Ladder Lattice Model of Soft Optical Phonon

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A linear lattice model for demonstrating a soft optical mode at a zone center is proposed. The unit cell consists of only two atoms. If the optical mode is sufficiently soft, anticrossing takes place between the optical and acoustic phonon branches. By using the generalized Langevin's equation method, the spectral function is calculated analytically. The intensity of the optical mode disappears at approximately the anticrossing wave number. In general, the spectral line shape of the optical mode is asymmetric because of the interaction between the two branches.

KEYWORDS: soft mode, anticrossing, acoustic and optical branch, dispersion relation, phonon spectrum, ferroelectric phase transition

1. Introduction

The concept of a soft-phonon mode has been introduced to explain ferroelectric and structural phase transitions.[1)] If an optical phonon freezes at a zone center, then the atomic configuration in a unit cell changes to induce ferroelectric or ferroelastic phases. Many examples have been found in perovskite crystals such as $PbTiO_3$ and $KNbO_3$.[2,3)]

An optical branch can be well understood using the two-atom lattice model described in standard textbooks of solid state physics.[4)] The dispersion relation of an optical branch is maximum at a zone center; therefore, such a model cannot describe ferroelectric phase transition.

On the other hand, the freezing of a phonon branch at a zone boundary or a general position in a Brillouin zone may be realized if interactions beyond second-nearest neighboring atoms are introduced. A typical example was observed at the normal- incommensurate transition in K_2SeO_4[5)] and related crystals.[6)]

Nowadays, computer programs can easily demonstrate phonon branches on the basis of first-principles calculations.[7)] However, an analytically tractable model will help us to understand the physical picture of soft modes. Here, another two-atom lattice model for demonstrating a soft optical mode at a zone center is proposed. Its dispersion relation is

shown in an analytical equation. Its spectral function is calculated with the addition of friction terms to the model's dynamic equations. Instead of the simple damped harmonic oscillator model, generalized Langevin's equations are considered in constructing a phonon spectrum. [8,9]

2. Model and Equations of Motion

Two atoms with masses m (closed circles) and M (open circles) exist in a cell; they interact with a spring whose constant is $K_0/2$, as shown in Fig. 1. Let us consider a transverse motion perpendicular to the chains denoted by solid and broken lines, and assume that deviations from equilibrium positions are the same within each layer. Since the projection on each chain takes a ladder form, as shown in Fig. 1(b), we call this model a ladder lattice.

The atomic vibration in the n-th layer from equilibrium positions is described by u_n and v_n. The equations of motion are as follows:

$$m\ddot{u}_n = K_0(v_n - u_n) + K_1(u_{n+1} + u_{n-1} - 2u_n), \tag{1}$$

$$M\ddot{v}_n = K_0(u_n - v_n) + K_2(v_{n+1} + v_{n-1} - 2v_n). \tag{2}$$

Under the periodic boundary condition with N unit cells, the solution takes the following forms:

$$u_n = \frac{1}{\sqrt{m}}\xi_q \exp(i2\pi qn), \quad v_n = \frac{1}{\sqrt{M}}\eta_q \exp(i2\pi qn) \quad , \tag{3}$$

where q is the reduced wave number. Then, eqs. (1) and (2) are written as

$$\frac{d^2}{dt^2}\begin{pmatrix}\xi_q \\ \eta_q\end{pmatrix} + \begin{pmatrix}V_{11} & V_{12} \\ V_{21} & V_{22}\end{pmatrix}\begin{pmatrix}\xi_q \\ \eta_q\end{pmatrix} = 0 \quad . \tag{4}$$

Here, the dynamical matrix V is symmetric and the elements are given by

$$\begin{aligned} V_{11} &= \frac{1}{m}\{K_0 + 2K_1(1-\cos 2\pi q)\}, \quad V_{12} = V_{21} = -\frac{K_0}{\sqrt{mM}}, \\ V_{22} &= \frac{1}{M}\{K_0 + 2K_2(1-\cos 2\pi q)\}. \end{aligned} \tag{5}$$

