Optical conductivity from local anharmonic phonons

Hideki Matsumoto

Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578 Japan
Institute for Materials Research, Tohoku University, Sendai, 980-8577 Japan and
CREST(JST), 4-1-8 Honcho, Kawauchi, Saitama 333-0012, Japan

Tatsuya Mori, Kei Iwamoto, Shohei Goshima, Syunsuke Kushibiki, and Naoki Toyota

Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578 Japan

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Recently there has been paid much attention to phenomena caused by local anharmonic vibrations of the guest ions encapsulated in polyhedral cages of materials such as pyrochlore oxides, filled skutterdites and clathrates. We theoretically investigate the optical conductivity solely due to these so-called rattling phonons in a one-dimensional anharmonic potential model. The dipole interaction of the guest ions with electric fields induces excitations expressed as transitions among vibrational states with non-equally spaced energies, resulting in a natural line broadening and a shift of the peak frequency as anharmonic effects. In the case of a single well potential, a softening of the peak frequency and an asymmetric narrowing of the line width with decreasing temperature are understood as a shift of the spectral weight to lower level transitions. On the other hand, the case of a double minima potential leads to a multi-splitting of a spectral peak in the conductivity spectrum with decreasing temperature.

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I. INTRODUCTION

Anharmonicity in lattice vibrations has been one of the old problems in condensed-matter physics. Anharmonic effects in acoustic phonons were treated by perturbation theory, while those in local vibrations were investigated in impurities or disordered systems. It was pointed out that the effects of the anharmonicity in local vibrations appear in the characteristic temperature dependence of the vibrational frequency and of the line width. Since an isolated irregular atom receives an anharmonic potential from the regular lattice, analysis has been made mostly on the anharmonic oscillation receiving effects of surrounding oscillation of the regular lattice.

Recently a revised interest on anharmonic phonons has arisen in relation to a material series of pyrochlore oxides, filled skutterdites and clathrates. Those materials, which are usually electrical conductors like metals, semimetals or heavily-doped semiconductors, have a common feature that some numbers of atoms form a three-dimensional network of polyhedral cages, in each of which a guest ions is accommodated. When the cages are oversized, the guest ion vibrates with a large amplitude in an anharmonic potential. Such vibrations are named as the rattling phonons. To note, depending on kinds of guest ions, on-centering or off-centering vibrations occur even in the same cage structure.

There have been reported various anomalous phenomena in the above materials, some of which have been discussed in relation to those rattling phonons. In applying some clathrate compounds to thermoelectric material devices, for example, the rattling phonons, in particular off-centered, are expected to suppress strongly the thermal conductivity by effectively scattering Debye-like acoustic phonons propagating through the cage network and carrying heat entropy. An alternative example is found in the superconductivity in a β-pyrochlore oxide KO$_2$S$_6$. It was suggested that rattling vibrations of the K$^+$ in the OsO$_6$ octahedral cage were responsible for the strong-coupling superconductivity and also for an electron-mass enhancement. It may be fair, however, to state that these interesting issues as for the question how rattling phonons interact with cage acoustic phonons and/or charge carriers are far from being well understood.

So far lattice vibrational modes including rattling phonons in the above cage materials have been studied rather extensively with use of spectroscopic measurements such as inelastic neutron and Raman scatterings. Some low-lying rattling modes are clarified to exhibit softening with decreasing temperatures. The softening phenomenon has been well recognized as one of the anharmonic effects from rattling phonons, which was discussed with a quasi-harmonic approximation. Beside these spectroscopies, an infrared-active optical measurements, particularly in the Terahertz range, would be, in principle, a powerful tool to clarify the charge dynamics in low-lying optical phonons near $q \sim 0$ with available optical conductivity spectra.

