

Phonon and electron contributions to the thermal conductivity of VN_x epitaxial layers

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ABSTRACT

Thermal conductivities of $\text{VN}_x/\text{MgO}(001)$ ($0.76 \leq x \leq 1.00$) epitaxial layers, grown by reactive magnetron sputter deposition, are measured in the temperature range $300 < T < 1000$ K using time-domain thermoreflectance (TDTR). Data for the total thermal conductivity are compared to the electronic contribution to the thermal conductivity calculated from the measured electrical conductivity, the Wiedemann-Franz law, and an estimate of the temperature dependence of the Lorenz number $L(T)$. The total thermal conductivity is dominated by electron contribution and varies between $13 \text{ W m}^{-1} \text{ K}^{-1}$ at $x = 0.76$ and $20 \text{ W m}^{-1} \text{ K}^{-1}$ at $x = 1.00$ for $T = 300$ K and between 25 and $35 \text{ W m}^{-1} \text{ K}^{-1}$ for $T = 1000$ K. The lattice thermal conductivity vs. x ranges from 5 to $7 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K and decreases by 20% at 500 K. The low magnitude and weak temperature dependence of the lattice thermal conductivity are attributed to strong electron-phonon coupling in VN.

I. INTRODUCTION

The phonon contribution to the thermal conductivity of a metal has a complex dependence on temperature, lattice anharmonicity, and the strength of electron-phonon coupling [1-3]. Typically, at temperatures greater than 1/3 of the Debye temperature, the lifetimes of phonons that dominate heat transport are limited by the anharmonicity of lattice vibrations [4]. Scattering of phonons by electrons is typically less important except at low phonon frequencies. Measurements of the thermal conductivity of alloys can often be used to determine the lattice thermal conductivity by introducing elastic scattering of electrons that suppresses the electronic component [5,6]. The high-temperature lattice thermal conductivities of metals with relatively weak electron-phonon coupling are typically in good agreement with the assumption of lattice thermal conductivity limited by anharmonicity [3].

Metallic transition-metal (TM) nitrides and carbides provide a contrast to metals for studying lattice thermal conductivities because their Debye temperatures are high and therefore the anharmonic phonon scattering rates are low, and electron-phonon coupling is strong [7]. The spectral integral of the Eliashberg function $\alpha^2F(\omega)$ yields a measure of the electron-phonon coupling strength: $\lambda = 2 \int \alpha^2F(\omega)\omega^{-1}d\omega$ [8-11]. For TM nitrides and carbides, λ is between 0.6 and 0.9, large values compared to common metals such as Al ($\lambda = 0.44$), Cu (0.13), Au (0.17), and Ti (0.38) [12,13]. The primary goal of this work is to determine the lattice contribution to the thermal conductivity of VN through studies of the thermal conductivity of stoichiometric VN and VN_x with varying concentrations of nitrogen vacancies.

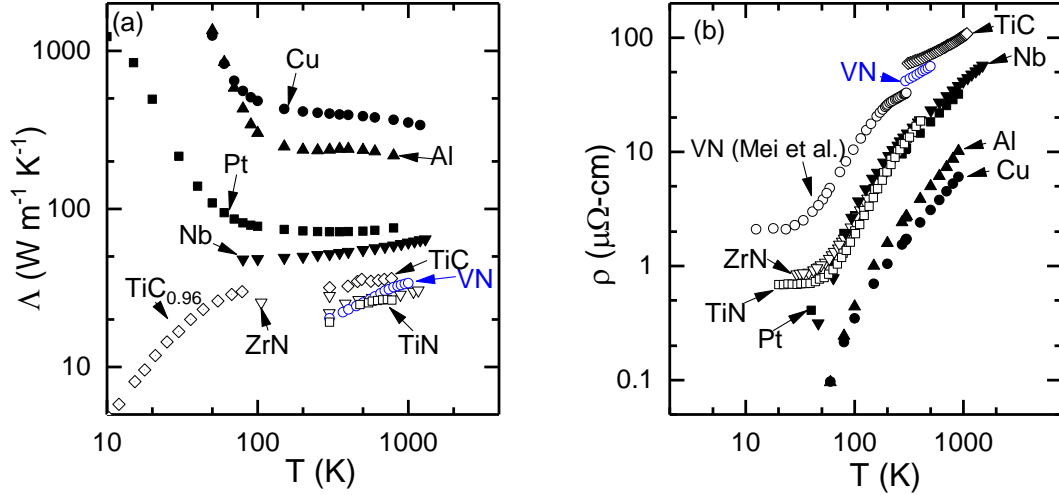


FIG. 1. (a) Temperature dependent thermal conductivity of representative metals and transition-metal nitrides and carbides. Black symbols: Al [14], Cu [14], Pt [14], Nb [15], TiC (bulk) [16,17], TiC_{0.96}(bulk) [5], ZrN (bulk) [18], TiN (RT) [19], and TiN (high T) [17], Blue open circles: VN epitaxial layers measured in this work. (b) Temperature-dependent electrical resistivity of representative metals and transition-metal nitride and carbide. Black symbols: Al [14], Cu [14], Pt [14], Nb [20], TiC [21], ZrN (bulk) [22], TiN (thin film) [23], and VN(thin film) [24]. Blue open circles: VN epitaxial layers measured in this work.

In Fig. 1(a), we compare representative data for the total thermal conductivities of elemental metals to selected data for TM nitrides and carbides. The temperature dependence of the thermal conductivity of TM nitrides and carbides has been discussed previously [21,25]. Fig. 1(b) summarizes the electrical resistivity of the same set of elemental metals and TM nitrides and carbides. In most cases, at temperatures greater than the Debye temperature Θ_D , the resistivity can be approximated as $\rho \approx \rho_0 + B + AT$, wherein we have distinguished between the residual resistivity ρ_0 created by elastic scattering by defects and a phenomenological constant B that describes the shift in the extrapolated intercept of ρ at $T = 0$ K relative to ρ_0 .

The Wiedemann-Franz (W-F) law predicts that the electronic thermal conductivity can be expressed as $\Lambda_{el} \approx L(T)T / (\rho_0 + B + AT)$, in which $L(T)$ is the temperature-dependent Lorenz number [26,27]. At low ($T \ll \Theta_D$) and high temperatures ($T \geq \Theta_D$), $L(T)$ approaches the

Sommerfeld value of $L_0 = 2.44 \times 10^{-8} \Omega \text{ W K}^{-2}$. In pure metallic elements at $T > \Theta_D/3$, the resistivity typically scales as $\rho \approx AT$ and therefore $\Lambda_{el} \approx L_0/A$ is nearly constant [2]. However, in TM nitrides and carbides, $\rho_0 + B$ is often large due to the high concentrations of point defects (e.g., oxygen and carbon impurities and nitrogen vacancies) [5,17]. Thus, the W-F law predicts that Λ_{el} should increase with increasing T at elevated temperatures (Fig. 1(a)).

