

Coupled phonons and transferred energies between Raman active phonons for LiTaO₃ crystal

Jun Suda^{1,*}

¹*Department of Electric Engineering, Kushiro National College of Technology ,
Otanoshike-nish 2-32-1, Kushiro, Hokkaido 084-0916, Japan*

(Received April 11, 2010)

The frequency shift for four TO modes in the LiTaO₃ was measured at 23–896K for ferroelectric rhombohedral phase (RH). The TO₂ mode (256 cm⁻¹) softens more rapidly than the TO₁ (206 cm⁻¹) and then pushes it down to lower frequencies. The temperature dependence of the frequency shift of the four TO modes was analyzed using the first-principles calculations. The calculated results reproduce the observed ones below 350 K. For the frequency shift of the soft TO₂ modes, it was explained that the thermal expansion effect $\Delta\omega_0$ was partly canceled by the quartic effect $\Delta\omega^{(4a)}$ with an increase in the temperature up to 350 K. For the TO₁ mode, the growth of $\Delta\omega^{(4a)}$ may cause suppression of softening above 350 K. For the frequency shift of the TO₁, TO₃, and TO₄ modes, it was explained that the thermal expansion effect $\Delta\omega_0$ and the cubic effect $\Delta\omega^{(3)}$ were partly canceled by the quartic effect $\Delta\omega^{(4a)}$ with an increase in the temperature up to 350 K. As a result, we found that phonon energies with TO₁ and TO₂ were transferred to each other at the temperature above 350 K. This may be because the ionic motions associated with the TO₁ and the TO₂ modes are transferred to each other.

PACS numbers: 63.20.D-, 63.20.Ry, 63.20.kg

I. INTRODUCTION

LiTaO₃ crystal is ferroelectric at room temperature (RT) and have rich applications in electromagnetic devices, i.e., surface acoustic filters, ultrasonic transducers, and optical device such as electro-optic, nonlinear optic, and photorefractive devices [1–3]. At RT, LiTaO₃ possesses rhombohedral (RH) space group and above 950 K undergoes a structural phase transition to the high-temperature paraelectric RH phase from the low-temperature ferroelectric RH phase. IR absorption and Raman scattering spectra of LO and TO phonons [4–8] have been measured by many researchers. Jayaraman and Ballman [4] have investigated the pressure dependence of Raman spectra of LiTaO₃. They concluded that the phase transition is order-disorder type. Penna *et al.* [5] found a Debye-like central peak in Raman spectra of the ferroelectric phase. Tomeno and Matsumura [6] measured the dielectric susceptibilities and conductivity, and reported that a comparison with light-scattering measurements, which an intermediate character between the displacive and order-disorder phase transition. Recently, the temperature dependence of Raman spectra of TO modes have been measured in the X(ZZ)Y configuration above room temperature [7]. They reported that the two low-frequency peaks (206 cm⁻¹ and 256 cm⁻¹) of TO mode show significant changes as the temperature increases above room temperature, and “Mode soft-

ening” and “frequency-repulsion” were observed [7]. However, the temperature dependence of Raman spectra of these modes has not been analyzed with respect to the anharmonicity of the phonon-modes by using the first-principles calculations in detail. Very recently, Hushur *et al.* [8], have reported that the central peak (CP) (quasi-elastic-scattering) has been investigated by the broadband Brillouin scattering and low-frequency Raman scattering in the wide temperature range of 300 to 1067 K. In Brillouin and Raman scattering, CP is observed at the polarized scattering geometry in all the temperatures studied. It is found that the relaxation time determined from the width of CP clearly shows a critical slowing down of an order-disorder phase transition in the vicinity of TC.

Previously, we studied the temperature dependence of Raman-active phonon spectra in certain GdFeO₃-type crystal (i.e., LaGaO₃ [9]) and found that the temperature dependence of the linewidth of the Ag modes in these Raman spectra was well described by the cubic anharmonic term in the expansion series of the crystal potential energy. We found that a large frequency gap in the DOS (phonon density of states) gives the difference between anharmonic effects on each peaks channel in the RH phase [9]. Very recently, we have reported that the observed temperature dependence of the Raman linewidth of four TO modes for LiTaO₃ is examined in terms of phonon-dispersion relations on the basis of the first-principles calculations in RH phase; it showed that the anharmonic effect on the linewidth was closely related to each ionic motion, and it was approximately dominated by cubic potential [10]. The variation of the linewidth of the TO₄ mode is a little greater than that of the TO₃ mode. This may be originated that in the TO₄ mode, the torsion of individual octahedra takes place, that costs much higher energy and has a strong anharmonic contribution, including low temperature range. Furthermore, “Mode softening” and “frequency-repulsion” were led to the interest for the origin of strong anharmonic effects on frequency shift. In spite of these phonon properties, the first-principles calculations of anharmonic effects on Raman shift for these modes have not been reported until now.