Recently, time-domain terahertz spectroscopy has been successfully applied for the first time to observe the rattling phonons around 1THz in a type-I clathrate Ba$_5$Ga$_{16}$Ge$_{30}$ (BGG). In this paper, we investigate systematically the optical conductivity spectra from the rattling phonons in an on-centered and off-centered potential, and apply the obtained theoretical classifica-
the polarization induced by an applied oscillatory electric field by considering the effects of acoustic phonons and electrons. We neglect essential features from the anharmonicity and multi-peak structures at low temperature in optical conductivity.

In the present paper, a one-dimensional model is used for simplicity. Essential effects from the anharmonicity are included. In the next section, the model and the expression of the optical conductivity are presented. In Sect. 3 some of numerical results are presented. Comparison with the recent experiment is discussed. Sect. 4 is devoted to the conclusion.

II. FORMULATION

As a model to describe the motion of a guest ion in the cage, we take the following one-dimensional anharmonic potential model, for simplicity,

\[ H = \frac{p^2}{2M} + \frac{1}{2}kx^2 + \frac{1}{4}\lambda x^4 , \quad (2.1) \]

where \( M \), \( p \) and \( x \) are the mass, momentum and spatial coordinate of the guest ion, respectively. We neglect effects of acoustic phonons and electrons.

The optical conductivity from the guest ion is obtained by considering the polarization induced by an applied oscillatory electric field \( E(t) \),

\[ H_I = -qE(t)x , \quad (2.2) \]

where \( q \) is the charge of the guest ion. By use of the linear response theory, the polarization \( P(t)(= \langle qx(t) \rangle) \) is obtained as

\[ P(t) = \frac{i}{\hbar} \int dt' q^2 \langle Rx(t)x(t') \rangle E(t') , \quad (2.3) \]

where \( \langle \cdots \rangle \) indicates the thermal average and ”\( R \)” means the retarded function. By taking the Fourier transform, the polarizability \( \alpha(\omega) \) defined by

\[ \langle Rx(t)x(t') \rangle = \frac{i}{2\pi} \int d\omega e^{-i\omega(t-t')}G_{xx}(\omega) . \quad (2.6) \]

where the density of the guest ion \( N \) is taken into account and \( G_{xx}(\omega) \) is defined by

\[ \langle Rx(t)x(t') \rangle = \frac{i}{2\pi} \int d\omega e^{-i\omega(t-t')}G_{xx}(\omega) . \quad (2.6) \]

Let us denote eigenstates and eigenvalues of the Hamiltonian \( H \) by \( |n\rangle \) and \( E_n \), respectively,

\[ H|n\rangle = E_n|n\rangle . \quad (2.7) \]

Then \( G_{xx}(\omega) \) is expressed as

\[ G_{xx}(\omega) = \sum_{nm} |\langle n|x|m \rangle|^2 \frac{(e^{-\beta E_m} - e^{-\beta E_n})/Z}{\omega + i\Gamma_0/2 - (E_n - E_m)/\hbar} \]

with \( \beta = 1/k_B T \) and \( Z = \sum_n e^{-\beta E_n} \). Here we have introduced a phenomenological parameter of the decay width \( \Gamma_0 \). Since the optical conductivity and the polarizability are related to each other as

\[ \sigma(\omega) = -i\omega\alpha(\omega) , \quad (2.9) \]

we have the complex optical conductivity as

\[ \sigma(\omega)/\sigma_0 = i\omega \sum_{\omega_{nm} > 0} |\langle n|x/x_0 \rangle|m|^2 e^{-E_m - \beta E_n} \]

\[ \times \left( \frac{1}{\omega - \omega_{nm} + i\Gamma_0/2} - \frac{1}{\omega + \omega_{nm} + i\Gamma_0/2} \right) \quad (2.10) \]

with

\[ \omega_{nm} = (E_n - E_m)/\hbar . \quad (2.11) \]

