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RESEARCH ARTICLE OPEN ACCESS

Resolving Basis Dependence in Point-Defect Scattering Models for Thermal Conductivity in Multi-Sublattice Ceramics

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ABSTRACT

Alloying is a widely used strategy for reducing lattice thermal conductivity through phonon scattering induced by mass and strain fluctuations. However, the evaluation of disorder-scattering parameters in multi-sublattice compounds remains inconsistent because both atomic- and unit-cell-based formulations are used in the literature. In this work, the origin of these discrepancies is systematically examined using ZrC and ZrB₂ as model systems. We show that the two approaches yield equivalent predictions only when a consistent basis is maintained throughout the calculation and the alloyed site has a degeneracy of unity. For compounds containing multiple sublattices or higher site degeneracy, the formulations diverge and can lead to substantially different estimates of alloying-induced phonon scattering. To address this issue, a generalized framework incorporating sublattice-selective disorder scattering is proposed. The formulation preserves basis consistency while accounting for the localized nature of disorder in complex compounds. The model is applied to W-doped ZrB₂ ceramics and compared with experimental thermal conductivity measurements. Improved agreement is obtained relative to conventional treatments. The proposed framework provides a physically consistent methodology for evaluating point-defect scattering in multi-sublattice solid solutions and enables more reliable prediction of lattice thermal conductivity in complex ceramic materials.

1 | Introduction

Thermal conductivity is an important material property for many applications, such as thermal barrier coatings, thermoelectric materials, and ultra-high-temperature ceramics. Taking ultra-high-temperature ceramics, for example, high thermal conductivity is a crucial material property for their application as adaptive thermal protection material, whereas low thermal conductivity could be enabling for thermal insulation purposes. In thermoelectric materials, low thermal conductivity is also preferred to maintain a temperature gradient in order to establish

voltage differences due to Seebeck effect and subsequent power generation. Both electrons and lattice contribute to the total thermal conductivity ($\kappa_{\text{total}} = \kappa_e + \kappa_l$). Lattice thermal conductivity κ_l is a measure of the phonon propagation in the lattice. These phonon waves can move unhindered until they encounter lattice imperfection, such as point defects, upon which phonons will be scattered. The time of free travel in between the scattering events is called relaxation time.

Depending on the types of lattice imperfection, various strategies can be applied to reduce κ_l , such as introducing point defects

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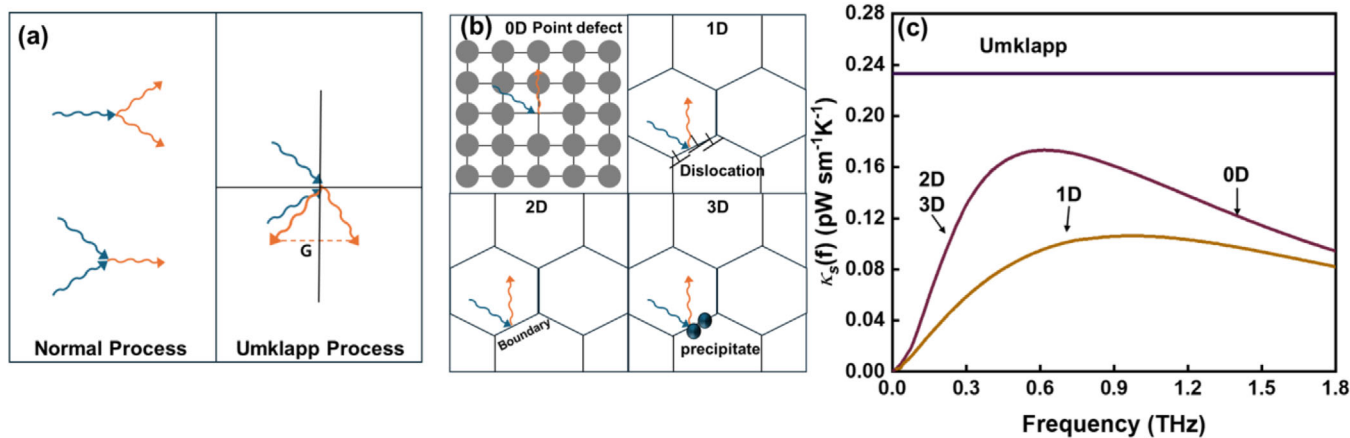


FIGURE 1 | (a) Phonon–phonon scattering processes. (b) Defects due to lattice imperfection with different dimensionalities. (c) Spectral thermal conductivity at high temperatures (assuming $T \gg \theta_D$) when Umklapp scattering (τ_U) dominates transport (top curve) and when defects in (b) are accounted for (lower curve) [1].

(0D), dislocations (1D), grain boundaries (2D), and nanoparticles (3D). The extent of effect mainly depends on the size and vibrational frequency of such imperfections. The smaller the imperfection, the higher frequency phonons it would be able to scatter, as shown in Figure 1. Specifically, 0D defects are most effective at suppressing high-frequency phonons, whereas 2D and 3D defects primarily scatter low-frequency phonons. Meanwhile, 1D defects are known to predominantly scatter mid-frequency phonons.

Here, in this article, we will mainly discuss how point-defect scattering or alloying effect (0D) will impact lattice thermal conductivity.

When a certain type of dopant is added into the material system, these dopants form point defects, which cause disturbance in phonon transport and subsequent phonon scattering, thus reducing lattice thermal conductivity. This point-defect scattering is often divided into two parts: One is from mass fluctuation effect Γ_M and the other from strain fluctuation effect Γ_S arising from different binding energy between the foreign atom and the original lattice. The total scattering parameter $\Gamma = \Gamma_M + \Gamma_S$ determines the extent to which the lattice thermal conductivity would be reduced given these introduced point defects.

This work revisits the evaluation of alloying-induced point-defect scattering in multi-sublattice ceramic compounds and examines how the choice of calculation basis influences predicted lattice thermal conductivity. First, the theoretical foundations of mass and strain fluctuation scattering and their incorporation into Debye–Callaway thermal conductivity models are reviewed. The derivation of disorder-scattering parameters is then reexamined using both atomic-based and unit (or primitive)-cell-based formulations, and the conditions under which the two approaches yield equivalent results are identified. Using ZrC and ZrB₂ as model systems, the effects of site degeneracy, sublattice structure, and multi-site alloying are analyzed, revealing the origin of discrepancies frequently encountered in the literature. To resolve these inconsistencies, a unified formulation incorporating sublattice-selective disorder scattering is proposed, providing a physically consistent treatment of alloying-induced phonon scat-

tering in complex compounds. Finally, the framework is applied to W-doped ZrB₂ ceramics, where thermal conductivity measurements are compared with Debye–Callaway calculations to evaluate the proposed model. The results demonstrate improved agreement with experiment and establish a more reliable methodology for predicting lattice thermal conductivity reduction in multi-sublattice solid solutions.

2 | Lattice Thermal Conductivity due to Disorder Scattering

In the 1950s, Klemens [2] derived the scattering probability of low-frequency lattice waves by static imperfections on the basis of the perturbation theory. In the case of an isolated imperfection in an otherwise perfect crystal, Klemens derived the reverse of the scattering time to scale as the fourth power of frequency. An important assumption made here is that the lattice is monatomic, and Klemens argued that this does not lead to errors at low frequency, as the crystal behaves like a continuous elastic medium and low-frequency phonons do not “see” the detailed multi-atom structure of the unit cell. Thus, we have the relaxation time τ_{PD} expressed as

$$\frac{1}{\tau_{PD}} = \Omega \Gamma \frac{\omega^4}{4\pi v^3} \quad (1)$$

where $v = \omega/k$ is the group velocity of the phonon waves, Ω is the volume per atom, and Γ is the scattering strength of the imperfection.

An imperfection is reasoned to contribute in three ways to the perturbation energy by producing an alteration in (a) the kinetic energy due to a mass difference Γ_M (Equation 2), (b) the potential energy due to a change in the elastic constant of some linkages, and (c) the potential energy due to an elastic strain field, which alters the elastic constants of the linkages as a result of deviations from Hooke’s law. The latter two (b + c) contribute to the scattering because of strain Γ_S (Equation 3). The total scattering Γ is due to both mass Γ_M and strain scattering Γ_S (Equation 4):

$$\Gamma_M = \left(\frac{\Delta M}{M} \right)^2 \quad (2)$$

$$\Gamma_S = 2 \left(\frac{\Delta K}{K} - 2Q\gamma \frac{\Delta R}{R} \right)^2 \quad (3)$$

$$\Gamma = \Gamma_M + \Gamma_S = \left(\frac{\Delta M}{M} \right)^2 + 2 \left(\frac{\Delta K}{K} - 2Q\gamma \frac{\Delta R}{R} \right)^2 \quad (4)$$

where M , K , and R are the atomic mass, bulk modulus, and atomic radius of the original crystal; and ΔM , ΔK , and ΔR are the difference of each quantity between original and introduced impurities. Q accounts for the accumulative influences on surrounding bonds from the point defect for which Klemens [2] used 4.2 for substitutional impurities and 3.2 for vacancies. γ is the Grüneisen parameter, which characterizes the anharmonicity of lattice vibrations.

