Native Point Defects in Boron Arsenide

Yaxian Wang and Wolfgang Wind

Department of Materials Science and Engineering,
The Ohio State University, Columbus, Ohio 43210-1178, USA

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We present ab initio results for structure and energetics of native point defects in BAs and examine their effect on its thermal conductivity, predicted to be ultrahigh. We find that antisites are the constitutional defects in B-rich and As-rich material, while B\textsubscript{As} antisites and B vacancies dominate stoichiometry. With the thermodynamically correct point defects treated as mass defects, extrapolation of experimental results for non-stoichiometric samples to perfect crystals suggests that the BAs thermal conductivity should indeed reach the theoretically predicted 2000 W/(mK), rivaling diamond.

INTRODUCTION

While 3D integrated circuits have supported the extension of Moore’s law to extremely small dimension by alleviating the interconnect bottleneck, they are pushing heat generation and thermal management requirements to unprecedented levels. Besides extreme solutions such as microfluidic cooling, semiconductors and substrates which are excellent thermal conductors and easy to fabricate and integrate are urgently needed for improved cooling [1]. In this situation, a recent prediction by computational modeling that cubic BAs could be the best thermal conductor known with an ultra-high lattice room-temperature thermal conductivity of 2000 W/(mK), even higher than diamond, has created significant excitement [2]. However, the difficulty of preparing crystals sufficiently pure and large for practical applications has limited the number and depth of previous investigations, while the growth of first, small crystals has been reported [3]–[5]. Recently, Lv et al. [6] synthesized pure BAs by growing single crystals from stoichiometric BAs powder via chemical vapor deposition, with a B to As ratio of \( \sim 50.7:49.3 \) and measured the thermal conductivity to be \( \sim 200 \) W/(mK). The authors argued that the As-deficiency resulted from As vacancies in the material and a thermal conductivity as high as 2000 W/(mK) may be achievable with improved crystal growth processes. Subsequently, a number of groups succeeded in synthesizing boron arsenide crystals of increasingly better quality [7]–[11] and high thermal conductivities above 1000 W/(mK) at room temperature have been achieved.

In parallel to these synthesis efforts, several theoretical attempts have been made to unravel the nature of the dominant native point defects, their connection to off-stoichiometry and their detrimental effect on the thermal conductivity in BAs [6]–[12]–[13]. However, to date there has been no convergence on the constitutional point defects, i.e. the point defects responsible for off-stoichiometric compositions [14]. Initial work has focused on vacancies, which were chosen in an ad-hoc fashion [6]–[12], but their predicted influence on thermal conductivity at a given stoichiometry was different from measured values by a factor of twenty [6]–[12]. Since however no evidence exists that in B-rich BAs, the constitutional point defect is indeed the As vacancy, the question arose if this ad-hoc assumption may be at the bottom of the unexpectedly strong discrepancy. To validate this assumption, more recent work included defect formation energy calculations and suggested B\textsubscript{As} and As\textsubscript{B} antisite pairs as lowest-energy defects [13]. However, this work contains inherent contradictions, such as the fact that antisite pairs maintain perfect stoichiometry and thus cannot explain non-stoichiometry, that BAs was assumed to be As-rich by the choice of chemical potential while calculations were performed for comparison to B-rich samples, or that BAs was found and discussed to be thermodynamically unstable based on an erroneous minus sign. Other previous theoretical studies have not addressed defects, but examined electronic [16]–[17], optical [18], mechanical [19] or thermal properties [2] of BAs. Thus, a theoretically rigorous and contradiction-free answer to the question about the energetics of point defects in BAs is still outstanding, along with a comprehensive examination of their connection to stoichiometry and thermal transport, which we will provide here.

In this letter, we present a systematic study of native point defects in cubic BAs, including vacancies, antisites and interstitials. Our results include the fully relaxed structures, their minimum-energy charge states, and their formation energies for the B-rich, As-rich and stoichiometric cases at 0 K and finite temperatures. For the latter, we calculated the fully temperature dependent free energy of formation within the quasi-harmonic approximation and the resulting equilibrium point defect concentrations. Our results at finite temperature show that it is the boron vacancy and antisite pair that play the most important role, instead of the antisite pair proposed in [13]. We finally discuss the previous suggestions of constitutional point defects in non-stoichiometric BAs in light of our results and their effect on the thermal conductivity. Using extrapolation of experimental measurement from Lv et al. [6] as an example, we show that in the absence of higher-dimensional defects such as dislo-
As the chemical potential of boron.

where \( Q \) is the charge state, \( E_F \) the Fermi level, and \( \mu_B \) the chemical potential of boron. \( E(V_B) \) and \( E(BA) \) are total energies of relaxed BAs cells with and without B vacancy, respectively.

