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Optical vibration modes and electron–phonon interaction in ternary mixed crystals of polar semiconductors*

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Optical vibrations of the lattice and the electron–phonon interaction in polar ternary mixed crystals are studied in the framework of the continuum model of Born and Huang and the random-element-isodisplacement model. A normal-coordinate system to describe the optical vibration in ternary mixed crystals is correctly adopted to derive a new Fröhlich-like Hamiltonian for the electron–phonon interaction including the unit-cell volume variation influence. The numerical results for the phonon modes, the electron–phonon coupling constants and the polaronic energies for several typical materials are obtained. It is verified that the nonlinearity of the electron–phonon coupling effects with the composition is essential and the unit-cell volume effects cannot be neglected for most ternary mixed crystals.

Keywords: optical vibration mode, electron–phonon interaction, ternary mixed crystal
PACC: 6320, 7138, 7340

1. Introduction

Many experimental and theoretical studies on the lattice dynamics of ternary mixed crystals (TMCs) of polar crystals have been performed.[1−11] It is well known that there are generally two frequency branches of phonon modes for either the transverse optical (TO) or the longitudinal optical (LO) vibration in TMCs instead of the single branch in the binary crystals. The characteristics of the polarization modes of the lattice vibration exhibit so-called "one-mode", "two-mode" behaviour or their intermediate case.[1−3] In the one-mode case, only one set of the LO and TO phonon modes whose frequencies move smoothly between the end-member crystals with compositional changes is observed. For the two-mode case, two optical phonon frequencies can be found close to the end-member frequencies for each LO and TO phonon branch. Some theoretical models have been proposed to discuss the properties of the lattice vibration in a TMC.[3] These properties may give rise to novel phenomena of electron–phonon (e–p) interaction and related problems in bulk [12] and layered semiconductors.[13,14] A simple and successful method in studying the mode behaviour of the lattice vibration in TMCs is to use the random-element-isodisplacement (REI) model [4] and its modifications.[5−8] The REI model introduced by Chen *et al* dealt with just the TO modes without including any Coulomb forces. Chang and Mitra modified the model and introduced the macroscopic electric field to split the transverse and longitudinal optical modes.[1,5] The model was called the modified random-element-isodisplacement (MREI) model. These models have been successfully used to explain the experimental results for the one-mode and two-mode behaviour.[1,7,8] The e–p interaction in TMCs has also been investigated theoretically.[11,12,15−17] Unfortunately, the e–p coupling constants has not yet been obtained experimentally in the whole range of the composition from x =0 to x =1.

One of the authors and his cooperator discussed the e–p interaction in TMCs on the basis of the MREI model and derived an e–p interaction Hamiltonian in Ref.[12]. The results gave a nonlinear relation between the e–p coupling constants and composition x. However, the normalization of the optical polarization modes was not correctly performed so that the results are over-sketchy. Zheng and Matsuura have derived

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the e–p interaction Hamiltonian in a recent work.[16] The so-called pseudo-unit-cell model they used is exactly the same as the MREI model, and the calculated results show nothing but the conclusions given by the linear interpolation method. Moreover, the effect of the unit-cell volume variation in considering the e–p interaction in TMCs was not considered. Some authors have investigated the e–p interaction in TMC heterostructures.[17] However, the normal modes of the lattice vibration in TMCs have not been constructed previously. Thus, the normal coordinates to describe the polarization modes and the corresponding normalization procedure in TMCs should be correctly carried out for the future work, in particular, for heterostructures. The unit-cell volume effect on the e–p interaction should also be considered.

In this paper we reconsider the optical vibration of TMC $A_xB_{1-x}C$ by taking the unit-cell volume variation into account to extend an early brief discussion.[18] Starting from the motion equations of the lattice vibration within the framework of the continuum model of Born and Huang [19] and the MREI model,[1,5] the Lagrangian function of the system is accurately and correctly constructed. The correct formulations for the optical vibration are given in the normal coordinate system by using a standard canonical transformation. A new Fröhlich-like Hamiltonian for the e–p interaction is obtained by taking the unit-cell volume variation into account. The numerical computations for the frequencies of LO phonons and the energies of polarons in several typical TMC materials are performed. The results show that the compositional dependence of the contribution of the e–p interaction to the polaronic energy is generally nonlinear. The unit-cell volume effects on the e–p interaction cannot be neglected for the systems with mismatch of the unit cell volumes of end-member materials.

2. Normal modes of optical vibration

To derive correctly the electron–LO-phonon interaction Hamiltonian in a TMC $A_xB_{1-x}C$, firstly we construct a normal coordinate system to describe the polarization modes of the lattice vibration in TMC $A_xB_{1-x}C$. The formulation for the normal modes of the optical vibration is also necessary for the further work, in particular for the research on the e–p interaction in heterostructures of TMCs.

In the framework of MREI model, the relative motion of the ion pairs and the polarization field in a TMC $A_xB_{1-x}C$ can be described by the following group of coupled equations,[12,15] which resemble the dynamical equations of the Born and Huang continuum model:[19]

$$\ddot{\boldsymbol{w}}_1 = b_{11}\boldsymbol{w}_1 + b_{12}\boldsymbol{w}_2 + b_{13}\boldsymbol{E}, \tag{1a}$$

$$\ddot{\boldsymbol{w}}_2 = b_{21}\boldsymbol{w}_1 + b_{22}\boldsymbol{w}_2 + b_{23}\boldsymbol{E}, \tag{1b}$$

$$\boldsymbol{P} = b_{31}\boldsymbol{w}_1 + b_{32}\boldsymbol{w}_2 + b_{33}\boldsymbol{E}. \tag{1c}$$

Here we have introduced the following quanta, similar to those used by Born and Huang for the vibration of a simple binary crystal, to describe the relative displacements of the A-C and B-C ion pairs:

$$\begin{aligned} \boldsymbol{w}_1 &= \left(\frac{\mu_{\rm A}}{\nu}\right)^{1/2}(\boldsymbol{u}_{\rm A} - \boldsymbol{u}_{\rm C}), \\ \boldsymbol{w}_2 &= \left(\frac{\mu_{\rm B}}{\nu}\right)^{1/2}(\boldsymbol{u}_{\rm B} - \boldsymbol{u}_{\rm C}), \end{aligned} \tag{2}$$

where $\mu_{\rm A}$ ($\mu_{\rm B}$) is the reduced mass of the ion pair of the end-member AC (BC)

$$\begin{aligned} \mu_{\rm A} &= \frac{M_{\rm A}M_{\rm C}}{M_{\rm A}+M_{\rm C}}, \\ \mu_{\rm B} &= \frac{M_{\rm B}M_{\rm C}}{M_{\rm B}+M_{\rm C}}. \end{aligned} \tag{3a}$$

