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# Theory of long-wavelength optical lattice vibrations in multinary mixed crystals: Application to group-III nitride alloys

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The optical lattice vibrations in multinary mixed crystals are investigated in the long-wavelength limit based on the pseudo-unit-cell approach and the Born-Huang procedure. A general equation for calculating the optical phonon frequencies in multinary mixed crystals is presented. The analytical expressions of phonon oscillator strength and dielectric constants of the multinary mixed crystal are obtained as functions of the phonon frequencies. The composition dependence of the oscillator strength shows clearly the phonon-mode behavior of the mixed crystals. As an application of our theory, a group of III-nitride mixed crystals is taken into numerical calculation. The concentration dependences of optical-phonon energy, lattice oscillator strength, and dielectric constants of the crystals are calculated in the whole compound range. It is found that the quaternary $\mathrm{Al}_y\mathrm{In}_x\mathrm{Ga}_{1-x-y}\mathrm{N}$ mixed crystal shows a two-mode behavior.

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## I. INTRODUCTION

In recent years, much attention has been focused on group-III nitride mixed crystals since the success of high efficient green/blue InGaN/GaN light-emitting diodes (LED's) and laser diodes (LD's) by Nakamura.[1] Recent developments in metal-organic chemical vapor deposition and molecular-beam-epitaxy technologies have made possible the fabrication of heterostructures from ternary and quaternary group-III nitride mixed crystals.[2–4] It has been shown in experiments that the group-III nitrides are polar semiconductors with direct band gap over the range of 2.0 eV (InN) to 3.5 eV (GaN) to 6.2 eV (AlN) in a wide range of the composition. The ternary and quaternary, and even multinary, III-nitride mixed crystals offer more flexible choices for consecutive layers in heterostructures and quantum wells with desirable lattice constants and band offsets, which makes an important potential application of III-nitrides in LED's and LD's with wavelengths from red to deep ultraviolet.

Although nitride-based LED's and LD's have been commercially available since 1993, many problems remain unknown to date. It is found in experiments that the optical properties of the III-nitride compounds are very complex and cannot be explained by usual properties of bulk crystals. Some authors have proposed that some kinds of self-formed nanostructures may exist in the III-nitride films due to the inherent property, immiscibility and phase separation, of the III-nitride compounds.[5–8] However, there rises a problem that, among the very complex phenomena of the III-nitrides films measured in experiments, which of these arise from the inherent property of mixed crystals and which from the property of the disordered quantum-confinement systems. The solutions depend on the developments of the theory of mixed crystals and the theory of disordered low-dimensional systems, and also, further more experimental works.

The optical properties of the ternary mixed crystals have been studied intensively by many authors.[9–16] Many theoretical methods and approaches have been well established and developed. The main features of ternary mixed crystals are known theoretically in a certain sense. On the other hand, the theoretical study of quaternary and multinary mixed crystals has only attracted limited attention because these kinds of compounds are very complex. In the past years, only a few papers concerning this issuer were published. Gupta *et al.* calculated the optical phonon frequencies of $\mathrm{CdTe}_{1-x-y}\mathrm{Se}_x\mathrm{S}_y$ quaternary mixed crystals by means of a concentration-dependent model.[17] Eunsoon *et al.* studied the optical properties of some II-VI quaternary compounds, such as, $\mathrm{Cd}_{1-x-y}\mathrm{Zn}_x\mathrm{Mn}_y\mathrm{Te}$[18] and $\mathrm{Cd}_{1-x-y}\mathrm{Mg}_x\mathrm{Mn}_y\mathrm{Te}$,[19] in terms of the modified random element isodisplacement (MREI) model. The equations of motion for the anion and cations were given out and the optical-phonon frequencies were calculated numerically. A schematic diagram showing the zone-center optical phonon frequencies in the mixed crystals as a function of $x$-$y$ was presented. It was shown that $\mathrm{Cd}_{1-x-y}\mathrm{Zn}_x\mathrm{Mn}_y\mathrm{Te}$ and $\mathrm{Cd}_{1-x-y}\mathrm{Mg}_x\mathrm{Mn}_y\mathrm{Te}$ mixed crystals exhibit a classic three-mode behavior, and the MREI model provides a fairly good agreement with experiments.

Very recently, the successful application of group-III nitrides in optoelectronic devices prompted us to perform a detailed theoretical analysis on the optical properties of the group-III nitrides. We extended our previous theoretical works on ternary mixed crystals[14,15] to multinary mixed crystals, and found with pleasure that we can treat the problems generally by using a simple method. The optical-phonon frequencies of a multinary mixed crystal can be calculated directly by using a matrix method. The oscillator strength of every phonon mode and the dielectric constants of the crystal can be given analytically as a function of the phonon frequencies. The phonon-mode behavior of the mixed crystal can be seen directly from the concentration dependency of the oscillator strength. By using this generalized theory, we have investigated the properties of group-III nitride ternary and quaternary compounds in a unitary theoretical framework. Some interesting results have been found.

