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# Thermal expansions in wurtzite AlN, GaN, and InN: First-principle phonon calculations

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Using the first-principle phonon calculations under the quasiharmonic approximation, thermal expansions in III-nitrides with wurtzite AlN, GaN, and InN are reported. The results showed that it is different for each thermal expansion of three III-nitrides at low temperatures, which is consistent with their Grüneisen parameters as the function of temperature. Below 50 K, negative thermal expansions occur in InN, while GaN and AlN follow the rule of positive thermal expansion. To seek the origin of positive/negative thermal expansion distinction, the mode Grüneisen parameters and the phonon spectra are investigated. They indicate that different low-frequency phonon vibration modes correspond to the change of thermal expansions. Below 5 THz, the significant weighted negative values of mode Grüneisen parameters, caused by the weakening of mixing-mode constituted with two transverse acoustic (TA) modes and a small overlapped part of optical modes, directly lead to the negative thermal expansion at low temperatures. © 2011 American Institute of Physics. [doi:10.1063/1.3627237]

## I. INTRODUCTION

III-nitrides have attracted much attention due to their fruitful electronic and optical properties.<sup>1</sup> The flexibility available in tuning the bandgap from 0.7 to 6.2 eV and the exceptional radiation resistance make them very suitable for aerospace applications. These applications of group-III nitrides mostly work with thin-layer structures in a wide range of temperatures. If the thermal expansions, lattice parameters and elastic constants among components are different, thermal stress could be introduced due to a larger difference of working temperatures. It can affect various important parameters of III-nitrides, such as bandgap energy, internal electric field, and device lifetime.<sup>2,3</sup> Therefore, accurate evaluation of the thermal expansion is essential not only from a physical point of view but also for device engineering.

Thermal expansion is one of the fundamental properties of a crystalline solid. It results from the anharmonicity of the interatomic potential and can be related to the intrinsic energy of the solid, similar to the specific heat and the thermal conductivity. Most solids expand upon heating due to anharmonicity of the chemical bond, and the distance between the chemically bonded atoms generally increases; negative thermal expansion (NTE) materials are the exception to this rule, and shrink when heated.<sup>4</sup> The special negative thermal expansion phenomenon at lower temperatures is found in most III–V phases,<sup>5</sup> such as InP and GaP. This phenomenon of NTE is attributed to the unique geometry of the crystal structure and the unusual lattice dynamics. The thermal expansion coefficients (TECs) of III-nitrides have been measured experimentally in a broad temperature range dur-

ing the past years.<sup>6–10</sup> The available TECs are based on powder diffraction and high resolution x-ray diffraction using different types of samples such as bulk crystals, GaN powder, and epitaxial layers. The thermal expansion of InN in a temperature range from 70 K to 750 K has been determined,<sup>10</sup> while those of GaN and AlN were in the range of 12~1250 K (Ref. 9) and 20~1250 K,<sup>8</sup> respectively. However, the available data scatter significantly and accurate low temperature experimental data is still lacking. Specifically, compared with GaN and AlN, there are scant experimental data on the thermal properties of InN below 70 K. Recently, Inushima *et al.*<sup>11,12</sup> have reported the observation of superconducting behavior of InN below 3 K, which is related to the lattice dynamics. Apparently, many aspects in the low-temperature thermodynamic property of these materials are still waiting for clarification.

In this report, the thermal expansions of wurtzite AlN, GaN, and InN were investigated using the first-principle phonon calculations, in order to compare the temperature dependence of thermal properties. In our work, we found that AlN and GaN follow the common positive expansion rule with different Grüneisen parameters. However, negative thermal expansions at lower temperatures (<50 K) occur in InN, but the NTE values are small, highlighting the fact that it can be challenging to determine such small NTE values with high accuracy. As far as we know, little attention has been devoted to the NTE of InN.