Here $M_{\rm A}, M_{\rm B}$ and $M_{\rm C}$ are respectively the masses of ions A, B, and C, ν is the volume of the two-ion unit-cell of the TMC. The x-ray examinations indicated that ν varies smoothly from the unit-cell volume of the end-member crystal $\nu_{\rm B}$ (for BC) to $\nu_{\rm A}$ (for AC) over the composition range (x=0 to 1) for the TMC $A_xB_{1-x}C$.[7–12,15–20] Thus, we can write the unit-cell volume of the TMC as

$$\nu = x\nu_{\rm A} + (1-x)\nu_{\rm B}. \tag{3b}$$

The dynamical coefficients b_{ij} (i,j=1, 2, 3) in Eqs.(1a)–(1c) have been given correctly in Ref.[15], where some errors for the corresponding coefficients in Ref.[12] were also corrected, and we do not rewrite them again here.

For the relation between the macroscopic electric field and the polarization, the following equation holds:

$$\boldsymbol{P}(\boldsymbol{r}) = \varepsilon_0\chi(\omega)\boldsymbol{E}(\boldsymbol{r}), \tag{4}$$

where

$$\chi(\omega) = \varepsilon(\omega) - 1 \tag{5}$$

is the isotropic dielectric susceptibility. Inserting Eq.(4) into Eq.(1c), we have

$$\boldsymbol{E}(\boldsymbol{r}) = \frac{b_{31}\boldsymbol{w}_1 + b_{32}\boldsymbol{w}_2}{\varepsilon_0\chi(\omega) - b_{33}}. \tag{6}$$

Inserting Eq.(6) into Eq.(1), one can obtain a group of coupled equations for the displacements $\boldsymbol{w}_1$ and $\boldsymbol{w}_2$:

$$\ddot{\boldsymbol{w}}_1 = b'_{11}\boldsymbol{w}_1 + b'_{12}\boldsymbol{w}_2, \tag{7a}$$

$$\ddot{\boldsymbol{w}}_2 = b'_{21}\boldsymbol{w}_1 + b'_{22}\boldsymbol{w}_2, \tag{7b}$$

with

$$b'_{ij} = b_{ij} + \frac{b_{i3}b_{3j}}{\varepsilon_0\chi(\omega) - b_{33}} \qquad (i,j = 1,2). \tag{7c}$$

Here b'_{ij} are generally functions of the frequency ω.

It is easy to verify that the Eqs.(2.35)–(2.36) and (2.39)–(2.40) in Ref.[16] are special forms of our universal equations (7a)–(7c) in the cases of transverse and longitudinal vibrations respectively.

Now let us write down the Lagrangian density describing the relative motion of the ions in the mass-centre system of a unit-cell of TMC $A_xB_{1-x}C$. Ignoring the motion of the mass-centre, the density of the kinetic energy of the system can be written as

$$T = \frac{1}{2}\sum_{ij} T_{ij}\dot{\boldsymbol{w}}_i \cdot \dot{\boldsymbol{w}}_j, \tag{8}$$

where

$$T_{11} = \frac{M_{\rm A}x[M_{\rm C} + M_{\rm B}(1-x)]}{\mu_{\rm A}M}, \tag{8a}$$

$$T_{12} = T_{21} = -\frac{M_{\rm A}M_{\rm B}x(1-x)}{\sqrt{\mu_{\rm A}\mu_{\rm B}}M}, \tag{8b}$$

$$T_{22} = \frac{M_{\rm B}(1-x)(M_{\rm C} + M_{\rm A}x)}{\mu_{\rm B}M}. \tag{8c}$$

In the above equations $M = M_{\rm C} + xM_{\rm A} + (1-x)M_{\rm B}$ is the effective unit-cell mass of the TMC. The Lagrangian density of the system then can be written as

$$L = \frac{1}{2}\sum_{ij}(T_{ij}\dot{\boldsymbol{w}}_i \cdot \dot{\boldsymbol{w}}_j - V_{ij}\boldsymbol{w}_i \cdot \boldsymbol{w}_j). \tag{9}$$

The potential coefficients is given by

$$V_{ij} = -\sum_l T_{il}b'_{lj}. \tag{10}$$

The motion equation group can be obtained by the Lagrangian equations as

$$\sum_j (T_{ij}\ddot{\boldsymbol{w}}_j + V_{ij}\boldsymbol{w}_j) = 0, \tag{11}$$

which is equivalent to Eq.(7) and also Eq.(1).

The Hamiltonian density of the lattice vibration of the system is then given by

$$H = \frac{1}{2}\sum_{ij}(T_{ij}\dot{\boldsymbol{w}}_i \cdot \dot{\boldsymbol{w}}_j + V_{ij}\boldsymbol{w}_i \cdot \boldsymbol{w}_j). \tag{12}$$

Some authors have performed partly the normalization for the polarization modes,[12,16] but only the longitudinal displacement of the ions was considered. It is necessary to re-seek a correct normal coordinate system that can completely describe the optical vibration including both the LO and TO vibrations by a standard procedure.[21]

Writing the solution in the form $w_i \propto S_i\exp(\mathrm{i}\omega t)$, the motion equation can then be expressed in the following matrix form:

$$(\mathbf{V} - \omega^2\mathbf{T})|\omega^2\rangle = 0, \tag{13}$$

where

$$|\omega^2\rangle = \begin{pmatrix} S_1(\omega^2) \\ S_2(\omega^2) \end{pmatrix}, \tag{13a}$$

and tensors $\mathbf{V}$ and $\mathbf{T}$ are defined by Eqs.(10) and (11) respectively. The requirement that this equation possesses a nontrivial solution is

$$\mathrm{Det}(V_{ij} - \omega^2 T_{ij}) = 0. \tag{14}$$

The frequencies are easy to obtain by solving Eq.(14) as

$$\omega_1^2 = \frac{-(b'_{22} + b'_{11}) + \sqrt{(b'_{22} - b'_{11})^2 + 4b'_{12}b'_{21}}}{2}, \tag{15a}$$

$$\omega_2^2 = \frac{-(b'_{22} + b'_{11}) - \sqrt{(b'_{22} - b'_{11})^2 + 4b'_{12}b'_{21}}}{2}. \tag{15b}$$

