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# Heat Capacity and Grüneisen Parameter for GaN with Zinc-Blende Structure

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A shell model molecular dynamics method is used to investigate the behavior of the pressure-volume relationship, heat capacities at constant pressure and constant volume, Grüneisen parameter for GaN with zinc-blende cubic structure at high pressures and high temperatures. The interactions between Ga−Ga, Ga−N, and N−N are described with polarizable potential models which have assigned two different partially ionic charges to Ga and N by taking into account of the ionic character of GaN. It is shown that the calculated thermodynamic parameters at ambient condition are in good agreement with the available theoretical results. Compared with the results from first-principles calculations, the discrepancy of constant-volume heat capacity at lower temperature may be explained well with different approximation mechanisms. The properties of GaN with zinc-blende structure are summarized in the temperature range of 300-2000 K and pressure up to 40 GPa.

**Key words:** Heat capacity, Grüneisen parameter, GaN, Molecular dynamics simulation

## I. INTRODUCTION

Among the III-V nitrides, GaN is a highly attractive material because of its great potential for development of short-wavelength optoelectronic devices, semiconductor lasers and optical detectors [1-3]. The compound exhibits some interesting properties, such as large band gap, strong interatomic bonds and high thermal conductivity, which make it an ideal material for optoelectronic, high-temperature and high-power devices. From a crystallography point of view and under ambient conditions GaN crystallizes in the hexagonal wurtzite structure. However, the zinc-blende structure has technological advantages compared with the wurtzite structure as it has the ability to produce cleaved laser cavities and to be doped easily. Several groups have synthesized the zinc-blende structure, which has basic problems including the poor quality of layers, the high density of planar defects and the tendency of phase transformation to the wurtzite, on different substrates [4,5]. Despite the technological developments of GaN, many fundamental problems, such as explaining the structural and thermodynamic mechanisms, still remain unsolved.

The investigation on the heat capacity of crystals is an old topic of condensed matter physics with which il-

lustrious names are associated [6-8]. Knowledge of the heat capacity of a substance not only provides essential insight into its vibrational properties but is also mandatory for many applications. Two famous limiting cases are correctly predicted by the standard elastic continuum theory [8]. At high temperatures, the constant-volume heat capacity $C_V$ tends to the Petit and Dulong limit in binary materials such as GaN [9]. At sufficiently low temperatures, $C_V$ is proportional to $T^3$ [8]. At intermediate temperatures, however, the temperature dependence of $C_V$ is governed by the details of vibrations of the atoms and for a long time could only be determined from experiments. In recent years, the temperature dependence of the specific heat of many systems has been calculated in the harmonic approximation. The calculations ranged from semiempirical, based on inelastic neutron scattering or X-ray data, to first-principles, based on total energy calculations.

Recently, an empirical pair potential was derived for GaN to reproduce the structural properties of wurtzite and zinc-blende cubic structures [10]. We have investigated lately the structural and thermodynamic properties of GaN with the empirical pair potential in wide temperature and pressure ranges. These properties, including phase transition, lattice constant, thermal expansion, isothermal bulk modulus, and specific heat, were calculated in a wide range of temperatures (300-3000 K) and pressures (0-65 GPa) [11,12]. The obtained structural and thermodynamic parameters under normal state are found to be in good agreement with

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the existing experimental data and theoretical results. Meanwhile, some thermodynamic parameters have been predicted at elevated temperatures and high pressures based on the reliable potential model. Here, a comparative study of heat capacity and Grüneisen parameter for GaN with zinc-blende structure is presented in the pressure range of 0-40 GPa and the temperature up to 2000 K, using molecular dynamics (MD) method with interactions due to the effective pair potentials which consist of two different partially ionic models [10,13]. The rationality of our theoretical results is verified by available experimental data and the latest theoretical results.

## II. THEORETICAL METHOD

MD simulations based on empirical interatomic potentials are now routinely performed to study structural and thermodynamic properties in a wide variety of materials [14-20]. Many successful applications and the modest requirements for computer resources of the method make it attractive for studies of various properties in wide-gap nitrides. The prerequisite condition for the success of any atomistic calculation is the availability of reliable interatomic potentials describing the interaction between atoms in the crystalline lattice. In contrast to the case for ionic materials such as oxides, semiconductors like silicon, and metals, there have been relatively few efforts devoted to the development of interatomic potentials for the group III nitrides.