The two frequencies

$$\omega^2(\nu) = \frac{V_{11}+V_{22}}{2} \mp \sqrt{\left(\frac{V_{11}-V_{22}}{2}\right)^2 + V_{12}V_{21}} \tag{6}$$

correspond to the acoustic and optical dispersion relations, respectively. At a zone center, the acoustic and optical frequencies are given by

$$\omega(1) \cong \sqrt{\frac{K_1 + K_2}{m + M}}\, 2\pi q \qquad \text{and} \qquad \omega(2) \cong \sqrt{\frac{(m+M)K_0}{mM}}\,, \tag{7}$$

respectively. Therefore, the optical frequency $\omega(2)$ at a zone center vanishes with decreasing spring constant, K_0. Typical dispersion relations are plotted in Fig. 2, where only K_0 is varied while the masses m and M and the other spring constants K_1 and K_2 are fixed. In the ladder model, the optical branch always has a minimum at a zone center. When $K_0 \le 2$, for the given numerical parameters in Fig. 2, the minimum of the optical branch becomes lower than the maximum of the acoustic branch at a zone boundary.

Generally, atoms vibrate within the anharmonic potential of a real crystal. Some anharmonic models have demonstrated that optical mode frequency softens as temperature decreases because of the temperature dependence of effective restoring force.[10,11,12] Thus, we may consider that spring constant depends on temperature or pressure. Thus, the K_0 dependence of the dispersion relation in Fig. 2 may simulate some characteristics of the soft-phonon mode in dielectric crystals.

The normalized eigenvector of the dynamical matrix V can be set to real quantities in the ladder model:

$$\begin{aligned} t_{11} &= t_{22} = \left(V_{22} - \omega(1)^2\right)\!/\zeta \equiv \cos\theta \\ t_{21} &= -t_{12} = -V_{21}/\zeta \equiv \sin\theta \end{aligned}\,, \tag{8}$$

where $\zeta = \sqrt{\left(-\omega(1)^2 + V_{22}\right)^2 + |V_{21}|^2}$. Using these transform matrix elements, we can write the general solutions for eqs. (1) and (2) as follows:

$$u_n = \frac{1}{\sqrt{mN}} \sum_{q,\nu} t_{1\nu} Q_q^{(\nu)} \exp(i2\pi qn)\,,\quad v_n = \frac{1}{\sqrt{MN}} \sum_{q,\nu} t_{2\nu} Q_q^{(\nu)} \exp(i2\pi qn)\,. \tag{9}$$

Here, $Q_q^{(\nu)}$ is the phonon normal coordinate belonging to the ν branch. In terms of phonon coordinates, the Hamiltonian can be represented in diagonal form, and the thermal expectation value is

$$\left\langle |Q_q^{(\nu)}|^2 \right\rangle = \frac{k_B T}{\omega(\nu)^2} \tag{10}$$

in a classical system. Here, k_B is the Boltzmann constant and T is the temperature. The phonon frequency $\omega(\nu)$ depends on the wave number q through eqs. (5) and (6).

Let us denote $u_q^{(\nu)}$ and $v_q^{(\nu)}$ as the Fourier amplitudes of the ν branch. At a zone center, the amplitude ratios are $u_0^{(1)} = v_0^{(1)}$ and $u_0^{(2)}/v_0^{(2)} = -M/m$. Calculating the dispersion relations in various cases, we can find that the curvatures of the two branches

repulsively change with each other, so that the separation between the two branches takes a minimum (see K_0=1 and 0.1 in Fig. 2). Such cases are realized for a small K_0 and a small K_1 (under the condition of $m<M$; otherwise, for a small K_2) . This phenomenon is understood from the fact that uncorrelated acoustic and optical branches cross and anticrossing takes place at a wave number q_x in a Brillouin zone, since the two branches have the same symmetry in our model. We observe that the optical mode strength

$$f_q^{(2)} = -\sin\theta/\sqrt{m} + \cos\theta/\sqrt{M} \propto u_q^{(2)} + v_q^{(2)} \qquad (11)$$

vanishes at q_x, i.e., $u_q^{(2)} / v_q^{(2)} = -1$ at the anticrossing point. For $q < q_x$, a light atom has a larger optical mode amplitude than a heavy atom, while a heavy atom has a larger amplitude for $q > q_x$.

