Computational Modeling of Grain Boundaries in ZrB$_2$: Implications for Lattice Thermal Conductivity

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A combination of ab initio, atomistic, and finite element methods (FEM) was used to investigate fundamental properties of grain boundaries and grain boundary networks and their impact on lattice thermal conductivity in the ultra high-temperature ceramic ZrB$_2$. The structure, energetics, and lattice thermal conductance of certain low energy grain boundaries were studied. Atomic models of these boundaries were relaxed using density functional theory. Information about bonding across the interfaces was determined from the electron localization function. Interfacial thermal conductances were computed using nonequilibrium molecular dynamics. Microstructural models were used to determine the reduction in lattice thermal conductivity due to grain boundary networks where FEM meshes were constructed on top of microstructural images.

I. Introduction

Ultra high-temperature ceramics (UHTC) are a class of materials with high melting points, good mechanical properties, and reasonable oxidation resistance. Among these materials, the metallic diborides, and especially ZrB$_2$, have been the object of considerable study, both as pure materials and as constituents in composites. These materials are of interest for applications in extreme environments which require little or no oxidation or ablation. In particular, they are candidate materials for sharp leading edges and nosecaps of hypersonic aircraft as well as propulsion systems, refractory crucibles, as well as other applications. Unlike most ceramics, UHTCs are distinguished by their high thermal conductivity. High thermal conductivity offers a number of advantages for high-temperature applications. For example, high thermal conductivity can improve thermal shock resistance. It can also improve the efficiency of thermal radiation by rapidly redistributing thermal energy across available surfaces.

The total thermal conductivity $\kappa_{\text{tot}}$ of the diborides has significant contributions from both electronic and lattice carriers. The electronic component $\kappa_e$ can be estimated approximately from knowledge of the electrical conductivity using the Weidemann-Franz (WF) empirical relation. The lattice contribution $\kappa_{\text{ph}}$, which results from phonon transport, cannot be measured directly and is usually inferred by subtracting $\kappa_e$ from $\kappa_{\text{tot}}$. For single crystal ZrB$_2$, thermal conductivity measurements at room temperature have been reported as 140 W/(m·K) in the basal direction and 100 W/(m·K) along the c-axis. These single sample results did not include either a characterization of the defect distribution, which will reduce $\kappa_{\text{tot}}$, or specific estimates of $\kappa_e$ and $\kappa_{\text{ph}}$. Polycrystalline ZrB$_2$ has been more thoroughly studied. Previously, room temperature measurements have been reported as 55 W/(m·K) for ZrB$_2$ where $\kappa_e$ was estimated to be 33 W/(m·K) and $\kappa_{\text{ph}}$ was given as 22 W/(m·K). More recent results based on different processing methods quote values for $\kappa_{\text{tot}}$ as high as 108 W/(m·K) for polycrystalline samples.

The reduction in $\kappa_{\text{tot}}$ relative to single crystals comes primarily from the thermal resistance of grain boundaries. Variations in $\kappa_{\text{tot}}$ with grain size can be substantial. Whereas $\kappa_e$ is expected to be relatively insensitive to grain boundaries due to the short electron mean free path, the lattice contribution $\kappa_{\text{ph}}$, which may be quite high in single crystals, can be reduced significantly due to grain boundary thermal resistance. Different processing methods can lead to very different grain sizes and grain boundary structures. Therefore, it is important to understand the effect of grain boundaries on the properties of these materials.

In this study, we use a combination of ab initio, atomistic, and finite element methods (FEM) to study grain boundaries as well as grain boundary networks to understand their impact on lattice thermal conductivity in polycrystalline ZrB$_2$. Although we focus primarily on thermal conductivity, our results also have implications for mechanical response. Interatomic potentials for this material were derived previously. These potentials have been used to compute the lattice thermal conductivity of single crystal ZrB$_2$. In the present study, we first constructed a series of atomic models of grain boundaries for this material, namely coincidence tilt and twist boundaries. Both ab initio methods and the interatomic potentials were used to relax the structures and evaluate their energetics. The electron localization function (ELF) was used to provide spatially resolved information about bonding across the boundaries. This is especially useful for studying extended defects such as grain boundaries where the structures may undergo significant reconstruction. Understanding how the character of bonding changes across an interface can have important implications for properties. Next, the thermal resistance of the grain boundaries was computed using nonequilibrium molecular dynamics. It is important to note that single crystal lattice thermal conductivities as well as lattice thermal resistances of grain boundaries are not directly accessible to experimental measurement in these materials. However, these quantities can be determined directly from molecular dynamics (MD) simulations. Finally, microstructural calculations were performed to determine the reduction in the bulk lattice conductivities...
thermal conductivity due to grain boundary networks. FEM computations were used to obtain the “effective thermal conductivity” of polycrystalline models where FEM meshes were constructed directly on SEM images.