To simplify the Γ_S term, in 1963 Abeles linked the elastic constant change to the atom size change [3]. G is defined as the sensitivity of bulk modulus change to that of atomic radius change (Equation 5):

$$G = -\frac{\Delta K}{K} / \frac{\Delta R}{R} \quad (5)$$

The strains' scattering strength becomes

$$\Gamma_S = 2 \left(\frac{\Delta K}{K} - 2Q\gamma \frac{\Delta R}{R} \right)^2 = 2 \left[(G + 2Q\gamma) \frac{\Delta R}{R} \right]^2 \quad (6)$$

$$\text{With } \Gamma_S = \varepsilon (\Delta R/R)^2 \quad (7)$$

$$\varepsilon = 2[G + 2Q\gamma]^2 \quad (8)$$

where $\Delta R = R_i - R$, and R_i is the radius of the impurity in the host lattice, unlike M_i , which does not change whether it is in its own lattice or the host lattice, R_i is different from R'_i , the radius of the impurity in its own lattice. According to the continuum theory of lattice defects [4], $\Delta R/R$ and $\Delta R'/R$ is related by

$$\frac{\Delta R}{R} = \frac{\Delta R'}{R} \frac{\mu}{1 + \mu} \quad (9)$$

where

$$\mu = \frac{1 + \sigma}{1 - 2\sigma} \frac{K'_i}{K} \quad (10)$$

where K'_i is the bulk modulus of the impurity sphere. K and σ are the bulk modulus and Poisson ratio of the matrix, respectively.

Integrating Equations (7)–(10) into Equation (6), we get

$$\Gamma_S = 2 \left[(G + 2Q\gamma) \left(\frac{1 + \sigma}{1 - 2\sigma} \frac{K'_i}{K} \right) \right]^2 \left(\frac{\Delta R'}{R} \right)^2 \quad (11)$$

If we assume $K'_i = K$, Equation (11) becomes

$$\Gamma_S = \frac{2}{9} \left[(G + 2Q\gamma) \left(\frac{1 + \sigma}{1 - \sigma} \right) \right]^2 \left(\frac{\Delta R'}{R} \right)^2 \quad (12)$$

Although Klemens' derivation is based on perturbation theory, Equation (1) has the exact expression in terms of frequency compared to the Raleigh scattering from classical physics [5].

In 1956, Ziman [6] proposed a way to quantify the scattering strength due to isotopes on the basis of Klemens' calculation, which further link the scattering parameter Γ to the site composition. If a particular element has several isotopes, of masses $M_1, M_2, \dots$, in proportions $f_1, f_2, \dots$, the scattering effect due to mass contrast is proportional to $f^k (M^k - \bar{M})^2$ according to Equation (2), and the total effect of all the isotopes of the element must be proportional to the variance of the isotopic masses in their natural abundances, that is,

$$\Gamma_M = \sum_k f^k \left(\frac{M^k - \bar{M}}{\bar{M}} \right)^2 = \frac{(\Delta M)^2}{\bar{M}^2} \quad (13)$$

Consider a compound material containing more than one site $M_{1,c1} M_{2,c2} \dots M_{n,cn}$, where c_i is the degeneracy on each site. In the same paper, Ziman proposed that for a compound, it is only necessary to take the average value of $(\Delta M)^2$ and $\bar{M}$ over the various elements of the chemical formula. This treatment of the compound material as a monatomic material with an average atomic mass $\bar{M}$ (Equation 16) has been adopted by Slack in 1962 [7] and later widely used in the thermoelectric community [8–10]:

$$\Gamma_M = \sum_i \frac{c_i}{\sum_i c_i} \frac{\bar{M}_i^2}{\bar{M}^2} \Gamma_{M,i} \quad (14)$$

$$\Gamma_{M,i} = \frac{\sum_k f_i^k (M_i^k - \bar{M}_i)^2}{\bar{M}_i^2} \quad (15)$$

$$\bar{M} = \frac{\sum_{i=1}^n c_i \bar{M}_i}{\sum_{i=1}^n c_i} \quad (16)$$

$$\Gamma_M = \sum_i \frac{c_i}{\sum_i c_i} \frac{\sum_k f_i^k (M_i^k - \bar{M}_i)^2}{\bar{M}_i^2} \frac{\bar{M}_i^2}{\bar{M}^2} = \frac{\sum_i c_i \sum_k f_i^k (M_i^k - \bar{M}_i)^2}{\sum_i c_i \bar{M}^2} \quad (17)$$

The mass scattering strength per atom (Equation 17) is thus an average based on the chemical composition (c_i), the mass contrast between each site $\bar{M}_i$ and $\bar{M}$ and the scattering strength $\Gamma_{M,i}$ on site i (Equation 15).

The strain scattering strength can be defined in a similar fashion (Equation 19), albeit with some complications due to the prefactor and radius difference of impurity atom in the host and its own lattice:

$$\Gamma_{S,i} = \frac{\sum_k f_i^k (R_i^{k'} - \bar{R}_i)^2}{\bar{R}_i^2} \quad (18)$$

$$\Gamma_S = \frac{\sum_i \varepsilon' c_i \sum_k f_i^k (R_i^{k'} - \bar{R}_i)^2}{\sum_i c_i \bar{R}^2} \quad (19)$$

$$\varepsilon' = 2 \left[(G + 2Q\gamma) \left(\frac{1+\sigma}{1-2\sigma} \frac{K'_L}{K} \right) \right]^2 \quad (20)$$

Once we have the disorder-scattering strength, we can move on to the calculation of lattice thermal conductivity. In 1960, Callaway [11] proposed a model on the basis of the following assumptions:

1. A linear dispersion $v = \omega/k$ is assumed for the phonons propagating through the lattice up to Debye temperature Θ_D .
2. All phonon scattering processes can be represented by frequency-dependent relaxation times. In addition to point-defect scattering (Equation 4), we also have other scattering, such as Umklapp scattering, normal scattering, and boundary scattering.

Although many expressions exist for Umklapp scattering τ_U^{-1} , there is a universality of

$$\tau_U^{-1} = B_1 \omega^2 T = \frac{2\hbar\gamma^2}{M v^2 \Theta_D} \exp\left(-\frac{\Theta_D}{3T}\right) \omega^2 T \quad (21)$$

Normal scattering is momentum-conserving: $\tau_N^{-1} = B_2 \omega^2 T$,

Is B_2 temperature independent? The total scattering due to phonon-phonon scattering $\tau_{ph}^{-1} = (B_1 + B_2) \omega^2 T$.

$$\text{Boundary scattering } \tau_B^{-1} = \frac{v}{L} \quad (22)$$

1. The additivity of the reciprocal relaxation times is assumed:

$$\tau_R^{-1} = \tau_B^{-1} + \tau_{PD}^{-1} + \tau_{ph}^{-1} = \frac{v}{L} + A\omega^4 + B_1 \omega^2 T \quad (23)$$

In the original Debye–Callaway model, normal scattering is treated separately from the resistive scattering term (τ_R^{-1}). This is because Umklapp scattering is assumed to dominate, and a single relaxation time approximation is adopted with the effect of normal scattering neglected, $\tau_C^{-1} = \tau_R^{-1}$.

The lattice thermal conductivity can be calculated as

$$\kappa_L = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \tau_C \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (24)$$

With $x = \frac{\hbar\omega}{k_B T}$

To further simplify, Callaway and von Baeyer [11] proposed Equations (25) and (26) as an approximate high-temperature Callaway–von Baeyer model. They assumed Umklapp-limited phonon transport in the pristine crystal and additional point-defect scattering in the disordered crystal and proposed the ratio of κ_L of the crystal with disorder to that without disorder, κ_L^p is

$$\frac{\kappa_L}{\kappa_L^p} = \frac{\arctan(u)}{u} \quad (25)$$

$$u^2 = \frac{\pi^2 \Theta_D \Omega}{\hbar v_s^2} \kappa_L^p \Gamma \quad (26)$$



FIGURE 2 | Zr as a monoatomic chain with vacancies.

where u , $\hbar$, v_s , Ω , and Γ are the disorder scaling parameter, the Planck constant, speed of sound, volume per atom, and the disorder-scattering parameter, respectively. Taking the decline of κ_L of the crystal with disorder to that without disorder, we can calculate the scattering parameter with experimentally determined κ_L , κ_L^p , Θ_D , v_s , and Ω . This has been proven to be a validation strategy for the calculation of scattering parameters at relatively high temperatures ($T > \Theta_D$) [10].

3 | Discrepancy in Calculating Γ

Although the treatment of the compound material as a monatomic material with an average atomic mass $\bar{M}$ (Equations 14–17) has been adopted widely, it is based on one important assumption that this holds for low-frequency phonons because long-wavelength phonons do not “see” the mass variations within a complex unit cell. However, as we have seen above, point-defects scatter mainly high-frequency (short-wavelength) phonons due to the high-order angular frequency dependence (ω^4). Near the Brillouin-zone boundary, phonon modes become increasingly polarized toward specific sublattices, particularly in materials with large mass contrast, making their scattering strongly dependent on the occupied sublattice. We need to look into the actual scattering strength given the mass variance from different sublattices, respectively.

