Anharmonicity on Raman active phonon modes of LaAlO$_3$

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Abstract. The phonon-dispersion relations of LaAlO$_3$ crystal are calculated using the first-principle calculations. The first-order Raman spectra in the LaGaO$_3$ were measured in the temperature range of 20-300K for the rhombohedral phase. The temperature dependence of the linewidth of the $A_{1g}$ ($132$ cm$^{-1}$) and that of $E_g$ ($489$ cm$^{-1}$) were analyzed using temperature-weighted two-phonon density of states (TDOS) due to the cubic term. The calculated results reproduce the observed ones in this temperature range. The scattering of a thermal phonon by observed phonons dominates phonon-phonon interaction on the rotational modes [the $A_{1g}$ ($132$ cm$^{-1}$)]. Phonon-phonon interaction on the bending mode [the $E_g$ ($489$ cm$^{-1}$)] 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 discrete spectra on the higher-frequency side in the phonon density of states that produces a difference in anharmonic effects on each peak’s channels in the HT. This result is similar to that in the high-temperature phase in the case of LaGaO$_3$[1].

1. Introduction

High-$\kappa$ oxides are currently the focus of intense research as potential replacements of silica as a gate dielectric in ultrahigh-integration Si-based electric devices based on the complementary-metal-oxide semiconductor paradigm [2]. Crystalline LaAlO$_3$, a rhombohedrally distorted pervoskite previously used as a substrate for ferroelectrics and high-Tc superconductors, has recently gained attention [3] in this context, and has been used in actual devices [4]. Another reason for interest in this compound is that it is closely related to other complex oxides, such as magnetic AMnO$_3$ (A=La,Y); in order to characterize, it is very important to understand the structures of these oxides as well as their Raman and infrared(IR) spectra [5].

Recently, we studied the temperature dependence of Raman-active phonon spectra in certain GdFeO$_3$-type crystals (NdGaO$_3$ [6, 7], YAlO$_3$ [8], and LaGaO$_3$ [1]) and found that the temperature dependence of the linewidths of the $A_g$ modes in these Raman spectra were 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. In LaGaO$_3$, the Raman shift for the 52cm$^{-1}$ mode shows very little change regarding line broadening as
the temperature increases in even a high-temperature phase [1]. The temperature dependence of the linewidth for the \( A_{2g} \) (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. We found that a large frequency gap in the DOS (phonon density of states) gives the difference between anharmonic effects on each peak’s channel in the rhombohedral phase [1]. Very recently, Choudhury et al. [9] reported on first-principle calculations and inelastic neutron scattering measurement of the DOS, dispersion relations, and electromechanical response of ATiO\(_3\) pervoskites. The large phonon band gap in ATiO\(_3\) pervoskites seems to be a characteristic of quantum paraelectrics; the anisotropy of phonon spectra correlates well with ferroelectric length [9]. In this study, the observed temperature dependence of the Raman spectra for LaAlO\(_3\) is examined in terms of phonon-dispersion relations based on the first-principle 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 single crystal (purity of 99.99%) and was cut perpendicularly on the c axis (7.2 x 6.0 x 8.0 (c axis) mm\(^3\) in dimensions), and its surface was optically polished. The nonpolarized Raman scattering spectra (Fig. 1) of several modes were measured in the range of 20-300K. These results above 77K were similar to those of a previous work [10]. The excitation source was the 514.5-Å 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. We used 90° scattering geometry. The scattered light from the surface was analyzed using a double monochromator (CT-1000D, JASCO) having a spectral resolution of about 2.0 cm\(^{-1}\), and the accuracy of the wave number was ± 1 cm\(^{-1}\).

![Fig. 1 Temperature dependence of Raman spectra in the low-temperature phase. The inset shows three spectra (at 100-160 cm\(^{-1}\)) of the experimental closed points and the calculated spectra (lines).](image)

3. Computational details
The phonon frequencies in this study are determined by the dynamical matrix obtained using the density functional theory (DFT) approach. Then a 4\( \times \)4\( \times \)4 supercell is considered, calculations are done with the Advance/PHASE [11] using norm-conserving pseudo-potentials and the plane waves (80 Ry cutoff) method. The phonon modes (Fig. 2(b)) 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...
Fig. 2 Phonon dispersion relations in the case of LaAlO$_3$. The (b) calculated vibrational patterns of the $A_{1g}$ (132 cm$^{-1}$) and the $E_g$ (489 cm$^{-1}$). The large and small open circles represent O and Al, respectively.

Fig. 3 Temperature dependence of the (a) 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 300 K (in lower). Temperature dependences of the (b) linewidths of the 132 cm$^{-1}$ and 489 cm$^{-1}$ peaks. The observed values were denoted by closed and open circles, respectively. The calculated values are denoted by the solid and dashed lines, respectively.
where the vector $\mathbf{q}$ is in the Brillouin zone and $V^{(3)}$ is the anharmonic coupling potential [6]. In a rough approximation, the anharmonic coupling potential in Eq. (1) is assumed to depend on neither $j_1$, $j_2$ nor on vector $\mathbf{q}$. The phonon width is proportional to the temperature-weighted two-phonon density of states (TDOS). TDOS (Fig. 3(a)) is calculated using the phonon-dispersion curves obtained from these calculations. The reciprocal-space summation has been performed with the linear tetrahedron method on a dense mesh of $\mathbf{q}$ vectors (16×16×16 grid mesh) in the first Brillouin zone. An increase in mesh quality gives no noticeable changes.

4. Results and discussion
In Fig. 3(a), we found that the TDOS for the 132 cm$^{-1}$ peak is dominated by the scattering processes. In Fig. 3(b), the variation of linewidth of the 132 cm$^{-1}$ peak is also about 1.6 times greater than those for the 489 cm$^{-1}$ peak. In Fig. 3(b), we found that the TDOS for the 132 cm$^{-1}$ peak is dominated by the scattering processes, while that for the 489 cm$^{-1}$ peak is dominated by both the scattering and decay processes. This can be seen in discrete spectra in the higher-frequency side in the DOS [Fig. 3(a)] showing the difference between anharmonic effects on each peak’s channel.

5. Conclusion
The first-order Raman spectra in the LaAlO$_3$ were measured in the temperature range of 20-300K. The temperature dependences of the linewidths of several low-frequency modes were analyzed using TDOS. The calculated results reproduce the observed ones in this temperature range. The temperature dependence of the linewidth for the $A_{1g}$ (132 cm$^{-1}$) is dominated by the scattering processes, while that for the $E_g$ (489 cm$^{-1}$) is dominated by both the scattering and decay processes including those in the low-temperature range. This is shown in discrete spectra in the higher-frequency side in the DOS expressing the difference between anharmonic effects on each peak’s channel. This result is similar to that in the high-temperature phase in the case of LaGaO$_3$.

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