A SUB-LATTICE MODEL FOR THE INCOMMENSURATE TRANSITION IN A_2BX_4-TYPE CRYSTALS

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In order to describe a normal-incommensurate transition in A_2BX_4-type crystals, a two-sublattice model is presented, which is modified from the discrete four-sublattice model proposed recently by Ishibashi and Janssen (J. Phys. Soc. Jpn. **69** (2000) 3870). The new model describes the softening of an optical phonon branch connected to an acoustic branch in the extended zone scheme. The dispersion relation of the soft mode in K_2SeO_4 can be reproduced by terms up to the second-neighbor interactions, although the third-neighbor interactions are usually considered to be necessary.

Keywords: two-sublattice model; soft mode; incommensurate transition; A_2BX_4-type crystal

1. INTRODUCTION

The A_2BX_4-type crystals are one of the typical system of the structurally incommensurate phase.[1,2] Among them K_2SeO_4 is a prototype crystal and has been best studied so far.[3] At room temperature it takes an orthorhombic system (*Pmcn*, *Z*=4). The optical phonon branch Λ_2 has a minimum around q~0.7c* in the extended zone scheme. With decreasing temperature, the mode softens and freezes at a general point on the Λ_2 branch, stabilizing the incommensurate phase. [3]

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Other A_2BX_4-type crystals have been investigated carefully whether they have the soft phonon mode at the normal-incommensurate transition. However, no underdamped soft mode has been recognized; only the critical increase of quasi-elastic scattering has been reported in Rb_2ZnBr_4.[4,5] But the amplitude and phase modes, which are characteristic of the incommensurate phase, have been observed to harden at low temperature.[5,6] The transition mechanism in many A_2BX_4-type crystals is expected to be the same as in K_2SeO_4, i.e. the softening of the Λ_2 mode is essential to the incommensurate transition.[7]

The stability of modulated structures was firstly discussed in a competing interactions of the Ising model, four decades ago.[8] Later the same model (named ANNNI model) was fully analyzed to explain the high-order commensurate phases.[9] The ANNNI and the derivative models[10,11] explain the incommensurate-commensurate transitions, but no dynamics can be discussed with the use of the Ising model.

Another type model is the ϕ^4-model, [12] which is a discrete lattice model with fourth-anharmonic terms in addition to next-neighbor interactions. Recently, Ishibashi and Janssen have proposed a new discrete model to describe the lattice instability in A_2BX_4-type crystals.[13] They analyzed the discrete four-sublattice model, and demonstrated that only a nearest-neighbor (n.n.) interaction can induce instability at a general point on the branch around $q \sim 0.7c^*$. It should be noted that such restricted short-range interactions were firstly introduced by Chen and Walker to explain the successive transitions in many A_2BX_4-type crystals.[14]

The observed soft optical branch connects to the acoustic one at zone boundary, and forms a single branch in the extended zone scheme.[3] Since the Ishibashi-Janssen (I-J) model treats only optical modes, it does not explain the whole phonon branches. Here we present a two-sublattice model modified from the I-J model. Our model satisfies the translation symmetry so that the optical branch, connected to the acoustic one at zone boundary, softens as in the case of K_2SeO_4.

2. SUBLATTICE MODEL

The basic structure of A_2BX_4-type crystals consists of two layers, a-b planes perpendicular to the modulation wavenumber along the c-axis.

