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Thermodynamics of wurtzite GaN from first-principle calculation

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Abstract. The density function perturbation theory (DFPT) is employed to study the linear thermal expansion and heat capacity at constant pressure (with the quasiharmonic approximation) for wurtzite GaN. The calculated results of linear thermal expansion coefficient and heat capacity at constant pressure are compared with the available experimental data in a wide temperature range. Generally these properties calculated agree well with experimental data except at high temperature, thus it suggests the thermal expansion and heat capacity can be well calculated from this first-principle approach.

PACS. 65.40.De Thermal expansion; thermomechanical effects – 62.20.Dc Elasticity, elastic constants – 63.20.-e Phonons in crystal lattices

1 Introduction

The wide-band-gap semiconductor GaN is currently of great interest for optoelectronic applications at blue and near-ultraviolet wavelengths, as well as in high-temperature and high-frequency electronics, e.g., high-electron mobility transistors based on the two-dimensional electron gas at the GaN/AlGaN interface. In these important properties, the thermal properties are one of the most basic properties of any materials. Thermal expansion is connected not only with thermal properties (thermal conductivity, specific heat, etc.) but also it influences many other properties, such as the temperature (T) variation of the energy band gap. Moreover, the knowledge of the thermal expansion coefficient is especially important for epitaxial growth.

The phonon density of states (DOS), which includes contributions from all phonons over the entire Brillouin zone, is needed for the calculations of various thermodynamic characteristic, e.g. heat capacity and thermal conductivity. Because the growth of single crystals has been limited to rather small sizes (maximum mm in length) owing to the high melting point (2800 K) and high equilibrium pressure (4 GPa) of nitrogen [1], measurements of the full phonon DOS of GaN is lack, which directly affect the measurement of various thermal properties for WZ GaN. The available experimental data are very rare. The measurements of thermal expansion coefficient for WZ GaN were performed by Leszczynski [2] and Maruska [3] respectively at T 294–900 K, but the discrepancy was larger between them. In the 1990's, another approach had been made possible by the achievements of DFPT [4,5] which allowed exact calculation of vibrational frequencies in every point of the Brillouin zone. Since then, many applications have been made within DFPT [6,7]. The vibrational free energy can be obtained using the quasiharmonic approximation (QHA). In the approximation, anharmonic effects are included through the explicit volume dependence of the vibrational frequencies. In this paper we apply DFPT within QHA to the study of the anisotropic thermal expansion for wurtzite GaN, meanwhile bulk modulus and heat capacity at constant pressure (volume) are also calculated.

2 Theory and computational details

2.1 Theory

The knowledge of entire phonon spectrum of a given system enables the calculation of its thermodynamical properties and the relative stability of its different phases as functions of T. The thermodynamical properties are usually determined by the appropriate thermodynamical potential relevant to the given ensemble. The relevant potential, e.g. Helmholtz free energy (F) can be written as

$$F(a,T) = E_{tot}(a)+K_BT\sum_{q\lambda}\ln\left\{2\sinh\left(\frac{\hbar\omega_{q\lambda}(a)}{2K_BT}\right)\right\} \quad (1)$$

the equilibrium structure parameters $a = (a_1, a_2, ...)$ of a crystal at any T are obtained by minimizing F of a system. Where $E_{tot}(a)$ is the ground state ($T = 0$ K) total

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energy of the crystal. The next term is vibrational free energy. The electronic entropy contribution vanishes for semiconductor, and thus, it is not include in equation (1). Even for metal this contribution is usually neglected, although it is easy to calculate. $\omega_{q\lambda}(a)$ of equation (1) is the phonon frequency of the qth phonon mode with wave length λ. The QHA accounts only partially for the effects of anharmonicity. However, QHA is found to be a very good approximation at temperatures not too high.

In the case of anisotropic thermal expansion of a wurtzite structure crystal, the system is described by two parameters a and c. One can compute phonon dispersions in a grid of points in (a, c) space and obtain phonon spectrum at any lattice parameters by interpolation. The coefficients of linear expansion (CTEs) are given by

$$\alpha_a = \frac{1}{a(T)}\left(\frac{da(T)}{dT}\right)$$
$$\alpha_c = \frac{1}{c(T)}\left(\frac{dc(T)}{dT}\right) \qquad (2)$$

here a and c mean equilibrium lattice constants at corresponding temperatures. The coefficient of volume expansion α_v for wurtzite structure is $\alpha_v = 2\alpha_a + \alpha_c$.

