Anisotropic work function of elemental crystals

Richard Tran,† Xiang-Guo Li,† Joseph Montoya,† Donald Winston,‡ Kristin Aslaug Persson,¶ and Shyue Ping Ong* †

†Department of NanoEngineering, University of California San Diego, 9500 Gilman Dr, Mail Code 0448, La Jolla, CA 92093-0448, United States
‡Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States
¶Department of Materials Science & Engineering, University of California Berkeley, Berkeley, CA 94720-1760, United States

E-mail: ongsp@eng.ucsd.edu

Abstract

The work function is a fundamental electronic property of a solid that varies with the facets of a crystalline surface. It is a crucial parameter in spectroscopy as well as materials design, especially for technologies such as thermionic electron guns and Schottky barriers. In this work, we present the largest database of calculated work functions for elemental crystals to date. This database contains the anisotropic work functions of more than 100 polymorphs of about 72 elements and up to a maximum Miller index of two and three for non-cubic and cubic crystals, respectively. The database has been rigorously validated against previous experimental and computational data where available. We also propose a weighted work function based on the Wulff shape that can be compared to measurements from polycrystalline specimens, and show that this weighted work function can be modeled empirically using simple atomic parameters. Furthermore, for the first time, we were able to analyze simple bond breaking

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rules for metallic systems beyond a maximum Miller index of one, allowing for a more
generalized investigation of work function anisotropy.

Introduction

The work function (Φ) is an electronic surface property of crystalline solids and is crucial to
the understanding and design of materials in many applications. It can be directly applied
to the engineering of device specifications such as the Schottky barrier of semiconductor
junctions or the thermionic currents of electron guns. Furthermore, it has been used to
guide the engineering of interfacial interactions between metals and monolayer structures
for nanoscale self-assembly. The work function is also an important parameter in charac-
terization techniques where it can influence the tip tunneling current of scanning tunneling
microscopes or correct the binding energy in photo-electron spectroscopy (PES).

The work function has also been explored as a parameter for materials design. For
example, previous experimental and computational investigations of Ni-alloys by Lu et al. have
established a correlation between the work function and various mechanical properties
such as toughness, hardness, ductility and bulk modulus. A more recent study using first-
principle calculations found similar correlations for elemental crystalline solids. The work
function has also been proposed as a possible parameter for the desorption rate of surface
adsorbates. Calculated work functions of hcp materials have also been used to screen for
more effective metallic photocathodes.

Much effort has also been devoted to modelling Φ itself. Michaelson and Miedema
et al., for example, were previously successful in modelling the polycrystalline work function
as a linear function of electronegativity. The modeling of the anisotropic work function
(Φ_{hkl}) as a function of surface morphology and chemical environment has also garnered much
attention. Smoluchowski smoothing is one such model which describes the contributions
to the work function of metals as a result of isotropic electron spreading and anisotropic
The spreading of negative charges increases the work function while the anisotropic smoothing of negative charges at the surface decreases the work function. Smoothing increases with surface roughness (defined here as the reciprocal of the surface packing fraction) which decreases the work function. This model is supported by previous observations that the anisotropic surface energy ($\gamma_{hkl}$) is inversely proportional to $\Phi_{hkl}$ via the broken bond surface density. Similarly, the Brodie model attempts to explain $\Phi_{hkl}$ for transition metals as a function of (bulk) electron effective mass, surface atomic radius and inter-planar distance. A more recent model using a dielectric formalism has been proposed by Fazylov that describes $\Phi_{hkl}$ using surface roughness and surface plasmon dispersion.

An extensive database for $\Phi_{hkl}$ would be invaluable for validating and further expanding upon these models. However, experimentally measured work functions are usually for polycrystalline specimens ($\Phi_{\text{poly}}$) instead of single crystals. An example of this is the extensive collection of experimentally measured $\Phi_{\text{poly}}$ for 66 polycrystalline elemental solids compiled by Michaelson. Though measurements for anisotropic $\Phi_{hkl}$ are not uncommon, values often vary due to the many techniques used or non-standardized methods of implementing the same technique (e.g., PES). The sparsity of $\Phi_{hkl}$ and the lack of a comprehensive compilation with a single standardized technique makes it difficult to develop and gain insights into work function anisotropy using experimental measurements.

Here, density functional theory (DFT) has the advantage of calculating $\Phi_{hkl}$ for a model of any specific solid surface under a controllable set of parameters, making it possible to create a standardized collection of values. Many authors have attempted such compilations for $\Phi_{hkl}$, which are often times accompanied by the corresponding surface energy $\gamma_{hkl}$. For instance, Ji et al. and Wang and Wang have calculated $\Phi_{hkl}$ for numerous bcc, fcc and hcp materials. Waele et al. created a database of $\Phi_{hkl}$ for all elemental crystalline solids, but only for facets up to a max Miller index (MMI) of 1, using the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) and localized density approximation (LDA).
functionals. More recently, Patra et al.\textsuperscript{[23]} evaluated the performance of various functionals by calculating $\Phi_{hkl}$ for an MMI of one for Al, Cu, Ru, Rh, Pd, Ag, Pt and Au. Despite the wide variety of computational data, the majority of these studies are limited to small Miller indices (typically MMI of 1). In addition, computational data for lanthanide systems and different polymorphs is sparse.\textsuperscript{[22,24,25]} Furthermore, most compilations do not consider possible reconstructions, which can drastically affect the calculated work function.\textsuperscript{[21]}

Here, we report the development of a comprehensive, validated database of work functions for elemental crystalline solids using DFT calculations that addresses all the above limitations in the following ways:

1. Coverage of 142 polymorphs of 72 elements, including rare earth metals.

2. Facets up to an MMI of three and two for cubic and non-cubic crystals, respectively, are considered.

3. Common reconstruction schemes, such as the missing-row (110) fcc and the diamond-type reconstructions,\textsuperscript{[26]} have been taken into account.

We validate our computed work functions with past experimental and computational data for both $\Phi_{hkl}$ and $\Phi_{\text{expt poly}}$. Finally, we will discuss trends in the work function of the elements, and develop a predictive empirical model for $\Phi_{\text{expt poly}}$. 
Methods

Definitions

Figure 1: Plot of the electrostatic potential along the hcp Rb (0001) slab model. The Fermi energy ($E_F$), electrostatic potential of the vacuum region ($V_{\text{vac}}$), average electrostatic potential of the slab region ($V_{\text{interior}}$) and work function ($\Phi$) are indicated.

The work function is defined as the energy barrier required to move an electron from the surface of a solid material into free space, as given by the following expression:

$$\Phi = V_{\text{vac}} - E_F$$  \hspace{1cm} (1)

where $V_{\text{vac}}$ is the electrostatic potential of the vacuum region near the surface and $E_F$ is the Fermi energy of the slab. The energy barrier can be visualized in Figure 1 where $V_{\text{vac}}$ is
obtained when the electron is far enough away from the surface, that the potential remains constant over a small distance in the vacuum. This method has been widely used in previous studies for calculating the work function\textsuperscript{11,12,21,22} and has been shown to converge quickly with respect to slab thickness.\textsuperscript{19}

**Modeling non-uniform work functions**

For comparison to work functions obtained from polycrystalline specimens, one approach is to calculate the work function of a “patchy” surface by weighting each $\Phi_{hkl}$ by the area fraction of its corresponding facet\textsuperscript{5,27} as follows:

$$\bar{\Phi} = \frac{\sum_{\{hkl\}} \Phi_{hkl} A_{hkl}}{\sum A_{hkl}} = \sum_{\{hkl\}} \Phi_{hkl} f_{hkl}^{A}$$

where $A_{hkl}$ and $f_{hkl}^{A}$ are the total area and the area fraction of all facets in the $\{hkl\}$ family, respectively. A polycrystal is an extreme case of a patchy surface, and as such the same technique can be applied to $\Phi_{expt}^{poly}$. The PES signal of the patch with a lower work function will tend to eclipse those with higher work functions leading to an underestimated measurement of $\Phi_{expt}^{poly}$. Thus, experimental values of the lowest anisotropic work function ($\Phi_{hkl}^{\text{lowest}}$) are only $\sim 90$ meV lower than $\Phi_{expt}^{poly}$. Because of this, it has also been suggested that $\Phi_{hkl}^{\text{lowest}}$ is a good estimate of $\Phi_{expt}^{poly}$.\textsuperscript{5,18,21} In this study, we use the facets present in the Wulff shape previously calculated by the current authors\textsuperscript{28} as an estimate of the orientation and area fraction present in a polycrystalline sample to obtain $\bar{\Phi}$ and $\Phi_{hkl}^{\text{lowest}}$ as estimates for $\Phi_{expt}^{poly}$.