Taking Zr, for example, to start with, when vacancies have been introduced into a perfect Zr crystal, the occupancy of Zr f_{Zr} becomes less than 1 (Figure 2).

The mass difference between the vacancy and Zr atom is the atomic mass of Zr (91.22 u). The average atomic mass would be $f_{Zr} M_{Zr}$. The mass scattering parameter based on Equation (2) becomes

$$\begin{aligned} \Gamma_M &= \frac{f_{Zr}(M_{Zr} - f_{Zr} M_{Zr})^2 + (1 - f_{Zr})(M_V - f_{Zr} M_{Zr})^2}{(f_{Zr} M_{Zr})^2} = \frac{1 - f_{Zr}}{f_{Zr}} \\ &= (1 - f_{Zr}) f_{Zr} \frac{M_{Zr}^2}{\bar{M}^2} \end{aligned} \quad (27)$$

We can understand it to be the disorder arises from f_{Zr} fraction of the Zr lattice is occupied by Zr, and $(1 - f_{Zr})$ of the Zr lattice is occupied by vacancy. The same goes to vacancy defected C, where

$$\Gamma_M = \frac{1 - f_C}{f_C} = (1 - f_C) f_C \frac{M_C^2}{\bar{M}^2} \quad (28)$$

Note the average atomic mass $\bar{M}$ would change from $f_{Zr} M_{Zr}$ in vacancy-doped Zr to $f_C M_C$ in vacancy-doped carbon, both Equation (27) and (28) can be simplified as $\Gamma_M = \frac{1-f}{f}$.



FIGURE 3 | ZrC with vacancies on the Zr site.

Now we introduce a C sublattice to form a ZrC crystal, which has an FCC crystal structure with a unit cell of four Zr atoms and four C atoms, and its corresponding primitive cell of one Zr atom and one C atom. We assume C has partial occupancy f_C ($0 < f_C < 1$) due to vacancies, and Zr has full occupancy, which is in agreement with reported phase diagram [12] (Figure 3).

Only the C sublattice is disturbed by the vacancies. The average atomic mass on Zr site would be the same as it were in a Zr metal, M_{Zr} . The average atomic mass $\bar{M}$ on C site is $f_C M_C$. The average atomic mass $\bar{M}$ across the chemical formula (ZrC), however, would be $\frac{M_{Zr} + f_C M_C}{2}$. The difference between the two is shown in Figure 4.

When we consider the ZrC crystal as a monatomic chain, on the basis of Equation (17), the mass scattering parameter per atom $\Gamma_{M,A}$ becomes

$$\Gamma_{M,A} = \frac{f_C \left(M_C - \frac{f_C M_C}{2} \right)^2 + (1 - f_C) \left(M_V - \frac{f_C M_C}{2} \right)^2}{2 \left(\frac{M_{Zr} + f_C M_C}{2} \right)^2} \quad (29)$$

Compare to the scattering parameter in vacancy doped pure C (Equation 28), we see that the mass scattering parameter was largely reduced to $\bar{M}^2/2M^2$ times the original value when the Zr sublattice is introduced. This is in agreement with physical intuition that an unchanging sublattice helps stabilize the whole system. Meanwhile, the mass difference between Zr and C leads to mass difference between $\bar{M} = f_C M_C$ and $\bar{M} = (M_{Zr} + f_C M_C)/2$. The ratio of $\bar{M}$ on C site and average atomic mass $\bar{M}$ in ZrC_f is shown against the carbon site occupancy in Figure 4. The monatomic chain approach thus takes into account the mass contrast between heavy and light elements in different sublattices, in addition to the sum over the degeneracy of sublattices (which is two in this case).

In the original derivation of Klemens [2], Klemens proposed that for a polyatomic crystal, the M in Equation (2) should be the mass for the unit cell. However, no further information was given regarding the rest of the analysis. In Callaway and von Bayer's simplification, when taking a unit cell into consideration, both Equation (1) $\tau_{PD}^{-1} = (\Omega/4\pi v^3)\Gamma\omega^4$ and Equation (13) $\Gamma = \sum_i f_i ((M_i - \bar{M})/\bar{M})^2$ were adopted. However, a major change was made, instead of the volume per atom, Ω is now considered to be the volume of the unit cell. At the same time, instead of looking at atomic mass, M_i is the mass of a unit cell, f_i is the fraction of unit cells with mass M_i , and $\bar{M}$ is the average mass of all unit cells. We will follow this approach by taking ZrC again as an example to illustrate how discrepancies in the calculation of disorder-scattering parameter may occur. For the sake of simplicity, we will use primitive cell as a basis.

Now rather than considering the compound material as a monatomic chain, we consider a ZrC primitive cell with two sublattices, Zr and C. From the perspective of the C sublattice, f fraction of C is on the lattice of ZrC and $(1 - f)$ amount on the lattice of ZrVac (Vac signifies vacancy). On the basis of Equation (29), the mass difference and average compound mass are

$$\Delta M = M(\text{ZrC}) - M(\text{ZrVac}) = 12 \quad (30)$$

$$\bar{M}_{\text{primitive}} = f_C M^{\text{ZrC}} + (1 - f_C) M^{\text{ZrVac}} \quad (31)$$

$$\bar{M}_{\text{primitive}} = M_{Zr} + f_C M_C = 2\bar{M} \quad (32)$$

$$\Gamma_{M,P} =$$

$$\frac{f_C \left(M_{ZrC} - \bar{M}_{\text{primitive cell}} \right)^2 + (1 - f_C) \left(M_{ZrVac} - \bar{M}_{\text{primitive cell}} \right)^2}{\bar{M}_{\text{primitive cell}}^2} = \frac{f_C (1 - f_C) M_C^2}{4\bar{M}^2} \quad (33)$$

where $\Gamma_{M,P}$ signifies the mass scattering parameter on the basis of a primitive base.

A difference with a factor of 2 is thus observed when comparing Equations (29) and (33). The scattering strength based on the primitive cell is smaller (only half) of that using a monatomic chain model. This can be understood as disorder only arises when $f_C/2$ fraction of the total lattice site is occupied by C in the C sublattice and $(1 - f_{Zr})/2$ of the total lattice site is occupied by vacancy in the C sublattice (Figure 5).

The mathematical origin of this discrepancy comes from how we weigh the scattering factor per C site $(1 - f_C)/f_C$ in a complex compound $M_{1,c1}M_{2,c2}\dots M_{n,cn}$. In the atomic basis, this is weighted by the degeneracy on the atomic site divided by the total site degeneracy $c_i/\sum_{i=1}^n c_i$ multiplied by a factor of $[\bar{M}_i/\bar{M}]^2$. In the primitive cell basis, $\Gamma = \sum_i f_i \left(\frac{M_i - \bar{M}}{\bar{M}} \right)^2$ the sublattice degeneracy c_i has already been taken into account in the calculation of $\Delta \bar{M}_{i,ci} M_{j,cj}$ ($i \neq j$) = $c_i \bar{M}_i$, whereas the nominator becomes the mass of total primitive cell with $\sum_{i=1}^n c_i$ times the average atomic mass $\bar{M}$. Thus, in the primitive basis, the scattering factor per atom site $(1 - f_C)/f_C$ is weighted by a factor of $[c_i \bar{M}_i / \sum_{i=1}^n c_i \bar{M}]^2$ instead of $[c_i \bar{M}_i / \sum_{i=1}^n c_i \bar{M}]$. Note only the perturbation on the occupied sublattice is considered when evaluating the disorder-scattering parameter, whereas cross-sublattice coupling is neglected. This sublattice selectivity is excluded from the monatomic chain model, where each atom site scatters uniformly with scattering strength $\Gamma_{M,A}$:

$$\Gamma_{M,A} = \frac{\sum_i c_i \sum_k f_i^k \left(M_i^k - \bar{M}_i \right)^2}{\sum_i c_i \bar{M}^2} = \frac{\sum_i c_i \frac{\bar{M}_i^2}{\bar{M}^2} \Gamma_{M,A,i}}{\sum_i c_i} \quad (34)$$

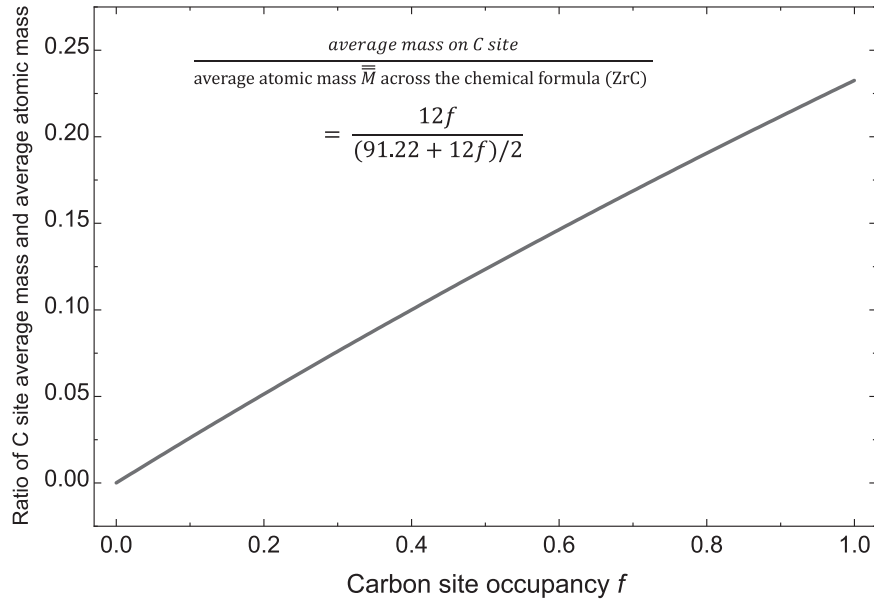


FIGURE 4 | Dependence on carbon site occupancy f of the ratio of $\bar{M}$ on C site and average atomic mass $\bar{M}$ in ZrC_f .