In order to calculate the vibrational contribution to the free energies of formation at finite temperatures, \( F_f(T) \), we use the quasi-harmonic approximation \( [20] \) based on supercell \( \Gamma \)-point calculations as described in previous work \( [21] \). Once the free energies for the different cells have been calculated, free energies of formation can be determined in analogy to Eq. (1).

For determining the necessary chemical potentials from Eq. (1), we use two approaches. For finite temperatures, we use the approach proposed by Mishra et al. \( [14] \), where the two constraints necessary to determine \( \mu_B \) and \( \mu_{As} \) are (i) that their sum is the total or free energy per formula unit of perfect BAs determined from DFT, and (ii) that the overall stoichiometry is balanced by point defect concentrations, such that the ratio of the As and B number densities equals a predefined stoichiometry. For off-stoichiometric cases, the chemical potentials saturate quickly to a constant value, and the most stable point defects for those cases are the "constitutional defects", which at zero temperature have a formation energy of zero \( [22] \). The point defect concentrations necessary to calculate the overall number densities of B and As atoms can be calculated from the free energy of formation,

\[
C_X(T) = \frac{C_s \theta_X \exp \left[-\frac{F'_X}{k_B T}\right]}{\frac{C_s \theta_X \exp \left[-\frac{F'_X}{k_B T}\right]}{1 + \sum_X C_s \theta_X \exp \left[-\frac{F'_X}{k_B T}\right]}},
\]

where \( C_s \) is the concentration of lattice sites in the perfect material, \( \theta_X \) is the multiplicity of the configuration (which is different from 1 e.g. for dumbbells which can have different orientations), and \( k_B \) is the Boltzmann constant. Since Eq. (2) is not practical at 0 K, we determined the thermodynamic stability range relative to the elemental phases, which limits the chemical potential of boron to a fairly narrow range of \(-7.43 \, eV\) to \(-7.14 \, eV\), of which we took the average as a reasonable guess for the chemical potential at stoichiometry, which was a posteriori justified by the high-temperature free energy calculations. The formation energies as a function of Fermi level relative to the top of the valence band \( E_F \) are shown in Fig. 2. We find antisites to be the constitutional defects in both B-rich and As-rich cases, while B_{As} and V_{B} balance each other to maintain stoichiometry. The charge neutrality point (CNP) for the stoichiometric case at 0 K is determined by the condition of equal electron and hole concentrations as described in Ref. \( [14] \) and is extrapolated from the finite-temperature results at varying temperatures to be \( 0.40 \, eV \) above the valence band edge (Fig. S2). Reasonable agreement is observed with Ref. \( [13] \), which reported the CNP at 0 K to be \( \sim 0.6 \, eV \) above the valence band edge. However, in Ref. \( [13] \) the constitutional defect is \( V_B \) at the proposed CNP, which indicates an As-rich sample. The As-rich stoichiometry is enforced in Ref. \( [13] \) by choosing the chemical potential of As to be equal to the energy of bulk