II. Method

*Ab initio* computations were performed using density functional theory (DFT) and utilizing the functional of Perdew, Burke, and Ernzerhof.1 Grain boundary structures were relaxed and their energetics evaluated. The plane wave code VASP and the projected augmented wave potentials were used for all calculations.8,9 All results were converged with respect to k-point sampling and plane wave energy cut-off $E_r$. Periodic cells were used which resulted in two boundaries per cell.

The ELF can be evaluated during a DFT calculation. Specifically, the ELF gives the probability of finding an electron near a reference electron at a given point and with a fixed spin.10 In this way, it is useful for identifying covalent bonds. The ELF is defined in terms of a dimensionless localization ratio $\chi_{\text{eff}}(r)$ which measures localization with respect to the uniform electron gas

$$\text{ELF}(r) = \frac{1}{1 + \chi_{\text{eff}}(r)}$$

The ELF takes values in the range $0 \leq \text{ELF} \leq 1$ where ELF = 1 corresponds to perfect localization and ELF = 0.5 gives the electron gas. $\chi_{\text{eff}}(r)$ is computed directly from DFT quantities. The ELF can be contrasted against the electron charge density $\rho(r)$ which is a single electron quantity whereas the ELF gives information about the two-body distribution.

The nonequilibrium molecular dynamics method of Muller-Plathe (MP) was used to compute interfacial thermal conductances.11,12 The LAMMPS package together with the ZrB$_2$ interatomic potential “Pot 1” of Daw, Lawson, and Bauschlicher (DLB) were used for these computations. Periodic unit cells with a long direction (~100 nm) normal to the boundaries were created to minimize reflections. Convergence studies for both the normal and lateral dimensions were performed. Results were only weakly dependent on the lateral dimensions, however, which was typically (~1–5 nm). A NPT simulation was run at the given temperature for 100 ps to equilibrate the system. NVE simulations were then performed in which a “hot” region and a “cold” region were formed in which a “hot” region and a “cold” region were swapped with the lowest energy atom in the hot region. A steady state was formed on opposite sides of the boundaries by exchanging created on opposite sides of the boundaries by exchanging $Q$- and $V_T$-point sampling and plane wave energy cut-off $E_r$. Periodic cells were used which resulted in two boundaries per cell.

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$$Q = \frac{1}{2A} \sum_{i} m \left( v_i^{\text{hot}} - v_i^{\text{cold}} \right)$$

and where the sum is over the number of exchanges, $i$ is the total simulation time, $A$ is the cross-sectional area normal to the direction of heat flow, $m$ is the atomic mass, and $v_i$ is the velocity of the exchanged atom. At the interface, a discontinuity in the temperature profile ($T$ versus $z$) will appear. The temperature discontinuity and the exchanged heat flux are related by the interfacial or Kapitza conductance $\sigma_k$

$$Q = \sigma_k \Delta T$$

where $q$ is the heat flux, $k_{\text{eff}}$ is the effective thermal conductivity, $\nabla T$ is the temperature gradient, and the brackets represent volume averages over the system. Note for UTG, we fix $\nabla T$ and measure $<q>$ after steady state is achieved. For UHF, we do the converse. Both methods were performed with boundary conditions applied in both the vertical and horizontal directions as well. It has been shown previously that $\kappa_{\text{UTG}} < \kappa < \kappa_{\text{UTG}}$.15

III. Structural Models

The crystal structure of single crystal ZrB$_2$, and the related material HfB$_2$, was discussed in detail in a previous publication.16 To summarize, the structure of ZrB$_2$ is the AlB$_2$ type, designated as C32 with space group symmetry $P6/mmm$. This is a layered arrangement with alternating planes of pure Zr and pure B atoms. The Zr planes have a hexagonal close-packed structure whereas the B planes are open, hexagonal with six-membered rings resembling graphite. The layers are situated such that each Zr atom lies directly above and below the centers of six-membered B rings in the adjacent planes. The $a$ and $b$-axis give symmetry equivalent in-plane directions whereas the $c$-axis is normal to the layers.