The extension of the mixed crystal theory to multinary crystals seems very worthwhile because it can give fundamental insight into the physics of the multinary compounds. It provides a powerful tool for analyzing the physical phenomena of compounds. In the present paper, we would like to introduce our improved mixed crystal theory, and also the application of the theory. The paper will be organized as follows: In Sec. II we present the theory of long-wavelength optical lattice vibrations in multinary mixed crystals. An application of the theory to group-III nitride compounds is shown in Sec. III. The main purpose of the application is to predicate the optical properties of $\mathrm{Al}_y\mathrm{In}_x\mathrm{Ga}_{1-x-y}\mathrm{N}$ quaternary mixed crystal as functions of the compositions. In order to give a good understanding of the quaternary mixed crystal, three correlated ternary mixed crystals, $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$, $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{N}$, and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$, are also calculated in the same theoretical framework for comparison. The conclusions are drawn in Sec. IV.

## II. GENERAL THEORY OF MULTINARY MIXED CRYSTALS

The multinary mixed polar crystals have been divided into three classes:[20] (1) purely anionic solutions, such as $A^{\mathrm{III}}B^{\mathrm{V}}_{1-x-y}C^{\mathrm{V}}_{x}D^{\mathrm{V}}_{y}$; (2) purely cationic solutions, such as $A^{\mathrm{III}}_{1-x-y}B^{\mathrm{III}}_{x}C^{\mathrm{III}}_{y}D^{\mathrm{V}}$; and (3) both anions and cations are mixed such as, $A^{\mathrm{III}}_{1-x}B^{\mathrm{III}}_{x}C^{\mathrm{V}}_{1-y}D^{\mathrm{V}}_{y}$. All of the mixed crystals considered here are assumed to be substitutional mixed crystals with completely miscibility. In the present work, we take the first two classes into consideration within a general theoretical frame. The third class is somewhat different and will be studied elsewhere.

### A. Theoretical model

Among various theoretical approaches used to study the optical properties of mixed crystals, the MREI model proposed by Chang and Mitra[9,11] is the most successful one. The main advantage of this model is not only simple enough for application, but also that it can give theoretical predications in good agreement with experiments. Therefore this model has been believed reliable and has been used extensively. Recently, Grille, Schnittler, and Bechstedt[16] published a detailed study on the phonons in ternary group-III nitride alloy with a generalized MREI model. By taking the lattice structure into consideration, their model can be used to describe various phonon modes in arbitrary crystal structures. The pseudo-unit-cell (PUC) model, also proposed by Chang and Mitra,[10,11] is another good theoretical model. This model simplifies greatly the concept of the many-body and random problem of the mixed crystals, and also has the advantage that the Hamiltonian of the mixed system can be obtained directly. The MREI model can be regard as a special case of the PUC model at the long-wavelength limit.

Using the PUC model, we have studied successfully the electron-phonon interaction in ternary mixed crystals in long-wavelength limit.[14,15] In our previous papers, we have explained in detail why the optical lattice vibration of mixed crystals can be described fairly well by the PUC model. In the present work, we begin our study from the PUC model directly.

We consider a multinary mixed polar crystal in form of $A_{x_0}B_{x_1}C_{x_2}\cdots X_{x_n}$ with

$$x_0=1 \quad \text{and} \quad \sum_{i=1}^{n} x_i=1, \tag{2.1}$$

where $i=0,1,2,\cdots,n$ $(n\geqslant 2)$, represents ions $A$, $B$, $C$, . . . , respectively. $x_i$ is the molar fraction of the $i$th ion in the mixed crystal. The $A$ ion is an anion and $B$, $C$, . . . ions are cations, or vice versa. The lattice of the mixed crystal consists of two sublattices. The $A$ ion is placed in one sublattice solely, and $B$, $C$, . . . ions with same polarity are distributed randomly in other one sublattice. The nearest neighbors of an A ion are always $B$, $C$, . . . ions. The probability of finding a $B$ ion as a nearest neighbor of an $A$ ion is equal to the concentration $x_1$, and so on for other ions.

In the PUC model, the effective unit cell of the mixed polar crystal consists of two ions with opposite polarity. In the present work, one of the ions is an $A$ ion, and the other is assumed to be a pseudoion which is like an aggregate of $B$, $C$, . . . ions weighted with their molar fractions. Therefore, one can understand that the multinary mixed crystals considered here is essentially a pseudo-binary crystal.

On the assumption mentioned above, the dynamic energy of the cell can be written in the form of

$$T=\frac{1}{2}\sum_{i=0}^{n} x_i m_i|\dot{\boldsymbol{r}}_i|^2, \tag{2.2}$$

where $m_i$ and $\boldsymbol{r}_i$ are the mass and the displacement of the $i$th ion, respectively.