The relations between the components of the ket-vectors corresponding to the frequencies ω_1 and ω_2 are obtained as

$$\begin{aligned} S_2(\omega_1^2) &= B_1 S_1(\omega_1^2), \\ S_2(\omega_2^2) &= B_2 S_1(\omega_2^2), \end{aligned} \tag{16}$$

where

$$B_1 = -\frac{\omega_1^2 T_{11} - V_{11}}{\omega_1^2 T_{12} - V_{12}}, \tag{16a}$$

and

$$B_2 = -\frac{\omega_2^2 T_{11} - V_{11}}{\omega_2^2 T_{12} - V_{12}}. \tag{16b}$$

The orthogonal and normalized relation of the eigen-solutions (13) can be chosen as

$$\langle\omega_i^2|\mathrm{T}|\omega_j^2\rangle = \delta_{ij} \tag{17}$$

in a space with the metric tensor $\mathbf{T}$. By using the above condition, the solutions can be determined as

$$|\omega_1^2\rangle = \begin{pmatrix} S_{11} \\ S_{21} \end{pmatrix}, \quad |\omega_2^2\rangle = \begin{pmatrix} S_{12} \\ S_{22} \end{pmatrix}, \tag{18}$$

where

$$S_{11}=\frac{1}{\sqrt{T_{11}+2B_1T_{12}+B_1^2T_{22}}},$$
$$S_{12}=\frac{1}{\sqrt{T_{11}+2B_2T_{12}+B_2^2T_{22}}},\qquad(18a)$$
$$S_{21}=\frac{B_1}{\sqrt{T_{11}+2B_1T_{12}+B_1^2T_{22}}},$$

and

$$S_{22}=\frac{B_2}{\sqrt{T_{11}+2B_2T_{12}+B_2^2T_{22}}}.\qquad(18b)$$

Now we transform the coordinate system to a new normal coordinate system $\boldsymbol{Q}_1$ and $\boldsymbol{Q}_2$ by

$$\begin{pmatrix}\boldsymbol{w}_1\\ \boldsymbol{w}_2\end{pmatrix}=\begin{pmatrix}S_{11}&S_{12}\\ S_{21}&S_{22}\end{pmatrix}\begin{pmatrix}\boldsymbol{Q}_1\\ \boldsymbol{Q}_2\end{pmatrix}.\qquad(19)$$

The kinetic matrix $\mathbf{T}$ is then transformed into the unit and the potential $\mathbf{V}$ a diagonal matrix with the eigenvalues ω_j^2. Thus the Lagrangian becomes a collection of simple harmonic oscillators

$$L=\frac{1}{2}\sum_j(\dot{Q}_j^2-\omega_j^2Q_j^2).\qquad(20)$$

Dividing the polarization into two perpendicular components, i.e. the transverse and longitudinal modes, a unitary motion equation can be finally obtained as

$$\ddot{\boldsymbol{Q}}_{n\nu}+\omega_{n\nu}^2\boldsymbol{Q}_{n\nu}=0,\qquad(21)$$

where the subscripts n=1, 2 stand for respectively the higher- and lower-frequency branches of phonon modes, and $\nu=T$, L for the transverse and longitudinal modes, whose frequencies are determined in Eq.(15) by choosing [12,15]

$$b'_{ij}=b_{ij}\qquad(22a)$$

for $\nu=T$, $\varepsilon=\infty$ and

$$b'_{ij}=b_{ij}-\frac{b_{i3}b_{3j}}{\varepsilon_0+b_{33}}\qquad(22b)$$

for $\nu=L$, $\varepsilon=0$.

3. e–p interaction

The energy density of the optical vibration in the normal coordinate system can be written as

$$H_{\rm vib}=\sum_{n\nu}\frac{1}{2}(\dot{\boldsymbol{Q}}_{n\nu}^2+\omega_{n\nu}^2\boldsymbol{Q}_{n\nu}^2).\qquad(23)$$

Here $\boldsymbol{Q}_{n\nu}$and $\dot{\boldsymbol{Q}}_{n\nu}$ are respectively the generalized coordinate and the conjugate momentum so that the following commutation relations are satisfied:

$$[\boldsymbol{Q}_{n\nu},\dot{\boldsymbol{Q}}_{n'\nu'}]=\mathrm{i}\hbar\delta_{nn'}\delta_{\nu\nu'},$$
$$[\boldsymbol{Q}_{n\nu},\boldsymbol{Q}_{n'\nu'}]=[\dot{\boldsymbol{Q}}_{n\nu},\dot{\boldsymbol{Q}}_{n'\nu'}]=0.\qquad(23a)$$

By using Fourier transformations we can write

$$Q_{n\nu}(\boldsymbol{r})=\frac{1}{\sqrt{V}}\sum_k Q_{n\nu}(\boldsymbol{k})\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\boldsymbol{e}_\nu,\qquad(24)$$

where $\boldsymbol{e}_\nu$ is the unit vector in the direction of the vibration and will be taken as $\boldsymbol{k}/k$ for the longitudinal vibrations. Furthermore, writing $\boldsymbol{Q}(\boldsymbol{k})$ in the following field operator form:

$$\boldsymbol{Q}_{n\nu}(\boldsymbol{k})=\left(\frac{\hbar}{2\omega_{n\nu}}\right)^{1/2}(a_{n\nu k}+a^\dagger_{n\nu,-k}),\qquad(25)$$

the commutation relations for the field operators can be derived as

$$[a_{n\nu k},a_{n'\nu'k'}]=[a^\dagger_{n\nu k},a^\dagger_{n'\nu'k'}]=0,$$
$$[a_{n\nu k},a^\dagger_{n'\nu'k'}]=\delta_{nn'}\delta_{\nu\nu'}\delta_{kk'}.\qquad(26)$$

The Hamiltonian of the phonon field is then given by

$$H_{\rm ph}=\sum_{n\nu k}\hbar\omega_{n\nu}a^\dagger_{n\nu k}a_{n\nu k}.\qquad(27)$$

