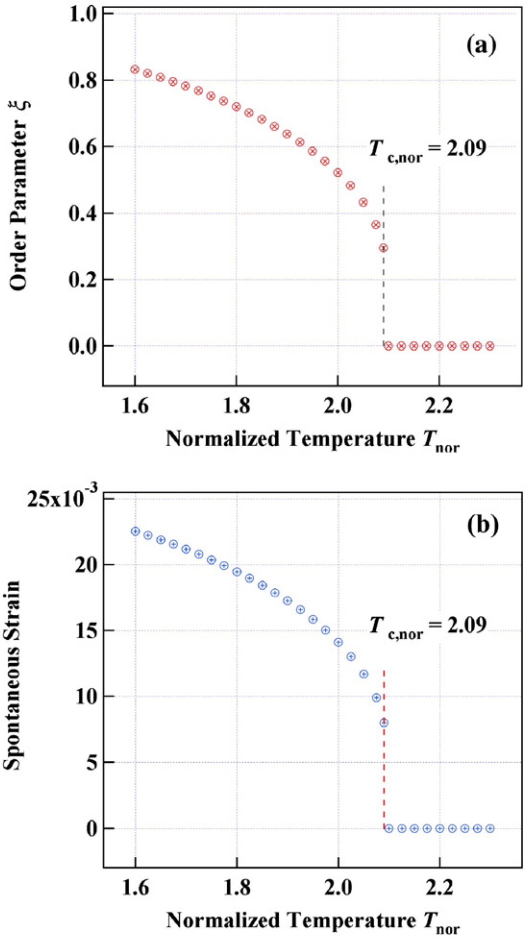

Fig. 2. Temperature dependence of (a) the order parameter and (b) the spontaneous strain: the normalized critical temperature is $T_{c,nor}=2.09$.

$$H = -\varepsilon\frac{1}{2}h\xi^2\ ,\ h = \frac{2K^2}{\varepsilon\mu} \tag{5}$$

with ε being the interaction energy between the nearest neighbor protons.

Now from CVM applied to the Kagome lattice, we have the free energy per unit cell given by

$$f = 2\varepsilon(y^{AB}_{11} + y^{BC}_{11} + y^{CA}_{11}) - k_B T \times\left[3\sum_{\substack{i=1,v\\ \alpha=A,B,C}} L(x^{\alpha}_i) - 2\sum_{\substack{i,j=1,v\\ \alpha\alpha'=AB,BC,CA}} L(y^{\alpha\alpha'}_{ij})\right] - \varepsilon\frac{1}{2}h\xi^2 \tag{6}$$

where $L(x)=x\ln x-x$ and $y^{\alpha\alpha'}_{ij}$ is the pair probability of finding particles i and j on α and α′ nearest neighbor sites, respectively, with $i, j=1$ (proton) and v (vacancy). The first term in the rhs of Eq. (6) is the interaction energy, the second term is the energy related to the entropy due to the on-site and pair probabilities under the temperature $\beta^{-1}=k_BT$ with k_B being the Boltzmann constant, and the last term is exactly the strain energy (Eq. (5)).