The potential energy of the cell can be written in form of

$$V=\frac{1}{2}\sum_{i=1}^{n} x_i\beta_i|\boldsymbol{r}_i-\boldsymbol{r}_0|^2-\frac{1}{2}\sum_{i=1}^{n} x_i e_i^*(\boldsymbol{r}_i-\boldsymbol{r}_0)\cdot\boldsymbol{E}_{loc}, \tag{2.3}$$

where $\beta_i$ and $e_i^*$ are the nearest-neighbor force constant and effective charge of the $i$th ion corresponding to the $A$ ion, respectively. $\boldsymbol{E}_{loc}$ is the local electric field defined by the well-known Lorentz equation

$$\boldsymbol{E}_{loc}=\boldsymbol{E}+\frac{\boldsymbol{P}}{3\epsilon_0}, \tag{2.4}$$

where $\boldsymbol{E}$ is the macroscopic electric field, $\epsilon_0$ the permittivity of vacuum, and $\boldsymbol{P}$ the polarization field. $\boldsymbol{P}$ is represented by

$$\boldsymbol{P}=\sum_{i=1}^{n} x_i n_e e_i^*(\boldsymbol{r}_i-\boldsymbol{r}_0)+\sum_{i=1}^{n} x_i n_e\gamma_i\boldsymbol{E}_{loc}, \tag{2.5}$$

where $n_e$ is the number of ion pairs per unit volume, $\gamma_i$ $(i=1,2,3,\ldots)$ is the electronic polarizability of the pairs of the $i$th ion and the $A$ ion.

We can introduce the center-of-mass coordinate $\boldsymbol{R}$ and relative coordinate $\boldsymbol{u}$ by

$$M=\sum_{i=0}^{n} x_i m_i , \tag{2.6}$$

$$\boldsymbol{R}=\frac{1}{M}\sum_{i=0}^{n} x_i m_i \boldsymbol{r}_i , \tag{2.7}$$

$$\boldsymbol{u}_i=\boldsymbol{r}_i-\boldsymbol{r}_0, \quad (i=1,2,3,\ldots,n); \tag{2.8}$$

then the expressions of $T$, $V$, and $P$ are reduced to

$$T=\frac{1}{2}M|\dot{\boldsymbol{R}}|^2+\frac{1}{2}\sum_{i=1}^{n} x_i m_i|\dot{\boldsymbol{u}}_i|^2-\frac{1}{2M}\left[\sum_{i=1}^{n} x_i m_i\dot{\boldsymbol{u}}_i\right]^2, \tag{2.9}$$

$$V=\frac{1}{2}\sum_{i=1}^{n} x_i\beta_i|\boldsymbol{u}_i|^2-\frac{n_e a}{18\epsilon_0}\left[\sum_{i=1}^{n} x_i e_i^*\boldsymbol{u}_i\right]^2 -\frac{a}{6}\left[\sum_{i=1}^{n} x_i e_i^*\boldsymbol{u}_i\right]\cdot\boldsymbol{E}, \tag{2.10}$$

$$\boldsymbol{P}=\frac{n_e a}{3}\sum_{i=1}^{n} x_i e_i^*\boldsymbol{u}_i+\epsilon_0(a-3)\boldsymbol{E}, \tag{2.11}$$

respectively. Here $a$ is calculated by

$$\frac{a-3}{a}=\frac{1}{3\epsilon_0}\sum_{i=1}^{n} x_i n_e\gamma_i . \tag{2.12}$$

It is easy to see that $\dot{\boldsymbol{R}}$ must be a constant because the potential $V$ is independent of $\boldsymbol{R}$. In the present work, we do not consider the motion of the mass center, so that we set $\dot{\boldsymbol{R}}=0$ in the following calculations. The Lagrange and the Hamiltonian for the system can be obtained straightforward from Eqs. (2.9) and (2.10), here we have no need to write them out since they are simple.

### B. Equation of motion

As usual, the variables of $\boldsymbol{E}$, $\boldsymbol{u}$, and $\boldsymbol{P}$ may be assumed to have a harmonic time dependence as $\exp(-i\omega t)$ for the study of long-wavelength lattice vibrations. $\boldsymbol{P}$ can also be calculated by

$$\boldsymbol{P}=[\epsilon(\omega)-1]\epsilon_0\boldsymbol{E}, \tag{2.13}$$

where $\epsilon(\omega)$ is the dielectric function of the mixed crystal, which is a function of the frequency of the lattice vibration. Using Eqs. (2.13) and (2.11), we have

$$\boldsymbol{E}=\frac{a n_e}{3\epsilon_0(\epsilon(\omega)+2-a)}\sum_{i=1}^{n} x_i e_i^*\boldsymbol{u}_i . \tag{2.14}$$

