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Anisotropy of hardness from first principles: The cases of ReB_2 and OsB_2

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The expression for hardness related to crystal orientation is proposed. Because all quantities in the equation are inherently coupled to the atomistic structure of matter, the anisotropy of hardness can be determined by first-principles methods. The calculations show the highest hardness is in ReB_2 and OsB_2 single crystals along the *c* axis, 50.3 and 45.5 GPa, respectively, and are in agreement with measurements. The presented model implies that hardness predominantly reflects the strength of bonds transversely oriented to the direction of indentation.

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I. INTRODUCTION

Hard materials are of considerable fundamental interest and practical importance due to their numerous technological applications. Unfortunately, almost all superhard materials (diamond, cubic BN, etc.) are expensive because they either occur naturally in limited supplies or have to be manufactured synthetically under high pressure. Therefore, the development of a new class of hard materials could be very useful. Simultaneously, quantitative material models need to be built that will compute macroscopic properties on the basis of the atomic and electronic structures of a material.

Several models expressing hardness by means of quantities inherently coupled to the atomistic structure of matter were presented,[1–4] however, in all methods anisotropic effects of hardness were neglected. In principle, hardness should be related to crystal orientation, therefore, for the description of hardness anisotropy we need a more general method. In this work the expression for hardness related to crystal orientation is presented and applied to new hard materials.

A substantial difference between the highest and lowest measured hardness was recently reported for ultraincompressible, superhard ReB_2.[5] The highest level of hardness was detected along the *c* axis and was attributed to the anisotropic structure of ReB_2. In addition, calculations by Zhang *et al.*[6] show a very low compressibility along the *c* axis of ReB_2. The hardness highly dependent on crystallographic orientation was observed also in OsB_2.[7] Moreover, Chung *et al.*[7] discovered that the *c* axis of OsB_2 is even less compressible than that of the comparable linear compressibility of diamond.[8] Hebbache *et al.*[9] and Chiodo *et al.*[10] also found that OsB_2 is extremely hard, in particular along the *c* axis.

The hardness of ReB_2 was directly calculated by Zhou *et al.*[11] using the first-principles method proposed by Šimůnek *et al.*[1] The calculated average, "isotropic" value of hardness $H=46.0$ GPa falls right within the range of the experimentally measured hardness 30–55 GPa.[5] The agreement found between the calculations and experiments indicates that the concept of bond strengths[1] captures the main interaction in this class of materials and can be utilized for the description of hardness anisotropy.

To find the equation expressing orientation dependence of hardness, the methods[1–4] based on bond strengths of the nearest neighbors have to be principally modified in two aspects. As the anisotropy of hardness is intrinsically determined by the crystal structure, the geometric or arithmetic averages over atomic or structural quantities have to be omitted. Therefore, all definitions of bond strengths in Refs. 1–4 have to be changed, and second, the directions of interatomic bonds have to be taken into account.

At first, compared to the definitions in Refs. 1–4, we redefine the bond strength $s(ij)$ between atoms i and j as

$$s(ij)=\frac{\sqrt{e_i e_j}}{n_i n_j d_{ij}} e^{-\sigma f_{ij}}, \tag{1}$$

$$f_{ij}=\left(\frac{e_i-e_j}{e_i+e_j}\right)^2, \tag{2}$$

where n_i and n_j are coordination numbers of atoms i and j, respectively, and d_{ij} is the interatomic distance of atoms i and j. The reference potential is defined as $e_i=Z_i/R_i$, with Z_i being the valence electron number of the atom i and R_i the radius of atom i within which the atom is electrically neutral. The definition of R_i by means of the crystal valence charge density with parameter $\sigma=4.0$ makes it possible to calculate hardness by the *ab initio* approach.[1] For the purpose of the determination R_i, the standard total-energy calculation within density functional theory can be applied. However, instead of the laborious first-principles calculations for R_i, Eqs. (1) and (2) using atomic radii with $\sigma=2.8$ can be applied.[2]

The hardness H of the ideal single crystal is proportional to the number of bonds $b(ij)$ between atoms i and j and their bond strength $s(ij)$ in the volume Ω of the unit cell of a crystal.[1,2] Therefore, for multibond complex crystals having different $s(ij), s(kl), \ldots, s(mn)$ bond strengths, the expression, still neglecting anisotropy of hardness, has the form

$$H=\frac{C}{\Omega}[b(ij)s(ij)+b(kl)s(kl)+\cdots+b(mn)s(mn)], \tag{3}$$

with parameters $C=1550$ or $C=1450$ in the case of *ab initio*[1] or atomic radii[2] approach, respectively. The parameters C and distances in angstroms yield the resulting values of the Vickers hardness in Eq. (3) in gigapascals (GPa). The tests of Eq. (3) give good agreement between theory and experiment for all crystals studied in Refs. 1–4 earlier.

