Vanishing Soft Mode in Phonon Spectrum of Ladder Lattice

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Abstract

A ladder lattice model is studied analytically to understand the coupling between the acoustic and optical phonons. When the optical phonon becomes soft at a Γ-point, the anticrossing between the two branches takes place. In a simple case, the optical spectral intensity vanishes around the anticrossing wave number. The coupled spectral function is not a simple superposition of two damped harmonic forms. It is shown that the off-diagonal component of static susceptibility for the elastic and polar waves is decisive to obtain the correct spectral intensity.

Keywords soft phonon, optical and acoustic branches, anticrossing, dispersion relation, phonon spectrum, ferroelectric transition

1. Introduction

Softening of optical phonon mode at a Γ-point is one of the mechanism to induce ferroelectricity.[1,2] Raman scattering measurements demonstrated that the soft phonon frequency vanished at the ferroelectric transition temperature.[3] Vigorous neutron scattering experiments revealed soft optical branches in 1960's.[4,5] Usually, lattice vibrations have been considered to show a damped harmonic oscillator form, which has been helpful to represent the phonon spectrum.[6]

If the optical mode couples with an acoustic phonon, then the spectral function should be modified. Couplings between elastic and polarization waves were investigated in late 1960's and early 1970's to understand complicated spectra observed in $BaTiO_3$, $PbTiO_3$, $AlPO_4$, KDP and other crystals, especially around the phase transition.[7-12]

On the other hand, interesting dielectric materials called relaxor have been investigated widely. A decade ago, a peculiar behavior was found in the optical phonon spectrum of relaxor; the soft optical branch disappeared in the long wave-length region around the characteristic temperature range of relaxor. This phenomenon was called 'waterfall', because the dispersion relation looked like a waterfall.[13,14] For a few years, it was considered that this is one of the peculiar properties of relaxor. But recently the similar behavior of the optical phonon has been reported in pure crystal $NaNbO_3$,[15] whose dispersion relation resembles that of $KNbO_3$.[16] These facts may suggest that the waterfall-like dispersion is not characteristic in relaxor but may be popular in dielectric crystals under some conditions.

Recently we have studied a coupling between the acoustic and optical phonons in a simple lattice model, called ladder lattice, that can display soft optical phonons.[17] It was found that the spectral intensity of the optical mode vanishes around the anti-crossing with the acoustic branch. Such disappearance of the optical branch has not been discussed previously. In order to investigate what is difference between the previous study and ours, we reinvestigate the ladder lattice model from the point of view of the traditional treatment of the coupling.

2. Ladder Lattice

A unit cell of ladder lattice is composed of two kind of atoms, whose displacements are demoted by u_n and v_n, where n is the number of the cell. The unit cell may be simple or base centered form as shown in Fig. 1(a). Two kinds of atoms are denoted by open and closed circles, respectively. If a transverse wave propagates along the horizontal line and the atomic displacement is in phase within each layer as shown with arrows, then the lattice is equivalent of a linear chain represented in Fig. 1(b). The equations of motion are written as following:

$$\begin{aligned} m\ddot{u}_n &= K_0(v_n - u_n) + K_1(u_{n+1} + u_{n-1} - 2u_n) - m\gamma_1\dot{u}_n \\ M\ddot{v}_n &= K_0(u_n - v_n) + K_2(v_{n+1} + v_{n-1} - 2v_n) - M\gamma_2\dot{v}_n \end{aligned}, \qquad (1)$$

where K_0, K_1 and K_2 are coupling constants, and γ_1 and γ_2 are damping coefficients for mass m and M atoms, respectively. Even if the mass M atom lies at other position in the unit cell, for example at body center, this model can be modified easily.

The dispersion relation consists of two branches; acoustic and optical ones. The optical

frequency at a Γ point,

$$\omega_{\mathrm{opt}}(0)=\sqrt{K_0\left(\frac{1}{m}+\frac{1}{M}\right)} \tag{2}$$

may be lower than the zone boundary frequency of the acoustic branch, if the coupling K_0 between the two kinds of atoms is small enough. Then the anticrossing between optical and acoustic branches may happen.