## II. THEORETICAL MODELS

To investigate the thermal expansions of wurtzite AlN, GaN, and InN, we employed the quasiharmonic approximation (QHA)<sup>13</sup> to calculate the thermal properties at constant pressure. In this approximation, volume

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dependence of phonon frequencies at finite temperature was introduced as a part of the anharmonic effect. The thermal properties of solids at constant volume can be calculated from their phonon density of states as a function of frequencies. The phonon frequencies at a constant volume were assumed to be independent from temperatures. In particular, the phonon contribution to the Helmholtz free energy  $F_{\text{phonon}}$  can be expressed in the following way:<sup>14,15</sup>

$$F_{\text{phonon}} = \frac{1}{2} \sum_{q,\nu} \hbar \omega_{q,\nu} + k_B T \sum_{q,\nu} \ln[1 - \exp(-\hbar \omega_{q,\nu}/k_B T)], \quad (1)$$

where  $q$  and  $\nu$  are the wave vector and band index, respectively;  $\omega_{q,\nu}$  is the phonon frequency at  $q$  and  $\nu$ ; and  $T$  is the temperature.  $k_B$  and  $\hbar$  are the Boltzmann constant and the reduced Planck constant, respectively. The Gibbs free energy  $G(T, p)$  is defined as<sup>15</sup>

$$G(T, p) = \min_V [U(V) + F_{\text{phonon}}(T; V) + pV], \quad (2)$$

where  $V$  and  $p$  are the volume and pressure, respectively, and  $U(V)$  is the total energy of electronic structure at constant volume. The definition of Gibbs free energy [Eq. (2)] is that, for each couple of  $T$  and  $p$  variables, the function inside the square brackets is minimized with respect to the volume. It is noticeable that only  $F_{\text{phonon}}(T; V)$  depends explicitly on temperature. At the given temperature  $T$ , the equilibrium volume results from a minimization of  $G(T, p)$  with respect to  $V$ . The calculated  $G(T, p)$  can be used to study thermal properties and thermodynamic parameters, such as the thermal expansion defined by  $\Delta V/V_0$ . The volume thermal expansion coefficient is defined as

$$\alpha_V(T) = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p. \quad (3)$$

The thermodynamic definition of the Grüneisen parameter can be obtained as

$$\gamma(T) = \frac{V \alpha_V B_T}{C_V}. \quad (4)$$

In the quasiharmonic approximation, the heat capacity  $C_V$  at constant volume is given by<sup>15</sup>

$$C_V = \sum_{q,\nu} k_B \left( \frac{\hbar \omega_{q,\nu}}{k_B T} \right)^2 \frac{\exp(\hbar \omega_{q,\nu}/k_B T)}{[\exp(\hbar \omega_{q,\nu}/k_B T) - 1]^2}. \quad (5)$$

Then the heat capacity at constant pressure is derived from  $G(T, p)$  by<sup>15</sup>

$$C_P(T, p) = -T \frac{\partial^2 G(T, p)}{\partial T^2} = T \frac{\partial V(T, p)}{\partial T} \frac{\partial S(T; V)}{\partial V} \Big|_{V=V(T, p)} + C_V[T, V(T, p)], \quad (6)$$

where  $V(T, p)$  is the equilibrium volume at  $T$  and  $p$ . The total energy of electronic structure  $U(V)$  and the Helmholtz free energy  $F_{\text{phonon}}(T; V)$  were calculated at 11 volume points, which were sufficient to fit the thermodynamic functions to the

integral form of the Vinet equation of state (EOS; Ref. 16) at  $p=0$ . Gibbs free energies at finite temperatures were obtained as the minimum values of the thermodynamic functions, and the corresponding equilibrium volumes were obtained simultaneously from the Vinet EOS. Unit cells used to calculate  $U(V)$  and  $F_{\text{phonon}}(T; V)$  were relaxed by the first-principle calculation under the hydrostatic-stress conditions. As a result of the stability at low temperatures, the structure of AlN, GaN, and InN is wurtzite. For the first-principle calculations, we employed the plane-wave basis projector augmented wave (PAW)<sup>17</sup> method in the framework of the density-functional theory, which is within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof form<sup>18</sup> as implemented in the VASP code.<sup>19–21</sup> A plane-wave energy cutoff of 500 eV was used. The Brillouin zones k-point sets were sampled by the Monkhorst-Pack scheme<sup>22</sup> with a  $10 \times 10 \times 8$  k-point mesh. Phonon calculations were performed by the supercell approach with atomic displacements of 0.01 Å implemented in the VASP (Refs. 19–21) and PHONOPY (Refs. 15 and 23) code. For the QHA calculations,  $3 \times 3 \times 2$  supercells containing 72 atoms were used.

