Anharmonicity on Raman active phonon modes of LaGaO₃

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Abstract. The phonon-dispersion relations of LaGaO₃ crystal are calculated using the first-principle calculations. The first-order Raman spectra in the LaGaO₃ were measured in the temperature range 20-690K. The temperature dependence of linewidth of several modes [the $A_g$ (57 cm⁻¹) and the $B_2g$ (118 cm⁻¹) for the low-temperature phase (LT), and the $E_g$ (52 cm⁻¹) and the $E_g$ (160 cm⁻¹) for the high-temperature phase (HT)] was analyzed using TDOS due to cubic term. The calculated results reproduce the observed ones in this temperature range without the temperature range (350-400 K) on the precursor effect of the phase transition. Temperature dependence of the linewidth for some rotational modes [the $A_g$ (57 cm⁻¹) and the $B_2g$ (118 cm⁻¹) for the LT, and the $E_g$ (52 cm⁻¹) for the HT] is dominated by the scattering of a thermal phonon by the observed phonon, while that for the bending mode [the $E_g$ (160 cm⁻¹) for the HT] is dominated by both the scattering and the decay of the observed phonons into two phonons having lower energies. We found that this originates in the large frequency gap in the DOS that produces a difference in anharmonic effects on each peak’s channels in the HT.

1. Introduction
Recently, we studied the temperature dependence of Raman-active phonon spectra in certain GdFeO₃-type crystals (i.e., NdGaO₃ [1,2]and YAlO₃ [3]) and found that the temperature dependence of the linewidth of the $A_g$ modes in these Raman spectra was well described by the cubic anharmonic term in the expansion series of the crystal potential energy. This temperature dependence indicates the importance of anharmonic interaction between rotational and other modes. LaGaO₃ crystal possesses this GdFeO₃-type structure (space group $Pnma$) at room temperature [4], and is composed of twenty atoms per unit cell in a highly complicated crystal structure. The optical active phonon spectra of LaGaO₃ have been studied by several researchers [4, 5]. Furthermore, the Raman shift for the 52 cm⁻¹ mode shows very little change regarding line broadening as the temperature increases in even a high-temperature phase [4]. Therefore, the temperature-behaviour of low-frequency Raman spectra is interesting in the anharmonic lattice dynamics, since the origin of the anharmonicity of these modes has not been known until now. In this study, the observed temperature dependence of the Raman spectra for LaGaO₃ is examined in terms of phonon-dispersion relations based on the
first-principles calculations. We also clarify the origin of anharmonic effects on the linewidth of several rotational modes using these calculations.

2. Experimental details
The specimen used in the present study was a polycrystalline sample (a purity of 99.99%), and was cut perpendicularly on the c axis (7.2×0.51×7.3 (c axis) mm$^3$ in dimension), and its surface was optically polished. The non polarized Raman scattering spectra (Fig.1) of several modes were measured in the range of 20-690 K. These results above 77 K were similar to the previous works [4,5]. The excitation source was the 514.5-nm line of an Ar$^+$-ion laser at a power level of 100-200 mW, and it was introduced to the thin side of the sample. 90° scattering geometry has been used. The scattered light from the surface was analyzed using a double monochromator (CT-1000D, JASCO Co.) having a spectral resolution of about 2.0 cm$^{-1}$ and the accuracy of the wave number was ±1 cm$^{-1}$.

