Thermal Conductivity of Rutile and Anatase TiO_2 from First-Principles

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Abstract

We compute the thermal conductivity of the most common polymorphs of titanium dioxide (TiO_2), rutile and anatase, within a first-principles approach and solving the phonon Boltzmann Transport Equation beyond the Relaxation Time Approximation. We find that both polytypes are anisotropic, as expected from their crystal structure, but while $\kappa_{xx} = \kappa_{yy} < \kappa_{zz}$ for rutile, the opposite holds for anatase. The modal decomposition of the thermal conductivity provides insight in this inversion in the anisotropy of the two polytypes.

Titanium dioxide (TiO_2) is a wide bandgap semiconductor that has applications in several fields. It is used as a white pigment in paints, where it is also known as *perfect white*, as a sunscreen, because of its high absorption of UV radiation, and in food industry (it is the common food colourant E171).¹ The interest towards TiO_2 has been further boosted by the rationalization of its photocatalytic properties, i.e. its ability of splitting water into hydrogen and oxygen upon irradiation, the so-called Honda-Fujishima effect;² the photocatalytic water splitting can be exploited for environmental purification³ and for the production of H_2 , a *clean* fuel for energy production.^{4,5} The two photocatalytic processes are anyway intrinsically different with the former only depending by the valence band maximum (VBM) position relative to the standard hydrogen electrode (photoexcited holes oxidize the organic pollutants towards harmless products). On the other hand, the latter process is much more complex, being the interplay of strict requirements that involve the gap of the photocatalyst and bandedges that straddle the water redox potential:⁶ not only VBM but also the proper conduction band minimum positioning is fundamental in such process. The surface of TiO_2 was also found to exhibit photoinduced *superhydrophilicity*,^{7,8} a property that confers the material with a self-cleaning function and that makes it a common choice for side view mirrors.⁹ Additionally, TiO_2 is also used as a substrate/electrode in dye-sensitized solar cells,^{10–12} where it collects electrons injected from the excited state of adsorbed photosensitizers.

TiO₂ occurs naturally in three polymorphs, anatase, rutile and (the less common) brookite,¹³ which are characterized minerals. Other phases, such as columbite (α -PbO₂), baddeleyite, and cotunnite have been observed at increasingly high pressures and hints of a cubic structure above 60 GPa have been reported.¹⁴ It is worth stressing that among the three mentioned most common polymorphs rutile is the most stable, followed by anatase and brookite. Importantly, anyway, at the nanoscale the order is inverted with anatase that becomes the most thermodynamically stable.¹⁵ This relevant result supports the fact that the vast majority of experimental^{16–18} and theoretical^{19–24} studies concern the mineral phases and predominantly, anatase and rutile, the most stable polymorphs.

The thermal properties of TiO₂ have received comparatively less attention, but they are important both from a fundamental standpoint and for applications related to thermal management and thermoelectricity.^{25–31} Experimentally, the thermal conductivity of rutile was first measured by McCarthy and Ballad³² in 1951, providing values of its anisotropy close to room temperature. Afterwards, Berman and Ziman³³ restricted their works to a rather low temperature range (2–90 K), while Charvat and Kingery studied the range from 350–1000 K.³⁴ A few years later Thurber and Mante²⁵ measured single-crystal TiO₂ samples cut from a boule grown by the Verneuil process from 2 K up to 1000 K. More recently, Harada *et al.*²⁷ studied its room-temperature thermoelectric properties, including lattice thermal conductivity, and several Ti_nO_{2n–1} stoichiometries. In the case of anatase only measurements of nanostructured samples are available and the thermal conductivity of nanotubes synthesized by electrochemical anodization³⁵ and nanowires synthesized electrosinning technique³⁶ have been reported. For bulk, only the room temperature thermal conductivity was reported by Touloukian *et al.*³⁷ A few theoretical works have studied the elastic and thermal properties of anatase and rutile from first principles,^{38–40} computing the phonon dispersions, the heat capacity, and the Grüneisen parameter. Regarding the thermal conductivity, however, the only available first principles results are based on the Cahill–Pohl model,^{41,42} which allows obtaining the so-called minimum thermal conductivity from harmonic properties, while a

full solution of the phonon Boltzmann Transport Equation (BTE) that includes anharmonic effects is still missing.