Structural models for ZrB$_2$ grain boundaries are considered for four situations: two twist boundaries and two tilt boundaries, one for each of the two independent axis, $a$ and $c$. Hexagonal crystals with irrational ratios of their lattice parameters $(c/a)^2$ only have exact coincidence site lattice (CSL) boundaries corresponding to rotations about the $c$-axis.17,18 We consider such CSL boundaries formed by twists and tilts about that axis. However, near coincidence boundaries about the $a$-axis can be formed by approximating $(c/a)^2$ as a rational number $(m/n)$. This approximation will introduce a strain into the system. Smaller $(n,m)$ values result in smaller, computationally efficient unit cells, but with larger strain. For larger values, the converse is true. For our structures, the strain was typically less than 1%. To accommodate *ab initio* computations, periodic cells were used, containing two boundaries per cell. With small cells, we expect nontrivial interaction between the boundaries. However we should
be able to obtain reliable information about relative structural and energetic differences.

For ceramics such as ZrB$_2$, grain boundaries are often disordered and may contain many impurities. However, such boundaries are usually the result of particular processing methods. Cleaner and more crystalline boundaries are expected to have low interfacial energies and therefore their formation should be favored with improved processing methods. Furthermore, such boundaries should have greater interfacial adhesion and reduced thermal resistance, and therefore are more desirable. Such boundaries are routinely observed in other ceramics such as alumina and zirconia. In this study, we focus on these relatively simple boundaries both because of their computational efficiency and also because of their expected superior properties. We expect grain boundary thermal properties to be somewhat insensitive to the exact atomic structure of the boundary. Therefore, it is not necessary to find the absolute, lowest energy boundary structure, which can be a highly nontrivial task as has been shown in a recent work.

The first boundary we consider is a $\Sigma 7$ symmetric tilt about the c-axis. This exact CSL boundary is shown in Fig. 1. As a shorthand we refer to this boundary as “c-tilt.” For tilt boundaries, the tilt axis is parallel to the boundary plane. Because the Boron sublattice in ZrB$_2$ is graphitic, we propose a c-tilt grain boundary structure in analogy with graphite. Related structures have been recently proposed for graphene. The boundary consists of a sequence of five and seven (5–7) membered Boron ring units that are separated by hexagonal rings. The distance between these units is related to the tilt angle where lower angles correspond to a larger separation between the five and seven pairs. The smallest such structure is the $\Sigma 7$ structure. To complete the structure for ZrB$_2$, Zr atoms are positioned over/above all Boron rings including the five- and seven-membered rings. This structure can also be viewed as an array of edge dislocations with a horizontal Burger’s vector where the five-membered rings represent the extra plane of atoms.

The second boundary is a $\Sigma 7$ symmetric twist about the c-axis. We call this boundary “c-twist” and it is displayed in Fig. 2. For twist boundaries, the twist axis is perpendicular to the boundary plane. This boundary is the simplest of the ones we will consider and shows the least reconstruction. The interface structure has a layer of Zr and a layer of B shifted relative to each other. Thus, across the interface, the Zr atoms are not centered directly above and below Boron six-membered rings. This twist results in a small degree of crumpling of the two layers, mainly in the Boron layer. However, large-scale reconstruction does not occur because the intralayer interactions (metallic Zr and covalent B) have not been disturbed significantly. The interfacial layers also are further stabilized by the compounded effect of additional layers away from the boundary.