In our previous paper, we used the phonon normal coordinates as representative variables to represent spectral function. Here let's consider the coordinate of the center of mass and the relative coordinate which are defined as

$$X_n=\frac{mu_n+Mv_n}{m+M},\quad x_n=\frac{\sqrt{mM}}{m+M}\left(u_n-v_n\right). \tag{3}$$

Assuming the periodic boundary condition, we perform the Fourier transformation of (1) and (3) as $X_n=\frac{1}{\sqrt{N}}\sum_q X_q\, e^{2\pi iqn}$, $x_n=\frac{1}{\sqrt{N}}\sum_q x_q\, e^{2\pi iqn}$, and obtain the following equations;

$$\begin{aligned}&\ddot{X}_q+\Gamma_{\mathrm{a}}\dot{X}_q+\omega_{\mathrm{a}}{}^2X_q+\Gamma_{\mathrm{ao}}\dot{x}_q+\Delta x_q=0\\&\ddot{x}_q+\Gamma_{\mathrm{o}}\dot{x}_q+\omega_{\mathrm{o}}{}^2x_q+\Gamma_{\mathrm{oa}}\dot{X}_q+\Delta X_q=0\end{aligned}. \tag{4}$$

Here, the wave number dependent coefficients are defined as;

$$\omega_{\mathrm{a}}{}^2=\frac{4(K_1+K_2)\sin^2\pi q}{m+M}, \tag{5}$$

$$\omega_{\mathrm{o}}{}^2=K_0\left(\frac{1}{m}+\frac{1}{M}\right)+\frac{4(K_1M^2+K_2m^2)\sin^2\pi q}{(m+M)mM}, \tag{6}$$

$$\Delta=4\frac{(K_1M-K_2m)\sin^2\pi q}{(m+M)\sqrt{mM}}, \tag{7}$$

$$\Gamma_{\mathrm{a}}=\frac{m\gamma_1+M\gamma_2}{m+M},\quad \Gamma_{\mathrm{o}}=\frac{M\gamma_1+m\gamma_2}{m+M},\quad \Gamma_{\mathrm{ao}}=\Gamma_{\mathrm{oa}}=\frac{(\gamma_1-\gamma_2)\sqrt{mM}}{m+M}. \tag{8}$$

Eqs. (5) and (6) give bare acoustic and optical phonon frequencies, respectively, if the coupling coefficient (7) is neglected. Figure 2 demonstrates the dispersion relation when the damping terms are neglected. The broken lines indicate (5) and (6); uncoupled dispersion. When the coupling coefficient (7) works, the anticrossing of the acoustic and optical branches

can be recognized as shown by solid curves.

3. Spectral Function

The neutron (or light) scattering intensity by phonon is represented with the use of the relaxation function as[18]

$$I(q,\omega) \propto \sum_{\mu,\nu} f_\mu f_\nu \,\mathrm{Re}\,\Xi_{\mu\nu}(q,\omega) \quad , \tag{9}$$

where the dynamical structure factor f_μ of mode μ is given explicitly as the following;

$$f_X = b_1 e^{-W_1} + b_2 e^{-W_2} \quad \text{and} \quad f_x = \sqrt{\frac{M}{m}} b_1 e^{-W_1} - \sqrt{\frac{m}{M}} b_2 e^{-W_2} \,. \tag{10}$$

Here b_1, W_1 and b_2, W_2 are the neutron scattering length and the Debye-Waller factor of atoms of mass *m* and *M*, respectively.

The Laplace transformation of the relaxation function of *X* and *x*, for example, is defined as

$$\Xi_{Xx} = \int_0^\infty dt\, e^{-i\omega t} \left\langle X_q(t) x_{-q}(0) \right\rangle . \tag{11}$$