### III. RESULTS AND DISCUSSIONS

In Fig. 1, the volume expansions of the three III-nitrides as a function of the temperature are shown in the temperature below 300 K with the inset image in the range from 0 to 1500 K. The volume expansion is defined by  $\Delta V/V_0$ , where  $V_0$  at 300 K and  $\Delta L = V - V_0$ . The calculated values of all III-nitrides are in good agreement with the experimental values. The little error is probably contributed by GGA and different experimental samples. In all III-nitrides, an almost linear expansion at temperatures above 600 K is shown in the inset of Fig. 1. This behavior is consistent with models based on the intrinsic phonon energy of a solid system. At low temperatures, almost no thermal expansion is observed below 120 K for AlN, while the temperature is 50 K for GaN and InN. The volume expansions of GaN and InN are similar and that of AlN is only half the size.

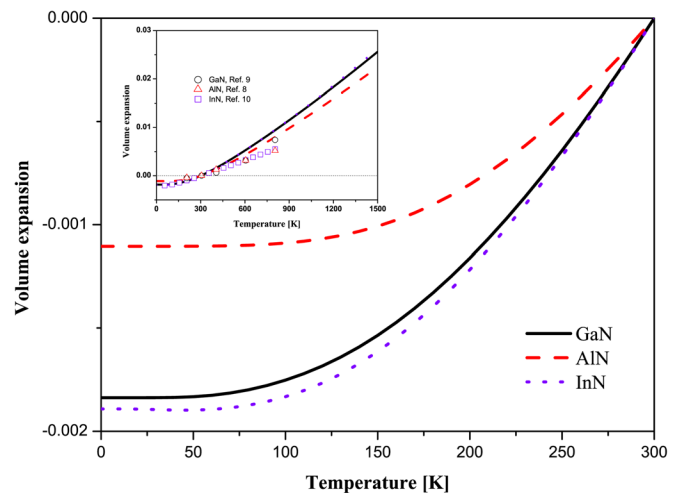


FIG. 1. (Color online) Volume expansions as a function of temperature below 300 K. Inset is the reduced figure between 0 and 1500 K. 300 K is set to the normal volume  $V_0$ . The experimental values of AlN, GaN, and InN are depicted by triangles (Ref. 8), circles (Ref. 9), and squares (Ref. 10), respectively.

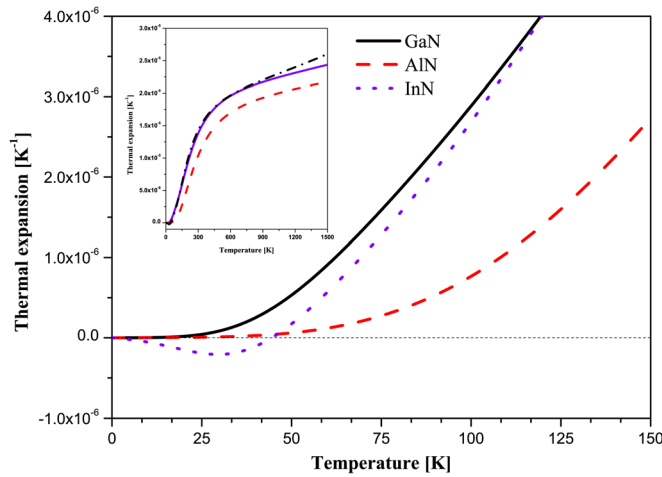


FIG. 2. (Color online) Thermal expansion coefficients as a function of temperature below 150 K. Inset is the reduced figure between 0 and 1500 K.