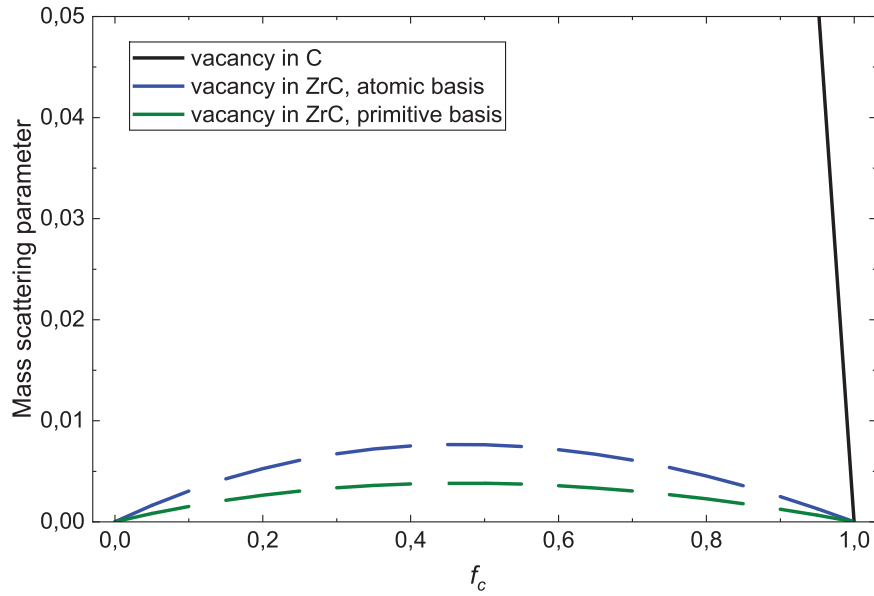


FIGURE 5 | Mass scattering parameter in vacancy-doped C (black curve), with occupancy of C f_c , per atom basis (blue curve) and per primitive cell basis (green curve).

$$\Gamma_{M,P} = \frac{\sum_i \sum_k f_i^k (c_i M_i^k - c_i \bar{M})^2}{(\sum c_i \bar{M})^2} = \frac{\sum_i c_i^2 \sum_k f_i^k (M_i^k - \bar{M})^2}{(\sum c_i)^2 \bar{M}^2}$$

$$= \frac{\sum_i c_i^2 \frac{\bar{M}_i^2}{\bar{M}^2} \Gamma_{M,A,i}}{(\sum c_i)^2} = \frac{\sum_i c_i \Gamma_{M,A}}{\sum c_i} \quad (35)$$

Similar conclusion holds for the strain or elastic constant

$$\text{scattering, } \Gamma_{S,P} = \frac{\sum_i c_i^2 \Gamma_{S,A,i}}{(\sum c_i)^2} = \frac{\sum_i c_i \Gamma_{S,A}}{\sum c_i} \quad (36)$$

So the discrepancy between the two bases can be expressed as

$$\Gamma_P = \frac{\sum_i c_i \Gamma_A}{\sum c_i} \quad (37)$$

It is crucial that we clarify between the scattering parameter Γ and cross section σ . The scattering parameter is a dimensionless measure of disorder strength, especially for point defects, which depends solely on the site composition, whereas the cross section σ is a physical area that measures the probability of a particle or phonon being scattered by a defect with the units of m^2 . Although Klemens derived from quantum perturbation theory $\tau_{PD}^{-1} = \frac{\Omega}{4\pi v^3} \Gamma \omega^4$, from classical kinetic theory, it can also

be expressed as $\tau_{PD}^{-1} = n\sigma v$, where n is the number density of scatterers, and v is the velocity of the waves. n can be expressed as $1/\Omega$, where Ω is the volume per scatterer. By correlating the two we have

$$\sigma = \frac{\Omega^2}{4\pi} \Gamma k^4 \quad (38)$$

The total cross section $n\sigma = \frac{\Omega}{4\pi} \Gamma k^4$ should be independent of the basis choice, this means $\Omega\Gamma$ should be independent of basis choice, whereas it depends on composition. In the dealing of compounds with multiple sublattices by Callaway and von Baeyer [11], Ω is that of unit cell $\sum_i c_i \Omega_{M,A}$, whereas the Γ is based on unit cell calculation $\sum_i c_i \Gamma_{M,A} / \sum_i c_i$. The multiplication of the two is the same when we treat with the primitive basis $\Omega_{M,P} \Gamma_{M,P}$, yet both lead to a divergence from monoatomic chain model as $\Omega_{M,P} \Gamma_{M,P} = \sum_i c_i \Omega_{M,A} \frac{\sum_i c_i \Gamma_{M,A}}{\sum_i c_i} = \Omega_{M,A} \sum_i c_i \Gamma_{M,A} \geq \Omega_{M,A} \Gamma_{M,A}$, given $c_i \geq 1$.

In sum, the atomic- and primitive-cell-based approaches yield equivalent predictions only when a consistent basis is maintained throughout the calculation and the alloyed site has a degeneracy of one ($c_i = 1$). For compounds with multiple sublattices of higher site degeneracy, the two approaches diverge and can lead to different estimates of alloying-induced phonon scattering.

Taking ZrB_2 , for example, when we repeat the calculation with $(1 - f_B)$ fraction of vacancy on the B site, we get

$$\Gamma_{M,A} = \frac{2f_B(1-f_B)M_B^2}{3M} \quad (\text{atomic basis}) \quad (39)$$

$$\Gamma_{M,P} = \frac{4f_B(1-f_B)M_B^2}{9M} \quad (\text{primitive cell basis}) \quad (40)$$

When we multiply the scattering parameter by the specific volume, we get

$$\Omega_{M,A} \Gamma_{M,A} = \frac{2f_B(1-f_B)M_B^2}{3M} \Omega_{M,A} \quad (41)$$

$$\begin{aligned} \Omega_{M,P} \Gamma_{M,P} &= \frac{4f_B(1-f_B)M_B^2}{9M} \Omega_{M,P} = \frac{4f_B(1-f_B)M_B^2}{9M} 3 \Omega_{M,A} \\ &= \frac{4f_B(1-f_B)M_B^2}{3M} \Omega_{M,A} \end{aligned} \quad (42)$$

As we can see from the equations above, when $c_i = 2$ (for B site), $\Omega_{M,P} \Gamma_{M,P} = 2\Omega_{M,A} \Gamma_{M,A}$.

4 | Unification of Bases and Site-Selective Disorder Scattering

The relation that $\Omega_{M,P} \Gamma_{M,P} \geq \Omega_{M,A} \Gamma_{M,A}$, given $c_i \geq 1$ is intriguing because on one hand, it violates the constant cross section law, on the other hand this is quite the opposite from what we expect with the introduction of sublattices, which should stabilize the structure and reduce the scattering parameter, as we have seen in the example of vacancy doped Zr_f and Zr_fC . In the atomic basis, the compound is assumed to be a monoatomic

chain with uniform scattering strength per atom site, $\Gamma_{M,A}$, the scattering unit being an atom, whereas in the primitive cell basis, the compound is assumed to have a repeating primitive cell with scattering strength $\Omega_{M,P}$ added up from each sublattice. Phonon scattering happens at a specific sublattice, with disorder arising with the occupancy probability of species (k) being $c_i f_{i,k} / \sum_{i=1}^n c_i$ at each sublattice i . When only vacancy is involved in the sublattice i , the probability becomes $c_i f_i / \sum_{i=1}^n c_i \times c_i(1 - f_i) / \sum_{i=1}^n c_i = \frac{c_i^2}{(\sum c_i)^2} f_i(1 - f_i)$. The selectivity of sublattice will thus reduce the probability of scattering compared to a monoatomic chain model $\frac{c_i}{\sum c_i} f_i(1 - f_i)$ given $\frac{c_i}{\sum c_i} < 1$.