Hereafter, we use the notation \( E_{nm} \), \( \omega_{nm} \) and \( \nu_{nm} \), respectively, as the energy, angular frequency and frequency for the transition from the \( m \)-state to the \( n \)-state. The normalization for the conductivity \( \sigma_0 \) is given by

\[ \sigma_0 = q^2 N x_0^2 /\hbar . \quad (2.12) \]

with a length scale \( x_0 \) determined shortly. In the following analysis, we choose a suitable energy scale \( \hbar \omega_0 \), which can be, for example, the energy corresponding to 1THz or a harmonic frequency evaluated from the quadratic term in the potential, or an observed phonon energy. The scaled parameters are defined as

\[ \bar{k} = \frac{k}{M\omega_0^2} , \quad \bar{\lambda} = \frac{h\lambda}{M^2\omega_0} . \quad (2.13) \]

and the length scale \( x_0 \) is given as

\[ x_0 = \sqrt{\frac{\hbar}{M\omega_0}} . \quad (2.14) \]

In the next section, we will calculate \( \sigma(\omega) \) for cases of \( \bar{k} > 0 \), \( \bar{k} = 0 \) and \( \bar{k} < 0 \), and discuss characteristic features of the optical conductivity from the rattling phonon.
III. NUMERICAL ANALYSIS

A. The case of $k > 0$

We can choose $\tilde{k} = 1$ without loss of generality. In this case, $\omega_0$ is given by $\omega_0 = \sqrt{k/M}$, the harmonic frequency. Let us estimate the magnitude of $\lambda$. In the band structure calculation for Ba$_8$Ga$_{16}$Ge$_{30}$, the coefficients $k$ and $\lambda$ were evaluated as $ka^2_B/2 = 2.813\text{mRy}$ and $\lambda a_B^4/4 = 1.602\text{mRy}$, where $a_B$ is the Bohr radius. Then using the mass of the Ba-atom 137.35 a.u., we have the harmonic frequency $\nu_0 = 0.6975\text{THz}$ and $\lambda = 4.292 \times 10^{-2}$. The actually observed phonon frequency lowest lying in Ba$_8$Ga$_{16}$Ge$_{30}$ is about 1THz and the parameters $k$ may vary about twice or so. Taking into account the above estimation and Eq. (2.13), we take the value of $\lambda$ in the range of $\lambda = 0.0 - 0.05$.

In Fig. 1 (a) we plot the optical conductivity for various $\lambda$ with $\tilde{k} = 1$ at $k_B T/\hbar \omega_0 = 10.0$. Hereafter, we introduce a constant decay width $\Gamma_0/2\omega_0 = 0.1$ by hand, in order to smooth the frequency dependence of the optical conductivity. How each level transition has a decay width depends on interactions with electrons or acoustic phonons. Details of such effects are not considered in this paper. Also in the following, $\sigma(\omega)$ denotes the real part of the complex conductivity. At $\lambda = 0$, the phonon mode has the single angular frequency $\omega = \omega_0$, and the line width is the decay width $\Gamma_0$. As $\lambda$ increases, both of the peak position and the line width increase. That is, the line width at higher temperature is determined by the anharmonic parameter $\lambda$. In Fig. 1 (b), we plot the excitation energy $\omega_{(n+1),n} = (E_{n+1} - E_n)/\hbar$. This is obtained by calculating the energy eigenvalues numerically. One example of the behavior of energy eigenvalues is shown in Fig. 1 (c) for $\lambda = 0.05$. The label "n" is identical with the boson number in the harmonic case of $\lambda = 0$. The energy eigenvalues deviate from the linear behavior as $E_n \approx e_0 + e_1 n + e_2 n^2$ but a perturbation calculation is not applicable, since $\lambda n^2$ becomes an order of one for $n \sim 10$. The calculation shows that the transition probability arises mostly from $\langle n + 1 | x | n \rangle$. As is seen in Fig. 1 (b), the excitation energies increase as eigenvalues (i.e. $n$) increase due to the anharmonicity; the larger the $\lambda$, the more spreading excitation energies become. The non-equal energy spacing of the phononic level transitions leads to the intrinsic spread of the line width in the optical conductivity, as is seen in Fig. 1 (a). It should be noted that excitations with larger $n$ ($\sim 30$) contribute at $k_B T/\hbar \omega_0 = 10.0$.