From the Langevin-type eq. (4), we obtain the following relation for the relaxation functions;

$$\begin{aligned} &\begin{pmatrix} {\omega_a}^2 - \omega^2 + i\omega\Gamma_a & \Delta + i\omega\Gamma_{ao} \\ \Delta + i\omega\Gamma_{oa} & {\omega_o}^2 - \omega^2 + i\omega\Gamma_o \end{pmatrix} \begin{pmatrix} \Xi_{XX} & \Xi_{Xx} \\ \Xi_{xX} & \Xi_{xx} \end{pmatrix} = \\ &\qquad = \begin{pmatrix} i\omega + \Gamma_a & \Gamma_{ao} \\ \Gamma_{oa} & i\omega + \Gamma_o \end{pmatrix} \begin{pmatrix} \left\langle XX^* \right\rangle & \left\langle Xx^* \right\rangle \\ \left\langle xX^* \right\rangle & \left\langle xx^* \right\rangle \end{pmatrix} \end{aligned} \,. \tag{12}$$

Here

$$\left\langle XX^* \right\rangle \equiv \left\langle X_q X_{-q} \right\rangle, \quad \text{etc.} \tag{13}$$

are the static susceptibility, and are calculated exactly for the ladder model. It is easily shown that the off-diagonal component $\left\langle Xx^* \right\rangle$ is vanishing at a Γ-point, however, the term makes an important effect on the spectral function if the anticrossing between the acoustic and optical branches takes place.

The contour maps of the scattering intensity are plotted in Fig. 3. The model parameters are m=1, M=2, K_1 =0.05, K_2 =2, γ_1 =0.2, γ_2 =0.15, b_1 =2, b_2 =1 and $W_1 = W_2$ =0. With decreasing K_0, the optical frequency $\omega_{\mathrm{opt}}(0)$ decreases with eq. (2). The anticrossing

between two branches takes place at a wave number q_x, around where the optical phonon intensity disappears. If the optical phonon is soft enough at a Γ-point, the weak optical mode is immersed under the wing of the acoustic branch; however, optical phonon exists anyhow.

4. Discussions

In the above calculation, we chose (2) as the representative variables. These coordinates correspond to the elastic and polarization waves in the traditional theories. Another choice of variables is phonon normal coordinates $Q_q(1)$ and $Q_q(2)$ as in our previous paper.[17] The similar relation holds for the relaxation function

$$\Xi_{\mu\nu}(q,\omega) = \int_0^\infty dt\, e^{-i\omega t} \left\langle Q_q^{(\mu)}(t) Q_{-q}^{(\nu)}(0) \right\rangle \tag{14}$$

as

$$\begin{pmatrix} \omega(1)^2 - \omega^2 + i\omega\Gamma_{11} & i\omega\Gamma_{12} \\ i\omega\Gamma_{21} & \omega(2)^2 - \omega^2 + i\omega\Gamma_{22} \end{pmatrix} \begin{pmatrix} \Xi_{11} & \Xi_{12} \\ \Xi_{21} & \Xi_{22} \end{pmatrix} = \\ = \begin{pmatrix} i\omega + \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & i\omega + \Gamma_{22} \end{pmatrix} \begin{pmatrix} \left\langle \left| Q^{(1)} \right|^2 \right\rangle & 0 \\ 0 & \left\langle \left| Q^{(2)} \right|^2 \right\rangle \end{pmatrix} . \tag{15}$$

The equation form of (12) and (15) are similar, but (15) is simpler because the last matrix of the right hand side is diagonal. The explicit matrix elements in (15) have been given in our previous paper.

Since these two set of coordinates are related by linear transformation with each other, and the dynamical equation (1) is linear on the coordinates, we can expect the same spectral intensity for both formulations. This is true, and we get the same spectral intensity both from (12) and (15), so far as the off-diagonal element in the right hand side of (12) is taken into account.

However, if the off-diagonal component $\langle Xx^* \rangle$ in (12) is neglected, the spectral intensity differs a little. A numerical result is demonstrated in Fig. 4. The left figure is the correct intensity contours given from either (12) or (15). But the right one is calculated by omitting the off-diagonal component $\langle Xx^* \rangle$. The dispersion frequencies manifested by the ridge lines

are almost identical with each other formulations. The distinguished difference is the vanishing intensity of the optical branch around the anticrossing wave number.