Figure 1: Sketch of the conventional cells of (a) rutile and (b) anatase. Our optimized structures have lattice parameters $a = b = 4.611 \text{ \AA}$ and $c = 2.957 \text{ \AA}$ for rutile and $a = b = 3.807 \text{ \AA}$ and $c = 9.464 \text{ \AA}$ for anatase, which agree well with the reported experimental values.^{43–46}

In this paper we study the thermal conductivity of the most common polymorphs of TiO_2 , anatase and rutile, within a first-principles approach (see the Supporting Information for the specific heat, entropy, internal energy and Helmholtz free energy). To this end we calculate the harmonic and third-order anharmonic interatomic force constants (IFCs) from density-functional theory (DFT) and then solve the phonon Boltzmann Transport Equation (BTE)

$$\left(\frac{\partial n_{\mathbf{q}}}{\partial t} \right)_{\text{drift}} \equiv \frac{\partial n_{\mathbf{q}}}{\partial t} + \mathbf{v}_{\mathbf{q}} \cdot \frac{\partial n_{\mathbf{q}}}{\partial \mathbf{r}} = \left(\frac{\partial n_{\mathbf{q}}}{\partial t} \right)_{\text{scattering}}, \quad (1)$$

which states that a perturbed distribution of phonons $n_{\mathbf{q}}$ restores its equilibrium state $n_{\mathbf{q}}^0$, expressed by the Bose-Einstein distribution function, through scattering (collision) processes.⁴⁷ To compute the IFCs we use the finite displacement method and the VASP code⁴⁸ under the Local Density Approximation (LDA)⁴⁹ by using projector augmented waves^{50,51} with an energy cutoff of 400 eV. For the effect of the functional on the computed thermal conductivity see e.g. Ref. 52. Born effective charges and the dielectric tensor are also computed in

order to account for non-analytical corrections. Both rutile and anatase have a tetragonal structure, belonging to the $P4_2/mnm$ (136) and $I4_1/amd$ (141) space groups, respectively (see the sketch in Fig. 1). For both the harmonic and anharmonic IFCs we used a $3 \times 3 \times 3$ supercell of the 6-atom (12-atom) cell of rutile (anatase), sampling the Brillouin zone with a $4 \times 4 \times 4$ ($4 \times 4 \times 2$) grid of $\mathbf{k}$ -points. This supercell sizes yield dispersion relations in good agreement with previously published results.^{39,40} We use the PHONO3PY code⁵³ to generate the inequivalent atomic displacements required to compute the IFCs and to calculate the thermal conductivity beyond the standard Relaxation Time Approximation (RTA), obtaining the direct solution of the BTE due to Chaput:^{54,55}

$$\kappa^{\alpha\beta}(\omega) = \int \frac{\rho_{\alpha\beta}(\omega')}{\omega' - i\omega} d\omega' , \quad (2)$$

where $\rho_{\alpha\beta}(\omega')$ is a spectral density. Although the RTA solution with TiO_2 works well at room temperature, we found that at 100 K the differences are larger than 30 %, as momentum conserving phonon scattering processes (Normal processes) become more relevant.⁵⁶ In addition to the intrinsic scattering events (Normal and Umklapp), isotope and boundary scattering have been also considered. For isotope disorder we consider the natural abundance of Ti and O isotopes and use the model due to Tamura.⁵⁷ The corresponding scattering term is

