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Polar isotope modes in crystals: Application to $RbClO_3$[†]

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The isotope effect of polar phonon modes in crystals has been treated with a phenomenological method. The coherent movement of the minor-isotope system was considered as additional phonon modes. The oscillator strengths of the isotope modes were found to be proportional to the concentrations of the isotopes. The TO-LO splitting and relative intensities of the phonons associated with the minor-isotope species can be calculated solely from the frequencies of the TO and LO modes associated with the major-isotope species. A generalized Lyddane-Sachs-Teller relation, which includes the isotope effect, has been derived; moreover, the effect of isotopes on the static and high-frequency dielectric constants has also been discussed. Upon application of the phenomenological method described above to the optical-phonon modes of $RbClO_3$, excellent agreement is obtained between the calculated values and experimental data.

I. INTRODUCTION

It is difficult to separate the various isotopes from their natural mixture. Most *pure* and *perfect* crystals contain a finite concentration of isotope *impurities* and experimentalists must often tolerate this type of crystal imperfection. It is the purpose of this paper to discuss the collective effect of the isotope impurities in a crystal with polar phonon modes.

Berman *et al.*[1] and Ziman[2] treated the minor-isotope species in a crystal as scattering centers and showed that a considerable part of the thermal resistivity of many crystalline solids at room temperature was contributed to by the scattering of phonons from the isotope impurities. However, the isotope impurities not only act as scattering centers, but also oscillate in the crystal with certain frequencies different from the normal-mode frequencies of the host crystal. When the concentrations of isotope *impurities* are comparable to that of the major-isotope species, the impurity *local* oscillators will couple to each other and form additional phonon branches. The coherent motion of the minor-isotope system is called the isotope mode.

Maradudin and Oitman[3] have considered the presence of a finite concentration of impurities in alkali halide crystals, and shown that the coherent motion of the impurity system can generate a macroscopic electric field. This field can act back on the impurity modes to split them into TO-LO pairs. The Maradudin-Oitman theory can be extended to cover the isotope impurities in crystals. However, the sole difference between the isotope modes and the major modes (or, more precisely, between the modes associated with the minor-isotope species and the modes associated with the major-isotope species) is their mode masses. The oscillator strengths of the isotope modes can be related to those of the major modes directly. With the simple phenomenological discussion presented in this paper, the behavior of the isotope modes can be understood completely without carrying out the tedious Ewald transformation as do Maradudin and Oitman.[3]

II. THEORY

The dielectric function of a crystal can be analyzed with the harmonic-oscillator formalism.[4] The optic vibrational modes with polar direction along one of the principle axes j are treated as a collection of N_j damped oscillators with vibrational amplitudes $W_{\nu j}$, effective charges $Z_{\nu j}$, mode masses $M_{\nu j}$, restoring force constants $M_{\nu j}\omega_{\nu j}^2$, and damping constants $\gamma_{\nu j}$. Here N_j is the number of normal modes predicted by group theory without considering the difference between various isotope species. In a crystal with more than one isotope species, the total number of normal modes becomes nN_j, where n is the number of distinguishable ways the primitive cells can be constructed with various isotope species. Since the chemical properties of different isotope species are identical, the atomic positions and electric charge distribution in all of the primitive cells should be the same. Therefore, the isotope modes and the major modes are subject to different mode masses, but subject to the same effective mode charges and restoring forces.

The normal-mode analysis of the unit cell is a classical problem and can be found in standard solid-state textbooks. Knowing the normal-mode frequencies of one of the isotope species and the structure, the force constants can be calculated.[5,6] Using the same force constants while varying mode masses, the mode frequencies of other isotope species can be obtained. But inside a crystal, both minor- and major-isotope modes will split further into TO-LO pairs owing to the long-range electrostatic force associated with the polar optical modes. A formalism including the effect of the macroscopic electric field must be used.

Let us consider the simplest case of the isotope effect. Assume that (i) only one element contained in the crystal has isotope impurities, (ii) there are only two isotope species of that element, and (iii) each primitive cell contains only one atom of that element. (It is straightforward to generalize the theory to crystals containing any number of isotope species.) There are only two distinguishable ways to construct the primitive cell and there are therefore two sets of normal modes. Let 1 and 2 denote the set of modes associated with the isotope species of percentage concentrations c_1 and c_2. Then the equations of motion for $W_{\nu j}(1)$ are

$$M_{\nu j}(1)[\ddot{W}_{\nu j}(1)+\gamma_{\nu j}(1)\,\dot{W}_{\nu j}(1)+\omega_{\nu j}^2(1)\,W_{\nu j}(1)]=Z_{\nu j}(1)E_j,\quad \nu=1,\cdots,N_j \tag{1}$$

and for $W_{\nu j}(2)$

$$M_{\nu j}(2)[\ddot{W}_{\nu j}(2)+\gamma_{\nu j}(2)\dot{W}_{\nu j}(2)+\omega_{\nu j}^2(2)W_{\nu j}(2)]=Z_{\nu j}(2)E_j,\quad \nu=1,\cdots,N_j\,. \tag{2}$$

Here E_j is the component of the macroscopic electric field along the j axis.