3. Spectral Function

Experimentally, the dispersion relations of a phonon are determined by neutron inelastic scattering; thus, we consider the scattering intensity for the scattering vector K: [13,14]

$$I(K,\omega) \propto \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{j,l} b_j b_l^{*} e^{-W_j - W_l} \sum_{n,n'} e^{iK(r_j(n) - r_l(n'))} \left\langle K\cdot u_j(n,t) K\cdot u_l(n',0)\right\rangle, \quad (12)$$

where b_j and W_j are the scattering length and the Debye-Waller factor of atom j, respectively. Substituting eq. (9) to eq. (12), and summing n and n' over N cells, we obtain the scattering intensity for a reduced wave number q as

$$I(q,\omega) \propto \sum_{j,l} \hat{b}_j \hat{b}_l^{*} \sum_{\nu,\mu} \left(K\cdot t_{j\nu}(q)\right)\left(K\cdot t_{l\mu}(-q)\right) S_{\nu\mu}(q,\omega)\Delta(K+q). \qquad (13)$$

Here, the Laue functioṇ Δ imposes $K+q$ to be some reciprocal vector, $\hat{b}_j = b_j e^{-W_j + iKr_j} \Big/ \sqrt{m_j}$ is the scattering factor for atom j, and the spectral function is defined as

$$S_{\nu\mu}(q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \left\langle Q_q^{(\nu)}(t) Q_{-q}^{(\mu)}(0)\right\rangle. \qquad (14)$$

This function can be given by the Laplace transformation of the relaxation function[15]

$$\Xi_{\nu\mu}(q,\omega) = \int_0^{\infty} dt e^{-i\omega t} \left\langle Q_q^{(\nu)}(t) Q_{-q}^{(\mu)}(0)\right\rangle \qquad (15)$$

as follows:

$$S_{\nu\mu}(q,\omega) = \frac{1}{2\pi}\left\{\Xi_{\nu\mu}(q,\omega) + \Xi_{\mu\nu}^{*}(q,\omega)\right\}. \qquad (16)$$

This quantity is directly related to dynamical susceptibility as

$$\mathrm{Re}\,\chi(q,\omega) = \chi(q) - \omega\,\mathrm{Im}\,\Xi(q,\omega) \quad \text{and} \quad \mathrm{Im}\,\chi(q,\omega) = \omega\,\mathrm{Re}\,\Xi(q,\omega). \qquad (17)$$

If a Hamiltonian is diagonal in phonon coordinates, phonons do not couple any more, and the damped harmonic oscillator may be a reasonable assumption when mode damping works:

$$\Xi_{\nu\mu}(q,\omega) = \frac{(i\omega + \Gamma_q)}{i\omega(i\omega + \Gamma_q) + \omega_q(\nu)^2} \left\langle | Q_q{}^{(\nu)} |^2 \right\rangle \delta_{\nu\mu}. \tag{18}$$

In real systems, anharmonic interactions of lattice vibration as well as the coupling with other degrees of freedom introduce linewidth into the spectra. In order to consider damping effects, we add the velocity-dependent friction terms $-m\gamma_1 \dot{u}_n$ and $-M\gamma_2 \dot{v}_n$ to the dynamic equations (1) and (2), respectively. Substituting eq. (9), we obtain the following Langevin's equation:

$$\left\{ \frac{d^2}{dt^2} + \mathrm{T} \begin{pmatrix} \gamma_1 & 0 \\ 0 & \gamma_2 \end{pmatrix} \widetilde{\mathrm{T}} \frac{d}{dt} + \begin{pmatrix} \omega(1)^2 & 0 \\ 0 & \omega(2)^2 \end{pmatrix} \right\} \begin{pmatrix} Q^{(1)} \\ Q^{(2)} \end{pmatrix} = \begin{pmatrix} f_1 \\ f_2 \end{pmatrix}. \tag{19}$$

where f_j is the random force, which satisfies $\left\langle Q^{(\nu)} f_j \right\rangle = 0$. The elements of the transform matrix T are given by eq. (8), and $\widetilde{\mathrm{T}}$ is the transposed matrix of T. By performing the Laplace transformation eq. (15) and performing partial integrating, we obtain the following equation for Ξ:

$$\begin{pmatrix} -\omega^2 + \omega(1)^2 + i\omega\Gamma_{11} & i\omega\Gamma_{12} \\ i\omega\Gamma_{21} & -\omega^2 + \omega(2)^2 + i\omega\Gamma_{22} \end{pmatrix} \Xi(\omega) = \begin{pmatrix} i\omega + \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & i\omega + \Gamma_{22} \end{pmatrix} \begin{pmatrix} \left\langle | Q^{(1)} |^2 \right\rangle & 0 \\ 0 & \left\langle | Q^{(2)} |^2 \right\rangle \end{pmatrix}. \tag{20}$$