In this paper, the observed temperature dependence of the Raman shift for LiTaO₃ is examined in terms of phonon-dispersion relations based on the first-principles calculations in ferroelectric RH phase. We also clarify the origin of anharmonic effects on the frequency shift of four TO modes using these calculations in view point of “Mode softening” and “frequency-repulsion,” including in the low-temperature range.

II. EXPERIMENT

The specimen used in the present study was a single crystal sample (purity of 99.99%), and it was cut perpendicularly along the c axis ($7.0 \times 6.0 \times 8.0$ (c axis) mm³ in dimension), and its surface was optically polished. 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. 90° geometric-scattering 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. The polarized Raman scattering spectra (Fig. 1(a)) of TO modes were measured in the range

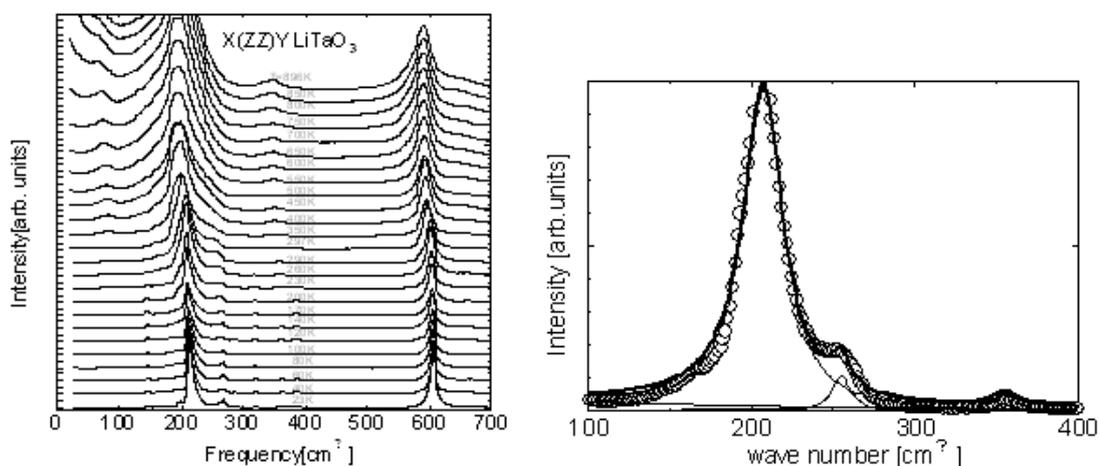


FIG. 1: Temperature dependence of polarized Raman spectra in a X(ZZ)Y configuration [(a)] and the polarized Raman spectra with the result of the fit calculations at 290 K [(b)].

of 23–896 K [10]. These results above 77 K were similar to the previous works [4–8] have corresponded with those according to the group theory.

In the case of a X(ZZ)Y configuration, for two lower-frequency modes, so we called them TO_1 and TO_2 modes corresponding to 206 cm^{-1} and 256 cm^{-1} of A_1 (TO) modes at room temperature (RT), respectively. As shown in Fig. 2(a), the TO_1 and TO_2 peaks broadened linearly and shifted to the lower-frequency side with increasing temperature up to 350 K. However, above 350 K, the TO_2 peak broadened with softening and shifted more to the lower-frequency side with increasing temperature up to 896 K. On the other hand, the TO_1 peak shows broadening linearly and shifts a little to the lower-frequency side as well as shows suppression of softening with increasing temperature. The TO_2 mode softens more rapidly than the TO_1 mode and then pushes it down to lower frequencies above 350 K as “Mode softening” and “frequency-repulsion.” For two higher-frequency modes, so we called