The dielectric function $\epsilon_j(\omega)$ relates E_j and P_j by

$$\epsilon_j(\omega)E_j=E_j+4\pi P_j, \tag{3}$$

where P_j is the jth component of the total polarization and is the sum of two terms:

$$P_j=P_j^{\text{electronic}}+P_j^{\text{ionic}}\,. \tag{4}$$

$P_j^{\text{electronic}}$ is the contribution due to the motion of electrons and is given by

$$P_j^{\text{electronic}}=(1/4\pi)\,(\epsilon_j^\infty-1)E_j\,. \tag{5}$$

P_j^{ionic} is the contribution due to the displacement of ions and is equal to the dipole moment of each unit cell multiplied by the density, i.e.,

$$P_j^{\text{ionic}}=\frac{c_1}{V}\sum_\nu^{N_j}Z_{\nu j}(1)W_{\nu j}(1)+\frac{c_2}{V}\sum_\nu^{N_j}Z_{\nu j}(2)W_{\nu j}(2), \tag{6}$$

where V is the volume of a primitive cell.

Consider only the harmonic plane-wave excitation of $W_{\nu j}(1)$, $W_{\nu j}(2)$, E_j, and P_j. Assume their space- and time-dependent part is $\exp[i(\vec{q}\cdot\vec{x}-\omega t)]$. Equations (1) and (2) yield

$$W_{\nu j}(1)=\frac{Z_{\nu j}(1)E_j}{M_{\nu j}(1)[\omega_{\nu j}^2(1)-\omega^2-i\omega\gamma_{\nu j}(1)]}, \tag{7}$$

$$W_{\nu j}(2)=\frac{Z_{\nu j}(2)E_j}{M_{\nu j}(2)[\omega_{\nu j}^2(2)-\omega^2-i\omega\gamma_{\nu j}(2)]}\,. \tag{8}$$

Substituting Eqs. (7) and (8) into Eq. (6) and then substituting Eqs. (4)–(6) into Eq. (3), we obtain the dielectric function

$$\epsilon_j(\omega)=\epsilon_j^\infty+4\pi\sum_\nu^{N_j}\left(\frac{c_1Z_{\nu j}^2(1)}{VM_{\nu j}(1)[\omega_{\nu j}^2(1)-\omega^2-i\omega\gamma_{\nu j}(1)]}+\frac{c_2Z_{\nu j}^2(2)}{VM_{\nu j}(2)[\omega_{\nu j}^2(2)-\omega^2-i\omega\gamma_{\nu j}(2)]}\right) \tag{9}$$

As discussed before, the modes associated with different isotope species are subject to the same effective charges and force constants, i.e., $Z_{\nu j}(1)=Z_{\nu j}(2)$ and $M_{\nu j}(1)\omega_{\nu j}^2(1)=M_{\nu j}(2)\omega_{\nu j}^2(2)$. We can therefore define the total oscillator strengths $S_{\nu j}$ as

$$S_{\nu j}=4\pi Z_{\nu j}^2(1)/VM_{\nu j}(1)\omega_{\nu j}^2(1)=4\pi Z_{\nu j}^2(2)/VM_{\nu j}(2)\omega_{\nu j}^2(2)\,. \tag{10}$$

Equation (9) then becomes

$$\epsilon_j(\omega)=\epsilon_j^\infty+\sum_\nu^{N_j}\left(\frac{c_1S_{\nu j}\omega_{\nu j}^2(1)}{\omega_{\nu j}^2(1)-\omega^2-i\omega\gamma_{\nu j}(1)}+\frac{c_2S_{\nu j}\omega_{\nu j}^2(2)}{\omega_{\nu j}^2(2)-\omega^2-i\omega\gamma_{\nu j}(2)}\right). \tag{11}$$

Equation (11) gives the dielectric function along the j axis and indicates that the total number of phonon modes is twice that predicted by group theory alone. Each phonon mode splits further into a TO-LO pair. Equation (11) also shows that the effective oscillator strengths are $S_{\nu j}(1)=c_1S_{\nu j}$ and $S_{\nu j}(2)=c_2S_{\nu j}$, and are linearly dependent on the isotope concentrations.