As mentioned earlier, Smoluchowski smoothing describes the anisotropic work function of metals as being inversely correlated with the broken bonds per surface area. As such, we model our values for $\Phi_{hkl}$ normalized by $\bar{\Phi}$ using the ratio of broken bonds-to-bulk coordination number ($\frac{N_{BB}}{CN_{bulk}}$) in a slab normalized by the surface area-to-atomic area ratio ($\frac{A_{surf}}{\pi r_{A}^{2}}$)
in order to compare across all systems:

\[ \overline{BB} = \frac{N_{BB}}{CN_{bulk}} \times \frac{A_{surf}}{\pi r^2} \]  

(3)

It is known that for bcc and hcp materials, the first nearest neighbors (1NN) and second nearest neighbors (2NN) are in close proximity to each other, leading to contributions from the latter to the anisotropy of surface energy.\cite{20} Hence, when defining \( \overline{BB} \) for a material, we will limit the maximum coordination number to the 1NN for fcc materials and explore both 1NN and 2NN for hcp and bcc materials. For hcp structures, we omitted \( \Phi_{0001} \) when investigating the effect of the 1NN as the number of broken bonds will always be 0 which is unphysical. The inverse correlation between \( \overline{BB} \) and \( \Phi_{hkl} \) for each element can be quantified by the Pearson correlation coefficient (\( r \)). We will define systems with a negative linear trend between \( \Phi_{hkl} \) and the normalized broken bonds with \( r < -0.75 \) as having a strong correlation, \(-0.75 < r < -0.5 \) as having a moderate correlation and \( r > -0.5 \) as having a weak correlation. Only ground state metallic fcc, bcc and hcp systems were explored under this context.

**Computational details and workflow**

For all slab calculations, we performed a full relaxation of the site positions under a fixed volume before obtaining the electrostatic potential of the slabs (see ref \cite{28} for a complete description of computational details). The electrostatic potentials only contains the electrostatic contributions (no contributions from the exchange correlation). All calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the exchange-correlation effects modeled using the PBE-GGA functional. Calculations using the revised PBE (rPBE) functional were performed on a smaller set of data using the same parameters for comparison.

We used the high-throughput workflow proposed by Sun and Ceder\cite{30} and implemented
by Tran et al.\textsuperscript{28} and Montoya and Persson\textsuperscript{31} to obtain all required data. The workflow was implemented using the open-source software packages Python Materials Genomics,\textsuperscript{32} Fire-Works,\textsuperscript{33} and Atomate.\textsuperscript{34} The work function is extracted from the calculations and inserted into the same database. To handle errors that may arise during calculations, the custodian software package was used as a wrapper around VASP together with a set of robust error handling rules. The database will be continuously improved and will continue growing as more structural data becomes available on the Materials Project.\textsuperscript{35}

**Data Availability**

The data can be accessed from the elemental-surface-data-focused Crystalium\textsuperscript{36} website, as well as from the Materials Project website\textsuperscript{37} on its detail pages for specific crystals.

**Results**

Due to the vast number of data points for $\Phi_{hkl}$ when comparing to literature values, we have adopted a consistent marker shape and color scheme for ease of reference (see Figure 2) for all subsequent plots. The shape and color represents the row and group of the element in the periodic table, respectively.
All values for $\Phi$ reported in this study, including those found in the literature, are listed in the Supplementary Information in Tables 1 and 2. Literature values for $\Phi$ were taken from the most recent experimental and computational studies available during the writing of this manuscript. Experimental values are explicitly annotated with a “expt” superscript, e.g., $\Phi_{\text{expt}}$, and unless otherwise indicated, all other values are computed values.
Experimental and computational validation

Figure 3: Plot of (a) experimentally measured $\Phi_{\text{expt}}$ vs the computed $\bar{\Phi}$ and (b) $\Phi_{\text{expt}}$ vs the computed $\Phi_{\text{hkl}}^{\text{lowest}}$. The single-factor linear regression line $y = x + c$ for both plots are indicated as dashed blue lines along with the $R^2$ value and standard error of the estimate (SEE). Values within the light blue (light yellow region) region are below (above) the SEE. (see refs 5,38,39).

Figures 3 shows a single-parameter $y = x + c$ least squares fit for $\bar{\Phi}$ vs $\Phi_{\text{expt}}$ and $\Phi_{\text{hkl}}^{\text{lowest}}$ vs $\Phi_{\text{poly}}^{\text{expt}}$ for the ground state polymorph of each element. We find that the PBE $\bar{\Phi}$ are on average 0.31 eV closer to $\Phi_{\text{poly}}^{\text{expt}}$ than the PBE $\Phi_{\text{hkl}}^{\text{lowest}}$. The linear fit for $\bar{\Phi}$ vs $\Phi_{\text{poly}}^{\text{expt}}$ also yielded a higher $R^2$ of 0.927 and a lower standard error of the estimate (SEE) of 0.246 eV compared to that of $\Phi_{\text{hkl}}^{\text{lowest}}$ vs $\Phi_{\text{poly}}^{\text{expt}}$ ($R^2 = 0.862$ eV and $\text{SEE} = 0.339$ eV). We find that $\bar{\Phi}$ systematically underestimates $\Phi_{\text{poly}}^{\text{expt}}$ by 0.18 eV on average. Notable outliers include $\Phi_{\text{poly}}^{\text{expt,As}}$ which is underestimated, and $\Phi_{\text{poly}}^{\text{expt,La}}$ and $\Phi_{\text{poly}}^{\text{expt,Se}}$ which are overestimated by more than the SEE. The largest error is for La, with an error of 0.86 eV. Although the Michaelson values of $\Phi_{\text{poly}}^{\text{expt,Re}}$ is 0.44 eV closer to our calculated value, the more recent value reported by Kawano is reported here.
Figure 4: Plot of computed facet-dependent $\Phi_{hkl}^{HT}$ in this work vs (a) experimental values, (b) literature PBE values, (c) literature LDA values and (d) RPBE values (this work).

Figure 4 compares the facet-dependent work functions obtained in this study to values obtained experimentally from single crystals and from other functionals, including LDA, PBE and RPBE. Again, we find that the experimental values in Figure 4(a) are on average 0.30 eV higher than the computed ones with an increasing deviation for work functions of
lower values. The (100), (310) and (311) facets of the early transition and refractory metals (Mo, W and Nb) have some of the lowest work functions, which also have the greatest deviation between the PBE and experimental values. For the same elements, facets with higher work functions have a smaller deviation ((110) and (210)). An exception to this is $\Phi_{\text{Ta}111}$ where computed and experimental values are in relative agreement despite having a value lower than other work functions. Meanwhile, the computed value of $\Phi_{\text{Graphite}0001}$ greatly overestimates the experimental value (see ref [5]). In general, the qualitative trends in work functions for different facets of each element are in agreement with the experimental trends, with the notable exception of Al. Eastmen and Mee [10] previously reported the order of $\Phi_{\text{Al}hkl}$ to be $\Phi_{\text{Al}111} > \Phi_{\text{Al}100} > \Phi_{\text{Al}110}$ which is typical of fcc metals while a later work by Grepstad et al. [41] reported that $\Phi_{\text{Al}100} > \Phi_{\text{Al}110} \sim \Phi_{\text{Al}111}$, which is consistent with our results (see Table 2 for values).

Our values for $\Phi_{\text{hkl}}$ are in excellent agreement with those calculated using PBE, LDA and RPBE (as shown in Figure 4(b), 4(c) and 4(d) respectively) with values of $R^2$ greater than 0.94 in all three cases. Unsurprisingly, there is smaller deviation when comparing our data to other GGA values (0.11 eV for PBE and 0.06 eV for rPBE) than to LDA values which are on average 0.38 eV higher. The major discrepancy between PBE and rPBE are for the (0001) surfaces of Y, Sc and Zn, with the PBE values being higher by 0.34 eV, 0.27 eV and 0.29 eV, respectively. Our values for $\Phi_{\text{Sc}2131}$ and $\Phi_{\text{Ba}210}$ are significantly lower when compared to PBE values obtained from the literature. Overall, the LDA-computed work functions are on average closer to the experimental values with a deviation of 0.11 eV (see Figure 9).
Work function of missing-row reconstructions

Figure 5: Plot of the (110) work function for an unreconstructed ($\Phi_{110}^{\text{unrecon}}$) and $1 \times 2$ missing-row reconstructed ($\Phi_{110}^{\text{recon}}$) surface for fcc materials. Data points corresponding to materials where reconstruction is thermodynamically favorable ($-2 \text{meV} \AA^{-2} < \gamma_{110}^{\text{recon}} - \gamma_{110}^{\text{unrecon}}$) are labelled in blue.