Inserting Eq. (2.14) into Eq. (2.10),

$$V=\frac{1}{2}\sum_{i=1}^{n} x_i\beta_i|\boldsymbol{u}_i|^2-\frac{n_e a}{18\epsilon_0}\left(1+\frac{a}{\epsilon(\omega)+2-a}\right)\times\left[\sum_{i=1}^{n} x_i e_i^*\boldsymbol{u}_i\right]^2. \tag{2.15}$$

The equation of motion for the lattice vibrations is calculated by the Euler-Lagrange equation

$$\frac{d}{dt}\frac{\partial T}{\partial\dot{u}}=-\frac{\partial V}{\partial u}. \tag{2.16}$$

Inserting expressions (2.9) and (2.15) into Eq. (2.16), we obtain a generalized equation of motion for optical lattice vibrations in the multinary mixed crystal:

$$\left(\frac{\beta_i}{m_i}-\omega^2\right)\boldsymbol{u}_i+\sum_{j=1}^{n}\left(x_j\frac{m_j}{M}\omega^2-\frac{x_j}{m_i}\frac{(\epsilon(\omega)+2)a}{\epsilon(\omega)+2-a}\frac{n_e e_i^* e_j^*}{9\epsilon_0}\right)\times\boldsymbol{u}_j=0 \quad (i=1,2,\ldots,n). \tag{2.17}$$

This equation can be rewritten in the form of a dynamical matrix,[18] that is, $[M][u]=0$. The frequency $\omega$ can be calculated by solving the equation of $\det[M(\omega)]=0$. Since $\det[M(\omega)]$ is a polynomial of degree $n$ for $\omega^2$, the roots of $\omega^2$ can be obtained analytically when $n\leqslant 4$ in principle, but their expressions are too lengthy to write them out if $n>2$. For a practical application, it seems convenient to solve the equation numerically by a personal computer.

The frequencies of transverse optical (TO) phonons are determined by the pole points of the dielectric function $\epsilon(\omega)$, that is to say, the TO modes correspond to the result of $\epsilon(\omega)\rightarrow\infty$ in Eq. (2.17). Obviously, this result can also be obtained by setting $\boldsymbol{E}=0$ in the expression (2.10) since the macroscopic electric filed $\boldsymbol{E}$ do not affects the TO mode. On the other hand, the frequencies of longitudinal-optical (LO) phonons can be determined by the zero points of the dielectric function, that is to say, the LO modes correspond to the result of $\epsilon(\omega)\rightarrow 0$, which means that $\epsilon_0\boldsymbol{E}+\boldsymbol{P}=0$ in Eq. (2.17). The eigenfrequencies of the TO and LO phonons are represented as $\omega_{Ti}$ and $\omega_{Li}$ $(i=1,2,\ldots,n)$, respectively.

### C. Physical parameters

In order to perform further calculation, one needs to determine the microscopic parameters that appeared in the above equations. As one advantage of the PUC model, the microscopic parameters can be expressed by the macroscopic measurable physical parameters according to the well-known Born-Huang procedure without any adjusting parameter.[12,21] This work is slightly tedious but without any difficulty.

In the present work, we will not consider the difference of the unit-cell volumes between the mixed crystal and the end binary crystals because (1) as we do not have sufficient knowledge of the lattice strain in mixed crystals, the lack of this information hinders us in proposing any reasonable modification; and (2) the difference is relatively small in practice. As explained early by Genzel *et al.*,[12] this approximation changes only slightly the curvature of the frequency curves inside the composition range, but has no effect at the end ranges of $x_i \rightarrow 0$ and $x_i \rightarrow 1$.

In fact, we do not need to give the expression for every microscopic parameter. The masses of the cations and anions, $m_i$ $(i=1,2,\ldots,n)$, are well known. The other parameters that need to be deduced are in three groups, they are

$$a, \quad \frac{\beta_i}{m_i} \quad \text{and} \quad \frac{n_e e_i^* e_j^*}{9\epsilon_0}. \tag{2.18}$$

Setting $x_i=1$ and $x_j=0$, $(j\neq 0,i)$, from Eq. (2.17) we obtain

$$\left(\frac{\beta_i}{m_i}-\omega^2\right)\boldsymbol{u}_i+\left(\frac{m_i}{M_i}\omega^2-\frac{1}{m_i}\frac{(\epsilon_i(\omega)+2)a_i}{\epsilon_i(\omega)+2-a_i}\frac{n_e e_i^{*2}}{9\epsilon_0}\right)\boldsymbol{u}_i=0, \tag{2.19}$$

with

$$M_i=m_0+m_i, \tag{2.20}$$

$$a_i=3\left[1-\frac{1}{3\epsilon_0}n_e\gamma_i\right]^{-1}. \tag{2.21}$$

Then, following the Born-Huang procedure, the parameters listed in Eq. (2.18) are deduced as

$$a=3\left[1-\sum_{i=1}^{n}x_i\frac{\epsilon_i(\infty)-1}{\epsilon_i(\infty)+2}\right]^{-1}, \tag{2.22}$$