Usually, the TO and LO frequencies and damping constants of the major modes can be obtained from Raman and/or infrared data, while the minor-isotope modes are difficult to resolve because of their weak intensities and small shifts from the major modes. With the approximation that $\gamma_{\nu j}(1)=\gamma_{\nu j}(2)$,[7] the only unknown parameters in Eq. (11) are $S_{\nu j}$. These N_j unknowns can be obtained by substituting the N_j LO major-mode frequencies into Eq. (11) and solving the simultaneous equations. Therefore, both the TO and LO frequencies of minor-isotope modes and their intensities relative to those of the major modes can be obtained solely from the known data of the major modes.

Let us rewrite Eq. (11) for the general case that there are n sets of isotope modes. Neglecting the damping terms, Eq. (11) becomes

$$\epsilon_j(\omega)=\epsilon_j^\infty+\sum_\nu^{N_j}\sum_i^n\frac{c_iS_{\nu j}\omega_{\nu j}^2(i)}{\omega_{\nu j}^2(i)-\omega^2}\,. \tag{12}$$

Equation (12) has 2 nN_j poles at $\pm\omega_{\nu j}(i)$ and 2 nN_j zeros at $\pm\omega_{\nu j}^{\mathrm{LO}}(i)$. Therefore the right-hand side of Eq. (12) can be written[4] as a product of the terms

$$[\omega_{\nu j}^{\mathrm{LO}^2}(i)-\omega^2]/[\omega_{\nu j}^2(i)-\omega^2]\,;$$

that is,

$$\epsilon_j(\omega)=\epsilon_j^\infty\prod_\nu^{N_j}\prod_i^n\frac{\omega_{\nu j}^{\mathrm{LO}^2}(i)-\omega^2}{\omega_{\nu j}^2(i)-\omega^2}\,, \tag{13}$$

where ϵ_j is included as a factor to yield the proper value of $\epsilon_j(\infty)$.

Letting $\omega=0$ in Eq. (13), we obtain the generalized Lyddane-Sachs-Teller (LST) relation which includes the isotope effect

$$\frac{\epsilon_j(0)}{\epsilon_j^\infty}=\prod_\nu^{N_j}\prod_i^n\left(\frac{\omega_{\nu j}^{\mathrm{LO}}(i)}{\omega_{\nu j}(i)}\right)^2 . \tag{14}$$

Equation (14) is perfectly general and applies to all crystals containing isotope impurities even when the isotope concentration is ~50%. Although Eq. (14) has additional factors due to the isotope modes, and the frequencies of both the major and minor LO modes are isotope concentration *dependent* [as can be seen from Eq. (12) and will be seen in Fig. 2], we can prove that the static dielectric constant is isotope concentration *independent*. Letting $\omega=0$ in Eq. (12), we have

$$\begin{aligned}\epsilon_j(0)&=\epsilon_j^\infty+\sum_\nu^{N_j}\sum_i^n c_iS_{\nu j}\\&=\epsilon_j^\infty+\sum_\nu^{N_j}\left(\sum_i^n c_i\right)S_{\nu j}\\&=\epsilon_j^\infty+\sum_\nu^{N_j}S_{\nu j}\end{aligned} \tag{15}$$

since $\sum_i^n c_i=1$. $S_{\nu j}$ is given in Eq. (10) and is isotope concentration independent. The high-frequency dielectric constant ϵ_j^∞ is due to the electron movement only, and crystals with different isotope concentrations have the identical electron distributions. Therefore, crystals with different isotope concentration ratio not only have the same ϵ_j^∞ but also have the same $\epsilon_j(0)$. The optical-phonon data of $\mathrm{RbClO_3}$ were analyzed to serve as an example of the application of the above theory.