Now we consider the interaction between an electron and the polarization field of the lattice vibrations. Our attention is focused on the LO vibrations hereafter, since the TO vibration modes generally do not induce the Coulomb field so that they do not couple with the electrons. The Hamiltonian of electron–polarization-field interaction is usually written as

$$H_{\rm I}=\frac{e}{4\pi\varepsilon_0}\int\frac{\boldsymbol{r}'-\boldsymbol{r}}{|\boldsymbol{r}'-\boldsymbol{r}|^3}\boldsymbol{P}(\boldsymbol{r}')\mathrm{d}\boldsymbol{r}'.\qquad(28)$$

By using Eqs.(4), (6) and (19), the polarization vector can be written as

$$\boldsymbol{P}=D_1\boldsymbol{Q}_{1L}+D_2\boldsymbol{Q}_{2L},\qquad(29)$$

where

$$D_1=\frac{\varepsilon_0}{\varepsilon_0+b_{33}}(b_{31}S_{11}+b_{32}S_{21}),\qquad(30a)$$

and

$$D_2=\frac{\varepsilon_0}{\varepsilon_0+b_{33}}(b_{31}S_{12}+b_{32}S_{22}).\qquad(30b)$$

In the above equations, all the coefficients are frequency dependent. The Fourier expansion of the polarization field (29) is given by

$$\boldsymbol{P}(\boldsymbol{r})=\frac{\varepsilon_0}{\varepsilon_0+b_{33}}\sum_{nk}\frac{\boldsymbol{k}}{k\sqrt{V}}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\times\left[\left(\frac{\hbar}{2\omega_{nL}}\right)^{1/2}(b_{31}S_{1n}+b_{32}S_{2n})(a_{1\boldsymbol{k}}+a^\dagger_{1,\boldsymbol{k}})\right].\qquad(31)$$

By using Eqs.(28) and (31), and also the Fourier transformation given by

$$\int \mathrm{e}^{\pm \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}'} \frac{\boldsymbol{r}'-\boldsymbol{r}}{|\boldsymbol{r}'-\boldsymbol{r}|^3}\mathrm{d}\boldsymbol{r}' = \mp 4\pi \mathrm{i}\frac{\boldsymbol{k}}{k^2}\mathrm{e}^{\pm \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}, \tag{32}$$

the e–p interaction Hamiltonian is finally obtained as

$$H_{\mathrm{I}} = \sum_{nk} G^*_{nk}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} a^\dagger_{nk} + \mathrm{H.c.}, \tag{33}$$

where

$$\begin{aligned} G^*_{1k} =& \frac{\mathrm{i}e}{\varepsilon_0 + b_{33}}\left(\frac{\hbar}{2\omega_{1L}}\right)^{1/2}\frac{1}{V^{1/2}k} \\ &\times \left(\frac{1}{T_{11}+2B_1T_{12}+B_1^2T_{22}}\right)^{1/2} \\ &\times (b_{31}+B_1b_{32}), \end{aligned} \tag{34a}$$

$$\begin{aligned} G^*_{2k} =& \frac{\mathrm{i}e}{\varepsilon_0 + b_{33}}\left(\frac{\hbar}{2\omega_{2L}}\right)^{1/2}\frac{1}{V^{1/2}k} \\ &\times \left(\frac{1}{T_{11}+2B_2T_{12}+B_2^2T_{22}}\right)^{1/2} \\ &\times (b_{31}+B_2b_{32}). \end{aligned} \tag{34b}$$

The e–p coupling constant is defined as

$$\alpha_{nL} = \frac{|g_n^2|}{4\pi\hbar^2\omega_{nL}^2}\left(\frac{2m\omega_{nL}}{\hbar}\right)^{1/2}, \tag{35}$$

where

$$g_n = V^{1/2}kG_{nk}. \tag{36a}$$

Here a linear interpolation for the electron band mass is used

$$m = xm_{\mathrm{A}} + (1-x)m_{\mathrm{B}}, \tag{36b}$$

where m_{A} and m_{B} are the electron band masses of the end-member materials AC and BC respectively. It is obvious that there are two branches of LO phonon modes coupling with the electrons in the TMC, in contrast to binary crystals. The e–p coupling constants depend on the composition x of TMC $\mathrm{A}_x\mathrm{B}_{1-x}\mathrm{C}$.

By using Eqs.(27) and (33), the Hamiltonian of the electron–phonon system in TMC $\mathrm{A}_x\mathrm{B}_{1-x}\mathrm{C}$ can be written as

$$\begin{aligned} H =& \frac{p^2}{2m} + \sum_{nk}\hbar\omega_{nL}a^\dagger_{nk}a_{nk} \\ &+ \sum_{nk} G^*_{nk}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}a^\dagger_{nk} + \mathrm{H.c.} \end{aligned} \tag{37}$$

This Hamiltonian can be solved by various techniques to obtain the polaron energy. A variational method used by Lee *et al* for the polaron problem in a binary polar crystal[22] has been generalized to calculate the polaron energy in a TMC.[23] The intermediate coupling polaron energy is obtained as follows:

$$E = -E_{\mathrm{tr}} + \frac{p^2}{2m^*}, \tag{38}$$

where the self-trapping energy and the renormalized effective mass are given by the following equations:

$$E_{\mathrm{tr}} = \alpha_{1L}\hbar\omega_{1L} + \alpha_{2L}\hbar\omega_{2L}, \tag{38a}$$

$$m^* = [1 + (\alpha_{1L}+\alpha_{2L})/6]m. \tag{38b}$$

4. Numerical results and discussions

We have computed numerically the phonon frequencies, the e–p coupling constants related to the two branches of LO phonon modes and the polaron energies for several polar TMC materials by using the new e–p Hamiltonian. The unit-cell volume variations

Table 1. Optical phonon energies, dielectric constants, effective masses of electrons and the lattice constants for several materials. Energy is measured in units of meV and m in the electron rest mass.