To show explicit details of volume expansion, the thermal expansion coefficients (TECs) of the three compounds are shown in Fig. 2. With increasing temperatures, the thermal expansion coefficients show strong temperature dependency and grow rapidly up to 600 K, and slopes become smaller and nearly constant at high temperatures. Below 900 K, the thermal expansion coefficients of GaN and InN are similar and are larger than that of AlN. At high temperatures, the thermal expansion coefficients of GaN and InN are different and the latter is larger. Particularly, for  $T < 50$  K, negative thermal expansion occurs in InN while positive thermal expansions are obtained in GaN and AlN. As far as we know, until now no observation about the negative thermal expansion of InN has been reported. Wang *et al.*<sup>10</sup> have reported that the thermal expansion coefficients of InN are small and possibly negative below 70–100 K, this experimental observation indirectly confirmed the prediction, in which InN appears to be NTE material at lower temperatures.

It is known that negative thermal expansion at lower temperatures is closely related to the negative Grüneisen parameter.<sup>24</sup> The Grüneisen parameter describes the effect of the temperature on the dynamics of the lattice, as shown in Eq. (4). Calculated Grüneisen parameters are shown in Fig. 3. It can be seen that for GaN and AlN, the Grüneisen parameter is always positive in the temperature range, although the Grüneisen parameter of AlN first decreases and then increases. The Grüneisen parameter of InN is initially negative from 0 K, and then it changes to a positive value close to 50 K. The change of the calculated Grüneisen parameter leads to different features of the thermal expansion at low temperatures. Although AlN, GaN, and InN belong to the same hexagonal structure, the difference of their mass, radii, and ionicity lead to different properties of thermal expansion.

Moreover, using the quasi-harmonic approximation for atomic vibrations, the Grüneisen parameter also can be related to the description of how the vibration frequencies (phonons) within a crystal are altered with changing volume, which are known as the “mode Grüneisen parameters.” For mode  $i$  and wave vector  $q$ , this is given as<sup>25</sup>

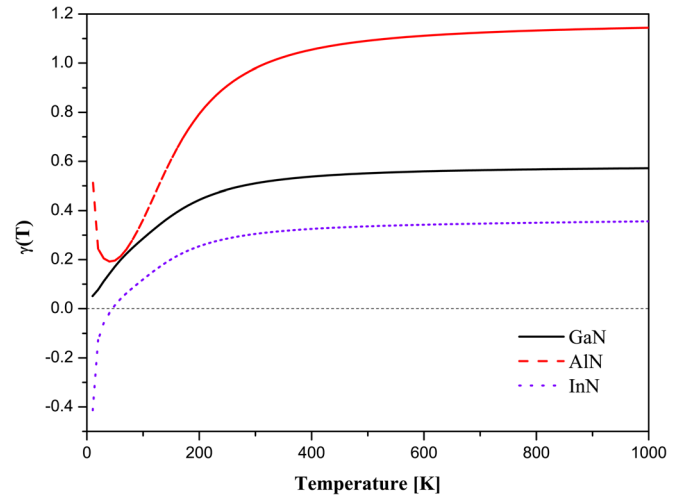


FIG. 3. (Color online) Temperature functions of the Grüneisen parameter.

$$\gamma_{i,q} = -\frac{d \ln \omega_{i,q}}{d \ln V}. \quad (7)$$

The negative mode Grüneisen parameter is due to the decrease of phonon frequency as the cell volume reduces. Therefore, if the partition of negative mode Grüneisen parameter is a majority, negative thermal expansion will occur at low temperatures due to the weakening of corresponding phonon frequencies as the cell volume reduces. This has been used to explain the negative thermal expansion for other materials.<sup>26</sup>