III. APPLICATION TO $\mathrm{RbClO_3}$ CRYSTALS

The chlorine element exists in nature as a mixture of 75.4% ^{35}Cl and 24.6% ^{37}Cl.[8] It is one of the most common elements with two isotope species of comparable concentrations. The Raman and infrared spectra of the chlorate ion, $\mathrm{ClO_3^-}$, in aqueous solution,[9] in alkali chlorate crystals,[6,10–12] and in doped solid solutions[13,14] have been studied extensively. Isotope splitting of some of the $\mathrm{ClO_3^-}$ internal modes has been reported.[6,10,12–14]

Hollenberg and Dows[6] have calculated the isotope splitting of the internal modes of the chlorate ion in $\mathrm{NaClO_3}$ crystals using a normal-mode analysis. The isotope frequency shifts they predicted are reasonable. However, a direct comparison of the result of Hollenberg and Dows with the experimental data is not possible since their calculation does not include the effects of factor-group splitting or long-range electrostatic forces in the crystal.

$\mathrm{RbClO_3}$ is an uniaxial crystal with a monomolecular rhombohedral primitive cell.[15] The spectra of normal and oblique optical phonons of this material have been reported recently.[12] Group theory predicts $3A_1+4E$ phonon modes each of which is simultaneously Raman and infrared active. The polarization direction of A_1 modes (E modes) is parallel (perpendicular) to the c axis. Two of the A_1 modes and two of the E modes correspond one to one to the internal vibration modes ν_1, ν_2 and ν_3, ν_4[5] of the free $\mathrm{ClO_3^-}$ ion. Only the isotope splitting of the $2A_1$(TO) and $3A_1$(TO) modes has been resolved.[12] The TO and LO frequencies and damping constants of the phonon modes associated with the ^{35}Cl isotope and the available experimental data on the ^{37}Cl isotope modes are given in Table I.

As is the case with chlorine, rubidium contains two isotope species with the following natural abundance: ^{85}Rb—72.15% and ^{87}Rb—27.85%.[8] Therefore, in a $\mathrm{RbClO_3}$ crystal, each of the $2A_1+2E$ internal modes will split into two isotope modes; while each of the $1A_1+2E$ external modes will split into four isotope modes. However, the isotope-mode mass differences of the external modes are small and their theoretical maximum isotope splitting can be shown to be $\lesssim 0.5\ \mathrm{cm^{-1}}$. Thus, in the following calculation, we concentrate our attention on the internal modes and neglect the isotope effect on the external modes.

Using Eq. (11), the dielectric function of $\mathrm{RbClO_3}$ can be expressed as

$$\epsilon_\parallel(\omega)=\epsilon_\parallel^\infty+\frac{S_{1A_1}\omega_{1A_1}^2}{\omega_{1A_1}^2-\omega^2}+\sum_{\nu=2,3}\left(\frac{c_{35}\,S_{\nu A_1}\omega_{\nu A_1}^2(35)}{\omega_{\nu A_1}^2(35)-\omega^2}+\frac{c_{37}\,S_{\nu A_1}\omega_{\nu A_1}^2(37)}{\omega_{\nu A_1}^2(37)-\omega^2}\right) \tag{16}$$

and

$$\epsilon_\perp(\omega)=\epsilon_\perp^\infty+\sum_{\nu=1,2}\frac{S_{\nu E}\,\omega_{\nu E}^2}{\omega_{\nu E}^2-\omega^2}+\sum_{\nu=3,4}\left(\frac{c_{35}S_{\nu E}\omega_{\nu E}^2(35)}{\omega_{\nu E}^2(35)-\omega^2}+\frac{c_{37}S_{\nu E}\omega_{\nu E}^2(37)}{\omega_{\nu E}^2(37)-\omega^2}\right) . \tag{17}$$

TABLE I. ^{35}Cl and ^{37}Cl isotope phonon modes in RbClO$_3$ at room temperature. The value given in columns 2–4 and inside parentheses in other columns are experimental data. Unless otherwise indicated, the frequency measurements were accurate to ±1 cm^{-1}. Only the isotope effect of the internal modes was considered.

Mode	$\omega^{TO}(35)$ (cm^{-1})	$\omega^{LO}(35)$ (cm^{-1})	$\gamma(35)$ (cm^{-1})	$\omega^{TO}(37)$ (cm^{-1})	$\omega^{LO}(37)$ (cm^{-1})	S	$\frac{I^{TO}(37)}{I^{TO}(35)}$	$\frac{I^{LO}(37)}{I^{LO}(35)}$
$1A_1$	81	119	2.4			2.6817		
$2A_1(\nu_2)$	612	621	2.6	606.6 (608)	607.5	0.0727	0.37 (~0.3)	0.04
$3A_1(\nu_1)$	928	935	3.5	921.5 (921)	922.4	0.0366	0.38 (~0.3)	0.07
$1E$	104	130	3.8			2.1384		
$2E$	141	150 ± 3	4.4			0.1281		
$3E(\nu_4)$	486	492	2.0	484.9	485.1	0.0748	a	a
$4E(\nu_3)$	943	1013	3.6	931.7	934.2	0.3879	0.34	0.004

[a] No peak associated with the minor isotope mode exists since the isotope splitting is smaller than the line width.