Here, the damping matrix is given as

$$\Gamma_{11} = \gamma_1 \cos^2\theta + \gamma_2 \sin^2\theta, \quad \Gamma_{12} = \Gamma_{21} = \left(-\gamma_1 + \gamma_2\right)\cos\theta \sin\theta, \quad \Gamma_{22} = \gamma_1 \sin^2\theta + \gamma_2 \cos^2\theta. \tag{21}$$

Furthermore we put $\left\langle Q^{(1)} Q^{(2)*} \right\rangle = 0$, because the Hamiltonian of the dynamic system is diagonal in terms of *Q*.

For our ladder model with two types of atom, the concrete form of scattering intensity is written as

$$I(q,\omega)/K^2 \propto \left(\hat{b}_1 \cos\theta + \hat{b}_2 \sin\theta\right)^2 S_{11}(q,\omega) + \left(-\hat{b}_1 \sin\theta + \hat{b}_2 \cos\theta\right)^2 S_{22}(q,\omega) + 2(\hat{b}_1 \cos\theta + \hat{b}_2 \sin\theta)(-\hat{b}_1 \sin\theta + \hat{b}_2 \cos\theta) S_{12}(q,\omega). \tag{22}$$

Hereafter, the scattering vector *K* is the component parallel to the atomic displacement.

Some typical scattering intensities, $I(q,\omega)/(k_B T K^2)$, are shown in Fig. 3 for a set of wave

numbers, q. The parameters are m=1, M=2, K_0=0.5, K_1=0.5, K_2=2, $\gamma_1 = \gamma_2 = 0.05$ and b_1=b_2=1, and the Debye-Waller factors are neglected, that is, W_1=W_2=0. The acoustic phonon branch is rather strong, and the optical phonon branch is weak. The peak positions correspond to the dispersion curve given by eq. (6) in weak-damping cases.

4. Discussion and Summary

In this report, we have demonstrated that a soft optical branch can be represented by the ladder lattice model. The dispersion relation is easily calculated analytically. The spectral function has been evaluated from the damped oscillator equations with the generalized Langevin's equation method. If the damping factors are the same, i.e., $\gamma_1 = \gamma_2$, then the dynamical equations can be diagonalized using the transform matrix T directly. Scattering intensity is just a superposition expressed as eq. (18).

Here, we comment on the scattering intensity of the optical mode. Figure 4 shows the line shape of the optical mode around the anticrossing point. The parameters in Fig. 4 are similar to those in Fig. 3, but the damping constants are assumed to be $\gamma_1 = \gamma_2 = 0.01$, in order to show the peaks sharply. With increasing wave number q, the mode strength of the optical mode of eq. (11) changes from negative to positive at q_x=1/6, for the given parameters. In the case of b_1=b_2, the coefficient $-\hat{b}_1 \sin\theta + \hat{b}_2 \cos\theta$ in (22) vanishes at q_x. The optical mode intensity disappears even if an optical phonon exists. Generally, the scattering lengths b_1 and b_2 are different; thus, the disappearance of optical mode intensity takes place at approximately q_x.

Although the line shapes in Fig. 4 seem symmetric, unbalanced damping parameters bring asymmetry in line shapes, which is shown in Fig. 5 for the same parameters except the unbalanced damping parameters. This is another effect of the anticrossing of the acoustic and optic branches in the ladder lattice model.

In the past, a number of experiments on and theories of the soft optical and acoustic mode couplings were published.[16,17] Relations similar to eq. (20) were used to explain experimental results. However, in many cases, the off-diagonal elements on the right-hand side of eq. (20) were set to zero.[17] Furthermore, the wave number dependence of the matrix element Γ_{ij} was often neglected. These approximations made the spectral function tractable to fit experimental data; however, they are reasonable only around a zone center. If mode mixing occurs at a general point in the reciprocal lattice, the wave number dependence of transform matrix elements should be taken into account. Since our model is simple, it will help us to understand

the significance and limit of the various approximations of mode coupling systems.