The third structure we consider is a 90°, near-coincidence, asymmetric tilt boundary about the a-axis, which we call “a-tilt.” This model contains two boundaries, which we designate Left and Right, as shown in Fig. 3. For the Left boundary, the inserted Zr layers match the middle section Boron layer. However, a deficit of Zr atoms now exists to match the Boron layer to the outer left. This results in an alternating series of flat and crumpled Boron rings in the Left interface. For the Right boundary, the Zr sheet matches perfectly the Boron layer to its right. However, there are too many Zr atoms in this layer to match the edge Boron layers on its left. These extra Zr atoms produce considerable crowding of the middle section Borons as can be seen in Fig. 8 from a different orientation where the Boron sheets are bent up or down at their edges.

The final boundary is a 90°, near coincidence, asymmetric twist about the a-axis, which we designate “a-twist.” Figure 4 shows the periodic model for a-twist with two boundaries, denoted Left and Right. Both Left and Right boundaries have two sets of 90° rotated edge-on Boron planes interacting with each other. On the Left boundary, there is one Zr

![Fig. 1. Atomic structure of $\Sigma 7$ symmetric c-axis tilt boundary for ZrB$_2$ with Zr (red) and B (gray) atoms shown. The boundary contains 5–7 membered ring pairs separated by hexagonal rings. This structure is similar to ones proposed for graphene. The c-axis is normal to the plane of the figure and parallel to the boundary.](image1)

![Fig. 2. Atomic structure of $\Sigma 7$ symmetric c-axis twist boundary for ZrB$_2$ with Zr (red) and B (gray) atoms shown. A layer of Zr has been shifted relative to a B layer resulting in crumpling. The c-axis is normal to the atomic layers and normal to the boundary.](image2)
reactive, but they are separated from the unreactive sheets by –
on configuration. This permits nontrivial Boron
both sides of both boundaries have the more reactive, edge-
active boundary. For the Boron planes interact with each other across their respec-
tory. We will have more to say about this when we examine
bonding across the interface and therefore a denser bound-
lattice that are aligned precisely with the locations of the
ELF for the boundary in Fig. 7. In particular, we consider
accumulation points in the Zr plane are no longer aligned with the Boron
relative to each other. Therefore, the ELF accumulation
high ELF values between neighboring Boron atoms. Between
atom too few per repeat unit, leaving an effective Zr vacancy
in the center of the boundary. This results in a complicated
four-membered Boron ring configuration. Above and below
this ring, Zr atoms are pushed away, resulting in the bending
of both Zr and B planes near that boundary. The Right
interface has an extra Zr atom (actually a column of Zr
going into the page of the figure) in this layer relative to the
middle section. The extra Zr atom is effectively attached to
the end of a Boron plane. Zr atoms above and below this
atom are pushed away causing bending of the middle planes
as they approach the boundary. We can see in the Boron
plane that is edge-on to the extra Zr atom that the Boron
rings are compressed along that edge.
Whereas a-twist and a-tilt have similar features, a-twist
appears more disordered than a-tilt. This is a result of how
the Boron planes interact with each other across their respec-
tive boundary. For a-tilt, the Boron planes on the left of the
Left boundary and on the right of Right boundary are flat,
chemically unreactive with no dangling bonds. The middle
section of a-tilt has exposed edge-on Borons that could be
reactive, but they are separated from the unreactive sheets by
layers of large Zr atoms. For a-twist, the Boron sheets on
both sides of both boundaries have the more reactive, edge-
on configuration. This permits nontrivial Boron–Boron
bonding across the interface and therefore a denser bound-
dary. We will have more to say about this when we examine
the electronic structure.