FIG. 1. Relaxed point defect structures for a B and b As vacancies, c B and d. As antisites, e B and f As (100) dumbbell interstitials, viewed from the (100) direction. As (B) atoms are represented by larger (smaller) balls.
As, although it seems the authors did not do that intentionally. In contrast, in our work, with effective masses obtained from DFT-HSE (see Supplement), the intrinsic carrier concentration is calculated to be \(6.8 \times 10^{16} \text{ cm}^{-3}\), while the intrinsic thermal point defects are predicted to provide a hole concentration of \(2.9 \times 10^{18} \text{ cm}^{-3}\), both at 1100 K. We also find that in B-rich samples, the excess of \(B_{As}^{-1}\) acceptors would increase the hole concentration, while in As-rich samples, the constitutive \(As_{B}^{+1}\) point defects act as donors, resulting in \(p\)-type BAs. Reported carrier density measurements always find \(p\)-type material with hole concentrations between \(7.6 \times 10^{18}\) and \(1.1 \times 10^{20} \text{ cm}^{-3}\) \([7,9,11]\), higher than what can be expected in intrinsic BAs. This then leads to the conclusion that standard growth techniques most likely produce \(p\)-type boron rich samples, which is in direct contradiction to the results of Ref. \([13]\), where the choice of chemical potentials enforces calculations for As-rich samples, for which the actually predicted neutral boron vacancy as constitutional defect does neither provide the experimental stoichiometry nor doping, which is also the case for the then studied antisite pair.

Since we have calculated the full free energies of formation, we can now plot the various defect concentrations as a function of (inverse) temperature in an Arrhenius plot as shown in Fig. 3 for intrinsic BAs with \(E_F\) at midgap. All lines are in very good approximation linear, and with \(F_f = H_f - TS_f\), we can use a linear fit to determine formation enthalpy and entropy for each defect, shown in Table 1. The number of digits shown in the enthalpy column indicates the degree of linearity of the fit, and the error bars shown limit the 95% confidence interval. The concentrations follow an Arrhenius temperature dependence to an excellent degree, although that does not necessarily have to be the case for the type of calculations performed here as previously found \([23]\).

While the agreement between calculated formation energies and fitted formation enthalpies is in general good with an average deviation of 5%, the considerable variations in the formation entropies shown in Table 1 cause some larger deviations up to 14%. However, the overall order of the energies is maintained. This suggests that a calculation of free energies is indeed an important step in case one is interested in accurate values, while the of course much easier to calculate zero-temperature formation energies may give a reasonable estimate for the general trends and for identification of the most relevant defect types. Fig. 3 shows that for B-rich material, the highest concentration of thermal, non-constitutional defects is below \(10^8 \text{ cm}^{-3}\), and thus all thermal defects should be negligible when calculating materials properties. This means that the only relevant defect in B-rich material, which is the relevant case for comparison to experiment as we just showed, is the boron antisite. The situation is different for As-rich BAs, where boron vacancies can reach concentrations in the \(10^{20} \text{ cm}^{-3}\) range, which may require including them into transport and carrier-concentration calculations in addition to the antisites. All other defects still have negligible concentrations. For stoichiometric BAs, we find that \(V_B\) and \(B_{As}\) balance the stoichiometry, with the equilibrium concentration of B vacancies twice that of BAs antisites, since one BAs needs two B vacancies to result in perfect stoichiometry. \(V_B\) and \(B_{As}\) concentrations have relatively low concentrations of \(\sim 10^{10} \text{ cm}^{-3}\) at elevated temperatures and significantly less around room temperature, giving them negligible relevance for electrical and thermal conduction in stoichiometric BAs. This rigorous examination at fi-
where \( \tau \) is other (Matthiessen’s rule \[24\]), the total scattering rate scattering mechanisms operate independently of each section, can be determined within the mass variance approximation, 

\[
\tau_{\text{total}} = \tau_{\text{lattice}} - \tau_{\text{defects}} - \cdots .
\]

According to Tamura \[25\], the defect-scattering rate \( \tau^{-1} \) in cubic BAs can be determined within the mass variance approximation,

\[
\tau^{-1}_{\text{defects}}(qj) = \frac{\pi}{6N} \omega^2 \sum_{\kappa} g(\kappa) |e(\kappa |qj)|^2 \times \sum_{q'j'} \delta [\omega(qj) - \omega(q'j')] |e(\kappa |q'j')|^2,
\]

where \( \omega(q) \) is the frequency of phonon branch \( j \) at point \( q \) in the Brillouin zone, \( e(\kappa |qj) \) its eigenvector for sublattice \( \kappa \), and \( g(\kappa) \) the mass variance parameter defined as

\[
g(\kappa) = \sum_i f_i(\kappa) \left( 1 - \frac{m_i(\kappa)}{\sum_{i} f_i(\kappa) m_i(\kappa)} \right)^2,
\]

where \( m_i \) are the masses of all isotopes and defect types \( i \) occupying sublattice \( \kappa \) with fraction \( f_i \).