Materials	$\hbar\omega_{\mathrm{TO}}$	$\hbar\omega_{\mathrm{LO}}$	ε_0	ε_∞	m	M/a.u.		a/nm
AlAs[a]	44.88	50.09	10.06	8.16	0.150	26.99	74.92	0.5660[c]
GaAs[a]	33.29	36.25	13.18	10.89	0.067	69.72	74.92	0.56419[c]
GaP[b]	45.33	49.97	10.28	8.46	0.338	69.72	30.97	0.54505[c]
GaSb[b]	28.58	29.79	15.69	14.44	0.047	69.72	121.7	0.60959[c]
ZnSe[b]	25.67	30.50	8.33	5.90	0.171	65.38	78.9	0.5668[c]
ZnS[b]	34.65	44.00	8.00	5.14	0.280	65.38	32.06	0.5410[c]
CdS[b]	30.25	38.24	8.42	5.27	0.155	112.4	32.06	0.5825[c]
AlP[c]	70.38	79.44	9.8	7.54	0.21	26.98	30.93	0.54635[c]
AlN[d]	82.70	112.83	8.5	4.68	0.33	26.99	14.01	0.4982[c]
GaN[d]	69.43	91.87	9.5	5.35	0.20	69.72	14.01	0.5185[c]
InN[d]	59.27	86.05	9.3	7.72	0.11	114.8	14.01	0.5760[c]
InP[b]	38.21	43.33	12.29	9.56	0.076	114.8	30.97	0.64794[c]

[a] Ref.[11], [b] Ref.[24], [c] Ref.[25], [d] Ref.[10].

are included in the calculations. As examples, the results for the e–p coupling constants, self-trapping energies and renormalized effective masses of some one- and two-mode behaviour TMCs are shown in Figs.1–3. The calculated e–p coupling constants and polaron self-trapping energies for some TMCs of nitride-based components are also illustrated in Figs.4 and 5. The parameters used in the computations are listed in Table 1.

4.1. e–p coupling

The coupling constants α_1 and α_2 between the electron and the higher and lower branches of LO phonon modes are illustrated as functions of the composition x for several TMC systems of III–V and II–VI compound semiconductors in Fig.1. It is found that the one- and two-mode behaviours can be reflected by the calculated results for the e–p coupling constants.

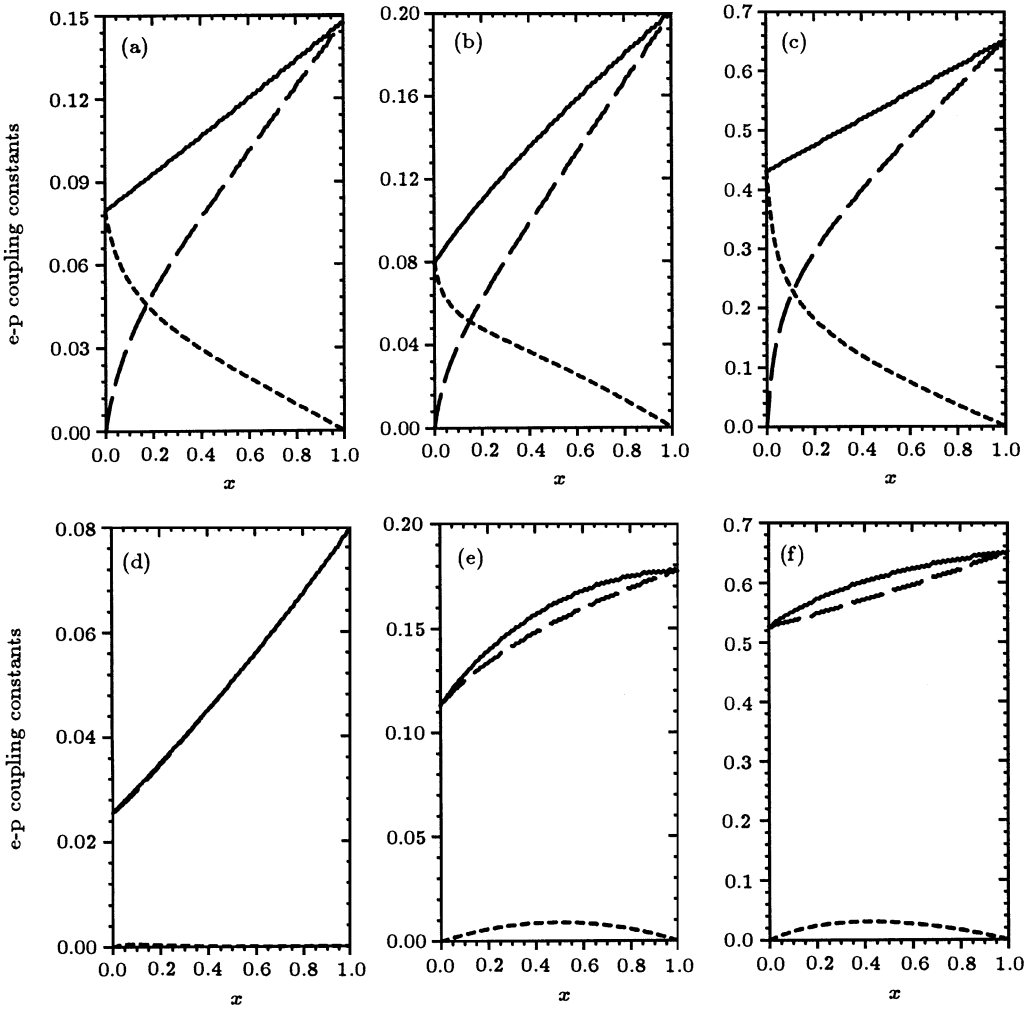


Fig.1. The e–p coupling constants α_1 (long dashed), α_2 (short dashed) and $\alpha_1+\alpha_2$ (solid) involving unit-cell volume variations as functions of the composition x for the TMCs: (a) $Al_xGa_{1-x}As$, (b) GaP_xAs_{1-x}, (c) ZnS_xSe_{1-x}; (d) $GaAs_xSb_{1-x}$, (e) $Ga_xIn_{1-x}P$, (f) $Zn_xCd_{1-x}S$.

TMC $Al_xGa_{1-x}As$, GaP_xAs_{1-x} and ZnS_xSe_{1-x} show their two-mode behaviour in the curves of the e–p interaction. It is clearly seen in Figs.1(a)–1(c) that the e–p coupling constant α_1 can be regarded as the coupling constants between the electron and the AlAs-, GaP- and ZnS-like LO phonons, and α_2 the GaAs-, GaAs- and ZnSe-like e–p coupling constants. The corresponding values of α_1 increase from zero at x =0 and finally have their end-values of AlAs-, GaP- and ZnS at x=1 respectively. Otherwise, α_2 has the end-values of GaAs, GaAs and ZnSe at x=0 and decays to zero at x=1 respectively.