Recently, a unique phenomenon has been reported in $NaNbO_3$. [18] A soft optical branch drops sharply at a general wave number in reciprocal space and disappears with decreasing wave number. Such a phenomenon has been observed in relaxor ferroelectrics, and is called a waterfall.[19] Although our model may be too simple to explain real systems, especially relaxor crystals, our model suggests that a waterfall-like phenomenon appears in a pure crystal if anticrossing takes place and the damping is sufficiently strong. When an optical mode becomes soft and anticrosses with an acoustic branch, careful treatments are highly expected to reduce the dispersion relations.

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Figures 1-5

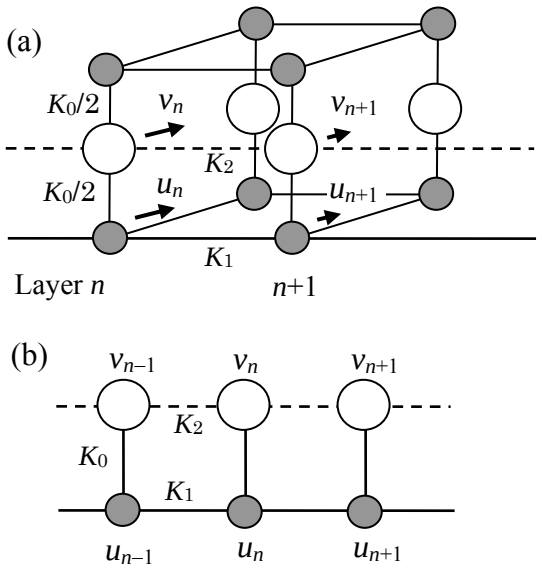

Fig. 1. Ladder lattice model: (a) three-dimensional and (b) one-dimensional schematics.

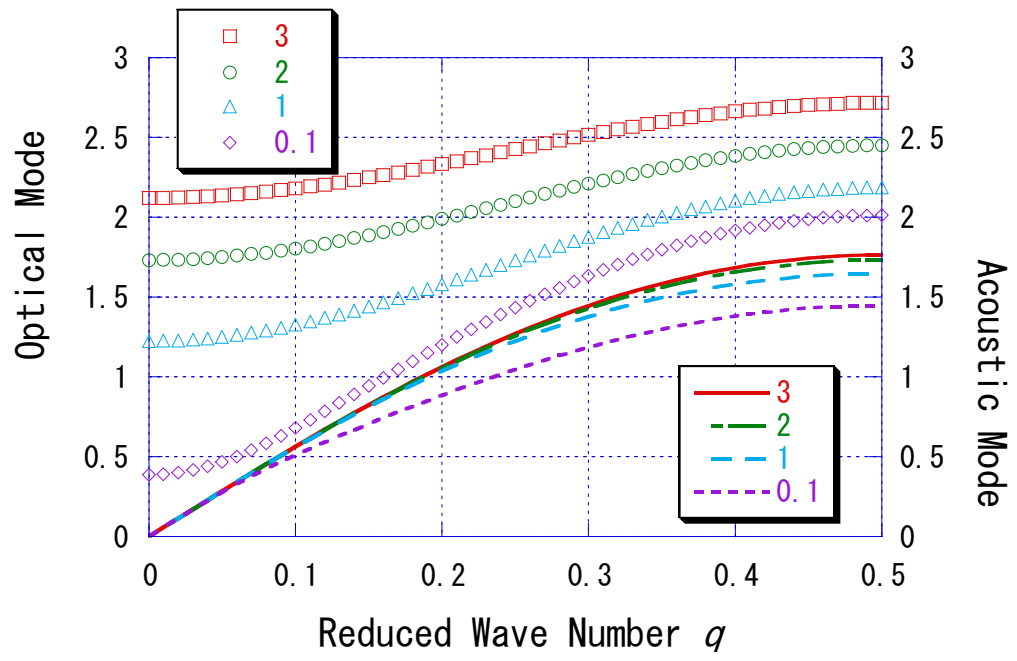

Fig. 2. Dispersion relation of the ladder lattice model. The parameters are m=1, M=2, K_1=0.5, K_2=2, and K_0=3, 2, 1 or 0.1, as indicated in the figure.