Using such an approach, Broido et al. \[20\] have previously examined the isotope effect in stoichiometric, defect-free BAs and found it to be lower than in diamond, since the motion of the isotopically pure heavy As atoms dominated for high-frequency acoustic phonons. Lv et al. \[4\] have then shown that if As-deficiency is considered as a mass variance effect based on As vacancies, the measured thermal conductivity for an experimentally determined B to As ratio of \( \sim 50.7:49.3 \) would extrapolate to a considerably lower perfect-material conductivity than the predicted \( \sim 2000 \text{ W/(mK)} \), which they speculated may be due to a plethora of additional effects compatible with their diffraction results. However, this disagreement may alternatively question either the modeling assumptions underlying the “perfect” predictions, or those underlying the mass variance calculations for the non-stoichiometric material which we will examine in the following. We will show that our results suggest that the disagreement mostly results from the ad-hoc assumption of As vacancies as the constitutional defect in B-rich BAs instead of the B antisites that our calculations suggest.

We start from validating the previous modeling prediction from Ref. \[2\] for phonon-phonon limited thermal conductivity in stoichiometric BAs using a similar approach based on \( 3^{rd} \)-order anharmonic force constants and Boltzmann transport theory as implemented in the phonopy package \[27\]. We found the intrinsic conductivity to be \( 1708 \text{ W/(mK)} \) at \( 200 \text{ K} \) and the specific heat to be \( 35 \text{ J/(Kmol)} \), in reasonable agreement with previous work. This results in a lattice scattering time of \( \tau_{\text{lattice}} = 20.4 \text{ ns} \) for isotopically pure perfect BAs, while the scattering from B isotopes results in \( \tau_{\text{isotope}} = 4.51 \text{ ns} \).

As we show in the supplement (Figs. S3 and S4), considering the effects of point defects on the phonon frequencies on the evaluation of Eq. (3) has negligible effect, which allows us to focus our analysis of non-stoichiometry on the difference in mass variance parameter between \( V_{\text{As}} \) and \( B_{\text{As}} \). Within the mass variance approach, either \( B_{\text{As}} \) antisite or As vacancy can be treated as an As isotope that possesses a mass of either \( m_B \) or 0, respectively. At the experimental stoichiometry where the B:As atom ratio is \( \sim 50.7:49.3 \), the mass variance parameters from Eq. (4) can be calculated to be \( g_{\text{As}} = 0.001 \) for antisites and \( g_{\text{As}} = 0.028 \) for As vacancies. With those and Eq. (3), the scattering rates of all phonon branches are calculated and the results for the dominant acoustic ones are shown in Fig. 4a. Both defects strongly increase the

### Table I. Summary of zero-temperature formation energies \( E_f \) and Arrhenius-fitted formation enthalpies \( H_f \) at mid gap for native point defects in cubic BAs, along with their relative differences \( \Delta E_{\text{rel}} \) and Arrhenius-fitted formation entropies \( S_f \).