IV. Electronic Structure
The electronic structure of single crystal ZrB2 was discussed in detail previously.16 To summarize, the electronic configur-
atation for Zr is [Kr]5s24d2, permitting two “s” and two “d”
valence electrons to be donated to the material. Boron’s elec-
tronic configuration is [He]2s22p1, giving it one less valence
electron than Carbon. Thus, Boron has an electron “defi-
ciency” which has a significant impact on its properties.
Despite its simple atomic structure, ZrB2 displays all three
major electronic bonding motifs. The electron localization
function (ELF) is a useful tool to identify and distinguish
different types of bonding in the real space structure. In sin-
gle crystal ZrB2, the ELF in the metallic Zr layers is diffuse
and relatively nonlocalized as expected for metallic bond-
ing.16 ELF accumulation points were identified in the Zr
planes which aligned with Boron atomic sites in the neigh-
bor ing planes. In the B planes, the electrons are well local-
ized into covalent, highly directional bonds as reflected by
high ELF values between neighboring Boron atoms. Between
layers, significant charge transfer was found as electron
“rich” Zr atoms donated electronic charge to the electron
“deficient” Borons resulting in ionic bonding between layers.
Thus, bonding in the Zr planes is metallic; bonding in the B
planes is covalent; and the bonding between layers is ionic.
The electronic structure of grain boundaries can provide
important information about interface properties.18 The for-
mation of an interface may result in significant reconstruc-
tion of the boundary atomic structure. The accompanying
changes to the electronic structure can result in significant
modifications to the bonding across the boundary. A range
of scenarios is possible from the formation of localized states
due to dangling bonds or impurity atoms to strong covalent
bonding across the interface. In Fig. 5, we show the density
of states (DOS) for the two simplest structures, c-tilt and
c-twist, and compare them to the single crystal DOS. As can
be seen, the electronic structures are largely similar for these
cases and indicate that there are no localized states in these
boundaries.
For grain boundaries, the ELF provides a spatially
resolved description of how the bonding changes across the
reconstructed interface; this can be correlated directly to
interfacial properties such as adhesion, formation energies,
and thermal conductance, among others. In Fig. 6, we show
the ELF for c-tilt. C-tilt is one of the least disrupted bound-
daries. The material is still layered in the same way as with
the single crystal, but at the boundary, 5–7 ring pairs are
inserted which results in the different crystal orientation on
either side of the boundary. The ELF clearly shows that the
same bonding motifs survive the formation of this boundary,
namely there is covalent bonding in the Boron planes includ-
ing among the 5–7 rings. Regions of high ELF are seen
between all Boron pairs regardless of the ring type (five-, six-,seven-membered rings). Interesting, the 5–7 rings remain flat
without crumpling. Because of the strong covalent bonding
across this interface, we expect especially strong interfacial
adhesion and thermal conductance for this boundary.
The bonding structure for c-twist is relatively simple. The
crystal structure on either side of the boundary remains
intact except at the interface where a boron and a zirconium
layer have been shifted relative to each other. We display the
ELF for the boundary in Fig. 7. In particular, we consider
the ELF in the plane on the Zr side of the boundary. This
particular plane is sandwiched between two Boron planes. In
the single crystal, the Boron planes are mirror images and
the Zr ELF forms accumulation points in an open hexagonal
lattice that are aligned precisely with the locations of the
Boron in the two neighboring planes. In the case of c-twist,
however, the Boron in the two neighboring planes is shifted
relative to each other. Therefore, the ELF accumulation
points in the Zr plane are no longer aligned with the Boron
atoms across the interface. The implication of this is not
completely clear, but it is expected that this mismatch will
weaken the ionic bonding across the interface.

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Fig. 4. Atomic structure of 90°, near coincidence, asymmetric a-axis twist boundary for ZrB2 with Zr (red) and B (gray) atoms shown. Unit cell has two boundaries designated Left and Right. Significant reconstruction makes this the most disordered boundary. The a-axis is in the plane of the figure and normal to the boundaries.

Fig. 5. Electronic densities of state for the c-axis tilt and c-axis twist boundaries compared to the single crystal result.

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In Fig. 8, the ELF for \(\alpha\)-tilt is shown in a plane crossing the boundary where the orientation has been rotated with respect to Fig. 3. The ELF plane displayed in Fig. 8 contains only Boron atoms on both sides of the interfaces. The \(\alpha\) atoms in the figure are in front of the contour plane. The plane that is displayed has the maximum ELF at the interface. The bonding across the \(\alpha\)-tilt boundary is expected to be ionic due to the \(\text{Zr}\)--\(\text{B}\) interaction. However, we see evidence from the ELF plot of some nontrivial electron localization inside the interface involving pairs of B atoms. These Boron ELF clouds are distorted slightly and may enhance the interaction across the interface. On the \(\alpha\)-twist boundary, Boron planes are bent due to crowding from extra \(\text{Zr}\) atoms.