Here ∥ and ⊥ refer to the directions parallel and perpendicular to the c axis. We have assumed zero damping constant in Eqs. (16) and (17). Since $\gamma_{\nu j}/\omega_{\nu j} \ll 1$, for all j, this assumption makes no essential difference in the frequencies of the modes.[16] The second term of Eq. (16) and first summation of Eq. (17) denote the external modes. The isotope splitting of the external modes is not included in these equations. The last summation terms of Eqs. (16) and (17) correspond to the internal modes.

The isotope splitting of the internal TO modes was calculated from a normal mode analysis.[5] The Cl–O–Cl angle α and Cl–O distance d are 109.53° and 1.443 Å,[15] respectively. From the four TO frequencies of the internal modes arising from the ^{35}ClO$_3^-$ ion, the force constants were calculated to be $f_d = 5.476\times10^5$ dyn/cm, $f_{dd} = 0.552\times10^5$ dyn/cm, $f_\alpha/d^2 = 2.290\times10^5$ dyn/cm, $f_{\alpha\alpha}/d^2 = 0.780\times10^5$ dyn/cm. Here f_d and f_{dd} are bond stretching force constants and f_α and $f_{\alpha\alpha}$ are bond bending force constants. The bond bending force constants shown above have been divided by the square of the bond length d to yield the same dimension as the bond stretching force constants.[5] By keeping the same force constants while changing the atomic mass of chlorine, the TO frequencies of ^{37}ClO$_3^-$ internal modes were obtained and are listed in the fifth column of Table I.

Now the only unknown parameters in Eqs. (16) and (17) are $S_{\nu A_1}$ and $S_{\nu E}$. Equations (16) and (17) become zero at the LO-mode frequencies.[4] Substituting the values of the LO frequencies of the major modes into Eqs. (12) and (13), we get

$$\epsilon_\parallel[\omega^{LO}_{\lambda A_1}(35)] = 0, \quad \lambda = 1, 2, 3 \tag{18}$$

$$\epsilon_\perp[\omega^{LO}_{\lambda E}(35)] = 0, \quad \lambda = 1, 2, 3, 4. \tag{19}$$

Solving the simultaneous equations (18) and (19) yields $S_{\nu A_1}$ and $S_{\nu E}$. Substituting the values of $S_{\nu A_1}$ and $S_{\nu E}$ back into Eqs. (16) and (17), we find two more roots in each equation. These roots are the LO frequencies of the ^{37}ClO$_3^-$ internal modes. The results are listed in Table I.

The dielectric function given by Eq. (17) is plotted in Fig. 1 for the frequency region of the $4E$ mode. The proper damping constants have been included.[12] The damping constants of the ^{37}Cl modes are assumed to be equal to those of the ^{35}Cl modes.[7]

The dielectric formalism relates the Raman intensity to the dielectric function as follows: $I^{TO} \propto \mathrm{Im}(\epsilon)$ and $I^{LO} \propto \mathrm{Im}(-1/\epsilon)$.[16] Comparing the peak values of $\mathrm{Im}[\epsilon_\perp(\omega)]$ at ω^{TO}_{4E} (37) in Fig. 1, we find that the theoretical intensity ratio, $I^{TO}_{4E}(37)/I^{TO}_{4E}(35) = 0.34$, which is almost identical to the concentration ratio of ^{37}Cl and ^{35}Cl, $c_{37}/c_{35} = 0.33$, and agrees well with the experimental result.[12] Comparing the peak values of $\mathrm{Im}[-1/\epsilon_\perp(\omega)]$ we find that $I^{LO}_{4E}(37)/I^{LO}_{4E}(35) = 0.004$. Therefore, the $4E$ LO mode of ^{37}Cl is not expected to be observed at all.[17] The

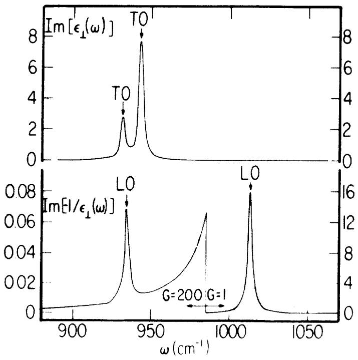

FIG. 1. Imaginary part of the ordinary dielectric function $\mathrm{Im}(\epsilon_\perp)$ and imaginary part of its inverse $\mathrm{Im}(-1/\epsilon_\perp)$ of RbClO$_2$ crystal in the frequency region of the $4E$ phonon mode. Note the relative gain is indicated by G. The Raman intensities of the TO and LO modes are proportional to $\mathrm{Im}(\epsilon_\perp)$ and $\mathrm{Im}(-1/\epsilon_\perp)$, respectively.