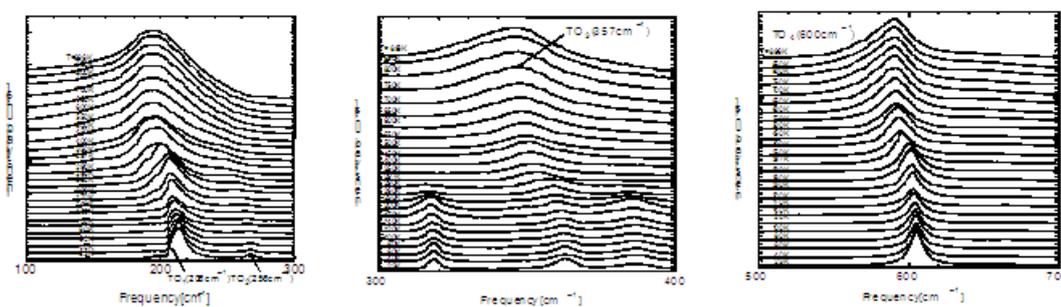


FIG. 2: Temperature dependence of polarized Raman spectra for (a) both TO_1 and TO_2 modes, and (b) TO_3 mode and the (c) TO_4 mode in a X(ZZ)Y configuration.

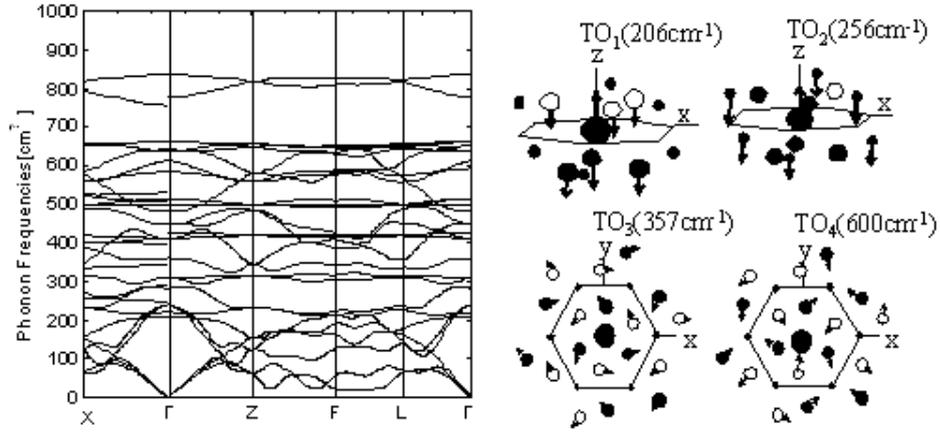


FIG. 3: The (a) phonon dispersion relations in LiTaO₃. The (b) calculated vibrational patterns of the TO₁ (206 cm⁻¹), TO₂ (256 cm⁻¹), TO₃ (357 cm⁻¹), and TO₄ (600 cm⁻¹) in a top-view along the z-axis.

them TO₃ and TO₄ modes corresponding to 356 cm⁻¹ and 600 cm⁻¹, at RT, respectively. As shown in Figs. 2(b) and 2(c), the TO₃ and TO₄ peaks show broadening linearly and shifted to the lower-frequency side with increasing temperature up to 350 K. However, in the case of the TO₃ mode, the linewidth variation changes with the temperature change at 350 K and shows broadening linearly as well as suppression of softening with increasing temperature above 350 K. On the other hand, the TO₄ mode shows broadening linearly as suppression of softening with increasing temperature. The variation of the linewidth of the TO₄ peak with temperature is a little greater than those for the TO₃ peak. The experimental center-frequencies in Fig. 4(b) were obtained by the fit calculations on the basis of the assumption of all spectra with a quasi-elastic-scattering [8] and three Raman spectra (TO₁, TO₂, and TO₃) with the Raman scattered intensities, which were written in terms of the imaginary part of the dielectric permittivity and the Bose-Einstein population factor for Stokes scattering. This procedure was employed in the case of LaGaO₃ [9] and LiNbO₃ [11]. As an example, the result of the fit calculations (at 290 K) is shown in Fig. 1(b). The obtained experimental frequencies in this study are in good agreement with those of ref. [7] above 300 K.