Due primarily to strong covalent bonds [28], VN exhibits high melting temperature (2050 °C), hardness (15.9 GPa), electrical conductivity (33 $\mu\Omega\text{-cm}$), and chemical stability [28-30]. As a consequence, VN films have been employed to enhance the properties of cutting and grinding tools, hard electrical contacts, cylinder linings, diffusion barriers, and rechargeable microbatteries and supercapacitors [25,31-35]. A better knowledge of VN thermal and electrical transport properties could improve materials design for new applications.

This work may also provide insights into the potential of TM nitride metal/semiconductor superlattices as high temperature materials for thermoelectric energy conversion. In our early work on (Zr,W)N/ScN superlattices, we attributed the minimum in the cross-plane thermal conductivity as a function of superlattice period to the intermixing of interfaces while a more recent work on TiN/Al_{0.72}Sc_{0.28}N attributed such a minimum to coherent phonon effects [36,37]. A better understanding of the lattice thermal conductivity in metallic TM nitrides could provide an important parameter for determining the efficiency of thermoelectric materials.

II. EXPERIMENTAL

VN_x/MgO(001) layers are grown in a load-locked ultra-high-vacuum magnetically-unbalanced dc magnetron sputter deposition system from a 7.6-cm diameter, 99.95%-pure, V disk target in 20-mTorr N₂ atmospheres as described in Ref [38]. Film N/V ratios, determined by

Rutherford backscattering spectrometry, are varied from 1.00 ± 0.05 to 0.76 ± 0.05 by increasing the growth temperature from 430 to 740 °C. The combination of x-ray diffraction ω - 2θ and ϕ scans with selected-area electron diffraction and high-resolution cross-sectional transmission electron microscopy analyses demonstrate that the VN_x films are NaCl-structure epitaxial single-crystals which grow cube-on-cube $(001)_{\text{VN}_x} \parallel (001)_{\text{MgO}}$ and $[100]_{\text{VN}_x} \parallel [100]_{\text{MgO}}$ with respect to the substrate [39]. Out-of-plane (a_{\perp}) and in-plane (a_{\parallel}) lattice parameters of the epitaxial $\text{VN}_x(001)$ films were obtained from high-resolution reciprocal lattice maps (HR-RLM) around symmetric 004 and asymmetric 113 reflections. The relaxed lattice parameters a_0 of VN_x epitaxial layers were determined from a_{\perp} and a_{\parallel} through the relationship $a_0 = a_{\perp} \left(1 - \frac{2\nu(a_{\perp} - a_{\parallel})}{a_{\parallel}(1 + \nu)} \right)$ in which the Poisson ratio, $\nu = 0.23$, is derived in our previous work on epitaxial $\text{VN}/\text{MgO}(001)$ [39]. a_0 decreases from 4.14 Å at $x = 1.00$ to 4.09 Å at $x = 0.76$ (see Table I), in good agreement with previous studies of bulk and sputter-deposited VN_x [39-42]. The quality of VN_x epitaxial layers determined from the XRD rocking curve peak FWHM is consistent with that of our previous work [24].

The thicknesses of the VN_x epitaxial layers are determined using RBS atomic areal density and HR-RLM lattice parameters to within $\pm 5\%$. For the five samples measured, the thickness varies from 160 to 229 nm (see Table I). The thickness of the stoichiometric VN sample is 192 nm, which is close to the value of 194 nm obtained using picosecond acoustics with the previously-reported longitudinal sound velocity $v_{001} = 9.8 \text{ km s}^{-1}$ [39]. The complex index of refraction of VN is $n \approx 1.49 + 3.44i$ at 785 nm as measured by ellipsometry, corresponding to an optical absorption depth of $\alpha^{-1} = \frac{\lambda}{4\pi k} = 18 \text{ nm}$, consistent with recent results on the optical properties of $\text{VN}_x/\text{MgO}(001)$ [38].

TABLE I. Composition x , growth temperature T , areal density, relaxed lattice constant a_0 , film thickness h , mass density ρ , and longitudinal sound velocity v_{001} of epitaxial VN_x samples.

x	T ($^{\circ}\text{C}$)	Areal density of atom (10^{18} cm^{-2})		a_0 (\AA)	h (nm)	ρ (g cm^{-3})	v_{001} (km s^{-1})
		V	N				
1.00	430	1.08	1.08	4.14	192	6.06	9.8
0.93	509	1.15	1.07	4.13	195	6.04	9.3
0.88	589	1.28	1.12	4.11	209	6.04	8.0
0.84	636	1.44	1.21	4.10	229	6.03	7.3
0.76	740	1.06	0.81	4.09	160	5.98	7.3

A modified time-domain thermoreflectance (TDTR) method, which required no additional transducer layer to be deposited on the sample surface, was used to measure the thermal conductivity of epitaxial VN_x thin films [43,44]. In our TDTR measurement, a train of optical pulses at a repetition rate of 80 MHz, generated by a mode-locked Ti:Sapphire laser at a wavelength of 785 nm, is split into separate pump and probe beams with the optical path of the pump beam controlled by a mechanical delay stage. The pump beam is modulated at a frequency of 4.1 MHz by an electro-optical modulator. This frequency is lower than the typical 10 MHz modulation used in our previous TDTR studies and was chosen to enhance the sensitivity to VN thermal conductivity (see Fig. 3). The pump and probe beams are focused on the sample through a $5\times$ objective lens to a $1/e^2$ intensity radius of $\approx 10.7 \mu\text{m}$. The total beam power of 15 mW creates a steady-state temperature rise of ≈ 4 K at room temperature and 8 K at 1000 K. The changes in the intensity of the reflected probe beam created by the pump beam are measured using phase-sensitive lock-in detection. The ratio of the in-phase (V_{in}) and out-of-phase (V_{out}) signals from the lock-in amplifier is then fit to a thermal diffusion model obtained from an analytical solution for heat flow

in a layered structure [43]. Based on the measured film thickness and the picosecond acoustic signal from TDTR [39], we also derived the longitudinal speed of sound v_{001} in the five VN_x samples to a precision of ± 0.4 km s⁻¹ (Table I).

In a conventional TDTR measurement, the sample is coated with a 60-90 nm metal transducer which provides the thermoreflectance signal. At the beginning of these studies, we tried using Pt as the transducer layer. However, a dramatic change in the interface thermal conductance between Pt and VN_x was observed at $T > 700$ K. We tentatively attribute this observation to reduction of the native oxide at the Pt/VN_x interface by the VN_x layer. This uncontrolled change in interface conductance often led to inconsistent measurements. Therefore, we instead studied bare VN_x films without an additional transducer layer. The room-temperature thermoreflectance dR/dT of VN_x is 2.2×10^{-5} K⁻¹ at 785 nm, significantly smaller than for Al or TiN, but still sufficient for TDTR measurements [45,46].