In Fig. 9, the ELF for \(\alpha\)-twist is shown in a plane crossing the boundary where the orientation has been rotated with respect to Fig. 3. The ELF plane displayed in Fig. 8 contains only Boron atoms on both sides of the interfaces. The \(\alpha\) atoms in the figure are in front of the contour plane. The plane that is displayed has the maximum ELF at the interface. The bonding across the \(\alpha\)-twist boundary is expected to be ionic due to the \(\text{Zr}\)--\(\text{B}\) interaction. However, we see evidence from the ELF plot of some nontrivial electron localization inside the interface involving pairs of B atoms. These Boron ELF clouds are distorted slightly and may enhance the interaction across the interface. On the \(\alpha\)-twist boundary, Boron planes are bent due to crowding from extra \(\text{Zr}\) atoms.

A central exotic feature of this structure is the horizontal Boron plane in the center of the middle section of Fig. 9. This Boron plane intersects the two boundaries in very different ways. At the Left boundary where there are missing \(\text{Zr}\) atoms, four-membered covalent Boron rings form. The ELF shows that there is strong covalent bonding in this ring that reaches across the Left interface. At the Right boundary, the same Boron plane encounters an extra \(\text{Zr}\) atom at that interface. Strong covalent bonding is seen across both Left and Right boundaries.
by Boron structures on five sides, instead of the single crystal configuration with Borons only above and below the Zr. Thus, there is nontrival and complex electronic structure between these Zr and their Boron-rich caged structures.

V. Grain Boundary Energies

The grain boundary interfacial excess energy was defined as

$$\gamma = \frac{(E_{GB} - nE_{bulk})}{2A}$$  \hspace{1cm} (5)

where $E_{GB}$ is the total energy of the grain boundary cell, $E_{bulk}$ is the total energy of a formula unit of single crystal bulk material, $n$ is the number of formula units to match the number of atoms in the grain boundary cell, and $A$ is the area of the interface. The volume of the interface was defined as

$$A_{c} = \frac{(z_{GB} - z_{bulk})}{2}$$  \hspace{1cm} (6)

where $z_{GB}$ is the length of the relaxed cell in the direction normal to the boundary and $z_{bulk}$ is the length of an equivalent cell with no boundary.

These quantities were calculated for unit cells corresponding to the structures shown in Figs. 1–4 using ab initio computations and also using the ZrB$_2$ DLB interatomic potentials. The results are shown in Table I. With such small cells (from 72 atoms for $c$-tilt to 1344 atoms for $a$-twist), significant interactions are expected between the two boundaries in each cell. As previously discussed, $c$-tilt and $c$-twist are exact CSL boundaries whereas $a$-tilt and $a$-twist are near-CSL structures. The near-CSL interfaces have a small amount of artificial strain (less than 1%). To maintain these structures, the volume was fixed during the optimization and only the articial strain (less than 1%). To maintain these structures, the volume was fixed during the optimization and only the

VII. Microstructural Modeling

The effect of grain boundary networks on the lattice thermal conductivity of polycrystal ZrB$_2$ is now considered. To begin, a Brick Layer Model (BLM) was used to estimate the reduction in thermal conductivity due to interfacial thermal resistance. The BLM, the effective thermal conductivity $\kappa_{eff}$ is given by

$$\frac{1}{\kappa_{eff}} = \frac{1}{\kappa_0} + \frac{R_K}{d}$$  \hspace{1cm} (7)

where $\kappa_0$ is the intrinsic lattice thermal conductivity of the material, $R_K$ is the interfacial (Kapitza) thermal resistance,
and $d$ is the grain size. This expression states that the effective resistance is a sum of the intrinsic resistance plus the sum of the resistances for each boundary crossed. The effective thermal conductivity $j_{\text{eff}}$ was evaluated using thermal parameters taken from our atomistic simulations. The value of $j_0$ cannot be measured directly therefore we assigned a value of $50 \text{ W/(m} \times \text{K)}$ which was obtained from our previous atomistic computations. This value is the average of the in-plane and normal conductivities obtained from those simulations. For $R_K$, we used the value for $\alpha$-tilt which has the highest interfacial resistance of our structures, $3.3 \text{ (m}^2 \times \text{K)/GW}$. For $d$ we used $6 \mu\text{m}$ which is typical for these materials.