The calculated phonon dispersion curves for AlN, GaN, and InN are shown in Fig. 4 and the phonon partial densities of states are shown in Fig. 5. As a result of their shared wurtzite structures, these curves have a similar framework with different dispersion relations. There is a bandgap in all curves. Below the bandgap, phonon frequencies exhibit overlap or mixing between acoustic and optical modes far from the gamma-point; the acoustic modes disperse up to 13 THz for AlN, 8 THz for GaN, and only 5 THz for InN. It is important that the low frequency phonons correlate predominantly as a function of temperature with the thermal expansion.<sup>27</sup> These modes ( $< 5$  THz) contribute significantly to the thermal expansion below 300 K. As shown in Fig. 4(c), the acoustic modes mixed with some optical modes disperse below 5 THz for InN, which are more flat than that of GaN and AlN as a function of wave vector. These flat bands give rise to local peaks below 5 THz in the phonon partial density of states [Fig. 5(c)], which are mainly composed of states of In atoms. The localization of these states behave like the “atomic states” of In. The low frequency peaks of Ga states have similar characters, but these modes have higher average energies and more states of N atoms. The states of AlN below 5 THz, however, are relatively delocalized due to the light atomic mass of Al. The difference of phonon vibration modes is most likely a result of the greater mass of In versus Al and Ga, corresponding to those of the thermal expansion observed in Fig. 1.

In order to check the frequency variations of three compounds at low temperatures, the mode Grüneisen parameters were calculated by Eq. (7). As shown in Fig. 6, the mode

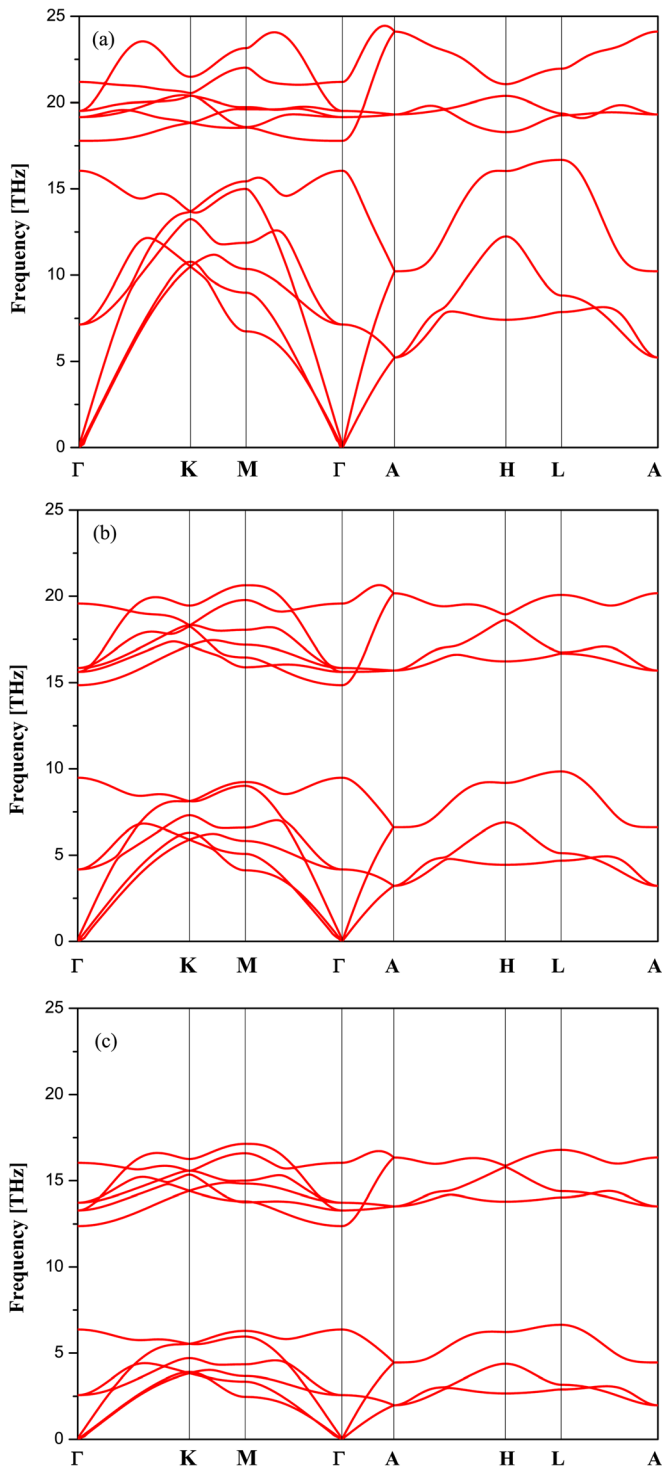


FIG. 4. (Color online) Phonon band structures of (a) AlN, (b) GaN, and (c) InN.