Temperature-dependent VN_x TDTR measurements from 300-1000 K are performed by mounting the VN_x/MgO(001) specimen on a heater stage in a vacuum chamber and monitoring the sample temperature with a Pt resistance thermometer. To minimize sample oxidation, the chamber was pumped with a turbo-molecular pump. The electrical resistivity ρ of the VN_x films was measured from 300 to 500 K by the Van der Pauw method using a heating stage in ambient air. To confirm the reliability of the data measured in ambient, we also performed four-point probe resistivity measurements of the VN_{0.84} sample from 300 to 920 K using a high vacuum furnace in a vacuum better than 5×10^{-7} Torr. The resistivity vs. temperature from 300 to 500 K obtained from the two facilities agrees to within 1%. The lateral dimensions of the other samples were too small to be measured with the high vacuum system.

III. RESULTS AND DISCUSSION

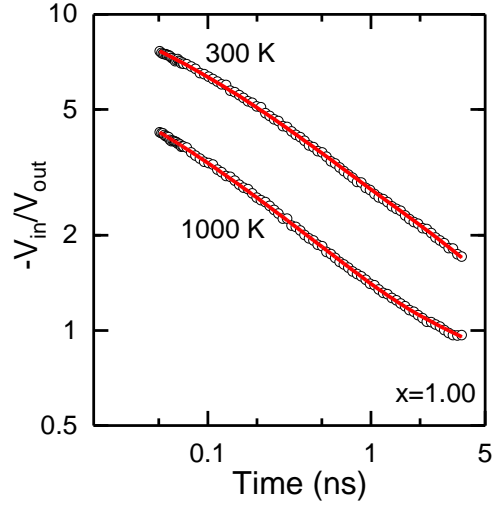


FIG. 2. Example TDTR data: $-V_{in}/V_{out}$ vs. delay time (open circles) for the 192-nm-thick epitaxial stoichiometric VN/MgO(001) film measured at 300 K and 1000 K. Data (black open circles) are compared to the predictions of the thermal transport model described in the text (red solid lines) with the optical absorption length and the thermal conductivity of the VN layer as free parameters.

Representative TDTR data and model fitting for a 192-nm-thick stoichiometric VN sample measured at 300 K and 1000 K are shown in Fig. 2. The thermal transport model used for fitting includes parameters for the thermal conductivity, heat capacity, and thicknesses of the optical absorption layer, the VN_x layers, and the substrate [43]. The most important fixed parameters in the model, in addition to the VN_x film thickness and composition, are the temperature-dependent thermal conductivity and heat capacity of the single-crystal MgO substrate and the temperature and composition-dependent heat capacity of VN_x , which were taken from references [47-49]. We also measured the thermal conductivity of the same MgO substrate used for VN_x growth by conventional TDTR with an 80-nm Al coating. The measured MgO thermal conductivity results from 300 to 600 K agree with reference data to within 5% [50].

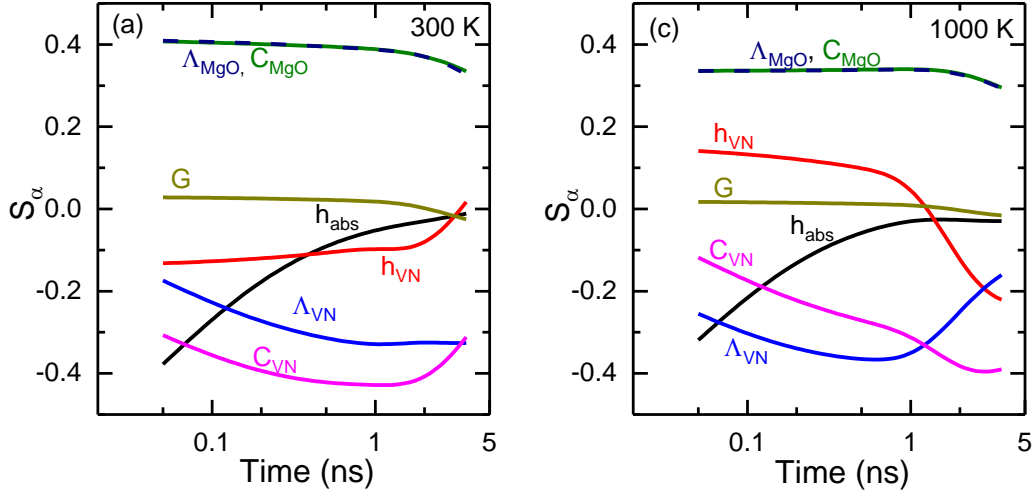


FIG. 3. Calculated sensitivity parameters in TDTR measurements as a function of delay time at (a) 300 K and (b) 1000 K for important parameters used in modeling 192-nm-thick VN/MgO: VN thermal conductivity and heat capacity (Λ_{VN} and C_{VN}), absorption layer thickness and VN thickness (h_{abs} and h_{VN}), VN/MgO interface thermal conductance (G), and MgO substrate thermal conductivity and heat capacity (Λ_{MgO} and C_{MgO}).

We define the sensitivity of the fit S_α as the logarithmic derivative $-V_{\text{in}}/V_{\text{out}}$ with respect to each of the parameters α in order to gauge how each parameter influences the output of the model. The larger the value of S_α , the smaller the error propagated from the other parameters into the measured thermal conductivity.

Figs. 3(a) and (b) show the sensitivity of the fits in Fig. 2 to changes in the various parameters in the thermal-transport model for VN_x/MgO . TDTR measurements of thick VN_x films have moderate sensitivity to Λ_{VN} (0.25-0.4) because the thermal resistance for heat transport through the thickness of the VN_x film is larger than the thermal resistance of the VN_x/MgO interface; *i.e.*, $h / \Lambda_{\text{VN}} > G^{-1}$. The measurement sensitivity to interfacial thermal conductance G is small ($|S_G| < 0.05$) so long as G is large ($> 0.7 \text{ GW m}^{-2}\text{K}^{-1}$). This limits the error propagation from our estimate

for G: a 20% error in G propagates into only an $\approx 3\%$ error in VN_x thermal conductivity. With increasing temperature from 300 to 1000 K, the thermal diffusivity of the VN layer, $D = \frac{\Lambda_{\text{VN}}}{C_{\text{VN}}}$, increases by $\approx 20\%$, while the effusivity of MgO substrate $\varepsilon = \sqrt{\Lambda C}$ decreases by $\approx 30\%$. These changes in thermal properties produce pronounced variations with temperature in the TDTR signal sensitivity to the VN thickness.