On the other hand, the one-mode behaviour of optical vibrations in $GaAs_xSb_{1-x}$, $Ga_xIn_{1-x}P$ and $Zn_xCd_{1-x}S$ systems is clearly seen in Figs.1(d)–1(f). For example, one cannot tell which is the e–p coupling of the GaAs-like or GaSb-like mode branch from the two branches of LO modes in the $GaAs_xSb_{1-x}$ system. The same situation also arises for the systems $Ga_xIn_{1-x}P$ and $Zn_xCd_{1-x}S$. A main branch in the e–p coupling constants, whose coupling is much stronger than the other one, is found in these systems. The weaker branch can usually be neglected in considering the e–p interaction, in particular for a much weaker coupling system like $GaAs_xSb_{1-x}$. Thus, the one-mode behaviour can also be understood since only one branch of LO phonon modes is important for the e–p interaction. The results are the same as in the previous consideration according to the oscillator strengths.[3,7]

For comparison with the previous theoretical results, we also plot the curves of the so-called "total" coupling constants $\alpha=\alpha_1+\alpha_2$ in Fig.1, even though its physical meaning is not very clear. A nonlinear dependence of the "total" coupling constants α on the composition x is obtained for either one-mode or two-mode behaviour systems and a few materials with extremely weak e–p coupling, such as $Al_xGa_{1-x}As$. The results are qualitatively different from that given by Ref.[16], in which Zheng *et al* calculated the e–p coupling constants for some TMC systems by using their Hamiltonian, and affirmed that the "total" coupling constants vary linearly with the composition. Unfortunately, as seen in Fig.1, the linearity of the "total" coupling constant with the composition is only an accidental phenomenon for a few systems. The nonlinearity is easily understood on the basis of the fact that the e–p coupling constant is a complicated function of the phonon-frequency, the electronic mass, the dielectric constants and other parameters, and thus of the composition. It can also be found that the flexure of the "total" coupling constant α is related generally to the e–p coupling strength. For example, the $Al_xGa_{1-x}As$ has a very small "total" e–p coupling constant (around 10^{-1}–10^{-2}) and then its corresponding curve versus x is almost linear. In contrast, the "total" e–p coupling constants of materials $Ga_xIn_{1-x}P$ and $ZnCd_xS_{1-x}$ are an order of magnitude larger than the former, hence the corresponding curves are obviously nonlinear.

Similar character can also be seen in the polaronic effects. The self-trapping energies and renormalized masses of polarons in the same TMC materials are respectively illustrated in Figs.2 and 3. The nonlinearity of the polaronic effect is also found for the majority of the systems calculated, even though the $Al_xGa_{1-x}As$ system keeps the almost linear dependence of the self-trapping energy and renormalized masses on the composition. The flexure of the corresponding curves is enhanced generally with increasing e–p coupling strength.

4.2. Unit-cell volume effect

For comparison, we have plotted the calculated curves of the self-trapping energies and renormalized effective masses of polarons as functions of the composition x respectively with and without including the unit-cell volume variations in Figs.2 and 3.

It is found from the figures that the effect of the unit-cell volume variation on the compositional dependence of the polaron effects cannot be entirely neglected generally. The mismatch between the lattice constants of the end-member materials enhances the nonlinearity of the self-trapping energies (see Fig.2). We have chosen the lattice constants to be 0.56611 and 0.56419nm for AlAs and GaAs, 0.5409 and 0.5669nm for ZnS and ZnSe respectively in the computations. The unit-cell volume mismatch rates are 0.3%, 4.8% and the corresponding maximal deviation from the values with the unit-cell volume variation to that without the variation are then 0.5% and 8.2 % respectively. The larger the mismatch rates, the bigger the deviation of the self-trapping energy. For the small mismatch and weak e–p coupling TMCs, such as $Al_xGa_{1-x}As$ and $GaAs_xSb_{1-x}$ systems, the curves of the self-trapping energies with and without the volume deviations coincide completely with each other, so that the volume effect can be ignored in considering polaron properties.