FIG. 1: (Color online) (a) Optical conductivity for various $\lambda$ with $\tilde{k} = 1$ at $k_B T/\hbar \omega_0 = 10.0$, (b) excitation energy $\omega_{10}$ and (c) energy eigenvalues for $\lambda = 0.05$.

In Fig. 2 (a), we plot the temperature dependence of the optical conductivity for $\lambda = 0.04$ and $\tilde{k} = 1$. (b) The corresponding spectral weight at $k_B T/\hbar \omega_0 = 0.05, 5.0$ and 10.0.

In Fig. 2 (a), we plot the temperature dependence of the optical conductivity. The optical conductivity shows the softening of the peak position and the narrowing of the line width with decreasing temperature. At low temperature, only the first level transition contributes. As temperature increases, the transition involves higher energy levels, resulting in a shift of the effective peak position. Also the line width increases, since more level transitions contribute. In order to see the line-distribution without the smoothening by the width $\Gamma_0$, we plot, in Fig. 2 (b), the spectral weight in the optical conductivity given by

$$F(\omega)/\sigma_0 = \pi \sum_{\omega \equiv \omega_m \equiv \omega} |\langle n | x | m \rangle|^2 \frac{e^{-\beta E_m} - e^{-\beta E_n}}{Z} \quad (3.1)$$

for $k_B T/\hbar \omega_0 = 0.05, 5.0$ and 10.0. Sharp lines arising from the non-equal spacing of the level transitions dis-
which deviates above the perturbation, \( T \) is shown, which gives the peak frequency at the present parameter region, the curve is fitted by

\[
\omega_0 = 1 + 0.7414\lambda - 0.7998\lambda^2,
\]

which deviates above \( \lambda \sim 0.05 \) from the result of the perturbation, \( \omega_{10} = 1 + (3/4)\lambda - (9/8)\lambda^2 \) (dashed line).

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In Fig. 4 (a) we plot the temperature dependence of the peak position and (b) line width for \( \lambda = 0.04 \) and \( k = 1 \).

In Fig. 4 (a) we plot the temperature dependence of the peak position and (b) line width for \( \lambda = 0.04 \) and \( k = 1 \).

We see that the averaged value (red dashed line) well agree with the mean field results (blue diagonal-crosses). However, our result of the peak structure is asymmetric, reflecting the spectral weight, Eq. (3.4). We express the line width at temperature \( T \) as

\[
\Gamma(T) = \gamma_a(T) + \gamma_l(T)
\]

with \( \gamma_a(T) \) \((\gamma_l(T))\) being the upper (lower) half width from the peak frequency, which is shown in Fig. 4 (b).

From the analysis of this subsection, we see that anharmonicity of the rattling phonon leads to softening of the phonon frequency and sharpening and asymmetric change of the line width with decreasing temperature.

B. \( k = 0 \)

When \( k = 0 \) (or \( |k| << \lambda a_B^2 \)), the peak position and the line width are solely determined by \( \lambda \). We choose

![Diagram of peak position and line width for different values of \( \lambda \) and \( k \).]
$\hbar \omega_0$ as a characteristic energy of the system, for example, $\omega_0/2\pi = 1$THz. In Figs. 6(a) and (b), the energy eigenvalues and the excitation energy $\omega_{(n+1),n} = (E_{n+1} - E_n)/\hbar$ are plotted. The lower excitation energies are softened and, just as well as in the case of $k > 0$, the effectively contributing $n$ decreases with decreasing temperatures, resulting in the characteristic behavior, softening and sharpening, of the optical conductivity as is shown in Figs. 6 and 7. Note that the lowest excitation energy is sharpening, of the optical conductivity as is shown in Figs. 6 and 7. Note that the lowest excitation energy is sharpening, of the optical conductivity as is shown in Figs. 6 and 7. 

The lower peak is reduced as temperature is further lowered. The broadening of the line width at higher temperature is enhanced as $\lambda$ increases. 