Figure 5 compares the work function for the (110) missing-row reconstructed surface of face-centered cubic metals ($\Phi_{110}^{\text{recon}}$) to the work function of the corresponding unreconstructed surface ($\Phi_{110}^{\text{unrecon}}$). As found in our previous work, only Pt, Au and Ir have significantly lower surface energies for the (110) missing-row reconstruction compared to the unreconstructed surface, which is in agreement with experimental observations. In general, we find that reconstruction leads to a relatively small increase in the work functions, though the three fcc metals exhibiting a thermodynamic driving force to reconstruct also have the largest work functions.
Discussion

Periodic trends in the work function

Figure 6: Plot of $\Phi$ versus (a) group number and (b) $\bar{\gamma}$ for transition metals, and (c) $\Phi$ versus group number for lanthanides. The left and right dashed lines in (a) corresponds to the parabolic peak when plotting group number against $\bar{\gamma}$ and $\Phi$ respectively.

Figure 6(a) plots $\Phi$ against the periodic group number for transition metals which demonstrates a parabolic behavior with the position of the parabolic maxima located at group 10 (Pt group). When plotting $\Phi$ against the weighted surface energy ($\bar{\gamma}$) in Figure 6(b), we observe a split between elements above and below group 8. A similar parabolic trend when plotting $\bar{\gamma}$ against group number results in a maxima observed at group 7 rather than 10. The position of these parabolic peaks are related to the increasing cohesive energy resulting
from the increasing number of half-filled \(d\)-orbitals as well as the width of the electronic \(s\), \(p\) and \(d\) bands. For a more in-depth discussion, the interested reader is referred to the references herein.\(^{20,12}\) We further note that cohesive energy and thus surface energy are strongly correlated with mechanical properties which suggests a cohesive energy origin to previously observed trends between \(\Phi\) and mechanical properties of transition metals.\(^{2,4,13}\)

To our knowledge, this work represents the first time DFT has been used to calculate the work functions of the lanthanides. Figure 6(c) plots \(\Phi\) against the group number. A gradual decrease is observed for the half-filled lanthanides from Ce to Sm with a sharp decrease for Eu. The latter half of the lanthanides has a relatively constant value from Gd to Tm with a sharp decrease for Yb. Afterwards, a sharp increase is observed for Lu. These trends are consistent with trends of the cohesive energies of the lanthanides (see Figure 10), which in turn may be attributed to the gradual filling of the \(4f\) orbitals. The two lowest \(\Phi\) are observed when the \(4f\) orbitals are half filled (Eu) and completely filled (Yb), and these two elements also have the lowest cohesive energy and melting point among the lanthanides. With the exception of Ce, the computed \(\Phi\) underestimates the experimental values of \(\Phi_{\text{expt}}\) for the lanthanides with a standard deviation of 0.136 eV from Ce to Yb (see Table 1).

**Discrepancies in the comparisons**

In general, our computed work functions are consistent with previous computational studies.\(^{11,21,23}\) It is well known that the GGA(PBE) functional underestimates the intermediate range van der Waals (vdW) forces and Fermi energy while having no long-range vdW forces, which generally leads to an underestimated work function. Although LDA generally yields values closer to experiment than GGA(PBE), this agreement is due to the various errors inherent in LDA that work in tandem to provide an error cancellation.\(^{23}\)

LDA/GGA are also known to have errors associated with overbinding/underbinding leading to smaller/larger cell volumes, lattice parameters and atomic distances, which can in turn influence surface properties. Larger atomic distances will decrease 2NN contributions to \(\gamma_{hkl}\)
and $\Phi_{hkl}$. This effect is especially prominent in the refractory metals Mo, Ta, Nb and W where the work function is shown to be dependent only on 1NN, but not 2NN (see Table 3). Without 2NN contributions, the work function will be severely underestimated in these metals when compared to experimental values, thus explaining the increasing deviation for refractory metals. Furthermore, the surface energy scales well with 2NN for Nb and Ta (which have the greatest deviation in $\Phi_{hkl}$ of the four refractory metals), indicating that underbinding in GGA(PBE) is more consequential for work function than it is for surface energy.

Experimental error is also a potential source of discrepancies in our comparisons. $\Phi^{As}$ is significantly higher while $\Phi^{La}$ and $\Phi^{Se}$ are significantly lower than that of their corresponding values for $\Phi^{expt}_{poly}$. Experimental values for these particular elements were taken from Michaelson where surface contamination could lead to inaccuracies of up to 0.5 eV in the reported measurements. $\Phi^{As}_{poly}$ is also known to range from 3.75 to 5.4 eV which our value for $\Phi^{As}$ lies between. Furthermore, the value of $\Phi^{Se}_{poly}$ was also determined using a photoelectric method which is known to yield erroneous values of work function for semiconductors. In addition, we opted to use the latest values available from the literature, which for $\Phi^{La}_{poly}$ came from Michaelson despite measurements from Rozkhov and Ye. being 0.54 eV closer to our DFT and previous linear muffin-tin orbital method values.

Although the calculated $\Phi^{\text{lowest hkl}}$ has previously been suggested as a good approximation of experimentally measured $\Phi^{\text{expt poly}}$, we have shown that the Wulff-area-weighted $\Phi$ provides a much closer estimate. This suggests that the eclipsing effect of lower work functions in PES signals of patchy surfaces may not be as prominent as once thought. Despite this, the values of $\Phi^{\text{expt poly}}$ are higher than $\Phi$ by an average value of 0.18 eV. Kawano has argued that the weighted work function is more likely to follow a Boltzmann distribution with a higher value than that provided by Equation. In this context, temperature becomes an important factor in determining the work function. However, it is unaccounted for in our calculations which are assumed to take place at 0K.
Effect of reconstruction on work function

In general, the work function of the reconstructed facets are slightly larger than that of the unreconstructed facets. This can be due to the exposure of the \{111\} facets during reconstruction which generally have larger values of $\Phi_{hkl}$ than the (110) facet due to the lack of Smoluchowski smoothing in the flat \{111\} surfaces. It is not coincidental that the disparity between $\Phi_{\text{recon}}^{110}$ and $\Phi_{\text{unrecon}}^{110}$ for metals with surface reconstruction (Au, Ir, and Pt) is larger than for other metals. Ho and Bohnen\textsuperscript{45} previously explained that missing row reconstruction was the result of competing forces that contributed to the kinetic energy (KE) contributions to surface energy. A missing-row introduces additional broken $d$-bonds for transition metals which increases KE. At the same time, a larger surface area is created from the newly exposed \{111\} facets which will better facilitate the spreading of $s$ and $p$ electrons. This increase in electron spreading will lower the surface KE and for some elements such as Au, Ir and Pt, is enough to overcome the KE increase. Recall that electron spreading will increase work function, a tenet of the Smoluchowski model (see later section), which explains the larger increase in $\Phi_{\text{recon}}^{110}$ for reconstructed surfaces relative to $\Phi_{\text{unrecon}}^{110}$.
Models for the work function

Smoluchowski rule

Figure 7: Plot of the normalized broken bonds vs Φ_{hkl}/Φ normalized by average work function for (a) fcc, (b) bcc and (c) hcp structures for elemental crystalline solids commonly observed in literature. A legend indicating the element of each corresponding marker is shown at the bottom right.

Figure 7 plots Φ_{hkl}/Φ normalized by the average work function for each element Φ as a function of the normalized broken bonds. All r values obtained from comparing Φ_{hkl} and γ_{hkl} to their respective normalized broken bonds and to each other are presented in Table 3. Strong negative correlations were observed for the anisotropic work functions of 23 metals: Au, Ni, Ag, Pd, Cu, Rh, Nb, Mo, Li, Ta, W, Y, Lu, Ru, Zr, La, Tc, Sc, Tm, Re, Eu, Er and Ho. Among these systems, similar trends have been confirmed in previous studies for Ni, Cu, Ag,
Mo and W, but not for Au and Pd. Ta and Nb are the only metals where a stronger correlation with surface energy (\( r_{Ta} = 0.96, r_{Nb} = 0.88 \)) is observed when modelling with 2NN and work function (\( r_{Ta} = -0.78, r_{Nb} = -0.86 \)) when modelling with 1NN. A moderate negative correlation is observed for 20 metals: Pt, Ir, Ca, Sr, Na, V, Cs, K, Cr, Mg, Ti, Zn, Pr, Hf, Tl, Co, Be, Nd, Sm and Os. The remaining 9 metals have weak negative correlations with Cd and Al having no negative correlation (\( r_{Cd} = 0.01, r_{Al} = 0.22 \)) at all.

