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LETTER TO THE EDITOR

Specific heat and entropy of GaN

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Abstract

The specific heat and entropy of (wurtzite) GaN are not well known experimentally. The literature values for C_p ($T > 298$ K) are based on a fit to an analytic function. The parameters include C_p (298 K) and the melting temperature T_m , both of which were poorly known when the parameters were first determined. The value of C_p (298 K) disagrees with the data measured in the range 5–305 K. Our first-principles calculations allow the values of the parameters to be established and lead to a more accurate prediction of specific heat and entropy of GaN.

(Some figures in this article are in colour only in the electronic version)

Although the story of GaN can be traced as far back as the late 1930s (see, e.g., [1]), the importance of this material for electronic applications has emerged only in the past decade or so [2]. Despite the large volume of research done on GaN, its basic thermodynamic properties are not well understood. In particular, there is a remarkably large discrepancy between the only two published values of C_p (298 K). Koshchenko *et al* [3] measured a GaN powder in the temperature range 5–305 K and found C_p (298 K) = 34.9 J mol⁻¹ K⁻¹, while Kubaschewski and Alcock [4], who fitted C_p in the range 298–1800 K, predicted C_p (298 K) = 40.8 J mol⁻¹ K⁻¹. Their high-temperature specific heat is widely used, for example by Barin [5], Levinshtein *et al* [6] and Nipko *et al* [7].

Kubaschewski and Alcock used a functional form for C_p first proposed by Kelley [8]

$$C_p = a + b \times 10^{-3}T \quad (1)$$

where the parameters a and b depend on the material. This formula predicts that the high-temperature specific heat is a linear of function of temperature and ignores the pronounced curvature at lower temperatures. In the case of GaN, the suggested values [4] are $a = 38.1$ J mol⁻¹ K⁻¹, $b = 8.96$ J mol⁻¹ K⁻² and C_p (298 K) = 40.8 J mol⁻¹ K⁻¹ (measured [3]: 34.9 J mol⁻¹ K⁻¹). Today, this C_p is used by almost everybody.

In order to extend this function, a T^{-2} curvature term was introduced for moderate temperatures [4] (here in joules, not calories)

$$C_p = a + b \times 10^{-3}T + c \times 10^5T^{-2}. \quad (2)$$

The parameters a J mol⁻¹ K⁻¹, b J mol⁻¹ K⁻² and c J K mol⁻¹ should be obtained by fitting this function to measured values of C_p above 298 K. If no such data are available, empirical forms for the parameters are proposed (for GaN, in the equations below, $n = 2$) [4]. Kubaschewski and Alcock use C_p (298) and the melting temperature T_m :

$$a = \frac{T_m 10^{-3} \{C_p(298) + 4.710n\} - 1.248n 10^5 T_m^{-2} - 9.04n}{T_m 10^{-3} - 0.298}$$

$$b = \frac{25.644n + 4.186n 10^5 T_m^{-2} - C_p(298)}{T_m 10^{-3} - 0.298}$$

$$c = -4.187n.$$

As abundantly illustrated in [4, 5], this procedure does predict accurate specific heats and entropies for a wide range of materials. A melting temperature of 2500 °C is listed in [9]. Under normal N₂ pressures, GaN sublimates at high temperatures and there would be nothing left but a sapphire substrate by the quoted temperature. However, GaN has been grown at high temperatures (up to 2000 K) under high gas pressures (up to 20 kbar) [10]. Nipko *et al* [7] measured the phonon density of states (pDoS), used it to calculate C_v in the harmonic approximation, and found a rather poor agreement above 298 K between their curve and the fitted equation (1) [5]. This leaves one guessing as to the correct temperature dependence of C_p for GaN.

In this letter, we argue that the parameters commonly used in equation (1) are inconsistent at and above 298 K with both the low-temperature measurements [3] and with first-principles calculations of C_v , even at temperatures at which $C_v \approx C_p$. We begin with first-principles calculations of the pDoS, at 0 K in the harmonic approximation. We use it to calculate the Helmholtz free energy, specific heat and vibrational entropy of GaN (at constant volume). Calculating vibrational spectra at $T = 0$ K and ignoring the temperature dependence of the lattice constant is justified at moderate temperatures and greatly simplifies the calculations [11]. Although our C_v does not match C_p at high temperatures, there is evidence that it is quite good up to at least 800–900 K for a range of materials [12]. The fit of C_p (equation (2)) to our calculated specific heat gives new values for a , b , and c , and leads to more accurate C_p and vibrational entropy for GaN.