$$\Gamma_{\mathbf{q}}^I = \frac{\pi}{4N_{\mathbf{q}}} \omega_{\mathbf{q}}^2 \sum_{\mathbf{q}'} \delta(\omega_{\mathbf{q}} - \omega_{\mathbf{q}'}) \sum_s \gamma(s) |e^*(s, \mathbf{q}') e(s, \mathbf{q})|^2 , \quad (3)$$

where $N_{\mathbf{q}}$ is the mesh sampling, $e_{\mathbf{q}}$ the phonon eigenvector and $\gamma(s)$ is the mass fluctuation factor:

$$\gamma(s) = \sum_i f_i(s) \left(1 - \frac{m_i(s)}{M_s} \right)^2 , \quad (4)$$

being f_i the fraction of the i th isotope with mass m_i and $M_s = \sum_i f_i m_i(s)$ the averaged mass. The boundary scattering, which accounts for the sample grain sizes, simply depends

on an effective size scale L and the phonon mode velocity ($v_{\mathbf{q}}$) as

$$\Gamma_{\mathbf{q}}^B = \frac{1}{2\pi} \frac{v_{\mathbf{q}}}{L}. \quad (5)$$

Converged values of the thermal conductivity at room temperature required to consider interactions up to eighth neighbors in three-phonon scattering processes and solving the phonon BTE on a $36 \times 36 \times 36$ and a $25 \times 25 \times 25$ $\mathbf{q}$ -point grid for rutile and anatase, respectively. At temperatures as low as 100 K we achieved convergence of the thermal conductivity by considering a sample grain size of 0.1 mm. Without including this boundary scattering term, much thicker $\mathbf{q}$ -point sampling, beyond our current computational capabilities, would be required.

Figure 2: Thermal conductivity of rutile and anatase as a function of temperature. Solid lines show the response in $\kappa_{xx} = \kappa_{yy}$ and dotted lines in κ_{zz} . The average value is represented with dotted dashed lines. The experimental points are taken from Ref. 27, 32, 34, and 37.

Fig. 2 shows the thermal conductivity of rutile and anatase, as computed from Eq. 2. For both polymorphs Umklapp is the dominant resistive scattering mechanism, in the temperature range investigated, and κ decreases with T . In the case of rutile the computed value

agree well with the experimental values, perhaps with the exception of the data of McCarthy *et al.*³² who reported somewhat larger values. We observe, nonetheless, that we obtain values within the dispersion of the experimentally reported magnitudes (see for instance the difference between the room temperature values measured of Refs. 27 and 32). For anatase, the average calculated room temperature thermal conductivity is also in good agreement with the value of $8.5 \text{ Wm}^{-1}\text{K}^{-1}$ reported by Touloukian *et al.*³⁷ Comparing both figures we observe that the two polytypes have an inverse anisotropy: while in anatase $\kappa_{xx} = \kappa_{yy}$ is higher than κ_{zz} , in rutile is the other way around. This result agrees with the report of Momenzadeh and coworkers⁵⁸ based on equilibrium molecular dynamics and with the experimental results from McCarthy and Charvat.³² In addition we observe some differences in the trend in temperature: in rutile as the temperature decreases all the components of the thermal conductivity tensor follow the same trend, while in anatase the variation in κ_{zz} is less pronounced and differs from the evolution of $\kappa_{xx} = \kappa_{yy}$. Notice that reducible TiO_2 may contain a large amount of oxygen vacancies in experimental samples and their presence, not accounted in our calculations, is expected to have an effect of the thermal conductivity.

To analyze in more detail the behavior of these two polytypes and see how the group velocities of each phonon branch affect the thermal conductivity we have calculated the mode-by-mode contribution to κ and the thermal conductivity accumulation function, defined as

$$\kappa_{acc}(\omega) = \int_0^\omega \kappa(\omega') d\omega' . \quad (6)$$

The results for rutile and anatase are shown in Fig. 3 and Fig. 4, respectively.