Grepstad et al.\textsuperscript{41} has previously suggested that the Smoluchowski rule is valid only for systems with densely packed planes. It is well known that the c/a ratio of Cd is significantly larger than other hcp metals leading to sparsely packed planes along the (0001) direction\textsuperscript{46} which can explain why Cd does not follow the Smoluchowski rule. However, although Grepstad et al.\textsuperscript{41} was able to show that the computed values of \( \Phi_{Cu}^{211} \) and \( \Phi_{Al}^{hkl} \) are consistent with this explanation, our results clearly show that even for facets of Cu with MMI>1, bond breaking trends are still valid.

Alternatively, Fall et al.\textsuperscript{47} associates the anomalously low value of \( \Phi_{Al}^{111} \) with the presence of \( p \) orbitals parallel to its surface which are highly favored in electronically dense facets. By decreasing the valence electrons at the surface, the \( p \) orbitals perpendicular to the surface become favored over the parallel \( p \) orbitals. This leads to an increase in \( \Phi_{111}^{Al} \) that will eventually lead to an anisotropy consistent with the Smoluchowski rule. It is possible that the same phenomenon can explain the lack of correlation in other \( p \)-block systems such as Pb (\( r = -0.05 \)).
An improved model for the work function of metals

Figure 8: Plot for the calculated $\Phi$ against (a) Pauling electronegativity $\chi$ and metallic radius $R$, and (b) predictions from improved model for $\Phi = 1.55 + 3.76 \frac{\chi}{r_{atom}}$, where $r_{atom} = \sqrt[3]{V_{atom}}$ and $V_{atom}$ is the unit cell volume per atom.

The comprehensive data set presented in this work affords us the ability to develop more robust models for the work function of the elemental metals. It has previously been well-established by Michaelson\(^7\) and Miedema et al.\(^8\) that the work functions of metals have a positive linear relationship with the electronegativity $\chi$ of the metal. This may be explained by the fact that $\chi$ is a measure of how strongly electrons are bounded to the atom, and hence, the higher the $\chi$, the greater the energy needed to bring an electron from the bulk to the free vacuum ($\Phi$). Nevertheless, as can be seen from Figure 8(a), it is clear that $\chi$ only explains $R^2 = 85.5\%$ of the variation in $\Phi$ across the metals.

We carried an investigation of the relationship between $\Phi$ and various atomic properties. As can be seen from Figure 8(a), a strong, albeit non-linear, negative relationship is observed between $\Phi$ and the metallic radius $R$. From Gauss’ law, the potential inside an infinite charged plate is proportional to the bulk charge density times the square of the thickness of the plate, i.e., it scales charge per unit length of material. We postulate that the average
work function is proportional to the electron density per unit length, similar in spirit to the
traditional jellium work function model for metals.\textsuperscript{12} We performed a linear regression of $\bar{\Phi}$
against $\frac{\chi}{r_{\text{atom}}}$, where $\chi$ is related to the electron charge contributed per atom (in line with
previous models) and $r_{\text{atom}} = $ $3 \sqrt{V_{\text{atom}}}$, where $V_{\text{atom}}$ is the unit cell volume per atom. As
shown in Figure 8(b), this optimized model $\bar{\Phi} = 1.55 + 3.76 \frac{\chi}{r_{\text{atom}}}$ exhibits a much improved
prediction accuracy for $\bar{\Phi}$, with a very high $R^2$ of 0.933 and a small SEE of 0.226 eV.

Conclusion

In conclusion we have constructed the largest database of anisotropic work functions to
date. We have validated our database by comparing to both experimental and computa-
tional results from the literature and by confirming previously observed trends. In addition,
we have also developed a technique for estimating the work function of a polycrystalline
specimen using the Wulff shape and showed that it is a significantly more accurate estimate
for experimental polycrystalline values than the lowest anisotropic work function. Using
this large dataset, we have also extensively probed well-known empirical relationships for
the work function, such as the Smoluchowski rule, and developed a substantially-improved
prediction model for the work function of the metals from atomic properties such as the
electronegativity and metallic radius.

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Table 1: The values of $\Phi$ and $\Phi_{\text{hkl}}^{\text{lowest}}$ (along with its corresponding Miller index) from high-throughput calculations and the experimental $\Phi_{\text{poly}}^{\text{expt}}$ from the literature.

| Material | $\Phi$ (eV) | Surface | $\Phi_{\text{hkl}}^{\text{lowest}}$ (eV) | $\Phi_{\text{poly}}^{\text{expt}}$ (eV) |
|----------|-------------|---------|----------------------------------------|---------------------------------------|
| Li       | 2.85        | (2, 2, 1) | 2.55                                   | 2.93\textsuperscript{16}              |
| Al       | 4.04        | (3, 3, 1) | 3.88                                   | 4.25\textsuperscript{15}              |
| Be       | 4.87        | (1, 1, -2, 0) | 3.88                           | 4.98\textsuperscript{13}              |
| B        | 4.67        | (1, 0, -1, 1) | 4.64                               | 4.47\textsuperscript{15}              |
| C        | 4.24        | (0, 0, 1) | 4.22                                   | 4.65\textsuperscript{15}              |
| Na       | 2.55        | (2, 1, 1) | 2.08                                   | 2.75\textsuperscript{16}              |
| Mg       | 3.55        | (2, 0, -2, 1) | 3.35                              | 3.66\textsuperscript{16}              |
| Si       | 4.73        | (3, 1, 1) | 4.23                                   | 4.82\textsuperscript{16}              |
| K        | 2.31        | (2, 1, 0) | 1.95                                   | 2.29\textsuperscript{15}              |
| Ca       | 2.77        | (3, 1, 0) | 2.39                                   | 2.87\textsuperscript{16}              |
| Sc       | 3.12        | (2, 0, -2, 1) | 2.66                              | 3.50\textsuperscript{16}              |
| Ti       | 3.65        | (1, 1, -2, 0) | 3.03                              | 4.33\textsuperscript{16}              |
| V        | 4.11        | (3, 2, 2) | 3.49                                   | 4.30\textsuperscript{15}              |
| Cr       | 4.11        | (3, 1, 1) | 3.53                                   | 4.50\textsuperscript{15}              |
| Mn       | 4.32        | (1, 1, 0) | 4.20                                   | 4.10\textsuperscript{16}              |
| Co       | 4.52        | (1, 0, -1, 2) | 3.85                             | 5.00\textsuperscript{15}              |
| Zn       | 4.01        | (1, 0, -1, 1) | 3.91                             | 4.33\textsuperscript{15}              |
| Ga       | 4.08        | (2, 1, 0) | 3.87                                   | 4.20\textsuperscript{15}              |
| Element | Atomic Weight | Crystal Data | Density (g/cm³) | Reference |
|---------|---------------|--------------|----------------|-----------|
| Ge      | 4.39          | (3, 1, 0)    | 4.05           | 5.00      |
| As      | 4.40          | (2, 2, -4, 1)| 4.31           | 3.75      |
| Se      | 5.22          | (0, 0, 1)    | 5.07           | 5.90      |
| Rb      | 2.20          | (2, 1, 1)    | 1.91           | 2.16      |
| Sr      | 2.51          | (2, 1, 0)    | 2.26           | 2.59      |
| Y       | 2.99          | (2, 2, -4, 1)| 2.57           | 3.10      |
| Zr      | 3.57          | (1, 1, -2, 0)| 2.83           | 4.03      |
| Ru      | 4.75          | (1, 1, -2, 1)| 4.12           | 4.70      |
| Cd      | 3.68          | (0, 0, 0, 1)| 3.63           | 4.05      |
| In      | 3.70          | (1, 0, 1)    | 3.67           | 4.12      |
| Sn      | 4.07          | (3, 2, 1)    | 3.87           | 4.42      |
| Sb      | 4.30          | (2, 2, -4, 1)| 4.20           | 4.55      |
| Te      | 4.51          | (1, 0, -1, 1)| 4.29           | 4.95      |
| Cs      | 2.03          | (1, 1, 1)    | 1.59           | 1.95      |
| Ba      | 2.33          | (2, 1, 0)    | 1.90           | 2.53      |
| La      | 2.64          | (2, 2, -4, 1)| 2.42           | 3.50      |
| Hf      | 3.54          | (1, 1, -2, 0)| 2.98           | 3.90      |
| W       | 4.47          | (3, 1, 0)    | 3.71           | 4.55      |
| Re      | 4.55          | (1, 1, -2, 1)| 4.06           | 4.95      |
| Os      | 4.78          | (1, 1, -2, 1)| 4.44           | 4.84      |
| Ti      | 3.47          | (1, 0, -1, 1)| 3.13           | 3.84      |
| Pb      | 3.69          | (1, 1, 0)    | 3.60           | 4.25      |
| Bi      | 4.06          | (2, 2, -4, 1)| 3.93           | 4.22      |
| Th      | 3.12          | (1, 1, 1)    | 2.99           | 3.40      |
| Ce      | 2.98          | (2, 1, 0)    | 2.69           | 2.90      |
| Nd      | 2.86          | (2, 2, -4, 1)| 2.48           | 3.20      |
| Element | Experimental Coordinates | Experimental Atomic Radius | Calculated Atomic Radius |
|---------|--------------------------|---------------------------|--------------------------|
| Sm      | 2.74 (1, 1, -2, 1)       | 2.54                      | 2.70^13^k                |
| Eu      | 2.43 (1, 0, -1, 0)       | 2.08                      | 2.50^13^k                |
| Gd      | 2.96 (2, 1, -3, 0)       | 2.38                      | 3.10^13^k                |
| Tb      | 2.98 (2, -1, -1, 2)      | 2.53                      | 3.00^13^k                |
| Lu      | 3.03 (2, 1, -3, 0)       | 2.36                      | 3.30^13^k                |
| Fe      | 4.31 (3, 2, 2)           | 3.30                      | 4.36^5^k                 |
| Ni      | 4.98 (2, 1, 0)           | 4.41                      | 5.02^5^k                 |
| Cu      | 4.53 (3, 1, 0)           | 4.17                      | 4.55^5^k                 |
| Nb      | 4.15 (3, 1, 0)           | 3.31                      | 3.99^5^k                 |
| Mo      | 4.11 (3, 1, 0)           | 3.53                      | 4.39^5^k                 |
| Rh      | 4.99 (1, 1, 0)           | 4.27                      | 4.88^5^k                 |
| Pd      | 5.06 (1, 1, 0)           | 4.63                      | 5.33^5^k                 |
| Ag      | 4.22 (2, 1, 1)           | 3.97                      | 4.33^5^k                 |
| Ta      | 4.26 (3, 1, 0)           | 3.49                      | 4.25^5^k                 |
| Ir      | 5.31 (3, 2, 0)           | 4.75                      | 5.27^5^k                 |
| Pt      | 5.54 (1, 1, 0)           | 5.19                      | 5.41^5^k                 |
| Au      | 5.06 (2, 1, 0)           | 4.71                      | 5.20^5^k                 |
| Pr      | 2.88 (2, 2, -4, 1)       | 2.48                      | 2.96^39^k                |
| Dy      | 2.98 (2, -1, -1, 2)      | 2.55                      | 3.25^39^k                |
| Ho      | 2.91 (2, 1, -3, 1)       | 2.56                      | 3.22^39^k                |
| Er      | 2.92 (2, 1, -3, 0)       | 2.37                      | 3.25^39^k                |
| Tm      | 2.95 (2, 1, -3, 1)       | 2.54                      | 3.10^39^k                |