Because the bond strengths $s(ij)$ do not depend on the orientation of bonds and (ij) bonds between atoms i and j have different directions in crystals, the key factor for the description of anisotropy lies in $b(ij)$, $b(kl)$, etc. numbers.

The important insight into the nature of hardness anisotropy was shown by the measurement of intrinsic strength of monolayer graphene.[12] Monolayer graphene is a true two-dimensional material which consists of covalently bonded carbon atoms. Atomic force microscope nanoindentation was applied to measure the mechanical properties of monolayer graphene membranes suspended over open holes. The intrinsic strength of graphene was measured by loading the membranes to the breaking point. These experiments established graphene as the strongest material ever measured. Also in the earlier report of Mao *et al.*,[13] the exceptional hardness in a high-pressure form of graphite was observed in the direction perpendicular to the basal carbon planes.

In graphene and in high-pressure forms of graphite, the exceptional hardness is due to strong carbon-carbon bonds in planar hexagons, the force of indentation only extends carbon bonds. Therefore, it is plausible to suppose that also in three dimensional material breaking bonds by their extension rather than by their compression determines hardness of material.

In the second step, let us denote $\mathbf{n}$—direction of indentation, $\mathbf{d}_r(ij)$—direction of the rth bond between atoms i and j, and the angle $\alpha_r^{\mathbf{n}}(ij)$ between $\mathbf{n}$ and $\mathbf{d}_r(ij)$, where $r=1,\ldots,b(ij)$. We introduce the projection $p_r(\mathbf{n},ij)$ of the bond with the direction $\mathbf{d}_r(ij)$, into the $\mathbf{n}$—plane of indentation as

$$p_r(\mathbf{n},ij) = \sin \alpha_r^{\mathbf{n}}(ij) \tag{4}$$

and for all $b(ij)$ bonds between i-j atoms, we define the sum $P(\mathbf{n},ij)$ as

$$P(\mathbf{n},ij) = \sum_{r=1}^{b(ij)} p_r(\mathbf{n},ij). \tag{5}$$

Analogously, $P(\mathbf{n},kl)=\sum_{r=1}^{b(kl)} p_r(\mathbf{n},kl)$ is the sum of all projection of $b(kl)$ bonds between k-l atoms. Because the mean value of bond projections over all planes of indentation is $\pi/4$, the mean values of the sums $P(\mathbf{n},ij)$ and $P(\mathbf{n},kl)$ are $\pi/4\ b(ij)$ and $\pi/4\ b(kl)$, respectively.

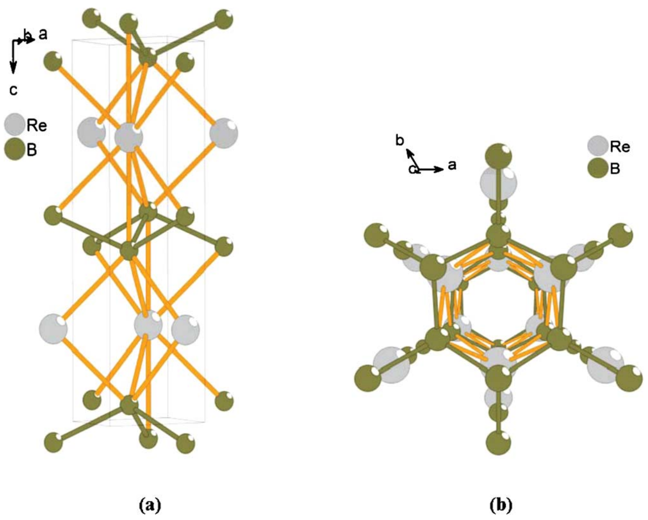
By means of the effective bond number $a(\mathbf{n},ij)$ defined as

$$a(\mathbf{n},ij) = b(ij) + A[4P(\mathbf{n},ij) - \pi b(ij)], \tag{6}$$

the hardness $H(\mathbf{n})$ in the direction of indentation $\mathbf{n}$ has the form

$$H(\mathbf{n}) = \frac{C}{\Omega}[a(\mathbf{n},ij)s(ij) + a(\mathbf{n},kl)s(kl) + \cdots + a(\mathbf{n},mn)s(mn)]. \tag{7}$$

To determine the parameter A in Eq. (6) the directional variations in the measured microhardness of covalently bonded wurtzite phase SiC were employed.[14] With $A=1$ and *ab initio* reference potentials $e_{\mathrm{Si}}=2.922$ and $e_{\mathrm{C}}=3.987$ for SiC, the theoretical hardness along the $\mathbf{c}$ axis $H(\mathbf{c})=21.1$ GPa(21.3), in directions perpendicular to the $\mathbf{c}$-axis hardness $H(\perp\mathbf{c})=29.4$–31.1 GPa(27.6). The experimental values are given in the brackets. In view of the spread of measured data depending on the load, temperature, purity of samples, etc., there is reasonable agreement between experiment and theoretical predictions. Therefore, we use the value $A=1$ throughout this work.