At very low frequencies (below $\sim 0.8 \text{ THz}$) both polytypes behave very similarly, but it is at higher values that they differ. In rutile almost all the contribution to the thermal conductivity comes from acoustic and low frequency phonons below 2 THz . The modal decomposition shows that all components have very similar contributions, but with a relative larger weight in the case of κ_{zz} . Notice that rutile has no phonons in a region between 18 and

Figure 3: Accumulated thermal conductivity (top) and phonon mode contribution (center and lower panel) as function of frequency at 300 K for rutile.

Figure 4: Accumulated thermal conductivity (top) and phonon mode contribution (center and lower panel) as function of frequency at 300 K for anatase.

20 THz due to the intrinsic phononic gap.³⁹ This fact, nevertheless, has no real impact on the thermal conductivity, as the contributions above 10 THz are already negligible. Anatase shows a different behavior. In this polymorph κ_{zz} starts its saturation above 1 THz, while at this point $\kappa_{xx} = \kappa_{yy}$ is still at barely the 20 % of its final value. Phonons between 1–3 THz have a contribution around 66 % and $\kappa_{xx} = \kappa_{yy}$ saturates only around 15 THz.

These results provide some hint to the different behavior in terms of anisotropy. While all the components of the thermal conductivity tensor of rutile and κ_{zz} of anatase are entirely determined by low frequency phonons, modes up to 15-20 THz contribute to $\kappa_{xx} = \kappa_{yy}$ of anatase. This unusual contribution of mid- and high-frequency phonons not only appear to be responsible for the inversion of the anisotropy, leading $\kappa_{xx} = \kappa_{yy}$ to largely exceed κ_{zz} in anatase; it also results in a considerable violation of the common assumption rule that prescribes the thermal conductivity to be inversely related to the complexity of the crystal structure. Anatase has more atoms in the primitive cell, more phonon modes and thus a larger phase space, i.e. more possible three-phonon scattering processes. For this reason, although counterexamples have been reported,^{59,60} one would expect its thermal conductivity to be lower. Indeed κ_{zz} of anatase is less than half of that of rutile. Conversely, however, $\kappa_{xx} = \kappa_{yy}$ in anatase is larger than κ_{zz} and roughly twice as large as its counterpart in rutile. These results suggest that the thermal conductivity of TiO_2 can be engineered not only by choosing the polytype, but also by selecting the direction of the heat transport, at least in the case of single-crystals.

In conclusion we have studied from first principles the thermal conductivity of the two most common polytypes of TiO_2 , rutile and anatase. We obtain the thermal conductivity of both crystal phases from the full solution of the Boltzmann Transport Equation and find that their anisotropy is inverted, with $\kappa_{zz} > \kappa_{xx} = \kappa_{yy}$ in rutile and $\kappa_{zz} < \kappa_{xx} = \kappa_{yy}$ in anatase. The frequency resolved analysis of the contribution to the thermal conductivity indicates that in anatase κ_{zz} is almost entirely determined by phonons with $\omega < 1$ THz (similarly to all the component of the thermal conductivity tensor in rutile), while higher frequency phonons still contribute to $\kappa_{xx} = \kappa_{yy}$. This increase is such that $\kappa_{xx} = \kappa_{yy}$ of anatase is the largest thermal conductivity that we computed, while one could naively expect that, owing to its simpler crystal structure, rutile should be more conductive.

Acknowledgement

We acknowledge financial support by the Ministerio de Economía, Industria y Competitividad (MINECO) under grant FEDER-MAT2017-90024-P and the Severo Ochoa Centres of Excellence Program under grant SEV-2015-0496 and by the Generalitat de Catalunya under grant no. 2017 SGR 1506. We thank Giacomo Giorgi for useful discussion.