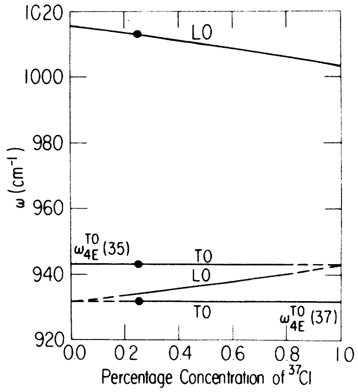

FIG. 2. Calculated TO and LO frequencies of the isotope modes of the $4E$ phonon in $RbClO_3$ crystal vs the percentage concentration of the ^{37}Cl isotope. The solid dots indicate the measured frequencies of the natural-isotope mixture. The dashed parts of the lines indicate that the intensities go to zero theoretically.

relative intensities of other isotope modes are given in the last two columns of Table I.

To understand the concentration dependence of the isotope effects, the mode frequencies of the $4E$ phonon were calculated from Eq. (17) with different isotope concentrations. The mode frequencies are plotted in Fig. 2 as a function of ^{37}Cl isotope concentration. We note that $\omega_{4E}^{LO} = 1016$ and 1004 cm^{-1} for pure $Rb^{35}ClO_3$ and pure $Rb^{37}ClO_3$, respectively. Upon changing the concentration of ^{37}Cl from 0 to 1, the major LO mode moves from 1016 to 1004 cm^{-1}, while an additional minor LO mode appears and moves from $\omega_{4E}^{TO}(37)$ to $\omega_{4E}^{TO}(35)$. The frequencies of the LO modes are almost but not exactly linearly dependent on the isotope concentration.

The product in the generalized LST relation, Eq. (14), theoretically should run over all isotope modes to yield the correct ratio of $\epsilon_j(0)$ and ϵ_j^∞. However, in the case of small isotope splitting or small isotope impurity concentration, some of the isotope modes may not be resolvable and the inclusion of all isotope modes in the L-S-T relation is not possible.

We notice from Eq. (12) and Fig. 2 that (i) the TO and LO modes occur alternatively, i.e., if $\omega^{TO}(1) < \omega^{TO}(2)$, then $\omega^{TO}(1) < \omega^{LO}(1) < \omega^{TO}(2) < \omega^{LO}(2)$; (ii) when one of the isotope concentrations approaches zero, the frequency of the LO modes approaches the frequency of one of the TO modes. Therefore, if either (i) the isotope splitting is small, or (ii) the concentration of the isotope impurities is small, inclusion of the isotope effect in Eq. (14) constitutes the addition of some factors, $\omega^{LO}/\omega^{TO} \approx 1$, to the product. Hence, considering only the major modes and the observable minor modes in the LST relation is a good approximation for crystals that satisfy conditions (1) and/or (2) above. For example, in $RbClO_3$, the maximum isotope splitting gives a ratio $\omega_{4E}^{TO}(35)/\omega_{4E}^{TO}(37) = 1.012$ even though the isotope impurity concentration is $c_{37} = 24.6\%$. Equation (14) yields $\epsilon_\parallel(0) = 4.99$ and $\epsilon_\perp(0) = 5.20$ when all the isotope modes are included. The values obtained by considering only the major modes[12] are $\epsilon_\parallel(0) = 4.97 \pm 0.14$ and $\epsilon_\perp(0) = 5.17 \pm 0.11$. The discrepancy is only 0.5% for $\epsilon_\parallel(0)$ and 0.6% for $\epsilon_\perp(0)$ and within the experimental errors.

IV. CONCLUSIONS

The isotope impurities in crystals not only act as scattering centers for phonons, but also form additional phonon modes. The isotope modes will split further into TO-LO pairs if the modes are polar. We have shown that the frequencies and intensities of the minor isotope modes can be calculated from the frequencies of the major modes. Although the minor isotope modes are hardly resolvable, the available data on the isotope modes of $RbClO_3$ agree well with our calculation.

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20% error in the relative intensities and very small error in the mode frequencies. See Refs. 2 and 16.

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