Grüneisen parameters of three III-nitrides are partial negative below 5 THz, which are mainly composed of two transverse acoustic (TA) modes and a small overlapped part of optical modes. When the cell volume reduces, the weakening modes consist of two parts, TA modes (two) and overlapped optical modes. These mixing phonon vibration modes cause the negative mode Grüneisen parameters. However, the negative thermal expansion is determined by the negative value of the overall Grüneisen parameter. If the partition of the

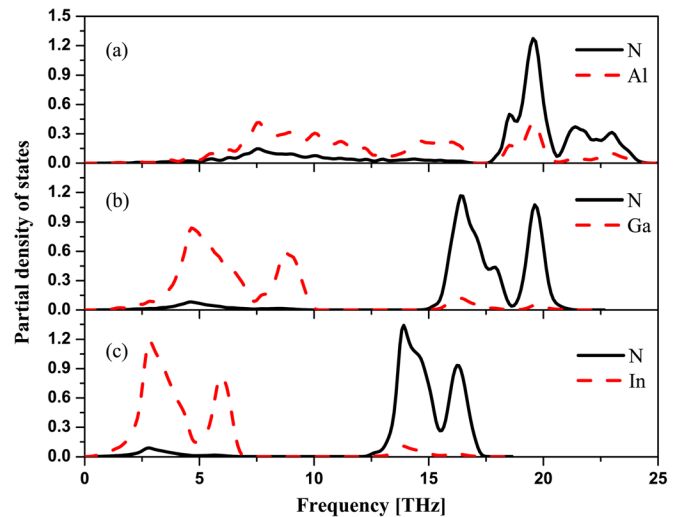


FIG. 5. (Color online) Phonon partial density of states of (a) AlN, (b) GaN, and (c) InN.

weakening modes is small, it will not cause a sign change in the overall Grüneisen parameter. For AlN, the negative values of mode Grüneisen parameters take a large proportion, which causes the shallow positive dip at low temperatures shown in Fig. 3. Moreover, the small partitions of negative mode Grüneisen parameters do not alter the overall Grüneisen parameter [Fig. 6(b)]. For InN [Fig. 6(c)], the large negative mode Grüneisen parameter below 5 THz, caused by the mixing phonon modes weakening, leads to the negative overall Grüneisen parameters (Fig. 3). Obviously, the significant weighted negative values of mode Grüneisen parameters cause a negative overall Grüneisen parameter, which originates from the mixing-modes weakening. In contrast, the proportion of negative mode Grüneisen parameters in AlN and GaN are small, which cannot cause the distinct change in the overall Grüneisen parameter, and it will not lead to negative thermal expansion. The weakening in the mixing modes of AlN only produces a shallow positive dip of its Grüneisen parameter curve as seen in Fig. 3, while the weakening in GaN does not make dramatic changes in the Grüneisen parameter. Therefore, it is easy to make a connection between the behavior of the lattice vibration and the thermal expansion in these compounds. The negative Grüneisen parameter originates from the weakening in mixing modes as the cell volume decreases, and it leads to the negative thermal expansion in InN.