As shown in the previous paper, vanishing optical intensity stems from the wave number dependence on the oscillator strength $f_2(q)$ of the optical mode in (9);

$$f_2(q) = -\frac{b_1}{\sqrt{m}} e^{-W_1} \sin\theta + \frac{b_2}{\sqrt{M}} e^{-W_2} \cos\theta \,, \tag{16}$$

where $\sin\theta$ and $\cos\theta$ are the matrix elements to diagonal the original bilinear equation (1) into the normal coordinates of phonons. On the other hand, f_x given by (10) is a constant. Therefore the coupling between X and x through the off-diagonal element $\langle Xx^* \rangle$ in (9) should not be neglected except for a Γ-point where $\langle Xx^* \rangle$=0, if the optical branch anticrosses with the acoustic branch.

The anticrossing point in our ladder lattice is a wave number that satisfies[17]

$$-\frac{\sin\theta}{\sqrt{m}} + \frac{\cos\theta}{\sqrt{M}} = 0 \,, \tag{17}$$

so the vanishing of the optical phonon intensity does not coincide exactly with the anticrossing. It depends on scattering lengths and Debye-Waller factors, however, the lengths and factors usually take the same order of magnitude. Therefore we could expect that the optical phonon intensity may vanish around the anticrossing point. Of course the expression (16) depends on the unit cell structure in actual crystals.

Any way, in order to obtain the soft phonon frequency experimentally, the fitting function must be carefully considered, if the soft optical mode anticrosses with the acoustic mode, as in the case of ferroelectric transition of displacive-type character. The waterfall-like spectra in some perovskite crystals will be explicitly investigated in near future.

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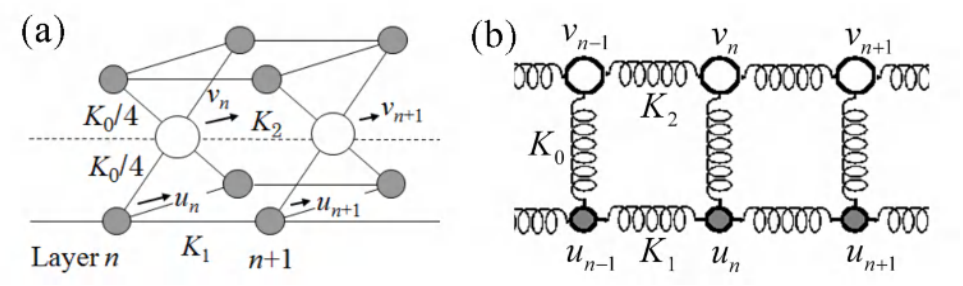

Figure 1. Unit cell of ladder lattice; a three dimensional image (a) and a one dimensional image (b).

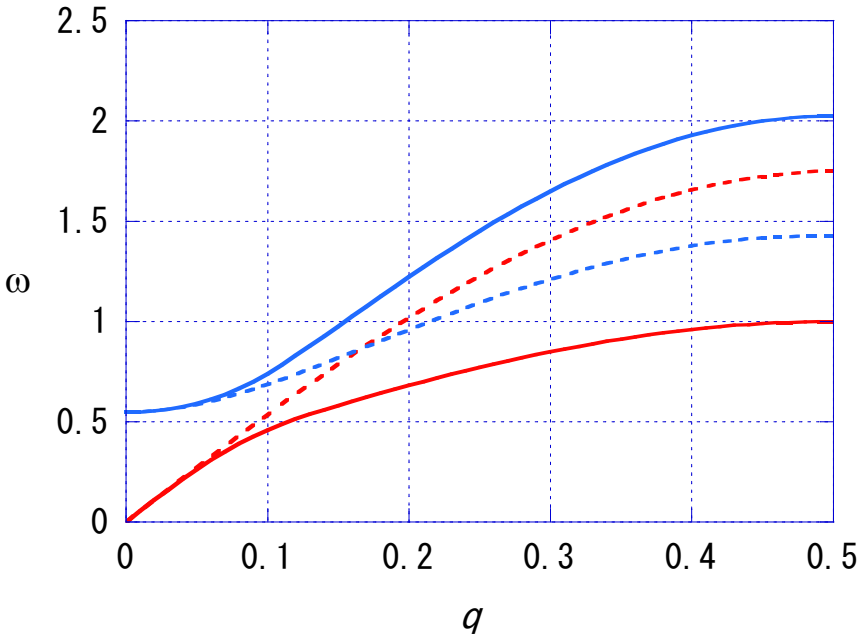

Figure 2. Dispersion relation of ladder lattice. Solid lines represent the acoustic and optical phonon branches for parameters m=1, M=2, K_0=0.1, K_1=0.2 and K_2=2. Broken lines show the uncoupled dispersions ω_a and ω_o calculated without the Δ term in (4).