Once phonon spectrum is obtained, one can easily calculate the vibrational heat capacity at constant volume as following

$$C_V^{ph} = K_B \sum_{q\lambda} \left(\frac{\hbar\omega_{q\lambda}(a)}{2K_BT}\right)^2 \csc h^2 \left(\frac{\hbar\omega_{q\lambda}(a)}{2K_BT}\right) \qquad (3)$$

due to anharmonicity effects, the heat capacity at constant pressure (C_P) is different from that at constant volume (C_V). The relation between C_P and C_V is

$$C_P = C_V + \alpha_v^2(T)BVT \qquad (4)$$

where B is bulk modulus.

2.2 Computational details

We use a first-principles pseudopotential method base on DFPT with wave function represented in a plane-wave basis set. This work is performed employing the ABINT package [8]. A review of the method (and of the algorithm used for the convergence of electronic density and atomic positions) can be found in reference [9]. The effect of the approximation to the exchange-correlation (XC) energy is considered. The pseudopotential for Ga, N atoms are generated according to scheme of Troullier and Martin [10]. Brillouin-zone integrations were performed using 12×12×8 k-point mesh, and phonon frequencies were computed on a 6×6×4 q-point mesh. Plane-wave basis sets with a cutoff of 40 Hartree were used. These calculating parameters are chosen to guarantee the total energy error in 0.1 mHartree.

To obtain the free energy, we perform 81 sets of first-principles ground-state and response-function calculations of WZ GaN by varying lattice parameters a/a_0 and c/c_0 from 0.97 to 1.05 with a step of 0.01, respectively. Next, the full phonon spectrums is obtained by the Fourier interpolation algorithm of dynamical matrices [7]. From the full phonon spectrum, the lattice vibration free energy and then the total Helmholtz free are calculated. In order to get the temperature dependence of lattice parameters, we calculated 81 sets of total free energy at temperature points with a step of 1 K from 0 to 1500 K. In order to get a relative mean error smaller than 1% for all studied thermodynamic quantities, we found it is sufficient to sample the phonon wave vectors q by a 40×40×40 MP mesh.

Table 1. Ground properties for wurtzite GaN.

	a (Å)	c (Å)	B (GPa)
Present	3.156	5.148	206
Calc (Ref. [12])	3.157	5.145	201
Expt (Ref. [13])	3.1872	5.1818	196
Expt (Ref. [14])	3.19	5.20	195

3 Results and analysis

3.1 Ground properties

We first calculated ground properties of WZ GaN. The equilibrium volume of ground state is determined by calculating the total energy per primitive unit cell as a function of volume. The Murnaghan's equation of state is then used to fit the calculated energy-volume data. The obtained structural parameters are compared with the available experimental data and other theoretical results. The Table 1 shows that our calculations are good agreement with other theoretical values. But, our calculation underestimate the equilibrium lattice parameter (a, c) by 1–2% and overestimate the static bulk modulus (B) by 5–7% with respect to experimental data. These errors are within the acceptable error bars due to the use of LDA [11], which reflects the reliability of our self-consistent calculations and the used pseudopotentials. On the other hand, the experimental data are obtained at room temperature mostly, which is easy to understand from the fact that increasing temperature leads to an increase in the equilibrium volume, and hence to a decrease in the bulk modulus.

Based on the ground equilibrium lattice parameters, we calculate the phonon DOS, which includes contributions from all the phonons over the entire Brillouin zone, and which provides the essential ingredient for the calculation of various thermodynamic properties. Figure 1 shows the calculated total phonon DOS at 0 K. The calculated results are good agreement with experimental data of reference [15]. The phonon DOS consists of a low-energy portion (0–360 cm^{-1}), a high-energy portion (590–850 cm^{-1}), and a gap in between. According to M. Cardona et al. [16], the low energy portion (mainly consisting of acoustic phonons) is mainly activated by Ga atoms, and high- energy portion (optic phonons) is activated by N atoms, which is mainly caused by big atomic mass discrepancy.

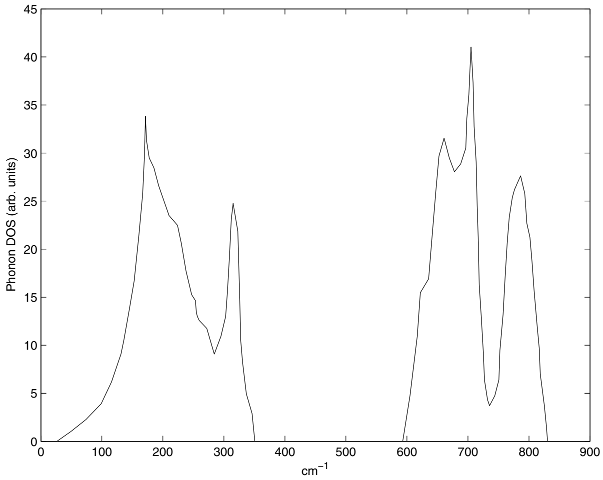

Fig. 1. The calculated phonon DOS of WZ GaN at 0 K.