Following our previous studies [11,12], the crystal is considered to consist of ions interacting via pair potential and polarizable by means of the shell model [21]. Here, guidance is taken from first-principles calculations which have assigned $+1.6e$ and $-1.6e$ charges to Ga and N (denoted as Model 1) [13], respectively, using a Mulliken population analysis. This is strong evidence of a significant ionic character of GaN. As mentioned in Ref.[10], the partially ionic model is chosen where charges of $+2e$ and $-2e$ are associated with Ga and N (denoted as Model 2) instead of the fully ionic charges $+3e$ and $-3e$, respectively, in the lattice. In general, covalent bonding requires an angle-dependent potential to describe its directional character. However, about a given point one can represent three-body effects as a sum of three two-body potentials. One can either use a formal charged model with three-body angle bending terms or use a partially charged model with only two-body terms. Here the two-body interatomic potential is adopted and it is represented by an analytical expression of the Buckingham form for atoms $i$ and $j$. Details about the mathematical formulation of the Buckingham potential and the corresponding parameters for GaN are given in Ref.[10]. The parameters of the short-range pair potentials as well as the polarizable parameters, N shell charge $Y$ and spring constant $K$, are obtained by fitting them to reproduce the properties of the wurtzite

structure. These properties include lattice, elastic, and dielectric constants. It is shown that the set of interatomic potentials for GaN developed in the framework of the shell model approach is able to successfully reproduce the structural, elastic and dielectric properties of the wurtzite, zinc-blende and rock-salt structures of the material at high pressures and temperatures [10-12].

In simulating the equilibrium structural and thermodynamic properties of GaN with zinc-blende structure under a desired temperature and pressure condition, the combination of the constant-temperature MD method proposed by Nosé [22] and constant-pressure MD technique by Parrinello and Rahman [23] was used on anisotropic crystals with any symmetry. The constant-volume heat capacity $C_V$ was evaluated from the variation of the internal energy of the system by fixed volume MD calculation. The MD basic cell was taken to be composed of 64 unit cells of GaN; then the basic cell contained 256 Ga and 256 N ions. Periodic boundary conditions are employed as usual. To facilitate the computation of the Coulomb and dispersion interactions, the Ewald sum method [24] and the convergence-acceleration technique described by Williams [25] were used. The equations of motion were solved by a fifth-order predictor-corrector algorithm with a time increment of 1.0 fs. In each MD run, a sufficiently long period of 5000 time steps (5 ps) was performed to establish equilibrium of the system under a desired temperature and pressure condition. After this, a subsequent period of 5000 time steps was used to simulate the structural and thermodynamic properties studied in this work.

## III. RESULTS AND DISCUSSION

It is well-known that GaN will undergo a phase transformation from zinc-blende to rock-salt structures at a sufficiently high pressure. The transition pressure is not higher than 44 GPa from our previous studies using the empirical pair potential model [12]. Figure 1 illustrates the simulated pressure dependence of relative volumes of GaN with the zinc-blende structure over the wide pressure range from 0 to 40 GPa at 300 and 2000 K using the polarizable potentials of Model 1 and Model 2. These MD results are compared with the theoretical results obtained by *ab initio* plane-wave pseudopotential density functional theory methods [26]. It is easily seen from Fig.1 that, as the pressure increases, the relative volume decreases at a given temperature. The calculated isotherm at 300 K using potential with Model 2 is in good agreement with the results from first-principles calculations, and isotherm obtained at 2000 K using potential with Model 1 is also close to the theoretical result. GaN is often thought of as a covalent material, and Model 1 used in the present work with $+1.6e$ and $-1.6e$ charges to Ga and N, yields strong evidence of a significant ionic character.
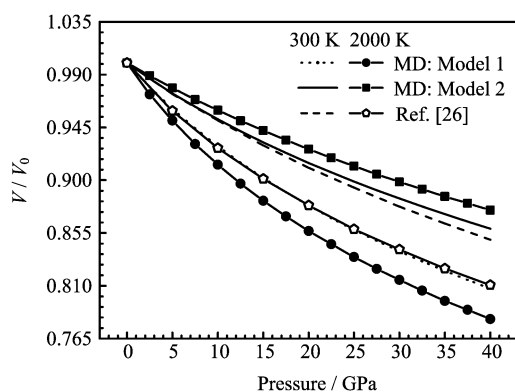
The heat capacity at constant pressure $C_p=$

FIG. 1 MD-calculated isotherms of GaN with the zinc-blende structure at 300 and 2000 K, in comparison with the theoretical result [26].



FIG. 2 MD-calculated heat capacities of GaN with the zinc-blende structure at zero pressure, in comparison with the theoretical results.

$(\partial H/\partial T)_P$ was obtained from a numerical differentiation of the enthalpy $H=U+PV$, where $U$ is the total energy, $P$ is the pressure, and $V$ is the volume. The heat capacity at constant volume $C_V=(\partial U/\partial T)_V$ was obtained from a numerical differentiation of the total energy. Figure 2 shows the constant-pressure heat capacity $C_P$, and constant-volume heat capacity $C_V$ of the zinc-blende phase of GaN from our simulations using the polarizable potentials of Model 1 and Model 2 over the temperature range 300-2000 K. Despite the publication of numerous theoretical studies on bulk GaN with zinc-blende cubic structure [12,26-29], experimental data on its heat capacity properties are still scarce. Moon and Hwang reported that the constant-volume heat capacity of the zinc-blende structure of GaN is 51.71 J/mol K at constant volume using the formula, $C_V=(\partial U/\partial T)_V$ [27]. Benkabou et al. reported the constant-volume heat capacity of the zinc-blende structure is 50.21 J/mol K by using the Tersoff potential [28]. However, the heat capacity $C_V$ of the zinc-blende structure in this work is 50.46 and 50.65 J/mol K using the polarizable potentials of Model 1 and Model 2, at zero pressure and ambient temperature respectively. The constant-pressure heat capacity $C_P$ obtained using the two models are 50.44 and 50.69 J/mol K, respectively. It is clear that these MD results agree well calculations. Meanwhile, we can see from Fig.2 that the constant-pressure heat capacity $C_P$ and constant-volume heat capacity $C_V$ increase as temperature grows.