References

- (1) Weir, A.; Westerhoff, P.; Fabricius, L.; Hristovski, K.; von Goetz, N. Titanium Dioxide Nanoparticles in Food and Personal Care Products. *Environ. Sci. Technol.* **2012**, *46*, 2242–2250.
- (2) Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238*, 37–38.
- (3) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96.
- (4) Ni, M.; Leung, M. K.; Leung, D. Y.; Sumathy, K. A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production. *Renew. Sustain. Energy Rev.* **2007**, *11*, 401–425.
- (5) Ma, Y.; Wang, X.; Jia, Y.; Chen, X.; Han, H.; Li, C. Titanium Dioxide-Based Nanomaterials for Photocatalytic Fuel Generations. *Chem. Rev.* **2014**, *114*, 9987–10043.
- (6) Giorgi, G.; Yamashita, K.; Palummo, M.; Fabris, S. A route for minimizing emissions: sun-mediated processes and clean batteries. *Curr. Opin. Green Sustain. Chem.* **2019**, *17*, A1–A4.
- (7) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shi-

- mohigoshi, M.; Watanabe, T. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1997**, *388*, 431–432.
- (8) Diebold, U. The surface science of titanium dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
- (9) Hashimoto, K.; Irie, H.; Fujishima, A. TiO₂ Photocatalysis: A Historical Overview and Future Prospects. *Jpn. J. Appl. Phys.* **2005**, *44*, 8269–8285.
- (10) O'Regan, B.; Gratzel, M. A low-cost, high-efficiency solar-cell based on dye-sensitized colloidal TiO₂ films. *Nature* **1991**, *353*, 737–740.
- (11) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110*, 6595–6663.
- (12) Bai, Y.; Mora-Seró, I.; De Angelis, F.; Bisquert, J.; Wang, P. Titanium Dioxide Nanomaterials for Photovoltaic Applications. *Chem. Rev.* **2014**, *114*, 10095–10130.
- (13) Di Paola, A.; Bellardita, M.; Palmisano, L. Brookite, the Least Known TiO₂ Photocatalyst. *Catalysts* **2013**, *3*, 36–73.
- (14) Zhu, T.; Gao, S.-P. The Stability, Electronic Structure, and Optical Property of TiO₂ Polymorphs. *J. Phys. Chem. C* **2014**, *118*, 11385–11396.
- (15) Gribb, A. A.; Banfield, J. F. Particle size effects on transformation kinetics and phase stability in nanocrystalline TiO₂. *Am. Mineral.* **1997**, *82*, 7–8.
- (16) Linsebigler, A. L.; Lu, G.; Yates, J. T. Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95*, 735–758.
- (17) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science* **2001**, *293*, 269–271.
- (18) Chen, X.; Mao, S. S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**, *107*, 2891–2959.

- (19) Vittadini, A.; Selloni, A.; Rotzinger, F. P.; Grätzel, M. Structure and Energetics of Water Adsorbed at TiO₂ Anatase 101 and 001 Surfaces. *Phys. Rev. Lett.* **1998**, *81*, 2954–2957.
- (20) Asahi, R.; Taga, Y.; Mannstadt, W.; Freeman, A. J. Electronic and optical properties of anatase TiO₂. *Phys. Rev. B* **2000**, *61*, 7459–7465.
- (21) Lazzeri, M.; Vittadini, A.; Selloni, A. Structure and energetics of stoichiometric TiO₂ anatase surfaces. *Phys. Rev. B* **2001**, *63*, 155409.
- (22) Rossmeisl, J.; Qu, Z.-W.; Zhu, H.; Kroes, G.-J.; Nørskov, J. Electrolysis of water on oxide surfaces. *J. Electroanal. Chem.* **2007**, *607*, 83–89.
- (23) Giorgi, G.; Yamashita, K. *Photoinduced Processes at Surfaces and in Nanomaterials*; 2015; Chapter 2, pp 47–80.
- (24) Varsano, D.; Giorgi, G.; Yamashita, K.; Palummo, M. Role of Quantum-Confinement in Anatase Nanosheets. *J. Phys. Chem. Lett.* **2017**, *8*, 3867–3873.
- (25) Thurber, W. R.; Mante, A. J. H. Thermal Conductivity and Thermoelectric Power of Rutile (TiO₂). *Phys. Rev.* **1965**, *139*, A1655–A1665.
- (26) He, Q.; Hao, Q.; Chen, G.; Poudel, B.; Wang, X.; Wang, D.; Ren, Z. Thermoelectric property studies on bulk TiO_x with x from 1 to 2. *Appl. Phys. Lett.* **2007**, *91*, 052505.
- (27) Harada, S.; Tanaka, K.; Inui, H. Thermoelectric properties and crystallographic shear structures in titanium oxides of the Magnéli phases. *J. Appl. Phys.* **2010**, *108*, 083703.
- (28) Kitagawa, H.; Kunisada, T.; Yamada, Y.; Kubo, S. Effect of boron-doping on thermoelectric properties of rutile-type titanium dioxide sintered materials. *J. Alloys Compd.* **2010**, *508*, 582–586.
- (29) Su, L.; Gan, Y. X. Formation and thermoelectric property of TiO₂ nanotubes covered by Te-Bi-Pb nanoparticles. *Electrochim. Acta* **2011**, *56*, 5794–5803.