(a) (b)

FIG. 1. (Color online) The unit cell of $\mathrm{ReB_2}$ with light gray Re-B bonds and dark gray B-B bonds. On the left side (a), the vertical and the horizontal directions are along the c and a axes, respectively. On the right (b), the perspective projection is along the c axis.

The model described above is applied for the calculations of the hardness anisotropy of $\mathrm{ReB_2}$ and $\mathrm{OsB_2}$ single crystals.

II. $\mathrm{ReB_2}$

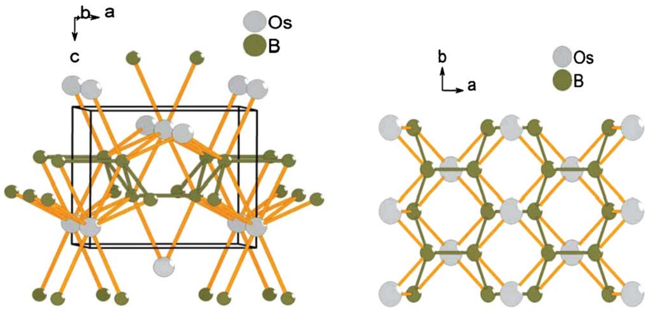
The $\mathrm{ReB_2}$ structure is hexagonal, containing two chemical formula per unit cell. The space group is $P6_3/mmc$, with the lattice parameters $a=2.900$ Å and $c=7.478$ Å.[11] Each Re atom forms eight bonds with B atoms $d_{\text{Re-B}}=2.255$ Å. In addition, each B atom forms three bonds with its neighboring B atoms, $d_{\text{B-B}}=1.822$ Å. There is 16 Re-B bonds and 6 B-B in the volume $\Omega=54.5$ Å^3 of the unit cell as shown in Fig. 1. The *ab initio* reference potentials for Re and B were calculated to be $e_{\mathrm{Re}}=4.878$ and $e_{\mathrm{B}}=3.09$, respectively.[11]

A. Hardness in the direction parallel to the c axis

There are only two different angles $\alpha_r^{\mathbf{c}}(ij)$ for Re-B (ij) bonds between $\mathbf{c}$ and $\mathbf{d}_r(ij)$; the angle $\alpha_r^{\mathbf{c}}(ij)=0°$ (four times, $r=1,\ldots,4$) and the angle $\alpha_r^{\mathbf{c}}(ij)=47.95°$ (12 times, $r=5,\ldots,16$). For B-B (kl) bonds is only one angle $\alpha_r^{\mathbf{c}}(kl)=66.79°$ (six times, $r=1,\ldots,6$). Then $a(\mathbf{c},ij)=1.376$, $a(\mathbf{c},kl)=9.209$, and finally hardness along the $\mathbf{c}$ axis is $H(\mathbf{c})=50.3$ GPa.

B. Hardness in the direction parallel to the a axis

There are three different angles $\alpha_r^{\mathbf{a}}(ij)$ for Re-B (ij) bonds between $\mathbf{a}$ and $\mathbf{d}_r(ij)$; angle $\alpha_r^{\mathbf{a}}(ij)=90°$ (eight times, $r=1,\ldots,8$), angle $\alpha_r^{\mathbf{a}}(ij)=49.98°$ (four times, $r=9,\ldots,12$),



(a) (b)

FIG. 2. (Color online) The unit cell of OsB_2 with light gray Os-B bonds and dark gray B-B bonds. On the left side (a), the vertical and the horizontal directions are along the c and a axes, respectively. On the right side (b), the projection is along the c axis, the vertical and horizontal directions are along the b and a axes, respectively.

and angle $\alpha_r^{\mathbf{a}}(ij)=130.02°$ (four times, $r=13,\ldots,16$). For B-B (kl) bonds there are also three different angles; $\alpha_r^{\mathbf{a}}(kl)=90°$ (two times, $r=1,2$), $\alpha_r^{\mathbf{a}}(kl)=37.26°$ (two times, $r=3,4$), and $\alpha_r^{\mathbf{a}}(kl)=142.74°$ (two times, $r=5,6$). Then $a(\mathbf{a},ij)=22.240$, $a(\mathbf{a},kl)=4.836$, and hardness along **a** axis $H(\mathbf{a})=41.8$ GPa. In the direction **x**, where **x** is perpendicular to the **c** and **a** axes $a(\mathbf{x},ij)=22.163$, $a(\mathbf{x},kl)=4.514$, and hardness $H(\mathbf{x})=40.0$ GPa.