$$\frac{\beta_i}{m_i}=\frac{m_0}{M_i}\frac{\epsilon_i(\infty)\omega_{Li}^2+2\omega_{Ti}^2}{\epsilon_i(\infty)+2}, \tag{2.23}$$

$$\frac{n_e e_i^* e_j^*}{9\epsilon_0}=m_0\sqrt{\frac{m_i m_j}{M_i M_j}}\frac{\sqrt{\epsilon_i(\infty)(\omega_{Li}^2-\omega_{Ti}^2)}}{\epsilon_i(\infty)+2}\times\frac{\sqrt{\epsilon_j(\infty)(\omega_{Lj}^2-\omega_{Tj}^2)}}{\epsilon_j(\infty)+2}. \tag{2.24}$$

Here $\epsilon_i(\infty)$ $(\epsilon_i(0))$ and $\omega_{Lj}$ $(\omega_{Tj})$ represent the high-frequency (static) dielectric constant and the frequency of LO (TO) phonon of the $i$th end binary crystal, respectively. It should be noted that, since the values $\epsilon(\infty)$, $\epsilon(0)$, $\omega_L$ and $\omega_T$ do not exactly obey the Lyddane-Sachs-Teller (LST) relation for a practical polar crystal, using or not using the LST relation to simplify the expressions will affect the final numerical results slightly.

Inserting above expressions into Eq. (2.17), then we obtain the dynamical equation expressed by the macroscopic measurable parameters of the end binary crystals. With the help of numerical linear algebra method, one can easily calculate the frequencies of the zone-center optical phonons in the multinary mixed crystals.

### D. Dielectric function and oscillator strength

The dielectric function is an important physical parameter to characterize materials. The concentration dependency of the dielectric function is a prerequisite for designing optoelectronic devices using mixed crystals. Since the dielectric function responds to the lattice vibrations, it can be calculated in the frame of phonon theory.

The high-frequency dielectric constant, $\epsilon(\infty)$, of the mixed crystal can be calculated simply since the lattice vibration has no effect on the polarization at high-frequency limit. From Eqs. (2.11) and (2.13) we obtain that

$$\epsilon(\infty)=a-2. \tag{2.25}$$

Since the expression of $a$ has been given in Eq. (2.22), we obtain an analytical expression for $\epsilon(\infty)$:

$$\frac{\epsilon(\infty)-1}{\epsilon(\infty)+2}=\sum_{i=1}^{n}x_i\frac{\epsilon_i(\infty)-1}{\epsilon_i(\infty)+2}. \tag{2.26}$$

This result appears in the form of a weighted summation of the Clausius-Mossotti equation from the high-frequency dielectric constants of the end binary members.

In general cases, by taking Eq. (2.14) into consideration, we can rewrite Eq. (2.17) in the form of

$$\left(\frac{\beta_i}{m_i}-\omega^2\right)\boldsymbol{u}_i+\sum_{j=1}^{n}\left(x_j\frac{m_j}{M}\omega^2-\frac{x_j a}{m_i}\frac{n_e e_i^* e_j^*}{9\epsilon_0}\right)\boldsymbol{u}_j=\frac{a e_i^*}{3m_i}\boldsymbol{E}. \tag{2.27}$$

We have noticed that the eigenfrequencies of the TO modes of the mixed crystal, $\omega_{Ti}$ $(i=1,2,\ldots,n)$, can be obtained by setting $\boldsymbol{E}=0$ in Eq. (2.27), and that the eigenfrequencies of the LO modes, $\omega_{Li}$ $(i=1,2,\ldots,n)$, can be obtained by setting $\epsilon_0\boldsymbol{E}+\boldsymbol{P}=0$ in Eq. (2.27). Then using relations (2.11) and (2.13), we obtain

$$\frac{\epsilon(\omega)}{\epsilon(\infty)}=\prod_{i=1}^{n}\frac{(\omega_{Li}^2-\omega^2)}{(\omega_{Ti}^2-\omega^2)}. \tag{2.28}$$

Obviously, this equation is the general dispersion relation for the dielectric function of a system consisted of $n$ uncoupled harmonic oscillators. The static dielectric constant $\epsilon(0)$ of the mixed crystal is calculated by setting $\omega\rightarrow 0$ in Eq. (2.28), that gives

$$\frac{\epsilon(0)}{\epsilon(\infty)}=\prod_{i=1}^{n}\frac{\omega_{Li}^2}{\omega_{Ti}^2}. \tag{2.29}$$

This is just the LST relation for multinary mixed crystals.