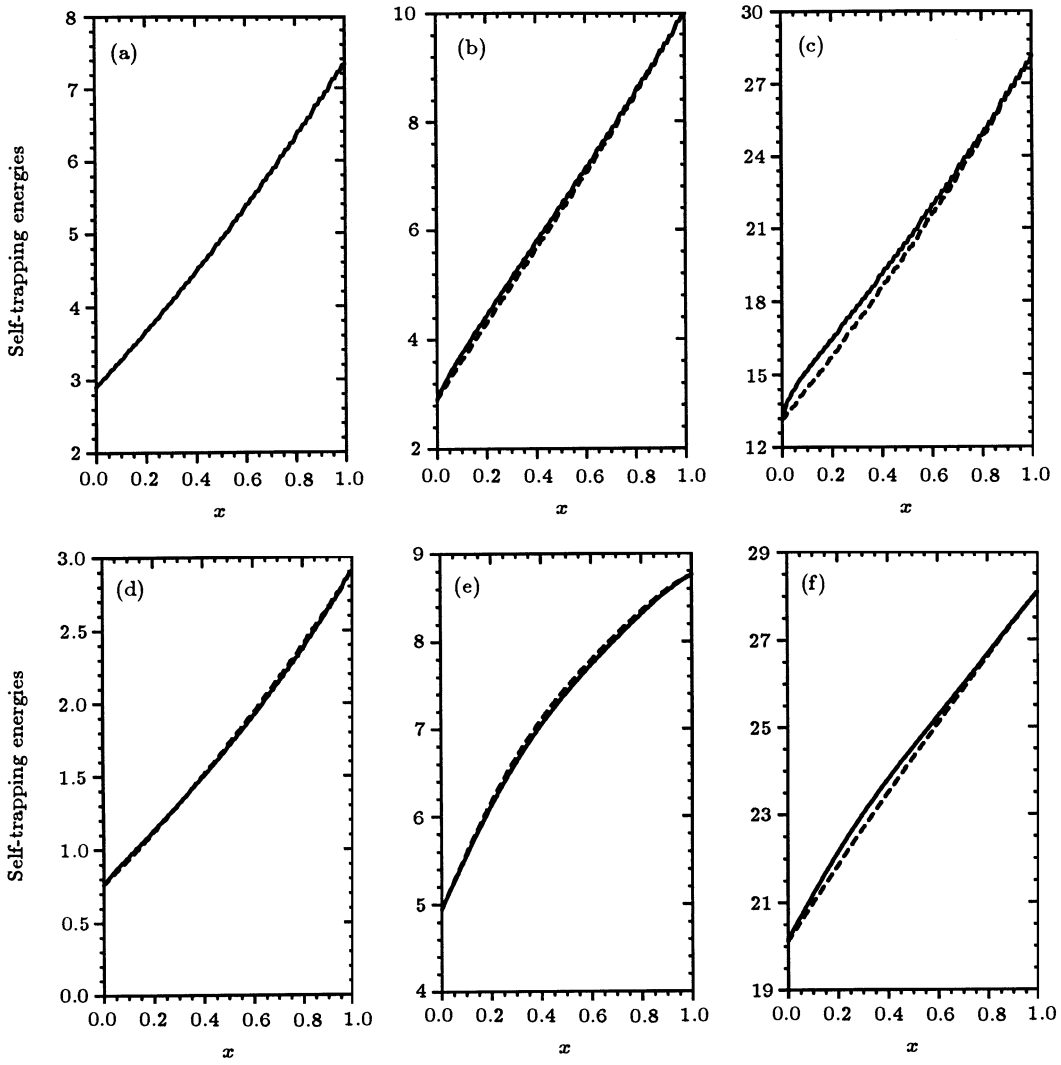


Fig.2. Self-trapping energies (in units of meV) of the polarons with (solid lines) and without (dashed lines) involving unit-cell volume variations as functions of the composition x for the TMCs: (a) $Al_xGa_{1-x}As$, (b) GaP_xAs_{1-x}, (c) ZnS_xSe_{1-x}; (d) $GaAs_xSb_{1-x}$, (e) $Ga_xIn_{1-x}P$, (f) $Zn_xCd_{1-x}S$.

Figure 3 shows the polaronic correction for the effective masses of polarons m^*/m with and without unit-cell volume variations as functions of x in TMCs. The characteristics of the curves for the renormalized masses is somewhat similar to that of the self-trapping energies, only the nonlinearity of the curves and the effect of the unit-cell volume variation on the effective mass are more obvious. It is also found that the unit-cell volume effect can be neglected only for the small mismatch and very weak e–p coupling TMCs, such as the $Al_xGa_{1-x}As$ and $GaAs_xSb_{1-x}$ systems.

4.3. Nitride-based compounds

The properties of column-III–nitride (III–N) compound semiconductors attract many scientists due to their potential developmental prospects. Some authors have investigated the phonon modes in III–N ternary mixed semiconductors theoretically.[25] We have calculated the e–p coupling constants and polaronic energies for several TMC systems of III–N compound semiconductors using our theory. The computed results of the e–p coupling constants and the self-trapping energies for the III–N TMC systems $Ga_xIn_{1-x}N$, $Al_xIn_{1-x}N$ and AlN_xP_{1-x}, as examples, are illustrated in Figs.4 and 5.

A one-mode behaviour is clearly shown in Fig.4, where there is a main branch of e–p coupling constants. It is found that the e–p coupling in III–N compounds is much stronger than that in other III–V compounds, and the nonlinearity is also more obvious than for the latter. One can also find from the curves of self-trapping energies in Fig.5 that the effect of the unit-cell volume variation on the compositional dependence of the polaron effects is remarkable and cannot be neglected for the III–N TMCs.

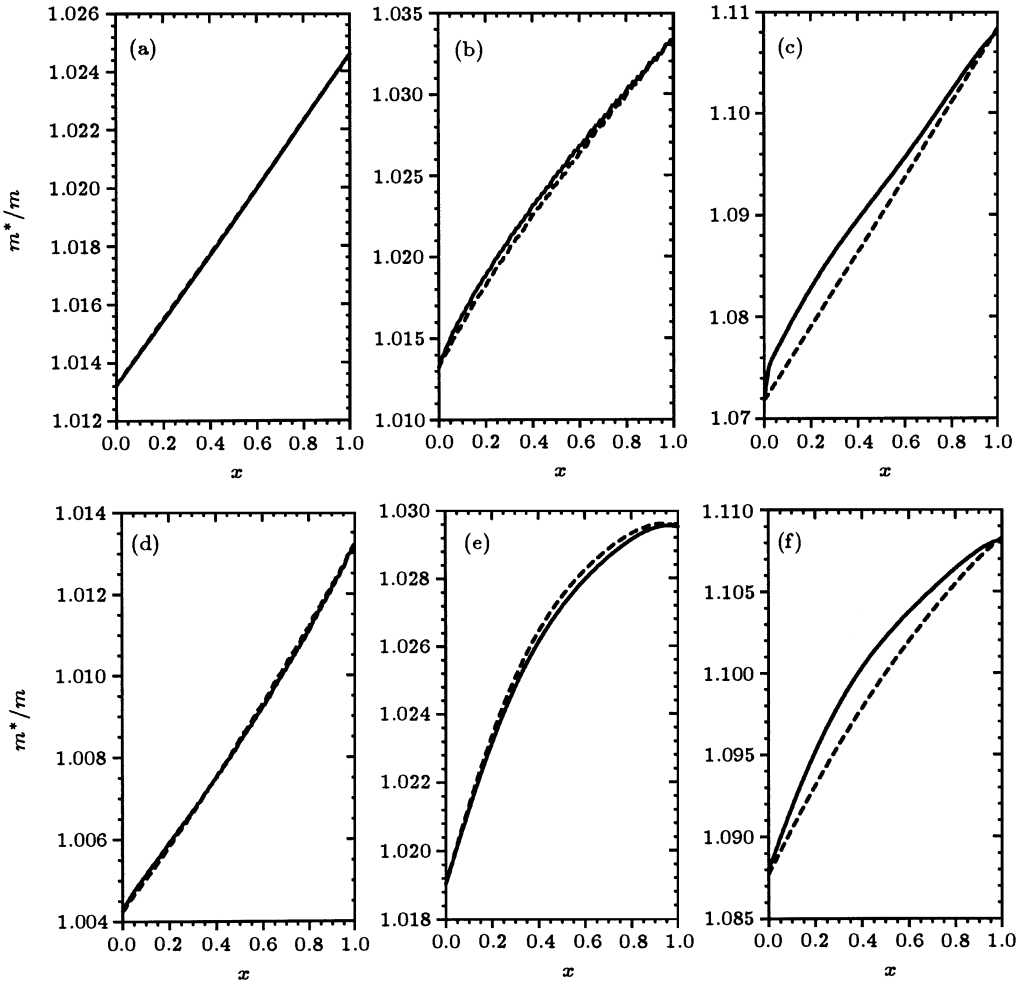


Fig.3. Renormalized coefficients m^*/m of polaron masses with (solid lines) and without (dashed lines) involving unit-cell volume variations as functions of the composition x for the TMCs: (a) $Al_xGa_{1-x}As$, (b) GaP_xAs_{1-x}, (c) ZnS_xSe_{1-x}; (d) $GaAs_xSb_{1-x}$, (e) $Ga_xIn_{1-x}P$, (f) $Zn_xCd_{1-x}S$.