III. COMPUTATIONAL DETAILS

The phonon-dispersion relations (Fig. 3(a)) of LiTaO₃ are calculated using the first-principles calculations approach [10]. The phonon modes (Fig. 3(b)) are also obtained as usual by the diagonalization of the dynamical matrix [10]. The lowest-order contribution to the phonon real part of the self-energy in a non-disordered single crystal near the Brillouin-

zone-center comes until three-phonon processes, such as [12, 13]

$$\Delta\omega_{obs}(0, J, \Omega) = \Delta\omega_0(0, J, \Omega) + \Delta\omega_A^{(3)}(0, J, \Omega) + \Delta\omega_A^{(4a)}(0, J, \Omega), \quad (1)$$

where $\Delta\omega_0(0, J, \Omega)$, $\Delta\omega_A^{(3)}(0, J, \Omega)$, and $\Delta\omega_A^{(4a)}(0, J, \Omega)$ corresponded to the thermal expansion, the cubic term of the second-order, and the quartic term of the first-order, and they are given by

$$\Delta\omega_0(0, J, \Omega) = -\omega_j(0)\gamma_j \int_{T_0}^T \beta(T') dT, \quad (2)$$

$$\begin{aligned} \Delta\omega_A^{(3)}(0, J, \Omega) = & \frac{-18}{\hbar^2} \sum_{q_1} \sum_{j_1, j_2} \left| V^{(3)}(0, j, q_1, j_1; -q_1, j_2) \right|^2 \\ & \times \left\{ \frac{n_{j_1}(q_1) + n_{j_2}(-q_1) + 1}{[\omega_{j_1}(q_1) + \omega_{j_2}(-q_1) + \Omega]_p} + \frac{n_{j_1}(q_1) + n_{j_2}(-q_1) + 1}{[\omega_{j_1}(q_1) + \omega_{j_2}(-q_1) - \Omega]_p} \right. \\ & \left. + \frac{n_{j_2}(-q_1) - n_{j_1}(q_1)}{[\omega_{j_1}(q_1) - \omega_{j_2}(-q_1) + \Omega]_p} + \frac{n_{j_2}(q_1) - n_{j_1}(-q_1)}{[\omega_{j_1}(q_1) - \omega_{j_2}(-q_1) - \Omega]_p} \right\}, \quad (3) \end{aligned}$$

and

$$\Delta\omega_A^{(4a)}(0, J, \Omega) = \frac{12}{\hbar^4} \sum_{q_1, j_1} V^{(4)}(q, j, -q, j, q_1, j_1; -q_1, j_1) [2n_{j_2}(q_2) + 1]. \quad (4)$$

Here, $n_j(q_j)$ is the phonon occupation number; $P(1/x)$, the principal value; γ_j , the mode Grüneisen parameter; $\beta(T')$, the thermal expansion of cell volume; and $V^{(4)}$, the anharmonic quartic coupling potential. The reciprocal-space summation has been performed with linear tetrahedron method on a dense mesh of \mathbf{q} vectors ($4 \times 4 \times 4$ grid mesh) in the first Brillouin zone. An increase in the quality of the mesh gives no noticeable changes in each phonon real part of the self-energy on the rhs of Eq. (3) and of Eq. (4), respectively.

IV. DISCUSSION

The temperature dependence of the frequency shift of the four TO modes was analyzed using the first-principles calculations. The calculated results reproduce the observed ones below 350 K. In Fig. 3(b), we found that TO₁ and TO₂ are the z-vibration of Li ions and of other ions, respectively. In Figs. 2(a), 4(a), and 4(b), we found that the TO₂ mode softens more rapidly than the TO₁ mode and then pushes it down to lower frequencies above 350 K (“Mode softening” and “frequency-repulsion”). For the TO₁ and the soft TO₂ modes, the calculated frequency shift (up to the cubic effect of the second order and the quartic effect of the first-order) reproduced the experimental shifts below 350 K [Fig. 4(b)]. For the frequency shift of the soft TO₂ modes, it was explained that the thermal expansion