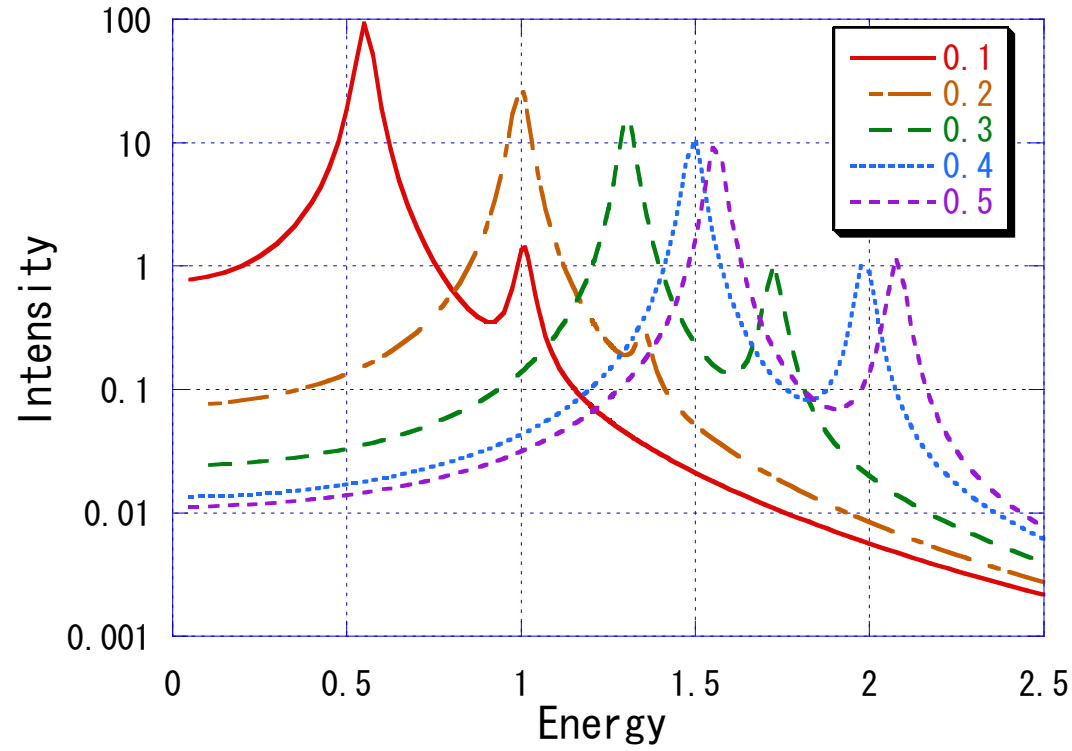

Fig. 3. Spectra of the ladder lattice model. The damping factors are $\gamma_1 = \gamma_2 = 0.05$, and the coupling constant is K_0=0.5. The wave numbers are given in the figure.