To independently measure the thermal conductance of the VN_x/MgO interface (G), we prepared a thinner 29-nm-thick VN/MgO(001) sample that enables higher sensitivity to G. We coated this sample with an 80-nm-thick layer of Al by magnetron sputtering to avoid artifacts that are sometimes encountered in TDTR studies of semi-transparent layers. By annealing the Al/VN/MgO sample overnight at 750 K in air, we obtained a metallic contact between Al/VN, presumably due to the reduction of the native oxide at the Al and VN interface by the VN layer; *i.e.*, we hypothesize that oxygen at the Al/VN interfaces diffuses into the bulk of the VN film during annealing. The Al/VN and VN/MgO interface thermal conductances were measured to be $\approx 1.1 \pm 0.3 \text{ GW m}^{-2} \text{ K}^{-1}$ and $\approx 0.8 \pm 0.2 \text{ GW m}^{-2} \text{ K}^{-1}$, respectively. The thermal conductances of the two interfaces are both weakly temperature dependent from 300 to 700 K. The value of $G_{\text{VN/MgO}}$ is close to that of epitaxial TiN/MgO(001), $G \approx 0.7 \text{ GW m}^{-2} \text{ K}^{-1}$ at room temperature [46].

In the measurement of Λ_{VN} with bare VN, the thickness of the absorption layer and the thermal conductivity of VN_x were chosen as the two free parameters in the model fitting. Since the sensitivity to these two parameters have maxima at short ($< 300 \text{ ps}$) and long ($> 1 \text{ ns}$) time delays, respectively, we could obtain their values independently. The TDTR measurement of the absorption layer thickness is $18 \pm 3 \text{ nm}$ for all VN_x samples at all temperatures. This result agrees with the ellipsometry measurement of the imaginary part of the refractive index for VN_x of varied compositions [38].

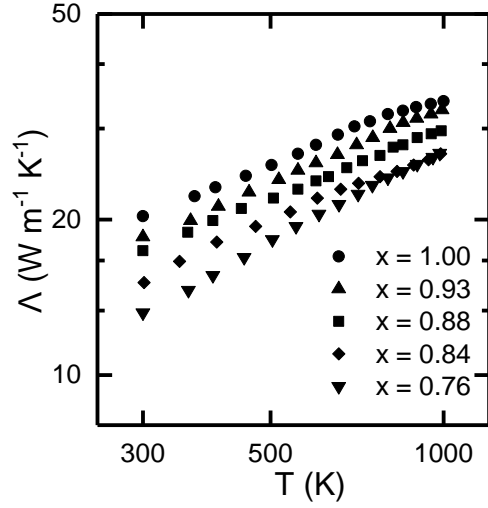


FIG. 4. Thermal conductivity of VN_x ($x = 0.76, 0.84, 0.88, 0.93, \text{ and } 1.00$) as a function of temperature.

We plot data for the thermal conductivity of VN_x as a function of temperature and composition x in Fig. 4. The thermal conductivities increase monotonically over the temperature range $300 < T < 1000$ K and decrease with increasing N vacancy concentration. The temperature dependence of the thermal conductivity becomes slightly stronger with decreasing x . Over this temperature range, Λ increases by a factor of 2 for $x = 0.76$, and increases by a factor of 1.7 for $x = 1.00$.