* See reference herein
Table 2: A comparison of the high-throughput values to experimental and computed values for materials from the literature.

| Material | Surface | Work function Φ (eV) | HT | GGA(RPBE) | GGA(PBE) | LDA | Experiment |
|----------|---------|----------------------|----|-----------|----------|-----|------------|
| Ru       | (0001)  |                      | 4.96 | 4.83      | 4.97<sup>12</sup> | 5.31<sup>12</sup> | 4.6<sup>12,*</sup> |
|          | (1010)  |                      | 4.7 | 4.79<sup>12</sup> | 5.13<sup>12</sup> |      |            |
|          | (1011)  |                      | 4.84 | 4.91<sup>12</sup> | 5.26<sup>12</sup> |      |            |
|          | (1012)  |                      | 4.45 | 4.5<sup>12</sup> | 4.85<sup>12</sup> |      |            |
|          | (1121)  |                      | 4.12 | 4.39<sup>12</sup> | 4.76<sup>12</sup> |      |            |
|          | (2130)  |                      | 4.28 | 4.47<sup>12</sup> | 4.86<sup>12</sup> |      |            |
| Pt       | (100)   |                      | 5.68 | 5.47      | 5.69<sup>22</sup> | 6.06<sup>21</sup> | 5.7<sup>17,*</sup> |
|          | (111)   |                      | 5.64 | 5.72      | 5.12<sup>23</sup> | 6.08<sup>21</sup> | 5.91<sup>17,*</sup> |
|          | (110)   |                      | 5.33 | 5.25      | 4.94<sup>23</sup> | 5.6<sup>21</sup> | 5.53<sup>17,*</sup> |
|          | (321)   |                      | 5.34 |           | 5.44<sup>11</sup> |      | 5.43<sup>5,*</sup> |
|          | (211)   |                      | 5.43 |           | 5.55<sup>11</sup> |      |            |
|          | (310)   |                      | 5.44 |           | 5.42<sup>11</sup> |      |            |
|          | (210)   |                      | 5.3  |           |                   |      | 5.18<sup>15,*</sup> |
|          | (311)   |                      | 5.47 |           |                   |      | 5.5<sup>15,*</sup> |
|          | (320)   |                      | 5.2  |           |                   |      | 5.2<sup>18,*</sup> |
|          | (331)   |                      | 5.24 |           |                   |      | 5.12<sup>5,*</sup> |
| Ni       | (100)   |                      | 4.95 | 4.71      | 4.9<sup>21</sup> | 5.33<sup>21</sup> | 5.1<sup>17,*</sup> |
|          | (111)   |                      | 5.1  | 4.89      | 5.09<sup>21</sup> | 5.5<sup>21</sup> | 5.36<sup>17,*</sup> |
|          | (110)   |                      | 4.43 | 4.26      | 4.49<sup>21</sup> | 4.95<sup>21</sup> | 4.53<sup>17,*</sup> |
| Nb       | (100)   |                      | 3.43 | 3.42      | 3.55<sup>11</sup> | 3.86<sup>21</sup> | 3.97<sup>17,*</sup> |
|          | (110)   |                      | 4.46 | 4.43      | 4.49<sup>11</sup> | 4.77<sup>21</sup> | 4.69<sup>17,*</sup> |
|          | (111)   |                      | 3.63 |           | 3.77<sup>11</sup> | 4.15<sup>21</sup> | 4.08<sup>17,*</sup> |
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| (210) | 3.86 |     | 3.97 |     |
| (331) | 4.08 |     | 4.15 |     |
| (311) | 3.4  |     | 3.64 |     |
| (310) | 3.31 |     | 4.18 |     |
| (211) | 3.77 |     | 4.45 |     |
| Y (0001) | 3.18 |     | 3.18 |     |
| (10\overline{1}0) | 3.23 |     | 3.31 |     |
| (2\overline{1}30) | 2.76 |     | 3.0  |     |
| Pd (111) | 5.21 | 4.94 | 5.32 | 5.07 |
| (110) | 4.63 | 4.56 | 4.95 | 4.86 |
| (100) | 5.13 |     | 5.12 |     |
| (321) | 4.86 |     | 4.89 |     |
| (211) | 4.92 |     | 4.99 |     |
| (310) | 4.93 |     | 4.86 |     |
| Rh (100) | 5.01 | 4.9  | 5.04 | 5.3  |
| (111) | 5.15 | 4.77 | 5.0  | 5.46 |
| (110) | 4.27 | 4.25 | 4.53 | 4.86 |
| (321) | 4.57 |     | 4.65 |     |
| (211) | 4.75 |     | 4.87 |     |
| (310) | 4.62 |     | 4.74 |     |
| Tc (0001) | 4.63 | 4.47 | 4.69 | 4.95 |
| (10\overline{1}0) | 4.22 |     | 4.5  |     |
| (10\overline{1}1) | 3.76 |     | 4.7  |     |
| (10\overline{1}2) | 4.35 |     | 4.31 |     |
| (11\overline{2}1) | 3.8  |     | 4.09 |     |
| (2\overline{1}12) | 4.19 |     | 4.28 |     |