![Figure 1. Temperature dependence of Raman spectra in the low-temperature phase [LT: (a)] and the high-temperature phase [HT: (b)].](image)

3. Computational details
The phonon frequencies in this study are determined by the dynamical matrix which is obtained using the density functional theory (DFT) approach. Then a 4×4×4 supercell is considered, calculations are done with the Advance/PHASE Package [6] using norm-conserving pseudo-potentials and plane waves (80 Ry cutoff) method. The phonon modes (Fig. 2) are also obtained as usual by the diagonalization of the dynamical matrix. The lowest-order contribution to the phonon imaginary part of the self-energy in a nondisordered single crystal near the Brillouin-zone center comes from three-phonon processes, such as

$$
\mathcal{V}^{(3)}(\mathbf{q}) = \frac{18\pi}{\hbar^2} \sum_{n_1 \neq n_2} |V^{(3)}(0,j_1,j_2,-j_3,-j_4)|^2 \delta[\omega_n(j_1)+\omega_n(-j_4)+1] \\
\times \left\{ \Omega - \omega_n(j_1) - \omega_n(-j_4) + [\omega_n(j_1) - \omega_n(-j_4)] + \omega_n(-j_4) \right\}.
$$

(1)

where the vector $\mathbf{q}$ is in the Brillouin zone and $V^{(3)}$ is the anharmonic coupling potential [1]. If in a rough approximation, the anharmonic coupling potential in Eq. (1) is assumed to depend neither on $j_1$, $j_2$, nor on the vector $\mathbf{q}$, the phonon width is proportional to the temperature weighted two-phonon density of states (TDOS). TDOS (Fig. 3) is calculated using the phonon-dispersion curves obtained from these calculations. The reciprocal-space summation has been performed with linear tetrahedron
method on a dense of mesh of \( q \) vectors (16×16×16 grid mesh) in the first Brillouin zone. An increase in the quality of the mesh gives no noticeable changes.

**Figure 2.** Phonon dispersion relations in the LT [(a)] and the HT [(b)]. The (c) calculated vibrational patterns of the \( A_g \) (57 cm\(^{-1}\)), the \( B_{2g} \) (118 cm\(^{-1}\)), the \( E_g \) (52 cm\(^{-1}\)), and the \( E_g \) (160 cm\(^{-1}\)).

**Figure 3.** Temperature dependence of TDOS in upper panel. A comparison between the TDOS related to the scattering term and the decay term (in middle), and one-phonon density of states (DOS) in the case of the (a) rhombohedral-phase at 450 K (in lower), (b) the orthorhombic-phase at 200 K.
4. Results and discussion

In the LT [Fig. 3(a)], we found that TDOS for both 57 cm$^{-1}$ and 118 cm$^{-1}$ is dominated by the scattering processes. Therefore, these peaks also show similar properties regarding the temperature dependence of the linewidth [Fig. 4(a)]. A large disagreement appears between the linewidth values at the temperature range of 350-400 K for the 57 cm$^{-1}$ and the 118 cm$^{-1}$ peaks, and the calculated values [Fig. 4(a)]. It is most likely that this discrepancy arises from the precursor effect (of the phase transition) with increasing temperature in the temperature range near $T_c$. In the HT [Fig. 4(b)], the variation of linewidth of the 52 cm$^{-1}$ peak is also about 1.6 times greater than those for the 160 cm$^{-1}$ peak. In the HT [Fig. 3(b)], we found that TDOS for the 52 cm$^{-1}$ peak is dominated by the scattering processes, while that for the 160 cm$^{-1}$ peak is dominated by both the scattering and the decay processes. This can be seen in a large frequency gap in the DOS [Fig. 3(b)] shown in HT expressing the difference between anharmonic effects on each peak’s channel.

4. Conclusion

The first-order Raman spectra in the LaGaO$_3$ were measured in the temperature range 20-690 K. The temperature dependence of linewidth of several low-frequency modes was analyzed using TDOS. The calculated results reproduce the observed ones in this temperature range without the temperature range (350-400 K). Temperature dependence of the linewidth for the $A_g$ (57 cm$^{-1}$), the $B_2g$ (118 cm$^{-1}$), and the $E_g$ (52 cm$^{-1}$) is dominated by the scattering processes, while that for the $E_g$ (160 cm$^{-1}$) is dominated by both the scattering and the decay processes. This is shown in a large frequency gap in the DOS expressing the difference between anharmonic effects on each peak’s channel.

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