The assumption we mentioned above of sublattice scattering selectivity is particularly true under the following cases: (1) Mass contrast is large, then different phonon branches become sublattice dominated; in the case of ZrB_2 , heavy Zr is more involved on low-frequency modes, whereas light B are more involved in high frequency modes. (2) Defects located on a specific sublattice predominantly scatter phonon modes whose eigenvectors are polarized toward that sublattice, whereas modes with little participation from that sublattice experience weaker scattering. (3) Bonding anisotropy exists, for example, high frequency phonons localize more on the B sublattice due to B layers having stiff covalent bonding. In all cases, mass or strain disorder on one sublattice will impact selectively the phonon spectrum, which should lead to a lower estimation of the scattering strength.

$$\Gamma_{M,UA} = \frac{\sum_i c_i \Gamma_{M,A}}{\sum_i c_i} \quad (43)$$

To unify the bases while taking the selectivity of sublattice into account, we propose a unified-atomic basis as the scattering strength per atom site with the volume per scatterer being $\Omega_{M,A}$, then not only we are keeping $\Omega\Gamma$ constant as the basis changes, but also $\Omega_{M,A} \Gamma_{M,UA} = \Omega_{M,A} \frac{\sum_i c_i \Gamma_{M,A}}{\sum_i c_i} < \Omega_{M,A} \Gamma_{M,A}$ as $\frac{c_i}{\sum c_i} < 1$. So by taking the sublattice selectivity into account, the scattering parameter estimation gives a lower bound compared to the work of Ziman [6], which will be more representative when we are dealing with compounds with either large mass contrast or large elastic constant contrast and defects localized on certain sites.

To sum up, this modified definition of scattering strength per atom thus offers as a unification for treating complex compounds as a monoatomic chain but with the sublattice selectivity taken into account:

$$\begin{aligned} \Gamma_{\text{unified atomic basis}} &= \frac{\sum_i \sum_k f_i^k (c_i M_i^k - c_i \bar{M}_i)^2}{(\sum_i c_i M)^2} \\ &= \frac{\sum_i c_i^2 \sum_k f_i^k (M_i^k - \bar{M}_i)^2}{(\sum_i c_i)^2 M^2} = \frac{\sum_i c_i \Gamma_{M,A}}{\sum_i c_i} \end{aligned} \quad (44)$$

with the volume per scatter Ω being the atomic volume.

As can be seen from Table 1, our proposed unified-atomic basis uses the primitive basis scattering parameter to account

TABLE 1 | A comparison of the two bases (atomic and primitive basis) and the unified-atomic basis proposed by this work.

	Atomic basis	Primitive basis	Unified-atomic basis (this work)
Γ	$\Gamma_{M,A} = \frac{\sum_i c_i \sum_k f_i^k (M_i^k - \bar{M}_i)^2}{\sum_i c_i \bar{M}_i^2}$	$\Gamma_{M,P} = \frac{\sum_i \sum_k f_i^k (c_i M_i^k - c_i \bar{M}_i)^2}{(\sum_i c_i \bar{M}_i)^2} = \frac{\sum_i c_i \Gamma_{M,A}}{\sum_i c_i}$	$\Gamma_{M,UA} = \frac{\sum_i \sum_k f_i^k (c_i M_i^k - c_i \bar{M}_i)^2}{(\sum_i c_i \bar{M}_i)^2} = \frac{\sum_i c_i \Gamma_{M,A}}{\sum_i c_i}$
Ω	$\Omega_{M,A}$	$\sum_i c_i \Omega_{M,A}$	$\Omega_{M,A}$
$\Omega\Gamma$	$\Omega_{M,A} \Gamma_{M,A}$	$\Omega_{M,A} \sum_i c_i \Gamma_{M,A} \geq \Omega_{M,A} \Gamma_{M,A}$, given $c_i \geq 1$	$\Omega_{M,A} \frac{\sum_i c_i \Gamma_{M,A}}{\sum_i c_i} < \Omega_{M,A} \Gamma_{M,A}$ since $\frac{c_i}{\sum_i c_i} < 1$

for selective scattering but maintains the atomic volume per scatterer.

5 | Application to ZrB₂

Given the large mass contrast between the metallic and non-metallic elements in ZrB₂, we have chosen this material system as an example to test our proposition.

6 | Experimental Methods

For the ZrB₂ samples, ZrB₂ (97%, Kosundo), B (2, 4, 6, and 8 at%) (99%, Aldrich), W (0, 1, 2, and 3 at%) (extra pure, Duksan Pure Chemical) powders were mixed by ball milling using WC balls at 210 rpm for 24 h with ethanol. The extra B was added to compensate for B loss during the synthesis to avoid ZrO₂ formation and achieve phase pure ZrB₂. The powders were then dried in a dry oven at 60°C for 24 h and sieved through a 60-mesh sieve. After drying, dry ball milling was additionally performed at 210 rpm for 20 min. Hot pressing was conducted under Ar flow at 32 MPa, with a 1 h holding step at 1500°C during heating, followed by holding at 2100°C for 1 h. Phase purity was checked by XRD analysis after pulverizing the samples. The measurements were performed using a D8 Advance A25 Plus diffractometer (Bruker, Germany) over a 2 θ range of 10°–90° with a step size of 0.005°. SEM and EDS analysis was performed using a scanning electron microscope (JSM-6010PLUS, JEOL, Japan). For LFA measurements, 6 × 6 × 1 mm³ square specimens were prepared and coated with graphite. Laser flash analysis was performed using an LFA 467 instrument (Netzsch, Germany) to measure diffusivity D up to 700 K. The specific heat C_p was taken from literature values [13], and the density ρ was measured using the Archimedes method. The total thermal conductivity was calculated using $\kappa = \rho C_p D$, electrical conductivity was measured using a ZEM-3 system (Ulvac) with 3 × 3 × 10 mm³ specimens up to 700 K. A 4-point probe measurement was also performed to measure the electrical resistivity at room temperature to cross-check, whereas the system is regularly calibrated using constantan.

7 | Phase Purity and Compositional Analysis

All Zr_(1-x)W_xB₂ ($x = 0, 1\%, 2\%$, and 3%) samples have a relative density of larger than 99%. Although XRD shows phase purity

(Figure 6) for all four samples, SEM and EDS analysis reveal that for the sample with $x = 3\%$, W-rich agglomerations start to show up, whereas the rest samples are phase pure. Actual compositions are calculated using only the ratio between measured Zr and W atomic percentages while keeping the metal/B ratio as 0.5 given the known inaccuracy of light element (such as B) characterization in EDS and the narrow phase width of ZrB₂ [14]. Both SEM images (Figure S1) and EDS compositions (Table S1) can be found in the Supporting Information data. We find that the actual W content in the Zr_(1-x)W_xB₂ phase of 2% and 3% samples saturates at 2%, indicating a solubility of W in ZrB₂ of around 2% at 2100°C, which is close to literature data where a 3% solubility was reported at 2100°C previously [15].

As the tungsten content increases, the lattice contracts due to smaller size of W (ionic radius 60–66 Å compared to 72 Å of Zr, metallic radius 1.39 Å compared to 1.60 Å of Zr), consequently the XRD peaks shift to larger angles as can be seen from Figure S2.

It can be noted from Figure S2 that our starting composition ($x = 0\%$) has a lattice parameter about 0.1% smaller compared to that of the reference, which is comparable to that of the lattice contraction due to W doping. It could be due to Zr vacancies with the extra 2% B we added in the synthesis, however, given the narrow phase width of ZrB₂ [14] and the difficulty to determine the Zr/B ratio accurately, we will consider ZrB₂ as a line compound.

The atomic mass of W (183.84 u) and Zr (91.224 u) also differs largely, we expect both the mass and size contrast to have an impact on the lattice thermal conductivity through disorder scattering.

8 | Thermal Conductivity Measurements

The total thermal conductivity of our ZrB₂ sample spans from 95.0 to 86.3 W/(m K), which is in agreement with previous data [16, 17].

Room temperature Seebeck coefficient was measured to be around $-5 \mu\text{V/K}$, suggesting metallic behavior. As a result, a Lorenz number of $2.44 \times 10^{-8} \text{ W } \Omega/\text{K}^2$ in the degenerate limit was taken to calculate the electronic thermal conductivity as a first estimation.

The similarity of total (Figure 7) and electronic (Figure 8) thermal conductivity between $x = 2\%$ and 3% samples indicates

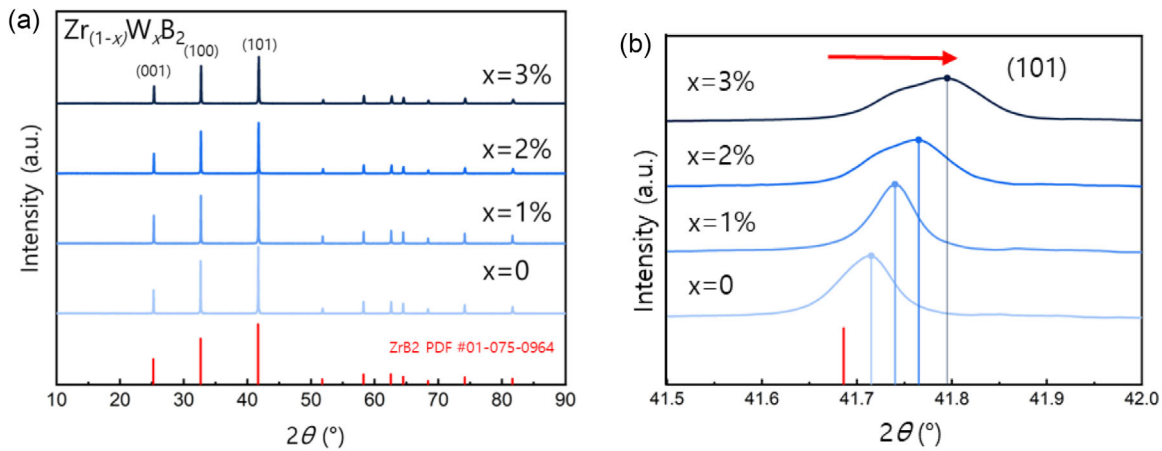


FIGURE 6 | (a) XRD patterns for $\text{Zr}_{(1-x)}\text{W}_x\text{B}_2$ ($x = 0, 1\%, 2\%, \text{ and } 3\%$) samples. (b) Zoom-in view around peak position (101).