The oscillator strength is a very useful parameter for us to judge the characteristic of the phonon modes, and its composition dependency shows the phonon-mode behavior of the mixed crystal. Since the harmonic-oscillator model is a good approximation of optical phonons, the dielectric function can be constructed as a linear superposition of the contributions of the individual oscillators. In this way, we can define the oscillator strengths $f_i$ $(i=1,2,\ldots,n)$ for phonon modes by following equation, as introduced by Genzel, Martin, and Perry:[12]

$$\epsilon(\omega)=\epsilon(\infty)+\sum_{i=1}^{n}\frac{f_i\omega_{Ti}^2}{(\omega_{Ti}^2-\omega^2)}. \tag{2.30}$$

TABLE I. The physical parameters of InN, GaN, and AlN crystals. The band gap $E_g$ is in units of eV, the phonon energy in units of meV. These data are taken from Ref. 26.

| Material | $E_g$ | $\hbar\omega_L$ | $\hbar\omega_T$ | $\epsilon_0$ | $\epsilon_\infty$ |
|---|---|---|---|---|---|
| InN | 2.05 | 86.0 | 59.3 | — | 9.3 |
| GaN | 3.5 | 92.5 | 69.3 | 10.4 | 5.8 |
| AlN | 6.2 | 111 | 83.3 | 9.14 | 4.84 |

Comparing Eq. (2.30) with Eq. (2.28) and performing a partial fraction decomposition, we obtain directly that

$$f_i=\epsilon(\infty)\prod_{j=1}^{n}\,(\omega_{Lj}^2-\omega_{Ti}^2)\left[\omega_{Ti}^2{\prod_{j=1}^{n}}'\,(\omega_{Tj}^2-\omega_{Ti}^2)\right]^{-1}, \tag{2.31}$$

where $\Pi'$ denotes the product for all terms excluding $j=i$.

If we obtain all of the eigenfrequencies of a mixed crystal, then we can use Eq. (2.31) to calculate the oscillator strength for every optical phonon mode. Equation (2.31) shows that the phonon oscillator strength $f_i$ will tend to zero if the frequency of the $i$th TO phonon mode is very close to any one of the LO-phonon frequencies; on the contrary, $f_i$ will tend to be larger if $\omega_{Ti}$ is near any other one of TO-phonon frequencies.

## III. OPTICAL PROPERTIES OF III-NITRIDE MIXED CRYSTALS

In recent years, the group-III nitride compounds have attracted considerable interest due to their applications for optoelectronic devices, which are active in the blue and ultraviolet spectral regions with high quantum efficiency.[2–4,22–25] A knowledge of these mixed compounds is urgently required for further investigations and applications. Using the multinary mixed theory described in Sec. II, we can give some predictions about the optical properties of these mixed crystals.

For the group-III nitrides, there are many optical-phonon modes due to the large unit cell of the wurtzite structure. Since we are interested in the mode behaviors and the qualitative optical properties of the III nitrides, we only focus our attention on the main branch $E_1$ mode in the present calculation. As we have mentioned in our previous paper,[15] the other modes may be some small different in values but have no qualitative different. The numerical results for other modes can be obtain by the same procedure by choosing different initial parameters.

The main purpose of this section is to study the composition dependency of optical properties of $\mathrm{Al}_y\mathrm{In}_x\mathrm{Ga}_{1-x-y}\mathrm{N}$ quaternary mixed crystal, but, in order to see the relationship between the ternary and quaternary mixed crystals and also to compare our theoretical results with other theoretical works, we also show briefly the numerical results of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$, $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{N}$, and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$, which are calculated within the same framework.

The parameters used in the calculation is listed in Table I. The numerical results of phonon energies, oscillator strengths and dielectric constants of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$, $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{N}$, and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ ternary mixed crystals are plotted in Fig. 1 in the form of a graphic matrix. It is seen clearly that $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{N}$ shows a typical two-mode behavior because of the large mass difference of In and Al atoms, $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ exhibits a typical one-mode behavior. The mode behavior of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ mixed crystals is slightly confused since the oscillator strength of the mode 2 is zero at the two end cases ($x=1$ and 0) and increases slightly inside the composition range, but, its amplitude is always much smaller than that of the mode 1. According to the early work of Chang and Mitra,[11] $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ can also be qualitatively classified to one-mode behavior, though mode 2 may be observed in experiments. This classification is in agreement with the work of Yu *et al.*[13] The phonon-mode behavior and the effect of atomic structures in ternary group-III nitride alloys have been discussed in detail in Ref. 16.