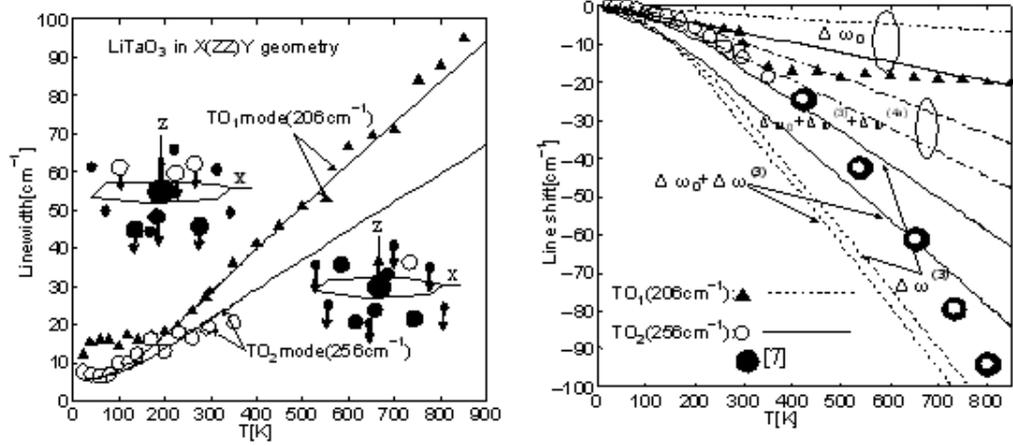


FIG. 4: Temperature dependence of the (a) linewidth [10] and the (b) line shift of the 206 cm⁻¹ and 256 cm⁻¹ peak. The observed values are denoted by open circles, closed triangles, and closed circles [7], respectively. Other lines denote the calculated values.

effect $\Delta\omega_0$ was partly canceled by the quartic effect $\Delta\omega^{(4a)}$ with increasing temperature up to 350 K. As seen in Fig. 4(b), the frequency shift of the soft TO₂ mode was dominated by the cubic effect $\Delta\omega^{(3)}$. For the frequency shift of the TO₁ mode, it was explained that the thermal expansion effect $\Delta\omega_0$ and the cubic effect $\Delta\omega^{(3)}$ were canceled by the quartic effect $\Delta\omega^{(4a)}$ with increasing temperature up to 350 K and that the growth of $\Delta\omega^{(4a)}$ may cause suppression of softening above 350 K [Fig. 4(b)]. As a result, we found that phonon energies with the TO₁ and TO₂ were transferred to each other at the temperature above 350 K. This may be because TO₁ and TO₂ are almost similar z-vibration of Li ions, so that the ionic motions associated with the TO₁ and the TO₂ modes are transferred to each other (Fig. 4(b)). Therefore, the difference between frequencies of the two peaks should be small. In Fig. 3(b), the z-displacements are negligible in the TO₃ and the TO₄ modes, and practically only oxygen ions are participating in them. For the TO₃ and the TO₄ modes, the calculated frequency shift (up to the cubic effect and the quartic effect) reproduce the experimental ones below 350 K (Fig. 5(b)). For both the frequency shift of the TO₃ and the TO₄ modes, it was explained that the thermal expansion effect $\Delta\omega_0$ and the cubic effect $\Delta\omega^{(3)}$ were partly canceled by the quartic effect $\Delta\omega^{(4a)}$ with increasing temperature up to 350 K (Fig. 5(b)). It suggests that the quartic anharmonicity may be related to suppression of softening of TO₃ and TO₄ with increasing temperature up to 350 K. However, above 350 K, there is a large upturn of the frequency shift for TO₃ and TO₄, and this origin will be the future investigation.