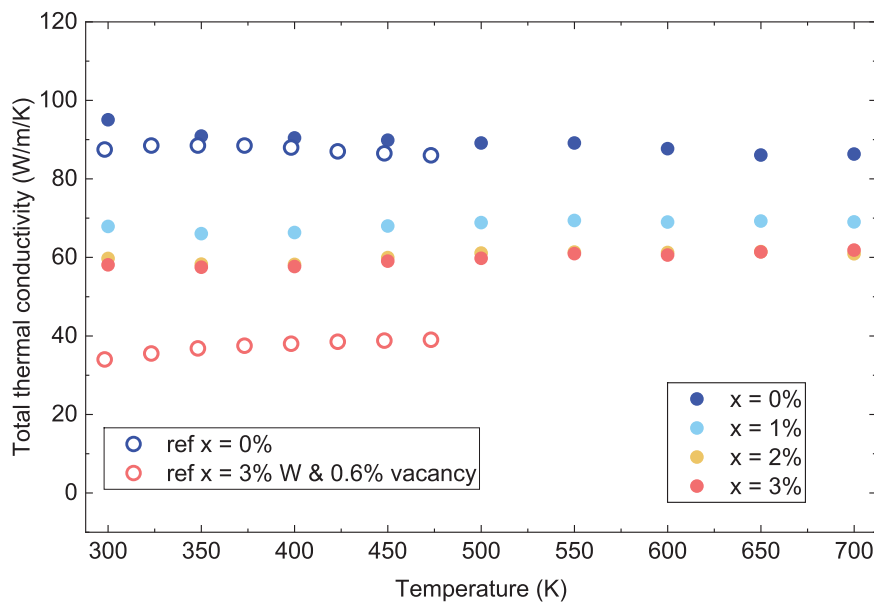


FIGURE 7 | Total thermal conductivity with temperature. Reference data are taken from [17].

the electronic dopant effect of W addition in the ZrB_2 system saturates, which is consistent with the EDS analysis

As x increases, the lattice thermal conductivity of $\text{Zr}_{(1-x)}\text{W}_x\text{B}_2$ samples reduces with $x = 1$ and 2% . However, the lattice thermal conductivity of 3% sample is higher than that of $x = 1\%$ and 2% samples, which could be due to the higher thermal conductivity of impurity phase W (175 W/(m K) at 300 K) [18] compared to that of ZrB_2 . Compared to our $x = 3\%$ sample, the reference sample with 3% W and 0.6% vacancy has slightly lower lattice thermal conductivity, most likely due to the extra vacancy doping in the system. Compared to our $x = 0\%$ sample, the reference sample with 0% has negative lattice thermal conductivity at room temperature despite the similar total thermal conductivity, indicating that their choice of Lorenz number as the degenerate limit being questionable (Figure 9).

9 | Thermal Conductivity Modeling

The details about Debye–Callaway model can be found in Table 2 and Tables S3, S4. On the basis of the speed of sound measurements of the $\text{Zr}_{(1-x)}\text{W}_x\text{B}_2$ samples, the Debye temperature Θ_D was calculated to be between 906 and 951 K depending on the W concentration. Θ_D decreases slightly because W increases the average atomic mass and introduces mass disorder, which results in lower speed of sound (Table S3), as can be seen from the following equations:

$$\Theta_D = \frac{h}{k_B} \left(\frac{3}{4\pi\Omega} \right)^{1/3} v_m \quad (45)$$

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (46)$$

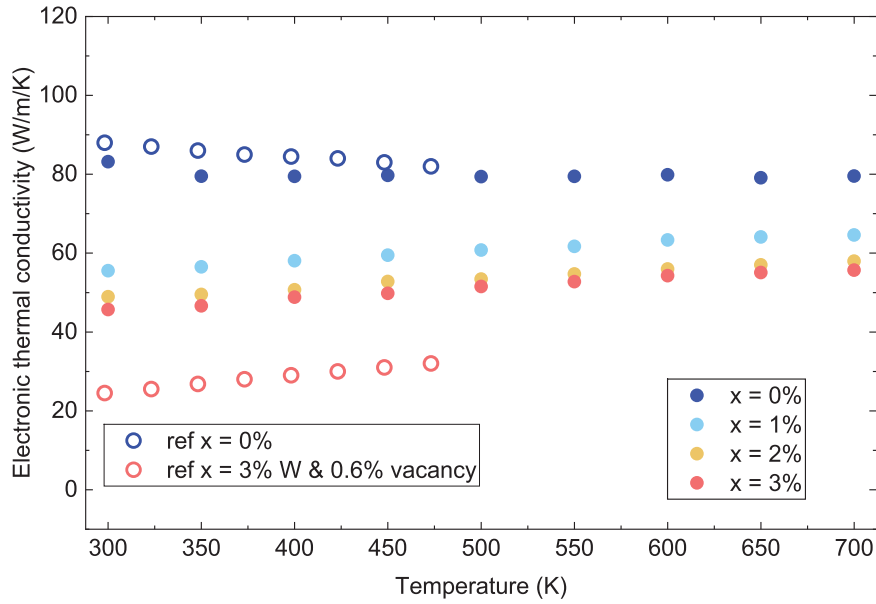


FIGURE 8 | Electronic thermal conductivity with temperature using the degenerate limit of Lorenz number $2.44 \times 10^{-8} \text{ W } \Omega/\text{K}^2$. Reference data are taken from [17].

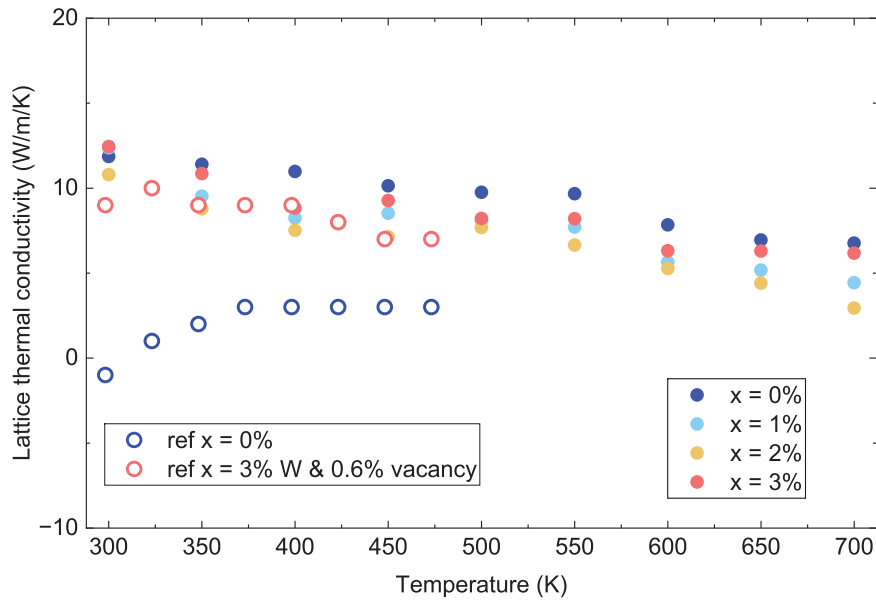


FIGURE 9 | Lattice thermal conductivity with temperature. Reference data are taken from [16].

TABLE 2 | Scattering parameters calculated with the unified-atomic basis (this work) and the atomic basis from literature.