#### IV. CONCLUSIONS

In summary, we have performed a theoretical study about the thermal expansions in AlN, GaN, and InN as a function of temperature using first-principle phonon calculations. The results showed that negative thermal expansions are found in InN below 50 K. GaN and AlN follow the rule of positive thermal expansions. The thermodynamic Grüneisen parameters correspond to those of thermal expansions, for which a negative value leads to negative thermal expansion. By comparing phonon vibrations and the mode Grüneisen parameters, it is found that the difference of



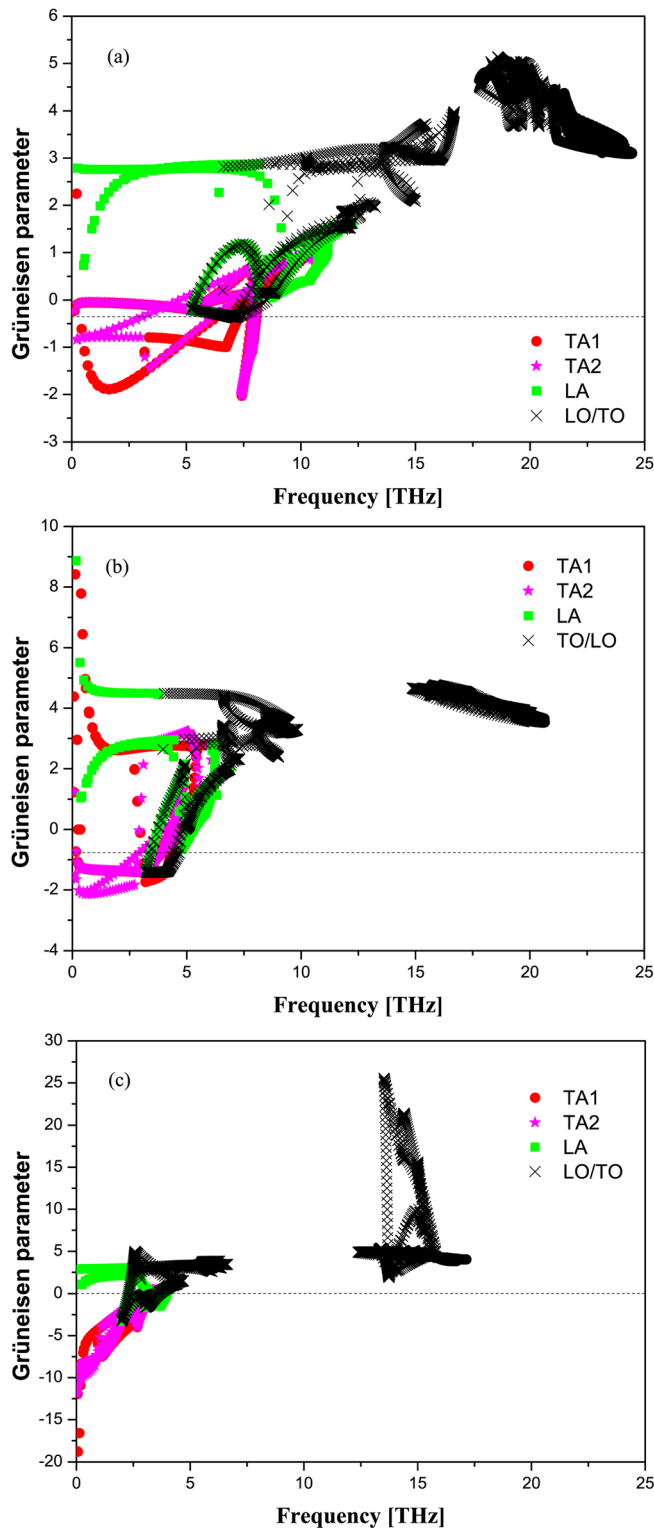


FIG. 6. (Color online) Calculated Grüneisen parameters for (a) AlN, (b) GaN, and (c) InN as a function of frequency. The labels are TA—transverse acoustic, LA—longitudinal acoustic, LO—longitudinal optical, and TO—transverse optical.

phonon vibration modes results from the greater mass of In versus Al and Ga. The low-frequency bands in InN give rise to local peaks below  $< 5$  THz, which behave like “atomic states.” The significant weighted negative values of mode Grüneisen parameters cause negative overall Grüneisen parameters below 5 THz, which originate from the weakening of the mixing mode composed of two transverse acoustic (TA) modes and a small overlapped part of optical modes. A majority of the modes show that negative Grüneisen parameters in InN lead to negative thermal expansion.

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