These results are first-principles results based on Zhou *et al.* data.[11] When anisotropy is not considered, the hardness $H=43.6$ GPa which corresponds well with the Zhou *et al.*[11] value of $H=46.0$ GPa. The calculated values fall right within the range of experimentally measured hardness 30.1–55.5 GPa.[5]

For comparison, an approach using atomic radii[2] with $C=1450$ and $\sigma=2.8$ yields the values of $H(\mathbf{c})=46.7$ GPa, $H(\mathbf{a})=39.7$ GPa, $H(\mathbf{x})=38.1$ GPa along the **c**, **a**, and **x** axes, respectively, the mean value $H=41.1$ GPa. Since the results based on the atomic radii values are in reasonable quantitative agreement with the first-principles results, the atomic-radii approach simplifying calculations will be applied for OsB_2.

III. OsB_2

The OsB_2 structure is orthorombic, containing two chemical formula units per unit cell. The space group is (*Pmmn*) and the lattice parameters a, b, and c are 4.679, 2.869, and 4.096 Å, respectively.[7] The corrugated boron layer is between two planar osmium layers perpendicular to the **c** axis (see Fig. 2). Each Os atom forms eight bonds with boron atoms. Additionally, each B atom forms three bonds with its neighboring B atoms. In contrast to the ReB_2 structure, the osmium-boron distances are not the same, $d_{\text{Os-B}}=2.16–2.31$ Å; for simplicity we use the averaged bond lengths $d_{\text{Os-B}}=2.23$ Å and $d_{\text{B-B}}=1.85$ Å. There are 16 Os-B and 6 B-B bonds in the volume $\Omega=55.1$ Å^3 of the unit cell. The atomic-radii reference potentials[2] for Os and B to be $e_{\text{Os}}=4.435$ and $e_{\text{B}}=3.061$, respectively.

A. Hardness in the direction parallel to the c axis

The projections of Os-B (ij) bonds between **c** and $\mathbf{d}_r(ij)$ yield $a(\mathbf{c},ij)=7.994$ and $a(\mathbf{c},kl)=8.230$ for B-B (kl) bonds. Then hardness along the **c** axis $H(\mathbf{c})=45.5$ GPa.

B. Hardness in the direction parallel to the a axis

For Os-B (ij) bonds $a(\mathbf{a},ij)=19.322$, and $a(\mathbf{a},kl)=2.465$ for B-B (kl) bonds. The hardness along the **a** axis $H(\mathbf{a})=25.6$ GPa.

C. Hardness in the direction parallel to the b axis

For Os-B (ij) bonds $a(\mathbf{b},ij)=22.119$, for B-B (kl) bonds $a(\mathbf{b},kl)=5.460$. The resulting $H(\mathbf{b})=42.1$ GPa. When anisotropy is neglected the calculated $H=40.3$ GPa, the experimental value $H=37$ GPa.[7]

It is interesting to note, that in the last example, the hardness $H(\mathbf{b})=42.1$ of OsB_2 is higher than the average value $H=40.3$ due to the effective number of osmium-boron bonds, $a(\mathbf{b},ij)=22.119$. This is an exception compared to the preceding cases, where the hardness is higher than average only if the effective number of boron-boron bonds $a(\mathbf{b},kl)$ is higher than the number of bonds $b(kl)=6$. Therefore, the contributions of different types of bonds to the anisotropy of hardness in different orientation can be analyzed.

The low compressibility of ReB_2 and OsB_2 crystals was studied by the first-principles density-functional electronic structure calculations.[6,9–11,15] The results show that in both crystals there are large electron densities in short and highly directional strong B-B bonds in contrast with the lower electron densities in weaker heavy-metal-boron bonds. The strong B-B bonds form hexagonal rings perpendicular to the c axes (Figs. 1 and 2) and result in the highest value of hardness along the c axes in these crystals.

It is common opinion that hardness is governed by the strongest bonds which prevent the close approach of atoms under compression.[9] This work indicates that this opinion is not a decisive feature in the nature of hardness. Contrary to common sense, hardness is determined mainly by the bonds which prevent breaking bonds by transversal extension of material under pressure.

In conclusion, the Eq. (7) for hardness related to crystal orientation is a model for first-principles calculation of hardness anisotropy of single crystals. The model is based on the bond strengths of the nearest neighbors and on the projections of the direction of these bonds into the plane of indentation. It is shown that transversely oriented bonds are the key factor determining hardness and elucidate, why in general, there is no clear relationship between hardness and bulk modulus of a material.

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