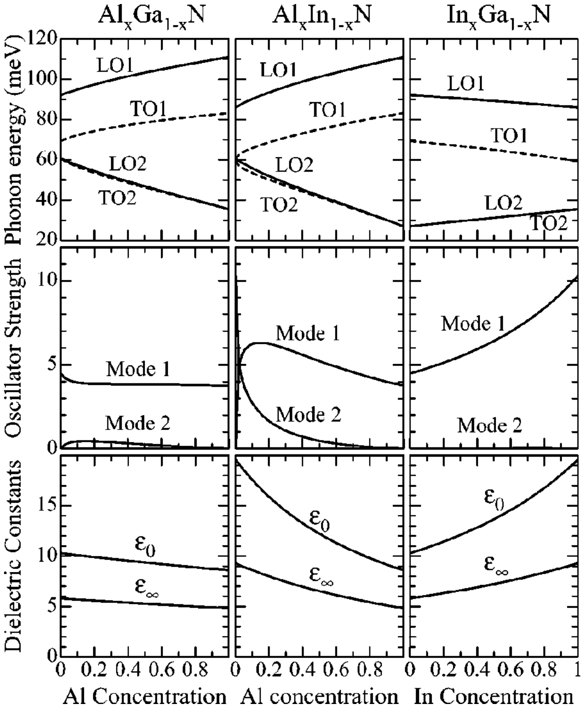

FIG. 1. Concentration dependence of optical-phonon energies, oscillator strengths, and high-frequency and static dielectric constants of (a) $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$, (b) $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{N}$, and (c) $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ ternary mixed crystals. The solid lines in the top graphs represent the LO-phonon energies, and the dashed lines represent the TO-phonon energies.

It is noticed that the oscillator strengths of $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{N}$ show a sudden change near the region of $x=0$. When Al concentration is nearly zero, the InN-like mode (mode 2) exhibits a very strong oscillation, but, when Al concentration is little more increased, the InN-like mode decreases abruptly with an abrupt increasing of the AlN-like mode (mode 1). The cross of the two strengths is at about $x=0.02$. When $x>0.1$, the AlN-like mode is dominant and the $\mathrm{Al}_x\mathrm{In}_{1-x}\mathrm{N}$ shows a behavior like a one-mode crystal. Recently, Kasic *et al.*[27] reported an investigation on the influence of strain and composition on the $E_1$(TO) phonon of undoped

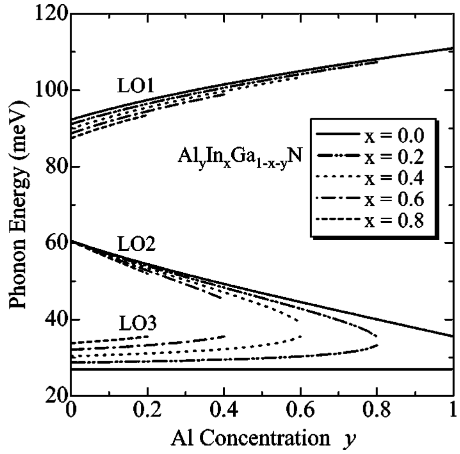

FIG. 2. Concentration dependence of LO-phonon energies in $Al_yIn_xGa_{1-x-y}N$.

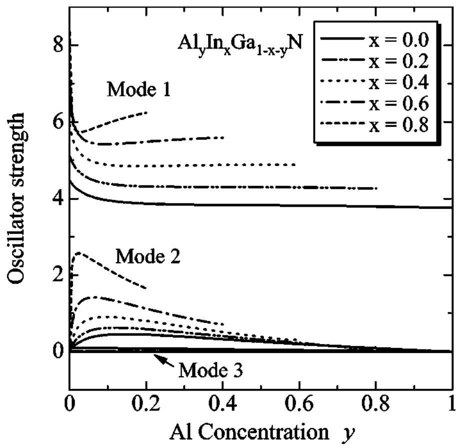

FIG. 4. Calculated phonon oscillator strengths as a function of $x$-$y$ in $Al_yIn_xGa_{1-x-y}N$.

$\alpha$-$Al_xIn_{1-x}N$ ($0.883 \geqslant x \geqslant 0.788$), and they found that the $Al_xIn_{1-x}N$ shows a one-mode behavior in contrast to the theoretical work of Grille *et al.*[16] However, this confusion can be explained reasonable by the present work. As shown in Fig. 1, in the range of $0.883 \geqslant x \geqslant 0.788$ the $Al_xIn_{1-x}N$ crystal indeed shows a one-mode behavior because the oscillator strength of the mode 1 is much larger than that of mode 2, even though $Al_xIn_{1-x}N$ is really a two-mode mixed crystal in the full composition range. Based on the present theoretical results, we suggest that, in order to judge the phonon modal behavior, one should perform experiments in the full range of concentration ratios, especially in the $x < 0.1$ range for $Al_xIn_{1-x}N$.

In Fig. 1, we see that the dielectric constants, $\epsilon_\infty$ and $\epsilon_0$, of the three ternary III-nitride mixed crystals vary smoothly and monotonically from one end-member value to the other end-member value over the composition range regardless of the one- or two-mode behavior. We are very interested in the modal behavior of optical phonons in $Al_yIn_xGa_{1-x-y}N$ quaternary mixed crystal since $Al_yIn_xGa_{1-x-y}N$ is regarded as a solid solution made up from two one-mode crystals (InGaN and AlGaN) and one two-mode crystal (AlInN). The optical-phonon energies, oscillator strengths, and dielectric constants of $Al_yIn_xGa_{1-x-y}N$ are calculated in the full $x$-$y$ range. Although the numerical results can be plotted in the form of three-dimensional (3D) objects, it seems difficult to show the numerical relation clearly by projecting the 3D geometry on the paper. In the present work, we plot the results as a function of $y$ while $x$ is fixed to several typical values. The LO phonon energies, the TO phonon energies, the oscillator strengths and the dielectric constants of $Al_yIn_xGa_{1-x-y}N$ are plotted in Figs. 2, 3, 4, and 5, respectively.