EDS concentration	$\Gamma_{M, UA}$	$\Gamma_{R, UA}$	$\Gamma_{\text{total, UA (this work)}}$	$\Gamma_{\text{total, atomic basis}}$
ZrB ₂	0.0000	0.0000	0.0000	0.0000
Zr _{0.99} W _{0.01} B ₂	0.0066	0.0009	0.0074	0.0223
Zr _{0.981±0.003} W _{0.019±0.003} B ₂	0.0128	0.0018	0.0146	0.0437
McClaine et al. [17] (Zr _{0.964} W _{0.03} V _{0.006})B ₂	0.0228	0.0337	0.0565	0.1695

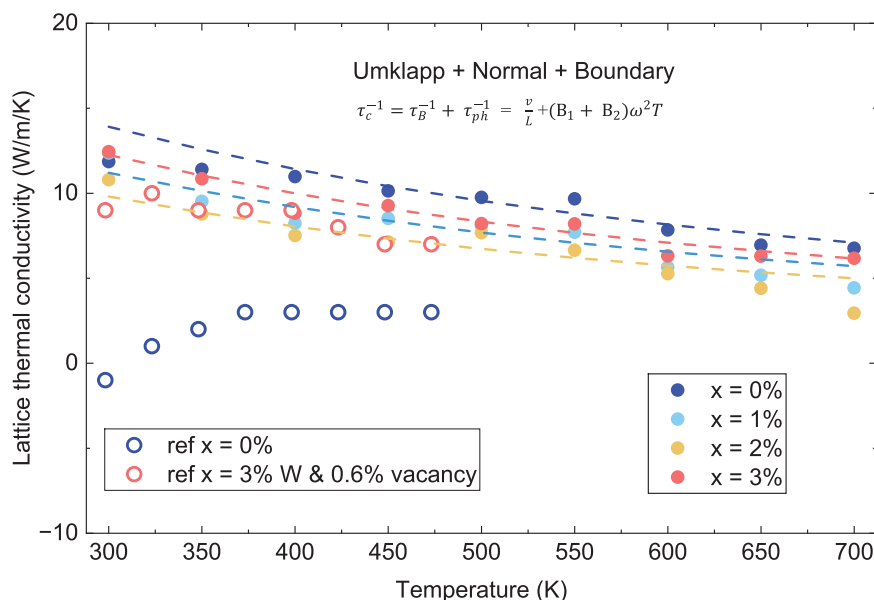


FIGURE 10 | Debye–Callaway modeling with Umklapp scattering, normal scattering, and boundary scattering. Dashed lines are Debye–Callaway modeling of sample with the same color [17].

Following the common Debye–Callaway approximation, Umklapp scattering is expected to become appreciable for $T \sim \frac{\Theta_D}{3}$ (Equation 21). The coefficient B_1 for Umklapp scattering is calculated on the basis of experimental data according to Equation (21) except γ , which was adopted from first-principle calculations in literature with a value of 1.38 [19]. A grain size of 20 μm is chosen to account for boundary scattering. A normal scattering term is added with the coefficient B_2 as a fitting parameter ($B_1 + B_2$ instead of B_1 alone in Equation 23), as pointed out by Wright et al. that although N-processes alone do not create thermal resistance, they do contribute to thermal resistance when U-processes (or scattering from defects or impurities) are present [20]. The fitted B_2 values are reported in Table S4. With B_2 being 100 times larger than B_1 , the effect of normal scattering is non-negligible. It is also worth noting that both B_1 (calculated on the basis of Equation 21) and B_2 (from fitting) increase as doping level increases, which could suggest missing electron–phonon scattering. Electron–phonon scattering is highly likely due to the low Seebeck coefficient ($\sim 5 \mu\text{V/K}$) and high electrical conductivity at room temperature ($1.08\text{E}7 \text{ S/m}$). Although electron–phonon scattering is expected to contribute to heat transport in semimetallic ZrB_2 . However, because the objective of this study is to establish the validity of the unified-atomic basis disorder-scattering model, this contribution has been omitted to avoid introducing additional fitting parameters. Incorporating electron–phonon coupling using first-principles calculations will be considered in future work, (Figure 10).

We then add the point-defect scattering to the model; Poisson ratio is derived from experimental results in this work (Table S5) and is consistent with literature [21], whereas the calculation of G (~ 5.94) is based on both literature [22] and our own experimental results. The as-calculated scattering parameters are listed in Table 2. It can be seen that the total disordering scattering stems mostly from mass difference rather than strain

influence, and the unified-atomic basis proposed in this work gives a value of 1/3 of that given by an atomic basis on the basis of the monoatomic chain assumption. The smaller value of Γ is due to the sublattice selectiveness in phonon scattering, which leads to less suppression of thermal conductivity due to disorder scattering, as can be seen in Figures 11 and 12.

10 | Discussion

A consistent underestimation of lattice thermal conductivity is observed when the conventional atomic-basis formulation is applied to ZrB_2 . This trend supports the central conclusion of the present work that alloying-induced disorder scattering in multi-sublattice compounds is more accurately described by considering sublattice-specific disorder rather than treating the material as an equivalent monoatomic medium, particularly in compounds such as ZrB_2 where large mass and bonding contrasts exist between crystallographic sublattices. Similar observations have been reported from first-principles studies, which show that phonon transport in ZrB_2 is dominated by specific phonon branches and that scattering processes can exhibit strong mode and sublattice dependence [19].

The proposed unified-atomic basis formulation modifies only the disorder-scattering term, whereas all other scattering mechanisms are assumed to remain unchanged. Nevertheless, electron–phonon scattering is expected to contribute to thermal transport in semimetallic ZrB_2 . Recent first-principles calculations [23] indicate that owing to its high carrier concentration ($\sim 10^{22} \text{ cm}^{-3}$), electron–phonon scattering rates can be comparable to, or even exceed, intrinsic phonon–phonon scattering rates for certain phonon modes. Consequently, the omission of electron–phonon scattering represents one of the principal limitations of the present model. Despite this limitation, the Debye–Callaway framework remains a valuable tool for interpreting experimental

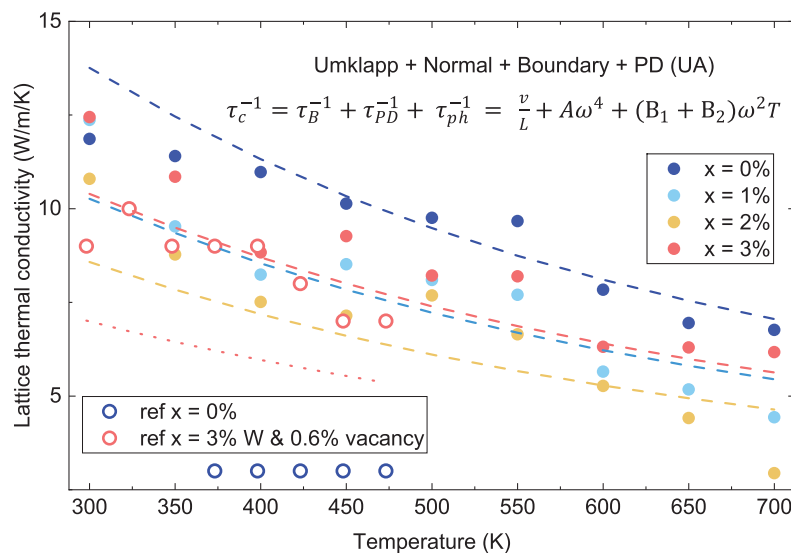


FIGURE 11 | Debye–Callaway modeling with Umklapp scattering, normal scattering, boundary scattering, and point-defect scattering with unified-atomic basis. Dotted line is for reference sample with $x = 3\%$ W and 0.6% vacancy [17].

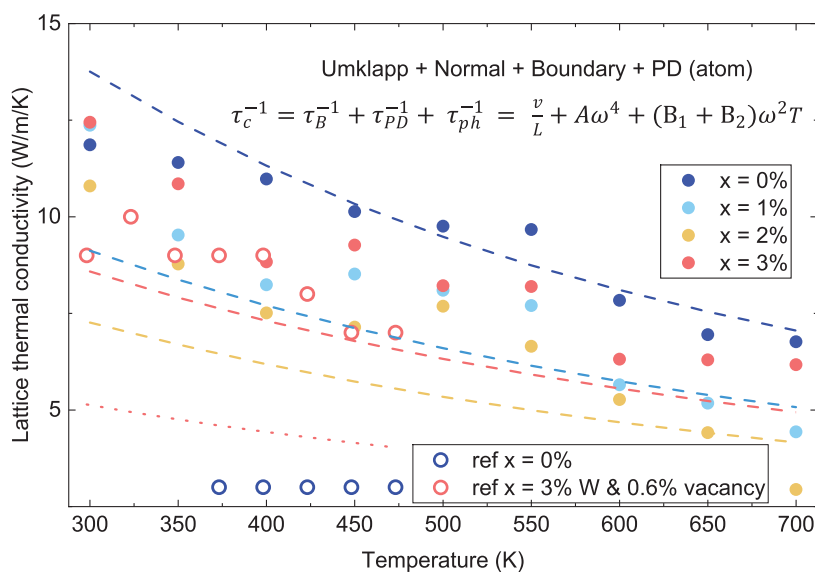


FIGURE 12 | Debye–Callaway modeling with Umklapp scattering, normal scattering, boundary scattering, and point-defect scattering with atomic basis. Dotted line is for reference sample with $x = 3\%$ W and 0.6% vacancy [17].

trends and comparing different disorder-scattering formulations. However, the fitted scattering parameter (B_2) should be regarded as effective parameter rather than unique microscopic scattering rate, as multiple scattering mechanisms—including normal phonon–phonon, electron–phonon—are incorporated phenomenologically and are not independently constrained within the model.