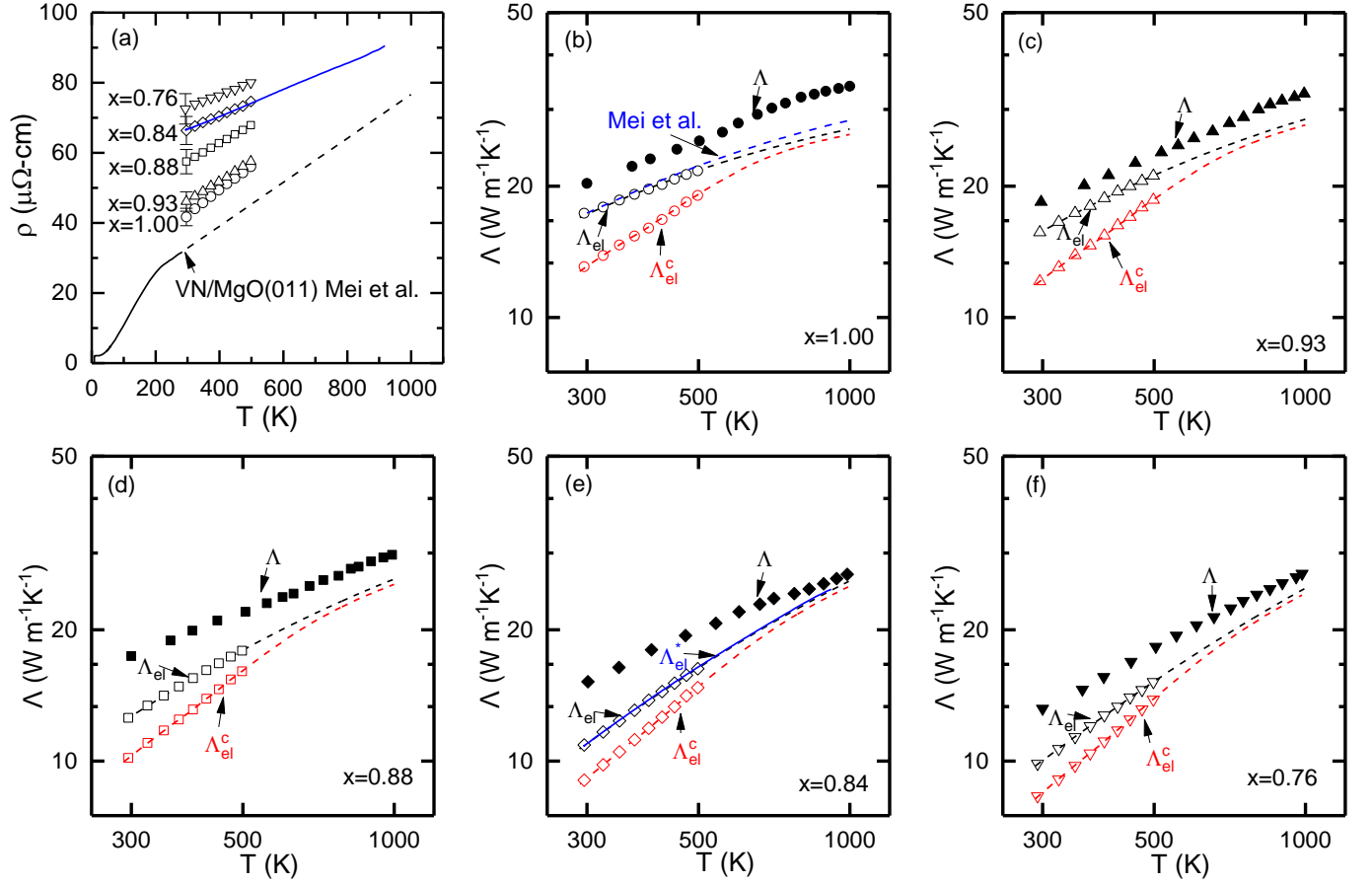


FIG. 5. (a) Electrical resistivity of $\text{VN}_x/\text{MgO}(001)$ layers as a function of temperature measured in ambient air (open symbols) and high vacuum (blue line). Previously published data for a stoichiometric epitaxial $\text{VN}/\text{MgO}(011)$ film deposited by the same method (solid line) together with a linear extrapolation of this data (dashed line) are included for comparison [24]. The blue line is the result for $\text{VN}_{0.84}$ measured with a different four-point probe system in a high-vacuum furnace as described in the text. (b-f) The same thermal conductivity of VN_x films as in Fig. 4 (filled black symbols) and their electronic thermal conductivity calculated from corresponding electrical resistivity by the W-F law with a constant Lorenz number $L = L_0$ (black open symbols = Λ_{el}) and $L = L(T)$ (red open symbols = Λ_{el}^c from Eq. (5)) [51] as a function of temperature from 300 to 1000 K. The black and red dashed lines are Λ_{el} and Λ_{el}^c calculated via the W-F law with $L = L_0$ and $L = L(T)$ obtained from a linear extrapolation of the electrical resistivity

data (open symbols) from 300 to 500 K. Λ_{el} calculated from $\rho(T)$ with the same 300 K resistivity as the stoichiometric VN sample and the TCR for epitaxial VN at 250-300 K in previous work [24] is also included in (b) (blue dashed line). The blue solid line in (e) shows the converted Λ_{el} values for VN_{0.84} from the direct high vacuum measurement result in (a) (blue line) from 300 to 920 K.

In Fig. 5(a), we plot our measurements of the electrical resistivity ρ of VN_x as a function of temperature. The VN_x(001) room-temperature resistivity, ρ_{300K} , increases from 42 to 73 $\mu\Omega\text{-cm}$ as x decreases from 1.00 to 0.76. The data for stoichiometric VN(001) are larger than the reported ρ_{300K} value of 33 $\mu\Omega\text{-cm}$ for VN/MgO(011) [24]. This larger resistivity suggests that the VN(001) sample may be slightly off-stoichiometry or contaminated by a small amount of carbon or oxygen that is not detectable in the RBS measurements.

The resistivity ρ increases with temperature due to the increasing strength of electron-phonon scattering. The temperature coefficient of resistivity (TCR) over this temperature range, defined as $(\rho_{500K} - \rho_{300K}) / \Delta T$, increases from $3.6 \times 10^{-8} \Omega \text{ cm K}^{-1}$ to $6.9 \times 10^{-8} \Omega \text{ cm K}^{-1}$ as x increases from 0.76 to 1.00.

We calculated the Debye temperature, Θ_D , using Houston's method [52] and the elastic constants measured in our previous work on stoichiometric VN [39], $\Theta_D \approx 800 \text{ K}$. The longitudinal elastic constant decreases with decreasing x (see Table I). If we assume that all 3 independent elastic constants of VN_x have the same dependence on x , then $700 < \Theta_D < 800 \text{ K}$ for $0.76 < x < 1.0$. The scaled temperatures in our work are therefore $0.4 < \frac{T}{\Theta_D} < 1.4$.

To understand the temperature-dependent behavior of Λ , we first apply the W-F law with a constant Lorenz number

$$\Lambda_{el}(T) \approx \frac{L_0 T}{\rho} = \frac{L_0 T}{(\rho_0 + AT)}, \quad (1)$$

in which L_0 is the Sommerfeld value of Lorenz number $L_0 = 2.44 \times 10^{-8} \Omega \text{ W K}^{-2}$. $\Lambda_{el}(T)$ results from Eq. (1) for each VN_x sample are compared to the total thermal conductivities measured by TDTR in Figs. 5(b)-(f). We conclude that the thermal conductivity of VN_x between 300 to 1000 K is predominantly electronic in origin.

An empirical relationship between the electrical resistivity ρ and thermal conductivity Λ of metal alloys was suggested by Smith and Palmer and is often used to predict the thermal conductivity of alloys from measurements of the electrical resistivity [53]

$$\Lambda = \frac{CL_0 T}{\rho} + \Lambda_L, \quad (2)$$

in which CL_0 is the effective Lorenz number and Λ_L is the lattice thermal conductivity; C and Λ_L are free parameters that are adjusted to fit the data. The Smith-Palmer equation is often a good description of the thermal conductivity of alloys, although significant deviations were observed by us in some Ni solid solutions [54]. Furthermore, application of the Smith-Palmer equation assumes that the Lorenz number does not depend strongly on temperature or alloy composition and that the lattice thermal conductivity does not depend on composition [55]. Nevertheless, we expect that the Smith-Palmer plot shown in Fig 6 provides a useful first estimate of the Lorenz number and lattice thermal conductivity. The linear fit of Fig. 6 gives $C = 0.90$ and $\Lambda_L = 5 \text{ W m}^{-1} \text{ K}^{-1}$.

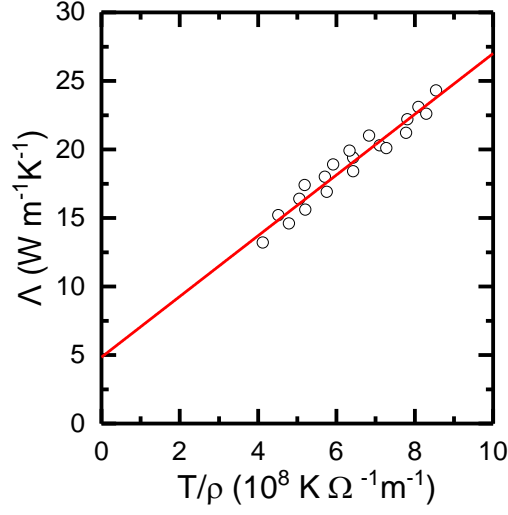


FIG. 6. Smith-Palmer plot, see Eq. (2), for VN_x from 300 to 500 K.

At the next level of sophistication, we consider the temperature dependence of the Lorenz number L . With the assumptions of spherical Fermi surfaces, equilibrium phonon distributions, a Debye phonon spectrum, and the predominance of normal processes for electron-phonon scattering [2,56], the theoretical expression for the Lorenz ratio, $L_{th}(T)/L_0$ as a function of temperature is [1,57]

$$\frac{L_{th}(T)}{L_0} = \frac{1}{1 + \frac{3}{\pi^2} \left(\frac{k_F}{q_D} \right)^2 \left(\frac{\Theta_D}{T} \right)^2 - \frac{1}{2\pi^2} \frac{J_7 \left(\frac{\Theta_D}{T} \right)}{J_5 \left(\frac{\Theta_D}{T} \right)}}. \quad (3)$$

Here, k_F is the Fermi wave vector, Θ_D and q_D are the Debye temperature and Debye wave vector, respectively. The Debye integrals J_n are defined as

$$J_n \left(\frac{\Theta_D}{T} \right) = \int_0^{\Theta_D/T} \frac{x^n e^x}{(e^x - 1)^2} dx. \quad (4)$$

Eq. (3) has been used to understand the electronic thermal transport in metals and alloys [3,56]. The second term in the denominator involving k_F / q_D is due to electron-phonon inelastic small-angle scattering (vertical processes). The third term is a correction that accounts for situations where large-angle scattering can reverse the electron direction without restoring the distribution back to equilibrium [56].