C. The case of $k < 0$

For negative $k$, the anharmonic potential has double minima. We investigate the temperature dependence of the optical conductivity for $\lambda = 0.04$ by changing $\lambda$. Depending on the depth of the double minima, various patterns of temperature-dependent optical conductivity are obtained. We choose $\hbar \omega_0$ as a characteristic energy of the system, for example, $\omega_0/2\pi = 1$THz.

In Fig. 6 we show the temperature dependence of the optical conductivity for various $k$. The softening of the peak position is seen in Figs. 6(a)-(c), but in Figs. 6(d)-(f) the softening of the peak frequency is followed by the sharpening, with decreasing temperature.

Low temperature behaviors have various variety, especially there appear structures with double or triple peaks, though it depends on the magnitude of the width $\Gamma_0$. This can be understood from the low energy level transition in the double well potential. In Fig. 6(a), one example of the potential with $k < 0$ is illustrated together with the eigenenergy levels. Low energy levels are much modified by the depth of the potential well. In Fig. 6(b) the $\tilde{k}$-dependence of $E_n$ for low energy levels are plotted. Dotted lines are the potential double minima with the value $V(\pm \sqrt{-k/\lambda})/\hbar \omega_0 = -\tilde{k}^2/4\lambda$ and the local maximum $V(0) = 0$, respectively. When $-\tilde{k}$ increases, the levels $(E_0, E_1)$, $(E_2, E_3)$, · · · , successively degenerate forming low-lying tunneling modes. In Fig. 6(c) the transition energies $\omega_{nm}$ are plotted among low-lying eigenstates. The dotted line is for the depth of the potential well. Transition energies $\omega_{10}$ and $\omega_{13}$ show successively soften as $-\tilde{k}$ increases, while the neighboring excitations $\omega_{21}$, $\omega_{43}$ increase and become larger than excitation energies among higher levels ($\omega_{11,10}$ in Fig. 6(c)). The upturn of the excitation energies of $\omega_{21}$ is correlated with the depth of the potential well. In the following we discuss more details of low temperature behaviors in Fig. 6.

Figs. 7(a) and (b) are for shallow double wells. Transition energy of $\hbar \omega_{10}$ is softened and it becomes smaller than $\hbar \omega_{21}$ due to the effect of the double well. Further, $(\omega_{21} - \omega_{10})$ is larger than $\Gamma_0$, so that there appears two peaks at low temperature and the higher peak of $\omega_{21}$ diminishes as $T \rightarrow 0$. The peak around $\omega/\omega_0 = 1$ which remains even at $T = 0$K corresponds to the transition $\hbar \omega_{30}$.

Fig. 7(c) is for $\tilde{k} = -0.3$. The states 0 and 1 become very close but still have finite difference. We can identify lower peak as $\omega_{10}$, $\omega_{21}$ and $\omega_{30}$. The peak for $\omega_{21}$ is reduced with decreasing temperature (See also Fig. 7(c)).

Fig. 7(d) is for $\tilde{k} = -0.4$. The states 0 and 1 are almost degenerate, and this soft mode does not appear
in the optical conductivity because of the factor $\omega$ in Eq. \textbf{(2.10)}. The state 2 is inside the double well and the state 3 is above the maximum at $x = 0$. Then $\omega_{21}$ is larger than $\omega_{32}$. We can identify the peaks in Fig. \textbf{(d)} as $\omega_{32}$, $\omega_{12}$ and $\omega_{03}$ from the low energy side. Note that the intensity of the peak $\omega_{32}$ increases and decreases as temperature decreases.

In Fig. \textbf{(e)}, $\tilde{k}$ is further reduced as $\tilde{k} = -0.5$. The state 2 and 3 start to degenerate and $\omega_{32}$ becomes lower than $\omega_{21}$. We can identify the peaks in Fig. \textbf{(e)} from the low energy side as $\omega_{13}$ and $(\omega_{12}, \omega_{03})$.