Second, the electronic contribution to thermal conductivity was estimated using the Sommerfeld Lorenz number ($2.44 \times 10^{-8} \text{ W } \Omega/\text{K}^2$), which is appropriate for degenerate metallic transport. Given the Lorenz number may vary with carrier concentration and scattering mechanism, a sensitivity analysis using a reduced value of $2.2 \times 10^{-8} \text{ W } \Omega/\text{K}^2$ was performed. We observe the extracted lattice thermal conductivity and corresponding scattering coefficients only change modestly

(Table S4). Importantly, the relative difference between the conventional atomic-basis treatment and the proposed unified-atomic basis formulation remains unchanged, indicating that the primary conclusions of this work are robust against reasonable uncertainty in the electronic thermal conductivity correction. Future work combining mode-resolved electron–phonon calculations with experimental validation across additional multi-sublattice systems would provide a more rigorous assessment of the proposed framework.

11 | Conclusion

This work reexamined the calculation of alloying-induced point-defect scattering parameters in multi-sublattice compounds and clarified the origin of discrepancies among formulations

commonly used in thermal conductivity modeling. Through analytical comparison of atomic-based and primitive/unit-cell-based representations, it was shown that the two approaches yield equivalent results only when a consistent basis is maintained and the alloyed site has a degeneracy of unity. For compounds containing multiple sublattices of higher site degeneracy, significant differences arise in the predicted disorder-scattering strength.

The discrepancy originates from the treatment of sublattice degeneracy and the implicit assumption regarding the sublattice dependence of phonon scattering. Although the conventional atomic formulation effectively treats disorder as uniformly distributed throughout an equivalent monoatomic medium, the primitive-cell formulation preserves the crystallographic identity of each sublattice and therefore captures sublattice-selective scattering. This distinction becomes increasingly important in materials with large mass contrast, localized defects, or strong bonding anisotropy, where phonon eigenvectors exhibit different amplitudes on different sublattices.

To bridge these two formulations, a unified-atomic basis expression was developed that combines the basis consistency of the atomic representation with the sublattice selectivity inherent to the primitive-cell description. The resulting disorder-scattering parameter preserves the physical interpretation of the scattering cross section while eliminating inconsistencies associated with the choice of basis.

Application of the framework to W-doped ZrB_2 resulted in closer agreement between Debye–Callaway calculations and experimentally measured lattice thermal conductivity. The analysis further suggests a W solubility limit of approximately 2 at% under the present processing conditions and highlights the important role of alloying-induced disorder in reducing lattice thermal conductivity.

Overall, the proposed methodology provides a physically motivated and internally consistent framework for evaluating mass- and strain-fluctuation scattering in multi-sublattice compounds. The approach is expected to be applicable to a broad range of ceramic solid solutions and may facilitate more reliable thermal conductivity modeling and alloy design for ultra-high-temperature ceramics, thermoelectric materials, and other functional materials.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

References

1. S. I. Kim, K. H. Lee, H. A. Mun, et al., “Dense Dislocation Arrays Embedded in Grain Boundaries for High-Performance Bulk Thermoelectrics,” *Science* 348, no. 6230 (2015): 109–114, <https://doi.org/10.1126/science.aaa4166>.
2. P. G. Klemens, “The Scattering of Low-Frequency Lattice Waves by Static Imperfections,” *Proceedings of the Physical Society Section A* 68 (1955): 1113–1128, <https://doi.org/10.1088/0370-1298/68/12/303>.
3. B. Abeles, “Lattice Thermal Conductivity of Disordered Semiconductor Alloys at High Temperatures,” *Physical Review* 131 (1963): 1906–1911, <https://doi.org/10.1103/PhysRev.131.1906>.
4. J. D. Eshelby, “The Continuum Theory of Lattice Defects,” *Solid State Physics* 3 (1956): 79–144.
5. L. Rayleigh, “On the Light From the Sky, Its Polarization and Color,” *Philosophical Magazine* 41 (1871): 107–120.
6. R. Berman, E. L. Foster, and J. M. Ziman, “The Thermal Conductivity of Dielectric Crystals: The Effect of Isotopes,” *Proceedings of the Royal Society of London Series A, Mathematical and Physical Sciences* 237 (1956): 344–354.
7. G. A. Slack, “Thermal Conductivity of MgO , Al_2O_3 , MgAl_2O_4 , and Fe_3O_4 Crystals From 3° to 300°K,” *Physical Review* 126, no. 2 (1962): 427–441, <https://doi.org/10.1103/PhysRev.126.427>.
8. J. Yang, G. P. Meisner, and L. Chen, “Strain Field Fluctuation Effects on Lattice Thermal Conductivity of ZrNiSn -Based Thermoelectric Compounds,” *Applied Physics Letters* 85 (2004): 1140–1142, <https://doi.org/10.1063/1.1783022>.
9. E. S. Toberer, A. Zevakink, and G. J. Snyder, “Phonon Engineering Through Crystal Chemistry,” *Journal of Materials Chemistry* 21 (2011): 15843, <https://doi.org/10.1039/c1jm11754h>.
10. H. Wang, A. D. LaLonde, Y. Pei, and G. J. Snyder, “The Criteria for Beneficial Disorder in Thermoelectric Solid Solutions,” *Advanced Functional Materials* 23 (2013): 1586–1596, <https://doi.org/10.1002/adfm.201201576>.
11. J. Callaway and H. C. von Baeyer, “Effect of Point Imperfections on Lattice Thermal Conductivity,” *Physical Review* 120, no. 4 (1960): 1149–1154, <https://doi.org/10.1103/PhysRev.120.1149>.
12. T. Davey and Y. Chen, “Vacancy Ordering in Substoichiometric Zirconium Carbide: A Review,” *International Journal of Ceramic Engineering & Science* 4 (2022): 134–157, <https://doi.org/10.1002/ces2.10126>.
13. E. W. Neuman, M. Thompson, W. G. Fahrenholtz, and G. E. Hilmas, “Elevated Temperature Thermal Properties of ZrB_2 - B_4C Ceramics,” *Journal of the European Ceramic Society* 42, no. 9 (2022): 4024–4029, <https://doi.org/10.1016/j.jeurceramsoc.2022.03.029>.
14. P. Rogl and P. E. Potter, “A Critical Review and Thermodynamic Calculation of the Binary System: Zirconium-Boron,” *Calphad* 12, no. 2 (1988): 191–204, [https://doi.org/10.1016/0364-5916\(88\)90021-1](https://doi.org/10.1016/0364-5916(88)90021-1).
15. A. Khadimallah, X. Li, and K. W. White, “Solubility of Tungsten in Zirconium Diboride Solid Solution,” *Journal of the European Ceramic Society* 37, no. 4 (2017): 1195–1203, <https://doi.org/10.1016/j.jeurceramsoc.2016.11.039>.
16. D. L. McClane, W. G. Fahrenholtz, and G. E. Hilmas, “Thermal Properties of $(\text{Zr, TM})\text{B}_2$ Solid Solutions With $\text{TM} = \text{Ta, Mo, Re, V, and Cr}$,” *Journal of the American Ceramic Society* 98, no. 2 (2015): 637–644, <https://doi.org/10.1111/jace.13341>.
17. D. L. McClane, W. G. Fahrenholtz, and G. E. Hilmas, “Thermal Properties of $(\text{Zr, TM})\text{B}_2$ Solid Solutions With $\text{TM} = \text{Hf, Nb, W, Ti, and Y}$,” *Journal of the American Ceramic Society* 97, no. 5 (2014): 1552–1558, <https://doi.org/10.1111/jace.12893>.
18. R. W. Powell, C. Y. Ho, and P. E. Liley, *Thermal Conductivity of Selected Materials* (U.S. Dept. of Commerce, National Bureau of Standards, 1966).
19. H. Xiang, J. Wang, and Y. Zhou, “Theoretical Predictions on Intrinsic Lattice Thermal Conductivity of ZrB_2 ,” *Journal of the European*

Ceramic Society 39, no. 10 (2019): 2982–2988, <https://doi.org/10.1016/j.jeurceramsoc.2019.04.011>.

20. A. A. Maznev and O. B. Wright, “Demystifying Umklapp vs Normal Scattering in Lattice Thermal Conductivity,” *American Journal of Physics* 82 (2014): 1062–1066, <https://doi.org/10.1119/1.4892612>.

21. F. Nakamori, Y. Ohishi, H. Muta, K. Kurosaki, K. I. Fukumoto, and S. Yamanaka, “Mechanical and Thermal Properties of Bulk ZrB_2 ,” *Journal of Nuclear Materials* 467 (2015): 612–617, <https://doi.org/10.1016/j.jnucmat.2015.10.024>.

22. C. Fuger, R. Hahn, L. Zauner, et al., “Anisotropic Super-Hardness of Hexagonal $\text{WB}_{2\pm z}$ Thin Films,” *Materials Research Letters* 10, no. 2 (2022): 70–77, <https://doi.org/10.1080/21663831.2021.2021308>.

23. J. Y. Yang, W. Zhang, C. Xu, J. Liu, L. Liu, and M. Hu, “Strong Electron–Phonon Coupling Induced Anomalous Phonon Transport in Ultrahigh Temperature Ceramics ZrB_2 and TiB_2 ,” *International Journal of Heat and Mass Transfer* 152 (2020): 119481, <https://doi.org/10.1016/j.ijheatmasstransfer.2020.119481>.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: jace70995-sup-0001-SuppMat.docx.