26
| Plane   | Ta   | Fe   | Hf   | Mo   | W    |
|---------|------|------|------|------|------|
| (2130)  | 4.05 | 5.28 | 4.58 | 4.44 | 4.65 |
| (100)   | 3.71 | 4.79 | 4.36 | 4.09 | 4.44 |
| (110)   | 4.64 | 3.96 | 4.86 | 4.51 | 4.76 |
| (111)   | 3.71 | 4.25 | 3.94 | 3.76 | 4.24 |
| (210)   | 4.04 | 3.96 | 4.34 | 4.04 | 4.22 |
| (331)   | 4.21 | 4.62 | 4.25 | 4.15 | 4.39 |
| (311)   | 3.5  | 4.1  | 4.1  | 3.61 | 4.25 |
| (211)   | 3.92 | 4.45 | 4.34 | 3.81 | 4.36 |
| (110)   | 4.64 | 3.96 | 4.34 | 3.81 | 4.22 |
| (111)   | 3.71 | 4.25 | 3.94 | 3.61 | 4.39 |
| (210)   | 4.04 | 3.96 | 4.34 | 3.81 | 4.22 |
| (331)   | 4.39 | 4.46 | 4.38 | 4.39 | 4.46 |
|     | (311) | 3.82 | 4.11 | 4.465 |
|-----|-------|------|------|-------|
|     | (211) | 4.29 |      | 4.766 |
|     | (321) | 4.13 |      | 4.499 |
|     | (310) | 3.71 |      | 4.329 |
| V   | (100) | 3.59 | 3.56 | 3.746 | 4.071 |
|     | (110) | 4.67 | 4.66 | 4.746 | 5.026 |
|     | (111) | 3.6  |      | 3.876 | 4.236 |
| Sc  | (0001) | 3.39 | 3.66 | 3.336 | 3.566 |
|     | (10\overline{1}0) | 3.35 |      | 3.566 | 3.776 |
|     | (21\overline{3}0) | 3.09 |      | 3.186 | 3.356 |
|     | (21\overline{3}1) | 2.84 |      | 3.426 | 3.396 |
| Os  | (0001) | 5.27 | 5.1  | 5.326 | 5.646 |
|     | (10\overline{1}0) | 4.44 |      | 5.176 | 5.456 |
|     | (10\overline{1}1) | 4.77 |      | 5.236 | 5.536 |
|     | (10\overline{1}2) | 4.78 |      | 4.856 | 5.156 |
|     | (11\overline{2}1) | 4.44 |      | 4.676 | 4.986 |
|     | (21\overline{1}2) | 4.93 |      | 4.916 | 5.226 |
|     | (21\overline{3}0) | 4.68 |      | 4.876 | 5.266 |
| Zn  | (0001) | 3.92 | 4.21 | 4.086 | 4.446 |
|     | (10\overline{1}0) | 4.08 |      | 4.336 | 4.766 |
|     | (21\overline{3}0) | 3.92 |      | 4.036 | 4.366 |
|     | (21\overline{3}1) | 3.93 |      | 4.136 | 4.436 |
| Co  | (0001) | 4.86 | 4.75 | 4.926 | 5.396 |
|     | (10\overline{1}0) | 4.55 |      | 4.766 | 5.146 |
|     | (21\overline{3}0) | 4.37 |      | 4.396 | 4.816 |
|     | (21\overline{3}1) | 4.34 |      | 4.336 | 4.766 |
|    | (0001) | 4.77  | 4.85  | 4.88 | 5.17 | 5.15 |
|----|--------|-------|-------|------|------|------|
| Ag | (100)  | 4.21  | 3.96  | 4.26 | 4.68 | 4.36 |
|    | (111)  | 4.34  | 4.21  | 4.49 | 4.84 | 4.53 |
|    | (110)  | 4.05  | 4.04  | 4.16 | 4.55 | 4.19 |
|    | (321)  | 4.01  |       |      |      |      |
|    | (211)  | 3.97  |       |      |      |      |
|    | (310)  | 4.06  | 4.08  |      |      |      |
| Re | (0001) | 4.77  | 4.85  | 4.88 | 5.17 | 5.15 |
|    | (1010) | 4.58  |       |      |      |      |
|    | (1011) | 4.67  |       |      |      |      |
|    | (1012) | 4.42  |       |      |      |      |
|    | (1121) | 4.06  |       |      |      |      |
|    | (2122) | 4.38  |       |      |      |      |
|    | (2130) | 4.06  |       |      |      |      |
| Ir | (100)  | 5.54  | 5.42  | 5.55 | 5.91 | 5.96 |
|    | (111)  | 5.42  | 5.18  | 5.5  | 5.86 | 5.78 |
|    | (110)  | 5.01  | 4.83  | 4.96 | 5.31 | 5.42 |
|    | (321)  | 5.0   |       |      |      |      |
|    | (211)  | 5.21  |       |      |      |      |
|    | (310)  | 5.04  |       |      |      |      |
|    | (210)  | 4.94  |       |      |      |      |
|    | (331)  | 4.87  |       |      |      |      |
| Cd | (0001) | 3.63  | 3.76  | 3.81 | 4.21 |     |
|    | (1010) | 3.72  |       |      |      |      |
|    | (2130) | 3.76  |       |      |      |      |
| Au | (100)  | 5.0   | 4.9   | 5.07 | 5.49 | 5.22 |
|    | (111)  | 5.16  | 4.98  | 5.12 | 5.49 | 5.33 |
|     |        |        |        |        |        |
|-----|--------|--------|--------|--------|--------|
|     | (110)  | 4.93   | 4.88   | 4.94   | 5.36   |
|     | (321)  | 4.89   |        | 4.98   |        |
|     | (211)  | 4.96   |        | 5.01   |        |
|     | (310)  | 4.93   |        | 4.92   |        |
|     | (210)  | 4.71   |        |        | 4.96   |
|     | (311)  | 4.94   |        |        | 5.16   |
| Cu  | (111)  | 4.71   | 4.74   | 4.88   | 5.2    |
|     | (110)  | 4.2    | 4.32   | 4.38   | 4.68   |
|     | (100)  | 4.47   |        | 4.42   | 4.79   |
|     | (321)  | 4.22   |        | 4.35   |        |
|     | (211)  | 4.22   |        | 4.45   |        |
|     | (310)  | 4.17   |        | 4.26   |        |
|     | (210)  | 4.18   |        |        | 4.37   |
|     | (311)  | 4.28   |        |        | 4.42   |
| Cr  | (110)  | 4.7    | 4.74   | 4.83   | 5.13   |
|     | (111)  | 4.04   |        | 4.09   | 4.39   |
|     | (100)  | 4.08   |        | 4.02   | 4.36   |
| Zr  | (0001) | 4.16   | 3.98   | 4.18   | 4.46   |
|     | (1010) | 3.52   |        | 3.84   | 4.16   |
|     | (2130) | 3.11   |        | 3.09   | 3.39   |
| Li  | (100)  | 2.96   |        | 2.99   | 3.13   |
|     | (110)  | 3.18   |        | 3.22   | 3.36   |
|     | (111)  | 2.6    |        | 2.75   | 2.92   |
|     | (210)  | 2.99   |        | 2.97   |        |
|     | (331)  | 2.94   |        | 3.01   |        |
|     | (311)  | 2.91   |        | 3.01   |        |
|     | (100) | (110) | (111) | (210) | (331) | (311) | K     | (100) | (110) | (111) | (210) | (331) | (311) | Rb    | (100) | (110) | (111) | (210) | (331) | (311) | Cs    | (100) | (110) | (111) | (210) | (311) | Cs    | (100) | (110) | (111) | (210) | (311) | Ca    | (100) | (110) | (111) | (210) | (311) | Ca    |
|-----|------|------|------|------|------|------|-------|------|------|------|------|------|------|-------|------|------|------|------|------|------|-------|------|------|------|------|------|-------|------|------|------|------|------|-------|------|------|------|------|------|-------|
| Na  | 2.53 | 2.71 | 2.5   | 2.65 | 2.49 | 2.45 | 2.53  | 2.15 | 2.37 | 2.13 | 1.95 | 2.29 | 2.15 | 2.1   | 2.23  | 2.05 | 1.94 | 2.18 | 2.08 | 2.18 | 1.97  | 2.04  | 1.59 | 1.77 | 1.65 | 2.56 | 2.74  | 2.94  | 2.76 | 2.81 | 2.94 | 3.01 |
|     | Sr  |     | Ba  |     |     |
|-----|-----|-----|-----|-----|-----|
|     |     |     |     |     |     |
|     |     |     |     |     |     |
| (321) | 2.52 |     | 2.78 |     |     |
| (211) | 2.55 |     | 2.83 |     |     |
| (310) | 2.39 |     | 2.71 |     |     |
| Sr   |     |     |     |     |     |
| (100) | 2.47 |     | 2.47 |     | 2.56 |
| (110) | 2.49 |     | 2.54 |     | 2.66 |
| (111) | 2.53 |     | 2.57 |     | 2.67 |
| (321) | 2.33 |     | 2.51 |     |     |
| (211) | 2.37 |     | 2.45 |     |     |
| (310) | 2.31 |     | 2.47 |     |     |
| Ba   |     |     |     |     |     |
| (100) | 2.28 |     | 2.31 |     | 2.54 |
| (110) | 2.35 |     | 2.38 |     | 2.58 |
| (111) | 2.24 |     | 2.29 |     | 2.58 |
| (210) | 1.9  |     | 2.35 |     |     |
| (331) | 2.35 |     | 2.34 |     |     |
| (311) | 2.21 |     | 2.33 |     |     |
| Be   |     |     |     |     |     |
| (0001) | 5.32 |     | 5.29 |     | 5.45 |
| (10\overline{1}0) | 4.48 |     | 4.52 |     | 4.7  |
| (10\overline{1}1) | 4.95 |     | 5.03 |     | 5.23 |
| (10\overline{1}2) | 4.71 |     | 4.81 |     | 5.04 |
| (11\overline{2}1) | 4.35 |     | 4.58 |     | 4.82 |
| (2\overline{1}12) | 4.79 |     | 4.81 |     | 4.94 |
| (21\overline{3}0) | 4.14 |     | 4.17 |     | 4.38 |
| Mg   |     |     |     |     |     |
| (0001) | 3.61 |     | 3.76 |     | 3.89 |
| (10\overline{1}0) | 3.39 |     | 3.64 |     | 3.76 |
| (10\overline{1}1) | 3.64 |     | 3.7  |     | 3.88 |
| (10\overline{1}2) | 3.58 |     | 3.63 |     | 3.74 |
|       | 3.4 | 3.56 | 3.68 |
|-------|-----|------|------|
|       | 3.62| 3.5  | 3.56 |
|       | 3.35| 3.49 | 3.72 |
| Al    | 4.0 | 4.2  | 4.97 |
|       | 4.18| 4.27 | 4.31 |
|       | 4.0 | 3.96 | 4.08 |
| Ga    | 3.9 | 4.01 | 4.33 |
|       | 4.19| 4.22 | 4.56 |
|       | 4.35| 4.61 | 4.96 |
| In    | 3.74| 3.88 | 4.22 |
|       | 3.81| 3.79 | 4.12 |
|       | 3.81| 3.92 | 4.3  |
| Tl    | 3.5 | 3.56 | 3.98 |
|       | 3.42| 3.56 | 3.98 |
|       | 3.34| 3.52 | 3.94 |
|       | 3.27| 3.52 | 3.95 |
| C(P6₃/mmc) | 5.02 | 4.57 | 4.76 |
|       | 4.61 | 4.36 | 4.54 |
|       | 5.17 | 5.63 | 5.63 |
|       | 5.22 | 5.3  | 5.56 |
| Si    | 4.64 | 4.67 | 4.81 |
|       | 4.79 | 4.56 | 4.71 |
|       | 4.97 | 5.0  | 5.23 |
| Ge    | 4.52 | 4.38 | 4.55 |
|       | 4.41 | 4.48 | 4.72 |
|       | 4.51 | 4.74 | 4.99 |
|   |  (111) |  (100) |  (110) |  (1010) |  (1120) |  (0001) |  (1120) |  (0001) |  (1010) |  (2130) |  (2131) |
|---|--------|--------|--------|---------|---------|---------|---------|---------|---------|---------|---------|
| Sn |  4.21  |  4.38  |  4.5   |  4.29   |  4.24   |  4.23   |  4.29   |  4.24   |  3.51   |  3.21   |  3.26   |
| Pb |  3.68  |  3.71  |  3.6   |  4.29   |  4.24   |  4.44   |  3.98   |  4.44   |  3.51   |  3.21   |  3.26   |
| As |  4.44  |  3.71  |  3.6   |  4.29   |  4.24   |  4.23   |  4.29   |  4.24   |  3.51   |  3.21   |  3.26   |
| Sb |  4.23  |  4.38  |  4.5   |  4.39   |  4.39   |  3.98   |  4.14   |  4.39   |  3.51   |  3.21   |  3.26   |
| Bi |  4.44  |  3.71  |  3.6   |  4.44   |  4.44   |  4.23   |  4.44   |  4.44   |  3.51   |  3.21   |  3.26   |
| Ti |  4.38  |  3.71  |  3.6   |  4.44   |  4.44   |  4.23   |  4.44   |  4.44   |  3.51   |  3.21   |  3.26   |