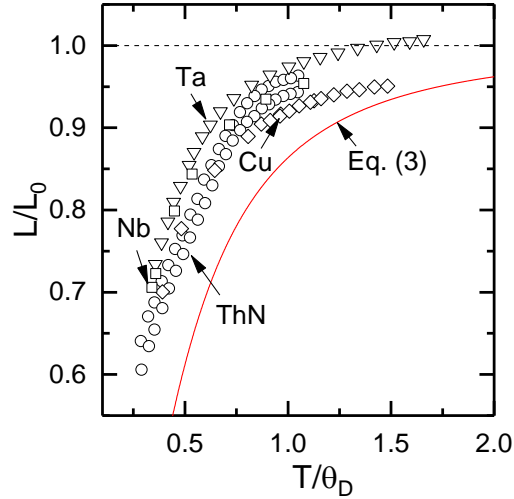


FIG. 7 Temperature variation of the Lorenz function normalized to the Sommerfeld value from experiments and theory as a function of reduced temperature for Cu [3,58], Ta [58], Nb [58], and ThN [51]. The red line is data calculated from Eq. (3) where $k_F / q_D = 2^{-1/3}$.

In Fig. 7, we plot the Lorenz ratio as a function of reduced temperature as predicted by Eq. (3) and give comparisons to experimental results for several metals. The similarity of the Lorenz ratios for Cu, Ta, Nb, and ThN is striking [3,51,58]. Here, the red line shows $L_{th}(T) / L_0$ for an ideal free-electron-like monovalent metal where $k_F / q_D = 2^{-1/3}$. The drop in $L_{th}(T)$ when the temperature is decreased below Θ_D is caused by the dominance of inelastic vertical scattering of electrons by phonons. At high temperature, the greater probability of large-angle quasi-elastic

scattering between electrons and high energy phonons reduces the deviation between $L(T)$ and L_0 .

Due to the lack of detailed knowledge about the electron-phonon coupling constant, Fermi wave vector, and residual resistance of our samples, a direct calculation of $L(T)$ for VN_x using Eq. (3) is not possible. Considering the relatively small difference among $L(T)$ values for normal metals shown in Fig. 7, we approximate the Lorenz function of VN_x with $L(T)$ interpolated from a similar NaCl-structure TM nitride, ThN, which also shows an increasing thermal conductivity with increasing temperature over a similar range [51].

Since static point defects typically elastically scatter electrons of different energy with equal effectiveness, the W-F law with $L(T) = L_0$ is usually valid for the residual resistivity due to point-defect scattering. Assuming negligible deviation from Matthiessen's rule, *i.e.* different scattering processes are independent of each other [59], an improved model by adding the thermal resistance from electron-phonon and electron-defect scattering based on the temperature-dependent Lorenz function follows as [6,58]

$$\Lambda_{el}^c = \left(\frac{\rho_i}{L(T)T} + \frac{\rho(x) - \rho_i}{L_0 T} \right)^{-1}. \quad (5)$$

ρ_i is the electrical resistivity of defect-free VN which is derived from subtracting the 9 $\mu\Omega\text{-cm}$ difference in ρ_{300K} between the stoichiometric VN in our previous work [24] and the VN in this work and the 2 $\mu\Omega\text{-cm}$ residual resistivity of VN in Ref. [24] from the ρ of the stoichiometric VN. $\rho(x)$ is the resistivity of VN_x with N vacancies.

Applying Eq. (5) to VN_x , we obtain the corrected electronic thermal conductivity Λ_{el}^c as a function of temperature. As shown in Figs. 5 (b)-(f), Λ_{el}^c is 20-30% smaller at 300 K than Λ_{el}

calculated with L_0 and approaches Λ_{el} at high temperature. As the concentration of nitrogen vacancies increases, *i.e.*, as x decreases, the difference between Λ_{el}^c and Λ_{el} decreases because the elastic scattering of electrons by defects becomes stronger, hence the contribution from the second term in Eq. (5) becomes larger.

In Fig. 8(a), we plot the total thermal conductivity Λ and our two calculations of the electronic component, Λ_{el} and Λ_{el}^c , for VN_x as a function of composition at three temperatures. The total and electronic thermal conductivities decrease as the vacancy concentration increases, and tends to flatten out at high vacancy concentration, a behavior similar to what has been observed in other TM carbides and nitrides [25].

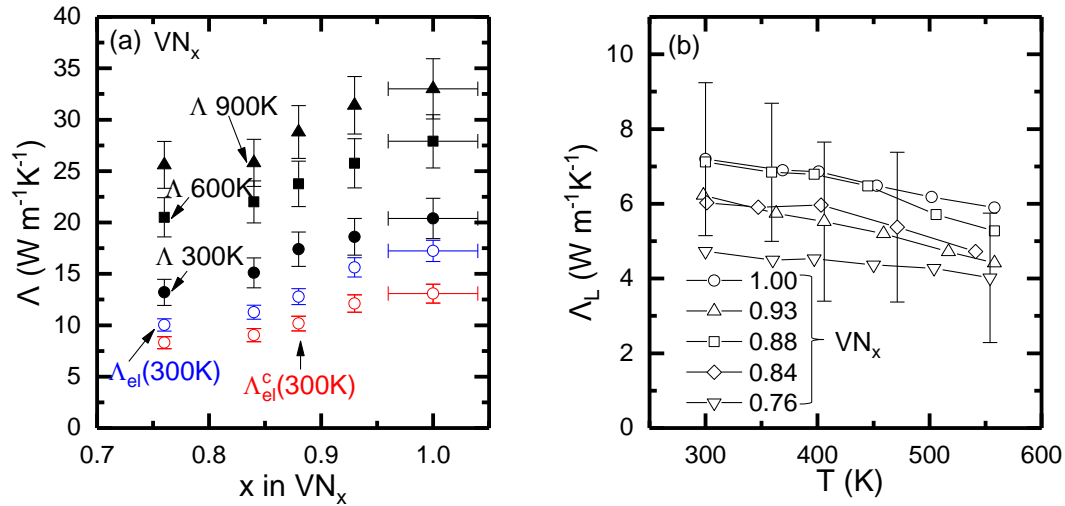


FIG. 8. (a) Thermal conductivity (Λ , black filled symbols) of VN_x films as a function of composition x at representative temperatures and 300 K electronic thermal conductivity with constant Lorenz number $L = L_0$ (black open symbols = Λ_{el}) and $L = L(T)$ (red open symbols = Λ_{el}^c from Eq. (5)) [51] (b) Lattice thermal conductivity Λ_L as a function of temperature and composition derived from $\Lambda_L = (\Lambda - \Lambda_{el}^c)$.