Our results are obtained from self-consistent, first-principles molecular-dynamics simulations based on local density-functional theory. The calculations are performed with the SIESTA code [13, 14]. The exchange–correlation potential is that of Ceperley–Alder [15] as parameterized by Perdew and Zunger [16]. Norm-conserving pseudopotentials in the Kleinman–Bylander form [17] remove the core regions from the calculations. The basis sets for the valence states are linear combinations of numerical atomic orbitals of the Sankey type [18–20], generalized to be arbitrarily complete with the inclusion of multiple-zeta orbitals and polarization states [13]. In the present calculations, double-zeta sets are used except for Ga, which has a set of polarization functions. The charge density is projected on a real-space grid with an equivalent cutoff of 150 Ryd to calculate the exchange–correlation and Hartree potentials.

The crystal is represented by a Ga₄₈N₄₈ periodic cell. The k -point sampling is limited to $k = 0$ for the calculation of the dynamical matrix (DM). The calculated crystal parameters $a = 3.185$ Å, $c = 5.245$ Å, bulk modulus 224.0 GPa, and Γ phonon frequency 769 cm⁻¹ compare well with the experimental values [9] $a = 3.189$ Å and $c = 5.125$ Å, 210.0 GPa and

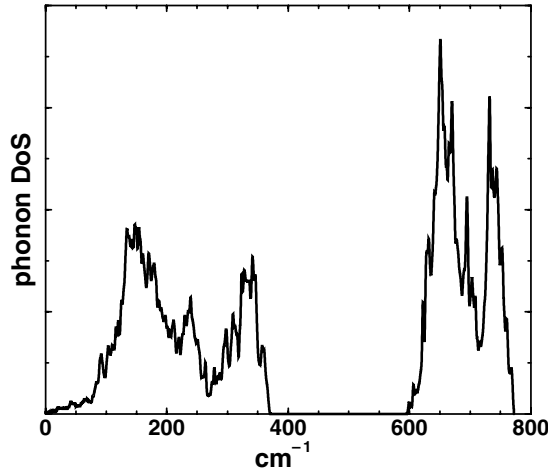


Figure 1. Calculated pDoS of wurtzite GaN.

742 cm^{-1} . The $T = 0$ K harmonic optical phonon is 3–4% off the anharmonic one measured at 300 K [9]. Note that while total energies are sensitive to the k point sampling, the vibrational frequencies are remarkably reliable with only $k = 0$. Indeed, our predictions [21] of some 70 known LVMS in Si have shown that the frequencies calculated this way have an average error relative to experiment of the order of 2% (less for highly harmonic modes). The matrix elements of the (harmonic) DM are extracted at $T = 0$ K from the derivatives of the density matrix relative to nuclear coordinates, using the perturbative approach developed by Gonze *et al* [22, 23] and implemented into SIESTA by Pruneda *et al* [21].

The eigenvalues of the DM are the 288 normal-mode frequencies ω_i ($i = 1, 2, \dots, 3N$). The Fourier transform of the DM is then evaluated at many k points along high-symmetry directions of the cell's Brillouin zone. Each k point generates another set of frequencies. The resulting pDoS is shown in figure 1. The *measured* one-photon excitation spectrum consists of two broad bands centred at 185.5 and 314.6 cm^{-1} (23 and 39 meV) corresponding to the acoustic and the first group of optical phonons, followed by a gap from 363 to 524.3 cm^{-1} (45–65 meV), then two sharp bands of upper optical modes at about 605.0 and 693.7 cm^{-1} (75 and 86 meV) [7]. The *calculated* pDoS (figure 1) has two broad bands centred at about 150 and 342 cm^{-1} (20.8 and 42.4 meV) followed by a gap from 370 to 595 cm^{-1} (45.9–73.8 meV), then two sharp bands at about 651 and 732 cm^{-1} (80.7 and 90.7 meV).