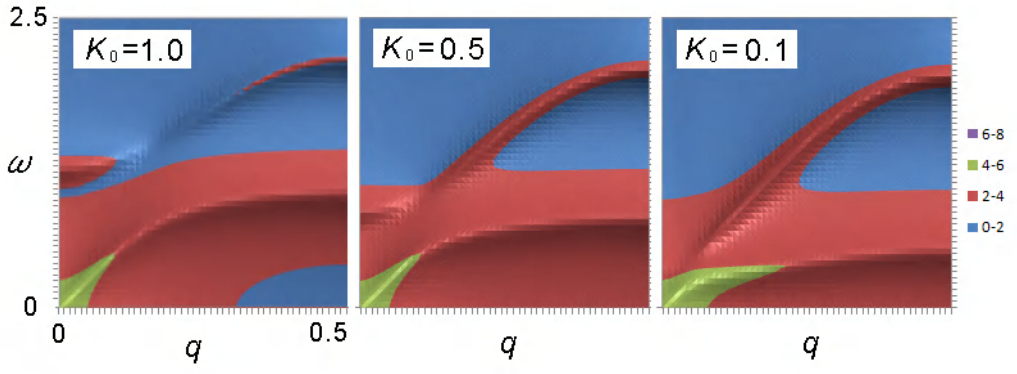

Figure 3. Contour map of spectral intensity for the ladder lattice model. Log-scaled intensity is shown for parameters m=1, M=2, K_1=0.05, K_2=2, γ_1=0.2, γ_2=0.15, b_1=2, and b_2=1. When $K_0 \le 0.1$, the optical branch with small wave number q<0.1 disappears under the wing of the acoustic branch.

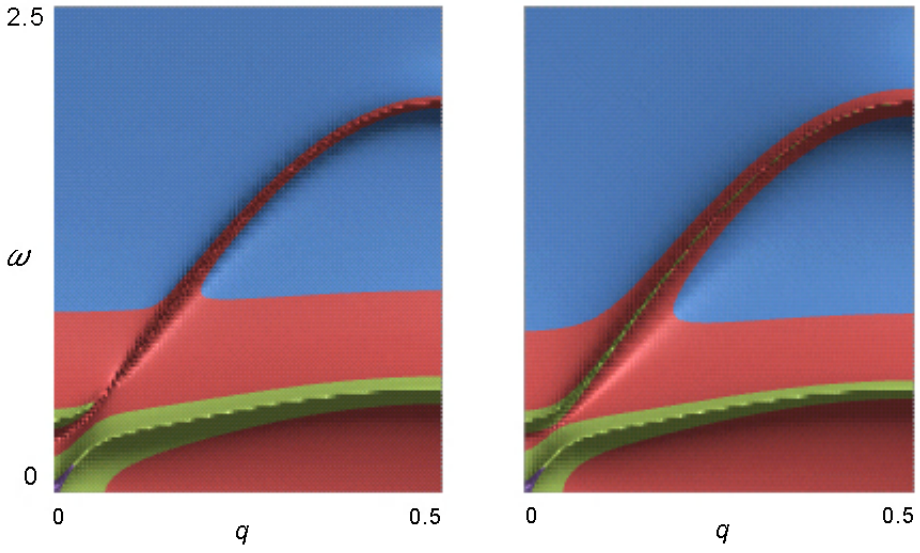

Figure 4. Contour map of the spectral intensity. The optical branch disappears around $q_x \cong 0.05$ if the coupling is properly taken into account (left), however, no anomaly is manifested without coupling (right). The model parameters are m=1, M=2, K_0=0.1, K_1=0.05, K_2=2, and $\gamma_1=\gamma_2$=0.05 (small damping terms are assigned to demonstrate phonon branches sharply).