| Defects     | \( E_f \) (eV) | \( H_f \) (eV) | \( \Delta E_{\text{rel}} \) (%) | \( S_f \) (kB) |
|-------------|--------------|--------------|----------------|-------------|
| \( V_{\text{As}}^0 \) | 4.79        | 4.773±0.001  | 0.42           | 1.39        |
| \( V_{\text{B}}^0 \) | 3.36        | 3.628±0.003  | 8.04           | 11.8        |
| B-rich      |              |              |                |             |
| \( B_{\text{As}}^{\text{2+}} \) | 5.36        | 5.702±0.004  | 6.74           | 10.8        |
| \( A_{\text{B}}^{\text{2+}} \) | 5.29        | 5.521±0.01    | 2.62           | 0.426       |
| \( B_{\text{As}}^{\text{2+}} \) | 4.20        | 4.312±0.01    | 2.62           | 0.426       |
| \( A_{\text{B}}^{\text{2+}} \) | 5.35        | 5.702±0.004  | 6.74           | 10.8        |
| \( V_{\text{As}}^0 \) | 5.98        | 5.982±0.001  | 0              | 5.12        |
| \( V_{\text{B}}^0 \) | 2.37        | 2.418±0.003  | 2.04           | 8.15        |
| Stoichiometric |           |              |                |             |
| \( B_{\text{As}}^{\text{2+}} \) | 3.04        | 3.646±0.018  | 13.9           | 2.55        |
| \( A_{\text{B}}^{\text{2+}} \) | 5.29        | 5.521±0.01    | 4.35           | 4.15        |
| \( V_{\text{As}}^0 \) | 7.45        | 7.442±0.001  | 0.8            | 5.05        |
total scattering rate by about two orders of magnitude throughout the whole frequency range while $V_{\text{As}}$ causes higher scattering rates than $B_{\text{As}}$. For a given stoichiometry, the ratio of the total scattering rates for As vacancies over $B_{\text{As}}$ antisites remains constant as evident from their identical but shifted curves in Fig. 4a. Furthermore, the ratio is also more or less constant when varying the stoichiometry. In the composition range shown in Fig. 4b, its values fall between 2.68 and 2.77. Fig. 4b shows our calculated thermal conductivity as a function of As deficiency in comparison to the previous results from Ref. [3]. It is evident that the thermal conductivity is significantly underestimated by assuming that the As vacancy is the constitutional point defect in B-rich BAs. By changing the constitutional defect to the energetically correct $B_{\text{As}}$, our result predicts that the experimentally measured thermal conductivity of 200 W/(mK) should correspond to an As deficiency of 2.33%, which agrees well with the measured value of 2.8% within our theoretical framework. This agreement is rather strong evidence that our physics-based approach without ad-hoc assumptions predicts antisites as the correct constitutional defects that are present in non-stoichiometric BAs, and confirms the previously predicted ultra high thermal conductivity values in defect-free material [2]. With that, we believe we have laid out here a scientifically sound pathway to correlate composition to expected thermal conductivity in a reliable way.

In summary, we have presented results for the energetics of native point defects in cubic boron arsenide and examined their effect on the bulk thermal conductivity, which has previously been speculated to be ultra-high. Based on thermodynamic equilibrium and overall stoichiometry, formation energies of vacancies, antisites and interstitials were determined. We find that antisites are the constitutional defects in both B-rich and As-rich material, while $B_{\text{As}}$ antisites and B vacancies balance to keep stoichiometry. In addition, full free energies of formation were calculated for a range of temperatures, and we find that considerable differences up to 14% exist between Arrhenius fitted formation energies and 0 K total-energy values. When the thermodynamically correct point defects are treated as mass defects in the crystal within perturbation theory, extrapolation of experimental results for non-stoichiometric samples to perfect crystals confirms the previously predicted value of ~2000 W/(mK) [2], while allowing now to correlate native-point defect population and stoichiometry in a physically rigorous way to the expected thermal conductivity of a sample.

METHODS

The calculations were performed within density-functional theory (DFT) using the plane wave projector augmented-wave (PAW) method [28] as implemented in the VASP code [29,30]. The cutoff energy of 560 eV and the BZ sampling grid of 6×6×6 Monkhorst-Pack k-point [31] in a 64-atom super cell were used in this work. A monopole correction $e^2Q^2\alpha/(a_0\varepsilon)$ ($\alpha$ is the Madelung constant, $a_0$ the lattice constant of the cubic cell and $\varepsilon$ the reported dielectric constant [32]) is applied to calculate energies of charged systems [33]. While structural relaxation was performed with the Perdew-Burke-Ernzerhof (PBE) functional [34]. Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [35] was employed for bandstructure calculation to get the correct band gap and final total-energy calculations to maintain the maximum accuracy. The fraction of exact exchange of 0.16 was chosen in the HSE calculations to obtain an indirect zero-temperature band gap of 1.60 eV, since typical semiconductors have band gaps that shrink between 0 K and room temperature by approximately 0.1 eV [36] and the measured room temperature gap for BAs is \(\sim 1.50 \text{ eV} \) [5].

DATA AVAILABILITY

The data are available from the corresponding author on request.

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AUTHOR CONTRIBUTIONS

Y. W. did all the calculations and wrote the paper. W. W. initiated and directed the research. Both authors discussed the results and contributed to the manuscript.

ADDITIONAL INFORMATION

Supplementary information

See supplemental material.