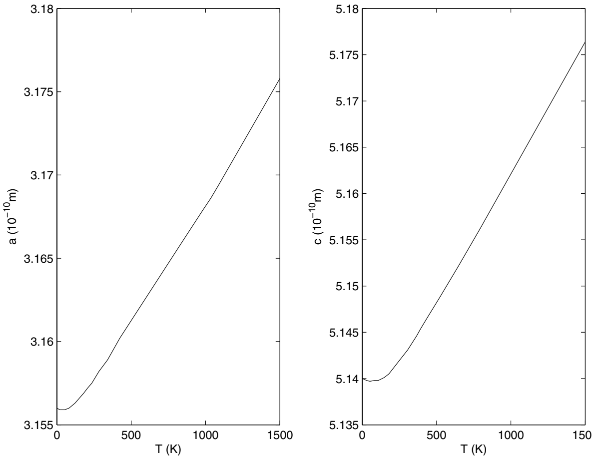

Fig. 2. The temperature dependences of lattice parameters a and c of WZ GaN.

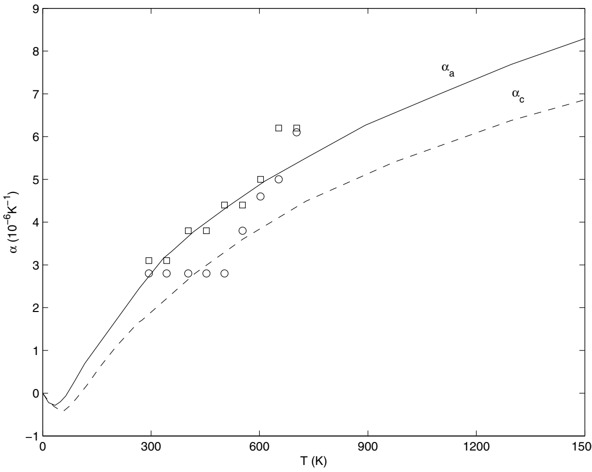

Fig. 3. The calculated coefficients of linear thermal expansion for WZ GaN. The solid and dashed lines are for α_a, α_c of WZ GaN. Circles and squares are experimental α_a and α_c of WZ GaN respectively from reference [3].

3.2 Thermal expansion

Figure 2 shows our ab initio results for the temperature dependence of lattice parameters a and c of WZ-GaN. The coefficients of linear thermal expansion along a and c axis are presented in Figure 3. The available experimental data from Leszczynski et al. [1] are also shown in same figure. The CTEs of leszczynski are from 294 K to 753 K. The calculated results are good agreement with experimental data for α_a at $T < 600$ K, but the discrepancy is large above this T. The experimental CTEs of Leszczynski increase sharply at 653 K. Our calculated result shows that α_a is always larger than α_c, and their ratio increases lightly with the increase of temperature. To be more specific, we find that α_a and α_c are negative at $T < 55$ K and $T < 86$ K respectively. They respectively have a minimum value of -0.29×10^{-6} K^{-1} at 35 K for α_a and -0.48×10^{-6} K^{-1} at 48 K for α_c. The negative values at low T can be explained as fellow. In the QHA, the CTE can be written as [18]

$$\alpha(T) = \frac{1}{3B_0V} \sum_{q,\lambda} \gamma_{q,\lambda}\, c^V_{q,\lambda}(T) \tag{5}$$

at low temperature, the excited phonon modes are predominantly of transverse acoustic type which have negative $\gamma_{q,\lambda}$, giving negative values of α. At high temperature, the calculated CTEs have larger errors with experimental data, and increase with temperature. It is instructive to verify how well the calculated and experimental CTE values follow the theoretical dependence on other thermodynamical material properties:

$$\alpha = \frac{\gamma C_V}{VB} \tag{6}$$

where Grüneisen parameter $\gamma = -d\ln\omega/d\ln V$. At high temperature, with the increase of temperature, the contribution of lattice anharmonicity can not be neglected. Recent measurements of the phonon density of states on WZ-GaN by reference [17] have shown an unusually large thermal softing of phonon frequencies at high temperature. The phonon softening comes from the weakening of force constants in a harmonic solid, as opposed to the softening in a anharmonic potential. We can rough estimate that the discrepancy between γ calculated within QHA and that, including anharmonic effect, is proportional to temperature, and then the discrepancy between calculated CTEs and experimental data is also proportional to temperature.