In the harmonic approximation, the Helmholtz free energy is given by [24]

$$F_{\text{vib.}}(T) = k_{\text{B}}T \int_0^{\Gamma} \ln\{\sinh(x/2)\}g(\omega) d\omega \quad (3)$$

where $x = \hbar\omega/k_{\text{B}}T$ and k_{B} is the Boltzmann constant. Here, the pDoS $g(\omega)$ is normalized so that $\int g(\omega) d\omega = 3N$, where N is the number of atoms. $F_{\text{vib.}}(T = 0 \text{ K})$ is the total zero-point energy. From $F_{\text{vib.}}(T)$, the vibrational entropy and specific heat at constant volume are

$$S_{\text{vib.}} = - \left(\frac{\partial F_{\text{vib.}}}{\partial T} \right)_V, \quad C_v = -T \left(\frac{\partial^2 F_{\text{vib.}}}{\partial T^2} \right)_V. \quad (4)$$

We use this C_v to determine the coefficients a , b , and c in equation (2). Since this function is valid only above 298 K and C_v is close to C_p only at moderate temperatures, we perform the fit in the range 298–700 K. This leads to $C_p \text{ J mol}^{-1} \text{ K}^{-1}$

$$C_p = 41.40 + 9.12 \times 10^{-3}T - 9.58 \times 10^5 T^{-2}. \quad (5)$$

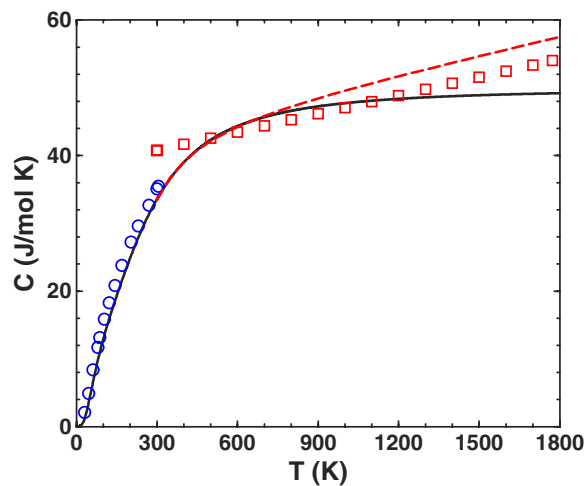


Figure 2. Calculated C_v (solid curve) versus the measured [3] C_p (circles), equation (1) (squares [5]), and equation (5) (dashed curve).

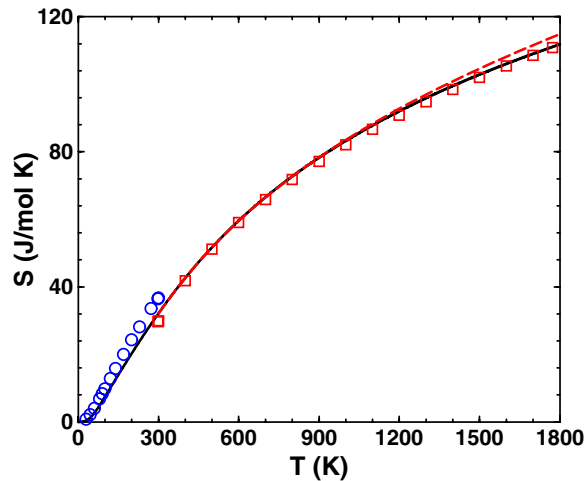


Figure 3. S_{vib} , calculated from first principles (solid curve) versus the values integrated from experiment [3] (circles), equation (1) (squares [5]), and equation (5) (dashed curve).

Figure 2 shows the comparison between C_v calculated from first-principles in the harmonic approximation (it is very close to that in [7]), C_p measured at low temperatures [3], Kelley's fitted functional for C_p with parameters from [4–6] and from our own fit, equation (5). Note that for $\sim 400 < T < 1000$ K, the original fit [4, 5] for C_p predicts values that are *smaller* than the harmonic C_v , which cannot be correct. Equation (5) (based on C_v) possibly underestimates somewhat the true C_p of GaN, which should ultimately be obtained experimentally.

We calculated S_{vib} in two different ways. The derivative of our Helmholtz free energy provides the entropy from first principles in the harmonic approximation. We also used our fitted C_p and integrated C_p/T . The constant of integration was fixed from the measured [3] value of S_{vib} (298). The results are shown in figure 3.

In conclusion, we have calculated from first principles the pDoS, Helmholtz free energy, specific heat and vibrational entropy at constant volume of wurtzite GaN in the harmonic approximation. Our C_v matches the measured C_p in the temperature range 5–305 K and the C_v obtained by Nipko *et al* from their measured pDoS. However, none of these specific heats matches the most commonly used C_p in the literature. We extract new values for the parameters in the empirical functional form of C_p , and predict the specific heat and vibrational entropy of GaN at constant pressure above room temperature. Our calculated C_v is an excellent approximation to C_p below 298 K.

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