We plot the VN_x lattice thermal conductivity derived by subtracting the electronic component $\Lambda_L = (\Lambda - \Lambda_{el}^c)$ in Fig 8(b). For all samples, Λ_L constitutes approximately 35-40% of the total thermal conductivity at 300 K and decreases as temperature increases, contributing 20-25% to the total thermal conductivity at 500 K. Λ_L values derived this way are approximately 20-30% smaller than those derived from the W-F law with the Sommerfeld Lorenz number at 300 K and are comparable to the lattice thermal conductivity of closely related materials, such as ThN and TaC, at high temperature [5,60]. However Λ_L is still small compared to estimates of the lattice thermal conductivity of TiC and ZrN in the intermediate and high temperature ranges [6,36,60]. We attribute this to relatively stronger electron-phonon scattering in VN and the significant contribution of phonon scattering by N vacancies.

Λ_L in VN_x does not show a $\Lambda_L \propto 1/T$ relation characteristic of anharmonic three phonon interactions (see Fig. 8(b)). In Makinson's transport theory for metals [1], the lattice thermal conductivity obtained from electron-phonon scattering alone should be nearly independent of temperature at $T > 0.6\Theta_D$. For the temperature range of our measurements, ($0.4 < \frac{T}{\Theta_D} < 0.7$ in Fig 8(b)) the weak temperature dependence of Λ_L indicates that the thermal resistance from electron-phonon scattering is of the same order as the thermal resistance from anharmonic phonon interactions.

As seen in Fig. 8(b), when the vacancy concentration increases, the lattice thermal conductivity Λ_L decreases and has a weaker dependence on temperature. In the high-temperature limit of a Debye model with the assumption of phonon scattering rates that scale quadratically with phonon frequency, the lattice thermal conductivity limited by point-defect scattering is

$$\Lambda_L^p = \Lambda_L^i \frac{\omega_0}{\omega_D} \tan^{-1} \left(\frac{\omega_D}{\omega_0} \right). \quad (6)$$

Λ_L^i is the lattice thermal conductivity of intrinsic phonon scattering, ω_D is the Debye frequency, and ω_0 is a characteristic frequency at which the phonon point-defect scattering rate is equal to the phonon-phonon scattering rate [3,61]. Eq. (6) predicts $\Lambda_L^p \propto T^{-1/2} \varepsilon^{-1/2}$ when point-defect scattering is strong and $\Lambda_L^p \propto \varepsilon^{-1}$ when point-defect scattering is weak, in which ε is proportional to the point-defect concentration [61,62]. Therefore, Λ_L^p is expected to become smaller as the vacancy concentration increases and should have a weaker temperature dependence than Λ_L^i . We also note that the longitudinal sound velocity in VN_x decreases with increasing vacancy concentration (see Table I) which reduces the velocity of acoustic phonons. This lattice softening with decreasing x may also contribute to the trend of decreasing lattice thermal conductivity with decreasing x .

IV. CONCLUSIONS

In summary, we measured the temperature-dependent thermal conductivity from 300 to 1000 K of epitaxial $\text{VN}_x/\text{MgO}(001)$ ($0.76 < x < 1.00$) thin films by TDTR and compared the result with the electronic thermal conductivity calculated from the Wiedemann-Franz law. The increase in the thermal conductivity in the temperature range of our measurement is predominantly electronic in origin. The relatively low lattice thermal conductivity and its weak temperature dependence are attributed to strong electron-phonon coupling in VN_x . Increasing vacancy concentration was found to reduce both the electron and lattice thermal conductivities and lead to weaker temperature dependence for the lattice contribution to the thermal conductivity.

V. ACKNOWLEDGEMENT

Experimental characterization was carried out in the Frederick Seitz Materials Research Laboratory (MRL) at the University of Illinois. Q. Z. gratefully thank the help from Professor Leslie H. Allen's group on the measurement of the electrical resistivity in the high vacuum system. We kindly acknowledge financial support from ICAMS, Ruhr-Universität Bochum, 44780 Bochum, Germany the Swedish Research Council (VR) Project Grants 2009-00971, 2013-4018, and 2014-5790, and the Swedish Government Strategic Research Area Grant in Materials Science (SFO Mat-LiU) on Advanced Functional Materials. D.G.S. gratefully acknowledges financial support from the Olle Engkvist Foundation and access to supercomputer resources provided by the Swedish National Infrastructure for Computing (SNIC).

- [1] R. E. B. Makinson, *Mathematical Proceedings of the Cambridge Philosophical Society* **34**, 474 (1938).
- [2] J. M. Ziman, *Electrons and Phonons: The Theory of Transport Phenomena in Solids* (OUP Oxford, 1960).
- [3] P. G. Klemens and R. K. Williams, *International Metals Reviews* **31**, 197 (1986).
- [4] A. Jain and A. J. H. McGaughey, *Physical Review B* **93**, 081206 (2016).
- [5] L. G. Radosevich and W. S. Williams, *Physical Review* **181**, 1110 (1969).
- [6] W. H. Butler and R. K. Williams, *Physical Review B* **18**, 6483 (1978).
- [7] W. Weber, *Physical Review B* **8**, 5093 (1973).
- [8] S. J. Poon and T. H. Geballe, *Physical Review B* **18**, 233 (1978).
- [9] P. B. Allen, *Physical Review Letters* **59**, 1460 (1987).
- [10] G. Grimvall, (North-Holland, New York, 1981).
- [11] A. B. Mei, A. Rockett, L. Hultman, I. Petrov, and J. E. Greene, *Journal of Applied Physics* **114**, 193708 (2013).
- [12] E. I. Isaev, S. I. Simak, I. A. Abrikosov, R. Ahuja, Y. K. Vekilov, M. I. Katsnelson, A. I. Lichtenstein, and B. Johansson, *Journal of Applied Physics* **101**, 123519 (2007).
- [13] Z. Lin, L. V. Zhigilei, and V. Celli, *Physical Review B* **77**, 075133 (2008).
- [14] W. M. Haynes, *CRC Handbook of Chemistry and Physics, 96th Edition* (CRC Press, 2015).
- [15] J. P. Moore, R. S. Graves, and R. K. Williams, *Thermal transport properties of niobium and some niobium base alloys from 80 to 1600 °K*, 1980.
- [16] D. G. Cahill, S. M. Lee, and T. r. I. Selinder, *Journal of Applied Physics* **83**, 5783 (1998).
- [17] R. E. Taylor and J. Morreale, *Journal of the American Ceramic Society* **47**, 69 (1964).
- [18] J. Adachi, K. Kurosaki, M. Uno, and S. Yamanaka, *Journal of Alloys and Compounds* **399**, 242 (2005).
- [19] H. O. Pierson, *Handbook of Refractory Carbides & Nitrides: Properties, Characteristics, Processing and Apps* (Elsevier Science, 1996).