- (30) Xu, L.; Garrett, M. P.; Hu, B. Doping Effects on Internally Coupled Seebeck Coefficient, Electrical, and Thermal Conductivities in Aluminum-Doped TiO₂. *J. Phys. Chem. C* **2012**, *116*, 13020–13025.
- (31) Liu, C.; Miao, L.; Zhou, J.; Huang, R.; Tanemura, S. Bottom-up assembly to Ag nanoparticles embedded Nb-doped TiO₂ nanobulks with improved n-type thermoelectric properties. *J. Mater. Chem.* **2012**, *22*, 14180–14190.
- (32) McCarthy, K. A.; Ballard, S. S. New Data on the Thermal Conductivity of Optical Crystals. *J. Opt. Soc. Am.* **1951**, *41*, 1062–1063.
- (33) Berman, R.; Foster, E. L.; Ziman, J. M.; Simon, F. E. The thermal conductivity of dielectric crystals: the effect of isotopes. *Proc. Royal Soc. Lond. A* **1956**, *237*, 344–354.
- (34) Charvat, F. R.; Kingery, W. D. Thermal Conductivity: XIII, Effect of Microstructure on Conductivity of Single-Phase Ceramics. *J. Am. Ceram. Soc.* **1957**, *40*, 306–315.
- (35) Guo, L.; Wang, J.; Lin, Z.; Gacek, S.; Wang, X. Anisotropic thermal transport in highly ordered TiO₂ nanotube arrays. *J. Appl. Phys.* **2009**, *106*, 123526.
- (36) Feng, X.; Huang, X.; Wang, X. Thermal conductivity and secondary porosity of single anatase TiO₂ nanowire. *Nanotechnology* **2012**, *23*, 185701.
- (37) Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermophysical Properties of Matter - The TPRC Data Series. Volume 2. Thermal Conductivity - Nonmetallic Solids*, (IFI/Plenum, New York, 1970).
- (38) Naffouti, W.; Ben Nasr, T.; Meradji, H.; Kamoun-Turki, N. First-Principles Investigation of Structural, Thermal and Transport Properties of Anatase TiO₂. *J. Electron. Mater.* **2016**, *45*, 5096–5103.
- (39) Shojaee, E.; Mohammadizadeh, M. R. First-principles elastic and thermal properties of TiO₂ : a phonon approach. *J. Phys.: Condens. Matter.* **2010**, *22*, 015401.