In the QHA, phonon frequencies depend on volume, while intrinsic effects arising from phonon-phonon interaction are neglected, these effects become more important at elevated T, and hence, QHA becomes increasingly less adequate at high temperature.

Another cause of large errors at high temperature is that the LDA underestimates lattice parameters and overestimates bulk modulus, then underestimates thermal expansion. Thus, as the temperature is increased, these two

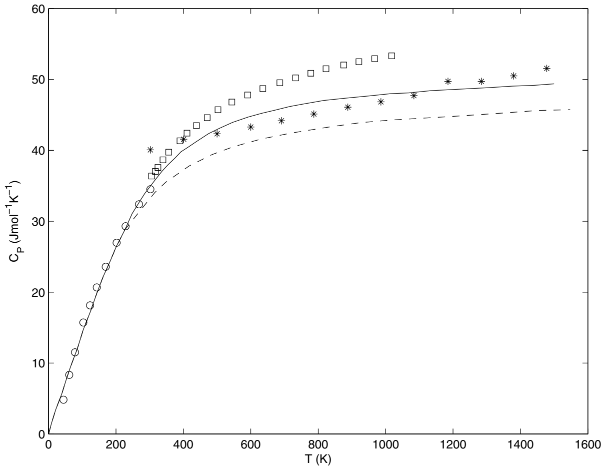

Fig. 4. The calculated heat capacity at constant pressure (solid line) and heat capacity at constant volume (dashed line) of WZ GaN. Circles, squares and asterisks are experimental C_P of WZ GaN from references [19,20] and [21] respectively.

effect are both aggravated further, resulting in increasing errors.

3.3 Heat capacity

Once the phonon spectrum over the entire Brillouin zone is available, the vibrational heat capacity at constant volume C_V^{ph} can be calculated by equation (3). Then, the specific heat at constant pressure can also be calculated by equation (4). The C_P, as a function of T is shown in Figure 4. The available experimental results are also shown in same figure. The important features to note from this figure are as fellows: (i) at low T, our results are in very good agreement with the experimental results of Koshcheko et al. [19], (ii) at 400–1100 K, our results is lower than that of reference [20], but higher than that of reference [21]. The C_P of Barin et al. shows an almostly linear dependence with temperature over 300–1500 K; (iii) at high T, our results are lower than other both. At 1300 K, the discrepancy is 2% with result of Barin [21], and increase with temperature. The calculated C_V is also shown in Figure 4, and the result is good agreement with other methods, such as heat flow method [22], molecular dynamics simulation [23] and rigid-ion model [13].

In the temperature range $0 < T < 250$ K, thermal expansion contributions to the heat capacity are negligible, and to a very good approximation, $C_P \approx C_V$. Above 250 K, the difference between constant-volume and constant-pressure specific heats become increasing important. The C_P and C_V are related by equation (4). At 600 K, the discrepancy between the calculated C_P and C_V is 5.8%. In temperature range 250–1100 K, due to the cause that the calculated C_P is between the experimental C_P of references [20] and [21], we have no means to compare the errors between the calculated results and experimental data, but this illustrates that our results are credible. At high T (above 1100 K), the calculate C_P is low to experimental data, and increase with temperature. At first sight, the discrepancy between the calculated and experimental C_p seems to be attribute to error α_v, however, the error due to underestimation of α_v is canceled out to some extent by the overestimation of bulk modulus, when we calculate difference. At high T, the contribution of lattice anharmonicity is important is important, and is proportional to temperature, then the discrepancy $C_P = C_V + \alpha_v^2 BVT$ between calculated C_P and experimental data is also proportional to temperature.

On the other hand, the measured samples themselves may have defects. The influence of defects on the C_P can not be separated from other effects, but one should expect that it is small in low temperatures where there is not enough energy in the system for new defect formation. Existing defects may only contribute very little to C_P since they do not have very strong influence on the phonon density of states distribution.

4 Conclusion

In conclusion, the anisotropic thermal expansion of WZ GaN is studied by DFT and DFPT calculations. α_a is always larger than α_c, and the ratio of α_a/α_c increases lightly with temperature. At low temperature, α_a and α_c are negative. We also calculate the C_P and C_V for WZ GaN. The calculated results are good agreement with available experimental data except at high temperature. We analysis the causes of error, and discrepancy is mainly resulted from anharmonic effect at high temperature.

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