- [20] N. Tralshawala, J. F. Zasadzinski, L. Coffey, W. Gai, M. Romalis, Q. Huang, R. Vaglio, and K. E. Gray, *Physical Review B* **51**, 3812 (1995).
- [21] W. S. Williams, *Journal of the American Ceramic Society* **49**, 156 (1966).
- [22] A. B. Mei, B. M. Howe, C. Zhang, M. Sardela, J. N. Eckstein, L. Hultman, A. Rockett, I. Petrov, and J. E. Greene, *Journal of Vacuum Science & Technology A* **31**, 061516 (2013).
- [23] M. A. Wall, D. G. Cahill, I. Petrov, D. Gall, and J. E. Greene, *Physical Review B* **70**, 035413 (2004).
- [24] A. B. Mei *et al.*, *Physical Review B* **91**, 054101 (2015).
- [25] W. S. Williams, *JOM* **50**, 62 (1998).
- [26] R. Franz and G. Wiedemann, *Annalen der Physik* **165**, 497 (1853).
- [27] U. Mizutani, *Introduction to the Electron Theory of Metals* (Cambridge University Press, 2001).
- [28] V. A. Gubanov, A. L. Ivanovsky, and V. P. Zhukov, *Electronic Structure of Refractory Carbides and Nitrides* (Cambridge University Press, 2005).
- [29] R. Sanjinés, C. Wiemer, P. Hones, and F. Lévy, *Journal of Applied Physics* **83**, 1396 (1998).
- [30] C. Stampfl, W. Mannstadt, R. Asahi, and A. J. Freeman, *Physical Review B* **63**, 155106 (2001).
- [31] M. B. Takeyama, T. Itoi, K. Satoh, M. Sakagami, and A. Noya, *Journal of Vacuum Science & Technology B* **22**, 2542 (2004).
- [32] X. Chu, S. A. Barnett, M. S. Wong, and W. D. Sproul, *Journal of Vacuum Science & Technology A* **14**, 3124 (1996).
- [33] L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic Press, 1971).
- [34] X. Zhou, H. Chen, D. Shu, C. He, and J. Nan, *Journal of Physics and Chemistry of Solids* **70**, 495 (2009).
- [35] Q. Sun and Z.-W. Fu, *Electrochimica Acta* **54**, 403 (2008).
- [36] V. Rawat, Y. K. Koh, D. G. Cahill, and T. D. Sands, *Journal of Applied Physics* **105**, 024909 (2009).
- [37] B. Saha, Y. R. Koh, J. P. Feser, S. Sadasivam, T. S. Fisher, A. Shakouri, and T. D. Sands, *Journal of Applied Physics* **121**, 015109 (2017).
- [38] A. B. Mei, M. Tuteja, D. G. Sangiovanni, R. T. Haasch, A. Rockett, L. Hultman, I. Petrov, and J. E. Greene, *Journal of Materials Chemistry C* **4**, 7924 (2016).
- [39] A. B. Mei, R. B. Wilson, D. Li, D. G. Cahill, A. Rockett, J. Birch, L. Hultman, J. E. Greene, and I. Petrov, *Journal of Applied Physics* **115**, 214908 (2014).
- [40] W. Lengauer and P. Ettmayer, *Monatshefte für Chemie / Chemical Monthly* **117**, 713.
- [41] T. Lee, K. Ohmori, C. S. Shin, D. G. Cahill, I. Petrov, and J. E. Greene, *Physical Review B* **71**, 144106 (2005).
- [42] B. R. Zhao, L. Chen, H. L. Luo, M. D. Jack, and D. P. Mullin, *Physical Review B* **29**, 6198 (1984).
- [43] D. G. Cahill, *Review of Scientific Instruments* **75**, 5119 (2004).
- [44] K. Kang, Y. K. Koh, C. Chiritescu, X. Zheng, and D. G. Cahill, *Review of Scientific Instruments* **79**, 114901 (2008).
- [45] Y. Wang, J. Y. Park, Y. K. Koh, and D. G. Cahill, *Journal of Applied Physics* **108**, 043507 (2010).
- [46] R. M. Costescu, M. A. Wall, and D. G. Cahill, *Physical Review B* **67**, 054302 (2003).

- [47] V. F. Litvinenko, A. S. Bolgar, V. I. Kas'yan, L. K. Shvedova, and I. I. Timofeeva, *Powder Metall Met Ceram* **19**, 109 (1980).
- [48] M. W. Chase, S. National Institute of, and Technology, *NIST-JANAF thermochemical tables* (American Chemical Society ; American Institute of Physics for the National Institute of Standards and Technology, [Washington, D.C.] : Woodbury, N.Y. :, 1998), 4th ed. edn., Journal of physical and chemical reference data. Monograph ; no. 9; Journal of physical and chemical reference data. no. 9. Monograph ;, p.^pp. 2 volumes (xi, 1951 pages) ; 29 cm.
- [49] V. F. Litvinenko, A. S. Bolgar, V. I. Kas'yan, L. K. Shvedova, and I. I. Timofeeva, *Powder Metall Met Ceram* **19**, 109.
- [50] A. M. Hofmeister, *Physics and Chemistry of Minerals* **41**, 361 (2014).
- [51] S. C. Weaver, University of Tennessee, 1972.
- [52] D. D. Betts, A. B. Bhatia, and M. Wyman, *Physical Review* **104**, 37 (1956).
- [53] C. S. Smith and E. Palmer, *Trans AIME Papers* **221**, 225 (1935).
- [54] X. Zheng, D. G. Cahill, P. Krasnochtchekov, R. S. Averback, and J. C. Zhao, *Acta Materialia* **55**, 5177 (2007).
- [55] X. Zheng, D. Cahill, P. Krasnochtchekov, R. Averback, and J.-C. Zhao, *Acta Materialia* **55**, 5177 (2007).
- [56] T. M. Tritt, *Thermal Conductivity: Theory, Properties, and Applications* (Springer US, 2006).
- [57] A. Wilson, in *Mathematical Proceedings of the Cambridge Philosophical Society* (Cambridge Univ Press, 1937), pp. 371.
- [58] R. K. Williams, R. S. Graves, T. L. Hebble, D. L. McElroy, and J. P. Moore, *Physical Review B* **26**, 2932 (1982).
- [59] G. Grimvall, *The electron-phonon interaction in metals* (North-Holland Amsterdam, 1981), Vol. 8, 9.
- [60] W. S. Williams, *JOM Journal of the Minerals, Metals and Materials Society* **50**, 62 (1998).
- [61] F. L. Madarasz and P. G. Klemens, *International Journal of Thermophysics* **8**, 257 (1987).
- [62] V. Ambegaokar, *Physical Review* **114**, 488 (1959).