There are two equivalent atoms on n-th layer, which are denoted by P_n and Q_n. If these variables are interacting through harmonic forces, the total potential energy is given by

$$U=1/2\ \Sigma\ \{\ b\ (P_n-Q_n)^2+\ c\ [(P_n-P_{n+1})^2\ +\ (Q_n-Q_{n+1})^2]\ +\ d\ (Q_n-P_{n+1})^2$$
$$+f\ (P_n-Q_{n+1})^2\ +\ g\ (Q_n-P_{n+2})^2\ +h\ (P_n-Q_{n+2})^2$$
$$+j\ [(P_n-P_{n+2})^2+\ (Q_n-Q_{n+2})^2]\ +k\ [(P_n-P_{n+3})^2+\ (Q_n-Q_{n+3})^2]\ \}\quad (1)$$

Here, parameters *b*, *c* and *d* are the same as -*B*, -*C* and -*D* in the I-J model, where the parameter *A* is arbitrary, but it should be *A*+*B*+2*C*+*D*=0 in order to satisfy the translation symmetry. We also take long-range interactions *g*, *h*, *j* and *k* into account. The schematic picture of the structure is drawn in Fig. 1.

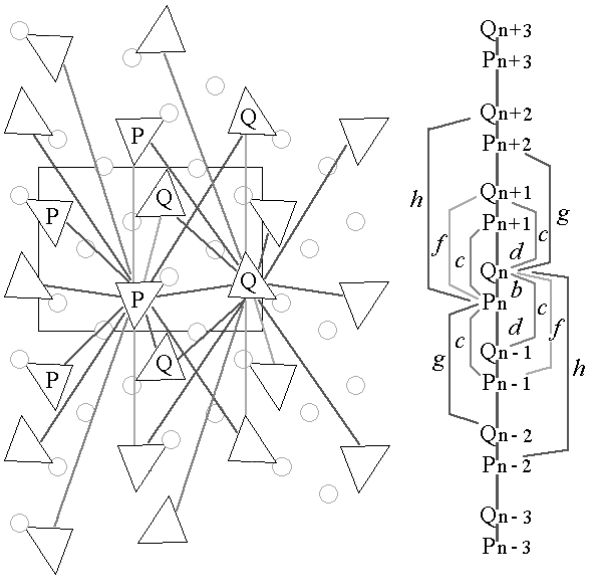

FIGURE 1 A_2BX_4 structure, showing force constants; left is a projection on the bc-plane, right is a projection onto the c-axis (an one-dimensional chain model). The squared box in the left indicates a unit cell. The triangles and circles represent BX_4 and A, respectively.

The Lagrange equation can be written with unit effective mass. The secular equation for the one-dimensional lattice is solved easily;

$$\omega^2=\alpha + |\beta|\ ,\quad \alpha - |\beta|\ , \qquad (2)$$

where

$$\alpha = b+d+f+g+h+2c(1-\cos(q/2))+2j(1-\cos q)+2k(1-\cos(3q/2)), \quad (3)$$

$$\beta = b + d\,e^{-iq/2} + f\,e^{iq/2} + g\,e^{-iq} + h\,e^{iq}\,. \quad (4)$$

The reduced wavenumber q is π at the zone boundary. Since the acoustic phonon should be stable, we impose that $b+d+f+g+h > 0$ and $2(b+d+f+g+h)(c+4j+9k)+bd+bf+dg+fh+4(bg+bh+df)+9(dh+fg)+16gh > 0$.

3. DISPERSION RELATION

In order to get a minimum on the acoustic phonon branch around $q=4\pi/3$ in the extended zone as in the case of K_2SeO_4, $k>0$ or $dh+fg>0$ must be imposed. This means that second- and third-layer interactions j and k are not necessarily important so far as both first-neighbor interaction d (and/or f) and second-neighbor interaction h (and/or g) work enough.

Now we shall show an example of the dispersion relation. Since the modulated phase of A_2BX_4-type crystals retains the n-glide symmetry, we assume a ferrodistortive coupling between P_n and Q_n within a layer, i.e. $b>0$.

For simplicity, let $b=1$ and $j=k=0$. As $dh+fg>0$ is necessary, we simply put $d=h=1$ and $f=g=-0.2$. A calculated dispersion relation is drawn in Fig. 2. The acoustic branch makes anti-crossing with the optical branch, and the optical branch becomes soft as the parameter c decreases (it is easily shown that the frequency vanishes at $c=-0.15$).