* See reference herein
Figure 9: Plot of computed facet-dependent $\Phi_{hkl}$ using LDA from the literature vs experimental values.

Figure 10: Plot of the cohesive energy ($E_{coh}$) versus the group number for lanthanides.
Table 3: The R values for $\gamma_{hkl}$ and $\Phi_{hkl}$ as a function of normalized broken bonds per surface area (BB) and $\Phi_{hkl}$ as a function of $\gamma_{hkl}$.

| Material | spacegroup | $\gamma_{hkl}$ vs BB | $\Phi_{hkl}$ vs BB | $\Phi_{hkl}$ vs $\gamma_{hkl}$ |
|----------|------------|----------------------|---------------------|-------------------------------|
| Cu       | $Fm - 3m$  | 0.99                 | -0.93               | -0.93                         |
| Er       | $P6_3/mmc$ | -0.06                | 0.84                | 0.24                          | -0.90 | -0.77         |
| La       | $P6_3/mmc$ | 0.53                 | 0.98                | -0.72                         | -0.89 | -0.73         |
| Re       | $P6_3/mmc$ | 0.57                 | 0.79                | 0.02                          | -0.89 | -0.28         |
| Ag       | $Fm - 3m$  | 0.96                 | -0.89               | -0.89                         | -0.88 |                 |
| Ni       | $Fm - 3m$  | 1.00                 | -0.89               | -0.89                         | -0.85 |                 |
| Ru       | $P6_3/mmc$ | -0.40                | 0.95                | 0.64                          | -0.88 | -0.91         |
| Ho       | $P6_3/mmc$ | 0.35                 | 0.75                | -0.24                         | -0.88 | -0.70         |
| Zr       | $P6_3/mmc$ | 0.52                 | 0.73                | -0.15                         | -0.87 | -0.48         |
| Nb       | $Im - 3m$  | 0.47                 | 0.88                | -0.86                         | -0.43 | -0.72         |
| Au       | $Fm - 3m$  | 0.92                 | -0.86               | -0.86                         | -0.74 |                 |
| Eu       | $P6_3/mmc$ | -0.02                | 0.77                | 0.20                          | -0.84 | -0.74         |
| Tc       | $P6_3/mmc$ | 0.80                 | 0.92                | -0.18                         | -0.84 | -0.42         |
| Y        | $P6_3/mmc$ | -0.07                | 0.78                | 0.23                          | -0.83 | -0.61         |
| Lu       | $P6_3/mmc$ | -0.01                | 0.70                | 0.05                          | -0.82 | -0.70         |
| Rh       | $Fm - 3m$  | 0.97                 | -0.82               | -0.82                         | -0.68 |                 |
| W        | $Im - 3m$  | 0.94                 | -0.00               | -0.81                         | -0.52 | -0.65         |
| Tm       | $P6_3/mmc$ | 0.34                 | 0.69                | -0.15                         | -0.80 | -0.47         |
| Li       | $Im - 3m$  | -0.38                | 0.77                | -0.34                         | -0.79 | -0.43         |
| Sc       | $P6_3/mmc$ | 0.67                 | 0.67                | -0.23                         | -0.79 | -0.66         |
|   |   |   |   |   |
|---|---|---|---|---|
| Ta | Im - 3m | 0.19 | 0.96 | -0.78 | -0.51 | -0.60 |
| Mo | Im - 3m | 0.47 | 0.21 | -0.78 | -0.53 | -0.55 |
| Pd | Fm - 3m | 0.95 |   | -0.78 |   | -0.71 |
| Cr | Im - 3m | 0.87 | 0.17 | -0.61 | -0.74 | -0.38 |
| Ti | P6₃/mmc | 0.67 | 0.21 | 0.34 | -0.74 | 0.42 |
| V  | Im - 3m | -0.27 | 0.89 | -0.74 | -0.67 | -0.40 |
| Cs | Im - 3m | 0.87 | 0.89 | -0.73 | -0.65 | -0.83 |
| Be | P6₃/mmc | 0.45 | 0.88 | 0.43 | -0.73 | -0.15 |
| Hf | P6₃/mmc | 0.80 | 0.82 | 0.11 | -0.73 | 0.07 |
| Ir | Fm - 3m | 0.93 |   | -0.72 |   | -0.50 |
| Co | P6₃/mmc | 0.57 | 0.95 | -0.68 | -0.71 | -0.47 |
| Pt | Fm - 3m | 0.88 |   | -0.71 |   | -0.51 |
| Ca | Fm - 3m | 0.86 |   | -0.70 |   | -0.41 |
| Nd | P6₃/mmc | 0.07 | 0.94 | 0.22 | -0.70 | -0.23 |
| Pr | P6₃/mmc | 0.03 | 0.95 | 0.28 | -0.65 | -0.15 |
| Tl | P6₃/mmc | 0.79 | 0.83 | -0.19 | -0.65 | -0.57 |
| Mg | P6₃/mmc | 0.30 | 0.82 | -0.64 | -0.26 | -0.23 |
| Na | Im - 3m | 0.38 | 0.97 | -0.49 | -0.62 | -0.62 |
| Os | P6₃/mmc | -0.10 | 0.94 | 0.24 | -0.60 | -0.30 |
| Sm | P6₃/mmc | 0.10 | 0.70 | -0.32 | -0.58 | 0.09 |
| Sr | Fm - 3m | 0.85 |   | -0.56 |   | -0.46 |
| K  | Im - 3m | 0.22 | 0.95 | -0.55 | -0.44 | -0.38 |
| Zn | P6₃/mmc | 0.59 | 0.48 | -0.51 | 0.44 | -0.20 |
| Ce | Fm - 3m | 0.96 |   | -0.49 |   | -0.49 |
| Fe | Im - 3m | 0.40 | 0.23 | -0.44 | -0.48 | -0.49 |
| Pm | P6₃/mmc | 0.46 | 0.88 | -0.40 | -0.44 | -0.21 |
| Element | Structure | Parameter 1 | Parameter 2 | Parameter 3 | Parameter 4 | Parameter 5 |
|---------|-----------|-------------|-------------|-------------|-------------|-------------|
| Yb      | Fm–3m     | 0.76        | –           | -0.44       | –           | -0.23       |
| Rb      | Im–3m     | 0.22        | 0.94        | -0.35       | -0.39       | -0.45       |
| Ba      | Im–3m     | -0.01       | 0.98        | -0.20       | -0.04       | 0.01        |
| Pb      | Fm–3m     | 0.94        | –           | -0.05       | –           | 0.02        |
| Cd      | P63/mmc   | 0.53        | 0.51        | 0.01        | 0.41        | 0.24        |
| Al      | Fm–3m     | 0.97        | –           | 0.22        | –           | 0.09        |