It is worth mentioning that for GaN the values of $C_P$ and $C_V$ obtained by MD simulations exhibited linear dependence on temperature. $C_V$ at high temperatures gives direct information on the intrinsic anharmonic effects. However, it is $C_P$ that is experimentally measured, and $C_P$ contains both intrinsic anharmonic and quasiharmonic contributions leading to the departure from the Dulong-Petit law; often it is difficult to separate these contributions accurately. First of all, from Fig.2 one can see that these results and first-principles calculated values of heat capacities are close with a few
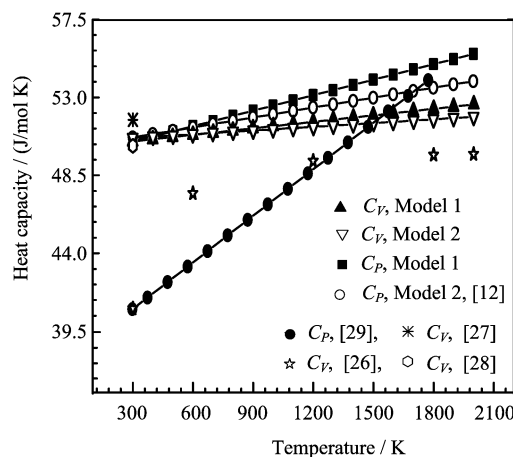
exceptions [26]. At low temperatures the differences are due to the approximations of the Debye model used by Lu et al. [26]; at high temperatures most of the difference can be reduced to experimental errors and theoretical errors in the Grüneisen parameter and intrinsic anharmonicity parameter.

The Grüneisen parameter $\gamma$ has been widely used to characterize and extrapolate the thermodynamic properties of materials at high pressures and temperatures. It is also used to place constraints on geophysically important parameters such as the pressure and temperature dependence of the thermal properties of the mantle and core, the adiabatic temperature gradient, and the geophysical interpretation of Hugoniot data. Meanwhile, it is closely related to classical melting equations: the Lindemann, Simon, and Kraut-Kennedy equations. But the experimental determination of $\gamma$ is extremely difficult [30]. Complementary to experiment, MD simulations have been employed to calculate the Grüneisen parameter GaN with zinc-blende structure.

The Grüneisen parameter is defined as the total energy derivative of pressure, $\gamma=V(\partial P/\partial U)_V$. Figure 3 shows the Grüneisen parameter of the zinc-blende phase of GaN as a function of volume using the polarizable potentials of Model 1 and Model 2. It was calculated by the method of constant volume MD simulations. Note that the Grüneisen parameter depends strongly on volume and it increases with increasing volume. The present value obtained by the shell potential of Model 2 is 1.04 at normal state. This result can be compared to Aouas's MD simulation 1.17 for LO phonon mode of the zinc-blende structure of GaN [31] and we see a good agreement. For the Grüneisen parameter, experimental measurements and other theoretical calculations are needed in order to confirm our results and also to know more about the thermodynamic properties in GaN under pressure.
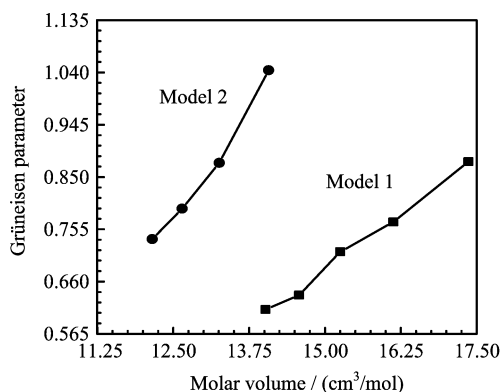
FIG. 3 MD-calculated Grüneisen parameters of the zinc-blende phase of GaN as a function of volume using the polarizable potentials of Model 1 and Model 2, respectively.

## IV. CONCLUSION

In summary, MD simulations of the GaN with zinc-blende cubic structure are presented using the shell model potentials in order to investigate the behavior of the heat capacities at constant pressure and constant volume, pressure-volume relationship, and Grüneisen parameter in the pressure range of 0-40 GPa and temperatures up to 2000 K. The calculated thermodynamic parameters were compared with the available theoretical results, and it was found that the model used and the empirical fitting potential parameters in this work performed very well to allow for a description of heat capacity and Grüneisen parameter properties of the zinc-blende phase of GaN at high temperatures. The results showed the constant-pressure heat capacity $C_P$ and constant-volume heat capacity $C_V$ increasing as temperature rises. The differences between the present work and Lu's theoretical calculations are due to the approximations of the Debye model used. The Grüneisen parameter is strongly dependent on volume.

## V. ACKNOWLEDGMENTS

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