The effective thermal conductivity $j_{\text{eff}}$ obtained was $48.6 \text{ W/(m} \times \text{K)}$ which represents a very small reduction in its thermal conductivity from the intrinsic value $j_0$. Experimental thermal conductivity values reported by Zimmerman et al. are around $22 \text{ W/(m} \times \text{K)}$ at room temperature. This suggests that the boundaries considered in this study have very low interfacial thermal resistance from the MD simulations compared with experimental data. This is not surprising as our structures are very pristine and current processing methods for this material typically give much more disordered boundaries with numerous impurities. On the other hand, this also shows that significant improvement in material properties can be obtained by improving the quality of the grain boundaries.

Next, we considered an experimentally more representative situation. First, we utilized a more realistic microstructure than BLM (1D boundaries “in series”). In particular, we evaluated $\kappa_{\text{eff}}$ using FEM computations whose mesh was constructed on an SEM micrograph taken from Ref. 1. Second, FEM thermal parameters were taken from experiment to obtain a nontrivial reduction in $\kappa_{\text{eff}}$. For the thermal conductivity of the grains, we again assigned a value $50 \text{ W/(m} \times \text{K)}$ obtained from MD simulations. However, as the MD interfacial resistances were very low (significantly lower than what is expected for these materials), a more realistic value for $\sigma_K$ was chosen to be $10.0 \text{ MW/(m}^2 \times \text{K)}$. An interphase conductivity $\kappa_K$ was obtained by multiplying $\sigma_K$ by a representative width, giving $\kappa_K = 1 \text{ W/(m} \times \text{K)}$. In Fig. 11, we show the original SEM image, the FEM mesh, and the steady-state temperature distribution in the material. As we can see, the conduction is not uniform as the grain boundary network impedes the flow, resulting in jagged thermal contours through the material. Remarkably, the result for the effective thermal conductivity of the material from the transient analysis is $18 \text{ W/(m} \times \text{K)}$ which is very close to the experimental value of $22 \text{ W/(m} \times \text{K)}$. In addition, results from the UTG and UHF steady-state computations are reported in Table II. Those numbers agree very well with each other and with the transient result.

It is interesting to compare the FEM result with the BLM and also with the rule of mixtures using the same parameters. Using the BLM expression and the more realistic interfacial
parameters, we obtain 10.1 W/(m·K) for $\kappa_{\text{eff}}$. This is a reasonable result as the BLM is a series resistance model and therefore should be lower than the FEM model which has both series and parallel contributions. As the FEM model is a two-phase system we can also apply the rule of mixtures which gives for this situation 44 W/(m·K). The rule of mixtures describes a system of parallel resistances, therefore, it should give an upper bound relative to the FEM model. These calculations show that a wide variation of results can be obtained depending on which model microstructure is used.

### VIII. Conclusion

In this study, we used a combination of ab initio computations, atomistic simulations, and FEM calculations to study the structure and properties of grain boundaries and grain boundary networks and investigate their impact on lattice thermal conductivity in ZrB$_2$. Ab initio results showed that the c-axis CSL boundaries, c-tilt and c-twist, had lower interfacial energies than the a-axis near-CSL boundaries, a-tilt and a-twist. Energies from the interatomic potential did not produce as clear an ordering, giving interfacial energies very similar to each other. However, the absolute values of the energies from the potentials were reasonable. The degree of energetic relaxation of the structures matched very well the ab initio results. In general, the new interatomic potential developed for this material seemed to give a reasonable description of the boundaries.

Interfacial thermal conductances $\sigma_{\text{K}}$ were evaluated using nonequilibrium molecular dynamics. For our boundaries, c-tilt had the lowest thermal resistance. The highest interfacial thermal resistances were for a-tilt which was both more disordered and more ionic than the other boundaries. In general, however, all four boundaries had very low thermal resistances compared with estimates based on experimental data. That is not surprising as these boundaries are very crystalline, highly ordered, and free of impurities. These calculations show, however, that low energy structures with very favorable properties exist for these materials and might be produced by improved processing methods.

The effect of the grain boundary network on the bulk lattice thermal conductivity of the material was also considered. A FEM thermal analysis was performed using a microstructure obtained from an SEM image. The FEM computations showed a reduction in lattice thermal conductivity that was much closer to experiments than results obtained from simple analytic models such as the BLM or the ROM.

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