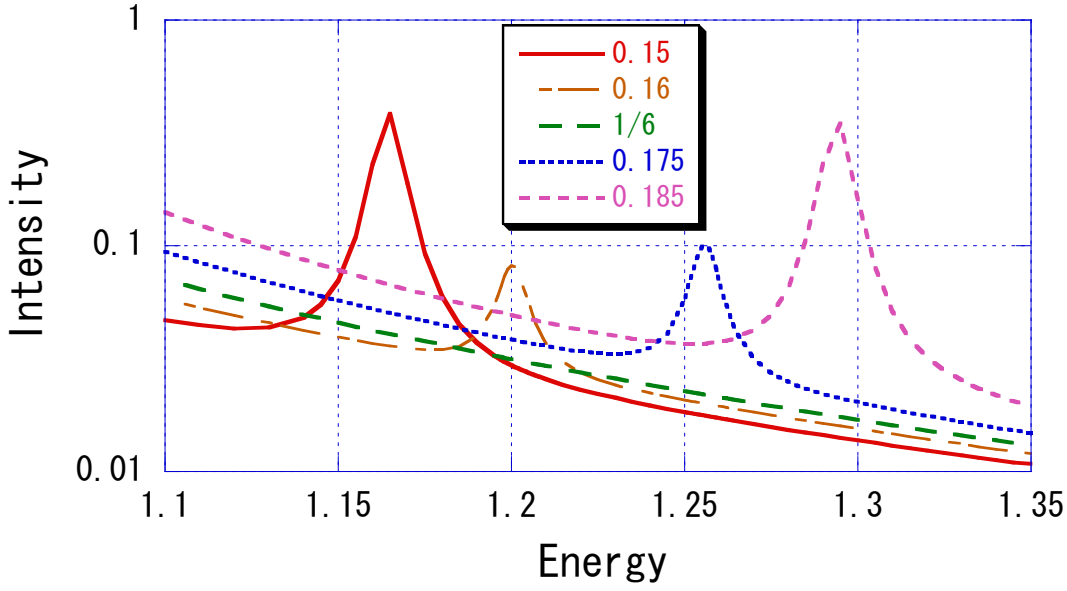

Fig. 4. Line shape of optical mode around the anticrossing point of the ladder lattice model. The spectra are given for the wave numbers q=0.15, 0.16, 1/6, 0175, and 0.185. The damping factors are $\gamma_1 = \gamma_2 = 0.01$.

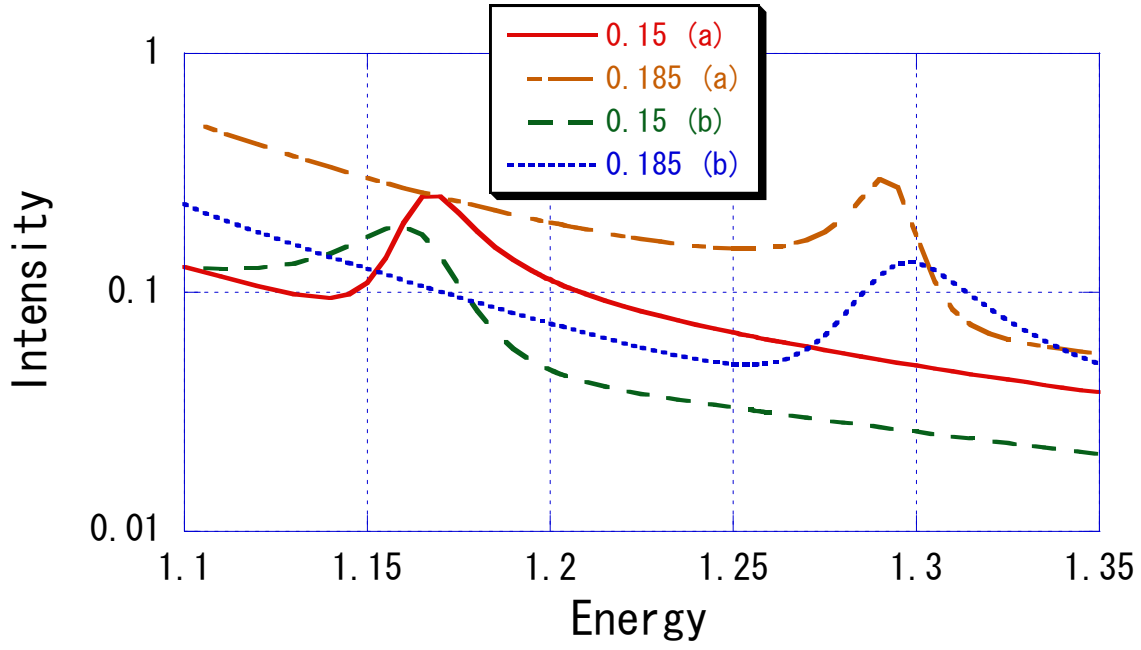

Fig. 5. Asymmetric line shapes of optical mode around the anticrossing point q_x=1/6. The damping factors are $\gamma_1 = 0.05$ and $\gamma_2 = 0.005$, and $\gamma_1 = 0.005$ and $\gamma_2 = 0.05$ in the (a) and (b) cases, respectively. The wave numbers are 0.15 and 0.185.