Comparing Figs. 2–5 with Fig. 1, we see that, in the cases of $x=0$, $y=0$, and $1-x-y=0$, all of the results can be reduced to that of AlGaN, InGaN, and AlInN ternary mixed crystals, respectively. For the $Al_yIn_xGa_{1-x-y}N$ quaternary mixed crystal, there should be three LO phonon modes and three TO phonon modes in principle, which can be calculated formally by the motion equation of Eq. (2.17). The results are shown in Figs. 2 and 3. However, the modal behavior of the phonons is very different. As shown in Fig. 4, since the oscillator strength of the mode 3 is almost zero for all composition ratios, $Al_yIn_xGa_{1-x-y}N$ is really a two-mode quaternary mixed crystal.

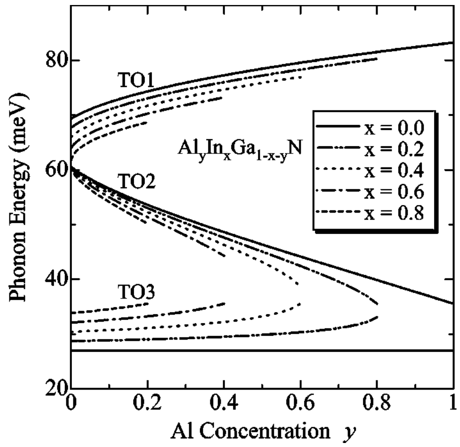

FIG. 3. Concentration dependence of TO-phonon energies in $Al_yIn_xGa_{1-x-y}N$.

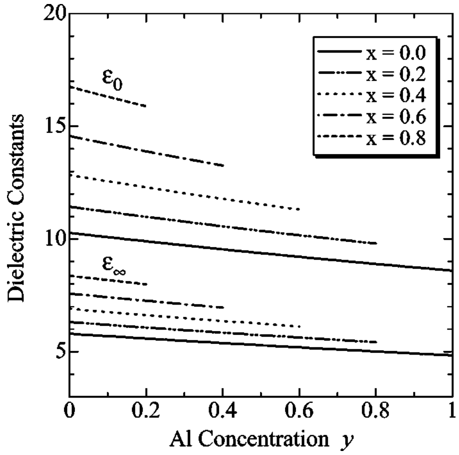

FIG. 5. Calculated static and high-frequency dielectric constants as a function of $x$-$y$ in $Al_yIn_xGa_{1-x-y}N$.

From Fig. 4 we also see that the oscillator strength of mode 1 is much larger than that of the mode 2 in nearly the full composition range expect the narrow region of $x > 0.8$. It can be predicted that when the In concentration is larger than 0.8, the oscillator strengths of $Al_yIn_xGa_{1-x-y}N$ will vary rapidly with adding a small amount of Al, as we have seen in Fig. 1 for $Al_xIn_{1-x}N$.

Figure 5 shows that the dielectric constants of the quaternary mixed crystal vary smoothly and monotonically with varying concentration ratios. This fact implies that the dielectric constants of the quaternary mixed crystal can be estimated reliably by the linear interpretation method. Due to the lack of systematic experimental study on the concentration dependence of optical phonons frequencies and dielectric constants for $Al_yIn_xGa_{1-x-y}N$ alloys in the full composition range, the comparison of the present theoretical results with experiments is hindered. It is expected that this work can be done in the near future.

## IV. CONCLUSION

The optical phonons of multinary mixed polar crystals have been studied theoretically in long-wavelength limit. The equation for calculating the optical-phonon frequencies in the multinary mixed crystals is obtained based on the PUC model. The lattice oscillator strength and dielectric constants of the multinary mixed crystal are obtained analytically. From the composition dependence of the oscillator strength we can see clearly the phonon-mode behavior of the mixed crystals. Since the present theory is given in a general form, it can be applied to ternary, quaternary, and so on, multinary mixed crystals. As an application of the theory, some III-nitride mixed crystals, which have attracted much attention, are taken into numerical calculation and comparison. The concentration dependences of the optical phonon energy, the lattice oscillator strength, and dielectric constants of the mixed crystals are calculated in the whole compound range. It is shown that the results are reasonable in the full composition range. Based on the theory, it is predicted that the $Al_yIn_xGa_{1-x-y}N$ mixed crystal will appear as a two-mode behavior. The present theory provides us with useful knowledge of the optical properties of multinary mixed crystals.

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