- (40) Kangarlou, H.; Abdollahi, A. Thermodynamic Properties of Rutile (TiO_2) Within the Phonon Calculations. *Int. J. Thermophys.* **2016**, *37*, 110.
- (41) Cahill, D. G.; Pohl, R. O. Thermal conductivity of amorphous solids above the plateau. *Phys. Rev. B* **1987**, *35*, 4067–4073.
- (42) Ding, Y.; Xiao, B. Anisotropic elasticity, sound velocity and thermal conductivity of TiO_2 polymorphs from first principles calculations. *Comput. Mater. Sci* **2014**, *82*, 202–218.
- (43) Sato, H.; Endo, S.; Sugiyama, M.; Kikegawa, T.; Shimomura, O.; Kusaba, K. Baddeleyite-Type High-Pressure Phase of TiO_2 . *Science* **1991**, *251*, 786–788.
- (44) Ma, X. G.; Liang, P.; Miao, L.; Bie, S. W.; Zhang, C. K.; Xu, L.; Jiang, J. J. Pressure-induced phase transition and elastic properties of TiO_2 polymorphs. *phys. stat. sol. (b)* **2009**, *246*, 2132–2139.
- (45) Djerdj, I.; Tonejc, A. Structural investigations of nanocrystalline TiO_2 samples. *J. Alloys Compd.* **2006**, *413*, 159–174.
- (46) Okrusch, M.; Hock, R.; Schüssler, U.; Brummer, A.; Baier, M.; Theisinger, H. Intergrown niobian rutile phases with Sc- and W-rich ferrocolumbite: An electron-microprobe and Rietveld study. *Am. Mineral.* **2003**, *88*, 986.
- (47) Fugallo, G.; Colombo, L. Calculating lattice thermal conductivity: a synopsis. *Physica Scripta* **2018**, *93*, 043002.
- (48) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169.
- (49) Labat, F.; Baranek, P.; Domain, C.; Minot, C.; Adamo, C. Density functional theory analysis of the structural and electronic properties of TiO_2 rutile and anatase polytypes:

- Performances of different exchange-correlation functionals. *J. Chem. Phys.* **2007**, *126*, 154703.
- (50) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953.
- (51) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758.
- (52) Arrigoni, M.; Madsen, G. K. Comparing the performance of LDA and GGA functionals in predicting the lattice thermal conductivity of III-V semiconductor materials in the zincblende structure: The cases of AlAs and BAs. *Comp. Mater. Sci.* **2019**, *156*, 354–360.
- (53) Togo, A.; Chaput, L.; Tanaka, I. Distributions of phonon lifetimes in Brillouin zones. *Phys. Rev. B* **2015**, *91*, 094306.
- (54) Chaput, L.; Togo, A.; Tanaka, I.; Hug, G. Phonon-phonon interactions in transition metals. *Phys. Rev. B* **2011**, *84*, 094302.
- (55) Chaput, L. Direct Solution to the Linearized Phonon Boltzmann Equation. *Phys. Rev. Lett.* **2013**, *110*, 265506.
- (56) Torres, P.; Alvarez, F. X.; Cartoixa, X.; Rurali, R. Thermal conductivity and phonon hydrodynamics in transition metal dichalcogenides from first-principles. *2D Mater.* **2019**, *6*, 035002.
- (57) Tamura, S. Isotope scattering of dispersive phonons in Ge. *Phys. Rev. B* **1983**, *27*, 858–866.
- (58) Momenzadeh, L.; Moghtaderi, B.; Belova, I. V.; Murch, G. E. Determination of the lattice thermal conductivity of the TiO₂ polymorphs rutile and anatase by molecular dynamics simulation. *Comput. Cond. Mater.* **2018**, *17*, e00342.

- (59) Carrete, J.; Gallego, L. J.; Mingo, N. Structural Complexity and Phonon Physics in 2D Arsenenes. *J. Phys. Chem. Lett.* **2017**, *8*, 1375–1380.
- (60) Raya-Moreno, M.; Rurali, R.; Cartoixà, X. Thermal conductivity for III-V and II-VI semiconductor wurtzite and zinc-blende polytypes: The role of anharmonicity and phase space. *Phys. Rev. Materials* **2019**, *3*, 084607.