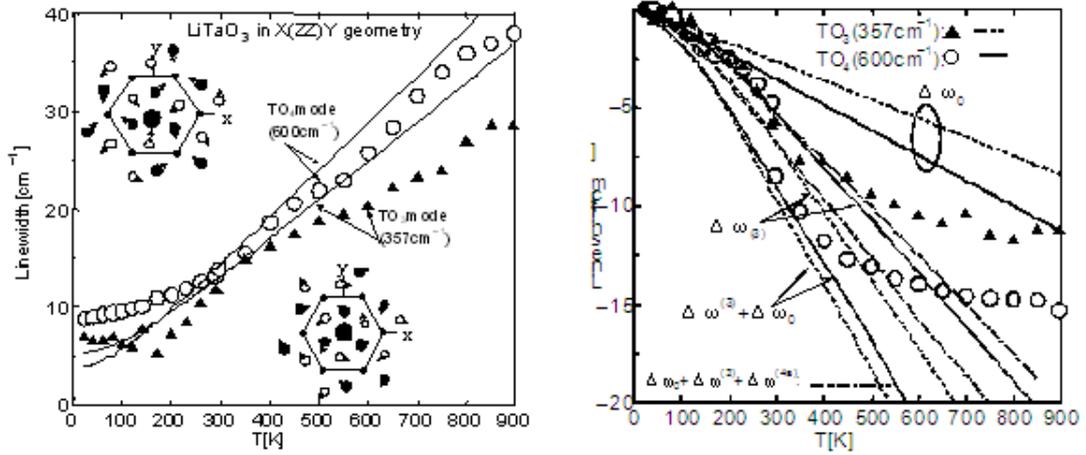


FIG. 5: Temperature dependence of the (a) linewidth [10] and the (b) line shift of the 357 cm⁻¹ and 600 cm⁻¹ peak. The observed values are denoted by open circles and closed triangles, respectively. Other lines denote the calculated values.

V. CONCLUSIONS

The temperature dependence of the frequency shift of the four TO modes of LiTaO₃ crystal is calculated using the first-principles calculations approach. We found that the TO₁ (206 cm⁻¹) and TO₂ (256 cm⁻¹) modes are the z-vibration of Li ions and of other ions, respectively, while the z-displacements are negligible in the TO₃ (357 cm⁻¹) and the TO₄ (600 cm⁻¹) modes using this calculation. The Raman frequency shift of these TO modes in the LiTaO₃ was measured in the temperature range 23–896 K for the ferroelectric rhombohedral phase. In the experiment, the TO₂ mode softens more rapidly than the TO₁ mode and then pushes it down to lower frequencies. The calculated results reproduce the observed ones below 350 K. For the frequency shift of the soft TO₂ modes, it was explained that the thermal expansion effect $\Delta\omega_0$ was partly canceled by the quartic effect $\Delta\omega^{(4a)}$ with increasing temperature up to 350 K. For the growth of $\Delta\omega^{(4a)}$ may cause suppression of softening above 350 K. For the TO₁, the TO₃ and the TO₄ modes, it was explained that the thermal expansion effect $\Delta\omega_0$ and the cubic effect $\Delta\omega^{(3)}$ were partly canceled by the quartic effect $\Delta\omega^{(4a)}$ with increasing temperature up to 350 K. As a result, we found that the phonon energies with the TO₁ and TO₂ were transferred to each other at the temperature above 350 K. This may be because the ionic motions associated with the TO₁ and the TO₂ modes are transferred to each other. Above 350 K, there is a large upturn of the frequency shift for TO₃ and TO₄, and this origin will be the future investigation.

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Science and Culture of Japan (Grant No. 20540322).

References

- * Electronic address: suda@kushiro-ct.ac.jp
- [1] Y. Xu, *Ferroelectric Materials and Their Applications* (North-Holland, Amsterdam, 1991).
 - [2] C. S. Abrahams, W. C. Hamilton, and A. Sequeira, *J. Phys. Chem. Solids* **28**, 1963 (1967).
 - [3] C. S. Abrahams and J. L. Bernstein, *J. Phys. Chem. Solids* **28**, 1685 (1967).
 - [4] A. Jayaraman and A. A. Ballman, *J. Appl. Phys.* **60**, 1208 (1986).
 - [5] A. F. Pena, S. P. S. Porto, and E. Wiener-Avnear, *Solid. State. Commun* **23**, 377 (1977).
 - [6] I. Tomeno and S. Matsumura, *Phys. Rev. B* **38**, 606 (1988).
 - [7] Y. C. Ge, X. L. Li, and C. Z. Zhao, *Spectro. Lett.* **30(3)**, 567(1997).
 - [8] A. Hushur, S. Gvasaliya, B. Roessli, S. Lushnikov, and S. Kojima, *Phys. Rev. B* **76**, 064104(2007).
 - [9] J. Suda, O. Kamishima, J. Kawamura, T. Hattori and T. Sato, *J. Phys. Conf. Ser* **92**, 012148(2007).
 - [10] J. Suda, O. Kamishima, J. Kawamura, and T. Hattori, *J. Phys. Conf. Ser* **150**, 052248(2009).
 - [11] A. Ridah, M. D. Fontana and P. Bourson, *Phys. Rev. B* **56**, 5967 (1997).
 - [12] J. Suda, H. Chiba, and T. Sato, *J. Phys. Soc. Japan* **67**, 20 (1998).
 - [13] J. Suda, O. Kamishima, T. Hattori, and T. Sato, *J. Phys. Soc. Japan* **73**, 2347(2004).