* See reference herein

**Declarations of interest:**

None
References

(1) Heimel, G.; Romaner, L.; Bredas, J. L.; Zojer, E. *Physical Review Letters* **2006**, *96*, 2–5.

(2) Lu, H.; Hua, G.; Li, D. *Applied Physics Letters* **2013**, *103*, 2619021–2619024.

(3) Lu, H.; Liu, Z.; Yan, X.; Li, D.; Parent, L.; Tian, H. *Nature Publishing Group* **2016**, 1–11.

(4) Hua, G.; Li, D. *Phys. Chem. Chem. Phys.* **2016**, *18*, 4753–4759.

(5) Kawano, H. *Progress in Surface Science* **2008**, *83*, 1–165.

(6) Li, T.; Rickman, B. L.; Schroeder, W. A. *Physical Review Special Topics - Accelerators and Beams* **2015**, *18*, 1–11.

(7) Michaelson, H. B. *IBM Journal of Research and Development* **1978**, *22*, 72–80.

(8) Miedema, A. R.; De Boer, F. R.; De Chatel, P. F. *Journal of Physics F: Metal Physics* **1973**, *3*, 1558–1576.

(9) Smoluchowski, R. *Physical Review* **1941**, *60*, 661–674.

(10) Sokolov, J.; Jona, F. *Solid State Communications* **1984**, *49*, 307–312.

(11) Wang, J.; Wang, S. Q. *Surface Science* **2014**, *630*, 216–224.

(12) Ji, D. P.; Zhu, Q.; Wang, S. Q. *Surface Science* **2016**, *651*, 137–146.

(13) Brodie, I. *Physical Review B* **1995**, *51*, 13660–13668.

(14) Wojciechowski, K. F.; Borna, M. *Vacuum* **1997**, *48*, 257–259.

(15) Fazylov, F. *Philosophical Magazine* **2014**, *94*, 1956–1966.

(16) Michaelson, H. B. *Journal of Applied Physics* **1977**, *48*, 4729–4733.
(17) Derry, G. N.; Kern, M. E.; Worth, E. H. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 2015, 33, 060801.

(18) Helander, M. G.; Greiner, M. T.; Wang, Z. B.; Lu, Z. H. *Applied Surf* 2010, 256, 2602–2605.

(19) Singh-Miller, N. E.; Marzari, N. *Physical Review B - Condensed Matter and Materials Physics* 2009, 80.

(20) Methfessel, M.; Hennig, D.; Scheffler, M. *Physical Review B* 1992, 46, 4816–4829.

(21) Waele, S. D.; Lejaeghere, K.; Sluydts, M.; Cottenier, S. *Physical Review B* 2016, 94, 1–13.

(22) Skriver, H. L.; Rosengaard, N. M. *Physical Review B* 1992, 46, 7157–7168.

(23) Patra, A.; Bates, J.; Sun, J.; Perdew, J. P. *Arxiv* 2017, 1–17.

(24) Durakiewicz, T.; Arko, A.; Joyce, J. J.; Moore, D. P.; Halas, S. *Physical Review B - Condensed Matter and Materials Physics* 2001, 64, 1–8.

(25) Aldén, M.; Johansson, B.; Skriver, H. L. *Physical Review B* 1995, 51, 5386–5396.

(26) Stekolnikov, a. A.; Furthmuller, J.; Bechstedt, F.; Furthmüller, J.; Bechstedt, F. *Physical Review B* 2002, 65, 115318.

(27) Delchar, T. A. *Modern Techniques of Surface Science*, 3rd ed.; Cambridge University Press: Cambridge, 1986; p 464.

(28) Tran, R.; Xu, Z.; Radhakrishnan, B.; Winston, D.; Sun, W.; Persson, K. A.; Ong, S. P. *Scientific Data* 2016, 3, 1–13.

(29) Frank, F. C.; Kasper, J. S. *Acta Crystallographica* 1958, 11, 184–190.

(30) Sun, W.; Ceder, G. *Surface Science* 2013, 617, 53–59.
(31) Montoya, J. H.; Persson, K. A. npj Computational Materials 2017, 3, 14.

(32) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Computational Materials Science 2013, 68, 314–319.

(33) Jain, A.; Ong, S. P.; Chen, W.; Medasani, B.; Qu, X.; Kocher, M.; Brafman, M.; Petretto, G.; Rignanese, G. M.; Hautier, G.; Gunter, D.; Persson, K. A. Concurrency Computation 2015, 27, 5037–5059.

(34) Mathew, K. et al. Computational Materials Science 2017, 139, 140–152.

(35) Winston, D.; Montoya, J. H.; Persson, K. A. 11th Gateway Computing Environments Conference 2016, doi:10.6084/m9.figshare.4491623.v2.

(36) Crystallium. http://crystallium.materialsvirtuallab.org/, 2016.

(37) The Materials Project. https://materialsproject.org/, 2015.

(38) Haynes, W. M.; Lide, D. R.; Bruno, T. J. CRC handbook of chemistry and physics, 97th ed.; CRC Press: Boca Raton, Fl, 2017.

(39) Rozkhov, O. K. K.; Ye., E. Rare Earth Metals and Alloys; Nauka: Moscow, 1971.

(40) Eastmen, R. M.; Mee, C. H. B. Journal of Physics F: Metal Physics 1973, 3, 1738–1745.

(41) Grepstad, J.; Gartland, P.; Slagsvold, B. Surface Science 1976, 57, 348–362.

(42) Michaelides, A.; Scheffler, M. . . . of Surface and Interface Science 2010, 1–40.

(43) Rahemi, R.; Li, D. Scripta Materialia 2015, 99, 41–44.

(44) Kiejna, A.; Wojciechowski, K. F.; Zebrowksi, J. Journal of Physics F: Metal Physics 1979, 9, 1361.

(45) Ho, K. M.; Bohnen, K. P. Physical Review Letters 1987, 59, 1833–1836.
(46) Gaston, N.; Andrae, D.; Paulus, B.; Wedig, U.; Jansen, M. *Phys. Chem. Chem. Phys.* 2010, *12*, 681–687.

(47) Fall, C. J.; Binggeli, N.; Baldereschi, A. *Physical Review B* 1998, *58*, R7544–R7547.

(48) Lang, N. D.; Kohn, W. *Physical Review B* 1971, *3*, 1215–1223.