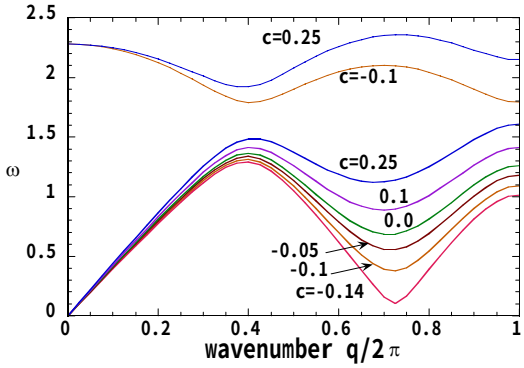

FIGURE 2 Calculated dispersion relation. Parameters are $b=1$, $d=h=1$, $f=g=-0.2$, $j=k=0$ and c is from -0.14 to 0.25.

4. DISCUSSION AND SUMMARY

Now we fit our model to the observed dispersion relation of K_2SeO_4.[3] In order to extract an essence, we select parameters as simple as possible. After some trials, we put c=-0.8, h=1, f=g=j=k=0, and b and d are determined by least-squares calculations. The result is shown in Fig. 3.

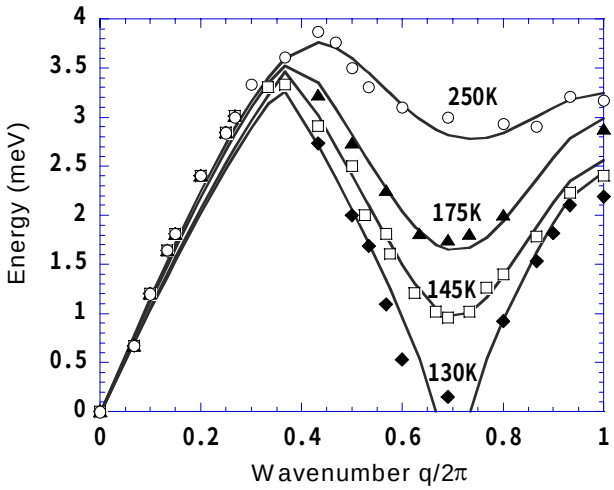

FIGURE 3 Observed dispersion(marks) after Iizumi *et al*.(1977) and the calculated dispersion relation(solid curves) by the two-sublattice model.

Though the fitting for 130K is not so good because of a small number of parameters, the observed dispersion relations are reproduced fairly well over the whole range of the wavenumber.

The fitted parameters are the followings:

T(K)	250	175	145	130
b	9.3	3.9	2.5	1.6
d	6.9	6.1	4.9	4.6

There is a tendency that b and d change with decreasing temperature. Since our model is not a thermodynamical but a dynamical one, we can only assume that the parameters depend on temperature in some way.

Iizumi *et al*.[3] decomposed the observed dispersion relation into Fourier components of the form

$$\omega^2 = \Sigma_{n=1}^{6} F_n \left(1 - \cos (nq/2) \right) . \qquad (5)$$

They found that the effective inter-layer force constants F_1 and F_2 decrease while F_3 increases a little with descending temperature. At about 45K above the transition temperature, F_1 vanishes and decreases further to induce the transition. There has been no explanation of such drastic change of nearest-neighbor interactions.

In our model, no direct interaction between third-neighbors is considered (k=0), and the intra-layer interaction b decreases with temperature mostly. However, it is still positive at the transition. As shown in Fig. 2, the negativity of c also promotes the softening of the branch.

In summary, the two-sublattice model, which reflects the structural character of A_2BX_4-type crystals, can reproduce fairly well the soft phonon branch. The short-range interactions b, c and d (or f) seems to be important. The second-layer interactions g and h (interactions between nearest-neighbor cells) are also indispensable to the incommensurate transition.

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