In Fig. \textbf{(f)}, the state 2 and 3 are completely degenerate and $\omega_{21}$ is the main transition at low temperature. Since this energy is much larger than energies for higher level transition, the peak position first decrease at higher temperature and then increase at low temperature.

When $\tilde{k}$ is further reduced and the double minima become deep enough, the hardening of the peak frequency is obtained rather than softening as was discussed in ref.\textsuperscript{30}.

In this way, we have various patterns depending on the strength of the double well.

D. Comparison with the experiment

We have performed the time-domain THz spectroscopy and obtained the optical conductivity\textsuperscript{29} in a type-I clathrate Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30} \textsuperscript{14,15,16,32}. The details of the experimental method and analysis will be presented in a separated paper\textsuperscript{29}. The obtained temperature-dependence of the phonon spectral for the lowest mode($\sim$1.2THz) is shown by colored symbols in Fig. \textbf{10}. No multi-peak structure is observed. Then from the patterns presented in this paper, we conclude $k > 0$ and we take $\tilde{k} = 1$.

We adjust $\omega_0$, $\tilde{\lambda}$, $\Gamma_0$ and $\sigma_0$ to fit overall behaviors and specially the higher frequency region (1.25$\sim$1.40 THz) of the spectral line. We choose $\omega_0/2\pi = 1.143$THz, $\tilde{\lambda} = 9.66 \times 10^{-3}$, $\Gamma_0/2\pi = 0.067$THz, and $\sigma_0 = 6.82 \Omega^{-1}$cm$^{-1}$. Theoretical results are presented by solid lines in Fig. \textbf{10}.

The agreement between the experimental and theoretical results in temperature-dependence is very good.
The temperature dependence of the peak frequency and the line width are estimated from the experimental data by the Lorentzian fit and are plotted by the solid rectangulars in Fig. 11(a) and (b), respectively. Theoretical results are plotted by solid and dashed lines. In Fig. 11(a), the red solid line is for the peak frequency $\nu_{\text{peak}}$ and the green dashed line is for the mid-frequency $\nu_{\text{mid}}$. In Fig. 11(b), the red solid, blue dashed and light blue short-dashed lines are frequencies $\nu_{T}/2$, $\nu_{d}$, and $\nu_{s}$ corresponding to the half width, the lower and upper half width, respectively. The experimental peak frequency situates between the theoretical peak and mid-frequency. Also the half-width is between the theoretical half-width and lower half-width. Since the Lorentzian fit is apt to lead a higher peak frequency and a narrower line width in an asymmetric line shape, the agreement between the experimental and theoretical results is reasonably good. The present comparison shows that the temperature-dependence of the rattling phonon in Ba$_8$Ga$_{16}$Ge$_{30}$ is well described by the anharmonicity of the potential without considering details of effects from other interactions.

It has been reported that a type-I clathrate Ba$_8$Ga$_{16}$Sn$_{30}$ has an off-centered potential of the guest ion.$^{17}$ It is an interesting problem to see if the optical conductivity of this material shows a behavior with $k < 0$ discussed in this paper.$^{12}$

**IV. CONCLUSION**

In this paper we have investigated theoretically the temperature dependence of the optical conductivity from the rattling phonon. The guest ion feels an anharmonic potential from the cage, and the anharmonic effect appears characteristically in the temperature dependence, that is, the softening of the peak frequency and sharpening of the line width with decreasing temperature.

In the case of the positive quadratic term, one can expect the quadratic coefficient is roughly determined from the saturated peak frequency at low temperature and the quartic term is determined from the line width and shift of the peak frequency.

In the case of the negative quadratic term, various patterns of the optical conductivity are expected depending on the strength of the double minima in the potential. Multi-peak structures appear at low temperature and increase and decrease of the peak frequency with temperature are obtained.

We have shown that measurements on the temperature dependence of the optical conductivity can provide a direct evidence for the anharmonicity.

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* Electronic address: matumoto@ldp.phys.tohoku.ac.jp  
† Electronic address: toyota-n@ldp.phys.tohoku.ac.jp

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