Competing interests

The authors declare no competing interests.

*windl.1@osu.edu*

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### TABLE OF CONTENTS

Section S.1 Supporting Information for Density-Functional Theory Calculations  
- Figure S1. Band structure and density of states of cubic BAs.  
- Figure S2. Charge neutrality point (CNP) in stoichiometric BAs.  

Section S.2 Effect of Point Defects on Phonons and Scattering Rates  
- Figure S3. Isotope scattering rate calculated for different approximation levels for phonon calculations.  
- Figure S4. Phonon density of state for perfect and defect BAs cells.  

## S.1 SUPPORTING INFORMATION FOR DENSITY-FUNCTIONAL THEORY CALCULATIONS

Fig. S1 shows band structure and density of states of perfect BAs. The effective mass of holes is obtained from an average of heavy hole and light hole and found to be 1.02 $m_e$, while the electron mass is 1.11 $m_e$. The intrinsic Fermi level (0.799 eV above the valence band edge) indicated in Fig. S1b has been calculated for a temperature of 1100 K, which is the temperature at which the BAs crystals of Lv *et al.* have been synthesized [6], using  

\[
E_i = \frac{E_V + E_C}{2} + \frac{3}{4}k_B T \ln\left(\frac{m^*_p}{m^*_n}\right),
\]

where $E_V$ and $E_C$ denotes the energies of valence band maximum and conduction band minimum, $k_B$ the Boltzmann constant and $T$ the temperature. $m^*_p$ and $m^*_n$ are effective masses of holes and electrons. Fig. S2a shows the charge neutrality point (CNP) obtained by the condition of stoichiometry balancing at 1200 K as a clear illustration that the system has equal amount of donors (electrons) and acceptors (holes). Fig. S2b clearly shows the temperature dependence of the CNP, which allows using linear extrapolation to obtain its value at 0 K.

## S.2 EFFECT OF POINT DEFECTS ON PHONONS AND SCATTERING RATES

Here, we examine the effect of the different approximations within the mass variance calculations for non-stoichiometric BAs on the phonon scattering rates. For that, we calculated phonon frequencies for perfect supercells from $3 \times 3 \times 3$ to $5 \times 5 \times 5$ conventional cells, as well as for defective $3 \times 3 \times 3$ cells with As vacancy and B antisite, respectively. By comparing to previous results and full calculations, we find that using normal modes from supercells is a reasonable approximation for scattering rates (Fig. S3), and that, as the $3 \times 3 \times 3$ supercell results show, the changes from explicitly using eigenvectors and frequencies from defective cells results in rather small changes, justifying the use of perfect-cell input. Next, phonon-DOS results for both defective cells with As vacancy and B$_{As}$ antisite are shown in comparison to the phonon DOS of perfect BAs in Fig. S4. Although the defects add additional peaks in the phonon gap, which has been shown to be partially responsible for BAs’s high thermal conductivity [2], we find that their effect is rather small and can be neglected (Fig. S3), since the thermal transport is mainly dominated by the low frequency acoustic phonons, where the DOS are very similar among the three cells.
FIG. S1. Electronic structure of BAs calculated within DFT-HSE. a Band structure of the perfect cell with band gap labeled. b Density of states of perfect BAs. The Fermi level is calculated for a temperature of 1100 K using Eq. (S1).

FIG. S2. a Charge neutrality point determined from the concentrations of electrons and holes due to charged point defects for stoichiometric BAs at 1200 K using Eq. (2). b Charge neutrality points as a function of temperature (circles) and linear fit (dashed line) to determine the charge neutrality point at zero temperature by extrapolation. All chemical potentials were determined by the condition of stoichiometry conservation[14].
FIG. S3. Isotope scattering rate from all phonon branches calculated on different levels of approximation as labeled, highlighting that normal modes from supercells allow a reasonable evaluation of isotope scattering with sufficient accuracy. Current results are benchmarked against previous results from Broido et al. [26].
FIG. S4. Phonon densities of states of perfect BAs (black) and defective BAs cells with $B_{As}$ antisite (red) and As vacancy (blue). While defects introduce additional peaks in the acoustic-optical phonon gap, their DOS at low frequency is approximately the same with that of the perfect cell.