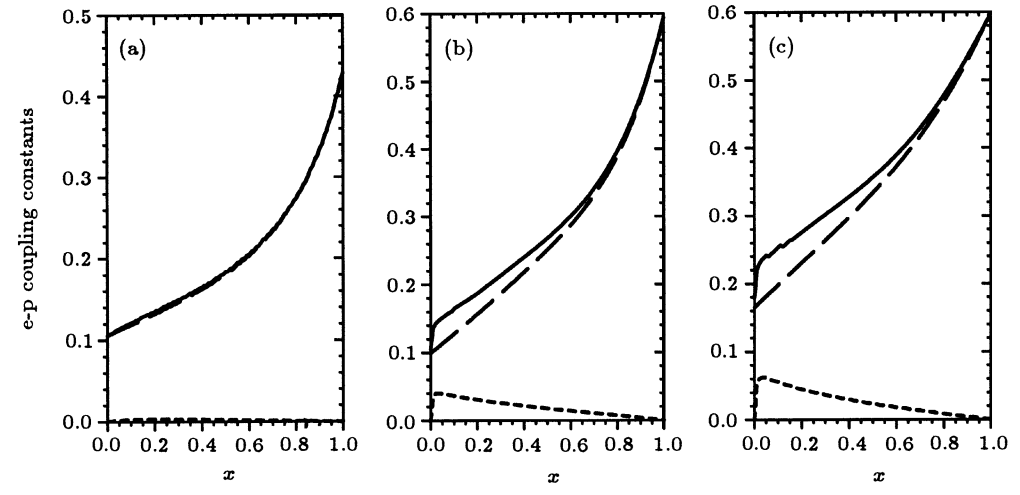


Fig.4. The e–p coupling constants α_1 (long dashed) and α_2 (short dashed) and the "total" coupling constants α (solid) involving unit-cell volume variations as functions of the composition x for several TMCs of nitride-based components: (a) $Ga_xIn_{1-x}N$, (b) $Al_xIn_{1-x}N$, (b) AlN_xP_{1-x}.

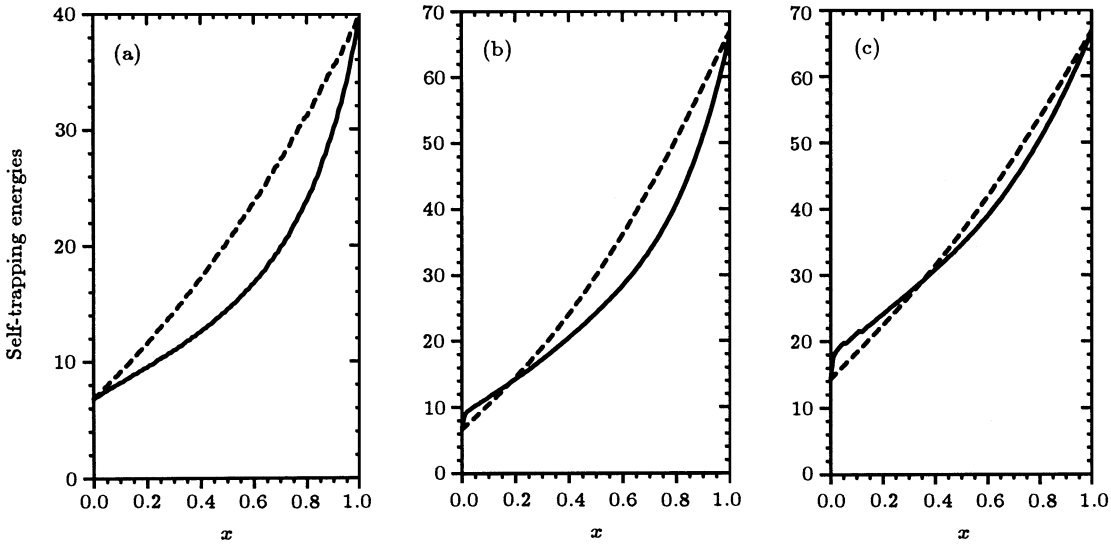


Fig.5. Polaron self-trapping energies (in units of meV) with (solid lines) and without (dashed lines) involving unit-cell volume variations as functions of the composition x for several TMCs of nitride-bases compounds: (a) $Ga_xIn_{1-x}N$, (b) $Al_xIn_{1-x}N$, (c) AlN_xP_{1-x}.

It should be pointed out that III–N compounds are usually grown in a wurtzite structure, which is not of a cubic lattice. For simplicity, in this paper we have used only one lattice constant to calculate the unit-cell volume and choose one pair of TO–LO frequencies for the binary crystals. This calculation is rather rough for the systems. However, the result for the volume effect is for reference. The correct calculation for III–N TMCs should take the non-cubic lattice and multi-branch phonon effects of binary crystals into account. This will be a subject of future investigations.

5. Summary

In summary, we have investigated the optical modes of the lattice vibration and the e–p interaction in ternary mixed crystals. In the framework of the continuum model of Born and Huang and the modified random-element-isodisplacement model, we have constructed a canonical normal coordinate system to describe the optical modes in a ternary mixed crystal $A_xB_{1-x}C$. A new Fröhlich-like Hamiltonian for the e–p interaction in the TMC system has been derived in the normal coordinate system. The unit-cell volume variation in forming the mixed crystals is also considered.

The numerical results of the e–p coupling constants and the polaronic energies for several typical ternary mixed crystal materials are obtained and discussed. The one-mode and two-mode behaviours of optical vibrations agree with the previous theoretical criteria and the experimental results. The nonlinear variation of the e–p coupling and polaron energy with the composition is verified, which is different from the previous conclusion of linearity. It is pointed out that the nonlinearity is related to the e–p coupling strength of the systems. It is also found that the volume deviation of the e–p coupling cannot be neglected generally, except for the materials with very weak e–p coupling.

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