

How to estimate hardness of crystals on a pocket calculator

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A generalization of the semiempirical microscopic model of hardness is presented and applied to currently studied borides, carbides, and nitrides of heavy transition metals. The hardness of OsB, OsC, OsN, PtN, RuC, RuB₂, ReB₂, OsB₂, IrN₂, PtN₂, and OsN₂ crystals in various structural phases is predicted. It is found that none of the transition metal crystals is superhard, i.e., with hardness greater than 40 GPa. The presented method provides materials researchers with a practical tool in the search for new hard materials.

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Hardness is a measure of a material's resistance to being scratched or dented, a measure to resist penetration, deformation, abrasion, and wear. These properties, important in a variety of industrial applications, drive the contemporary effort focused on the synthesis and characterization of hard or superhard materials.^{1–15} However, the physical processes connected with hardness are very complex, involving fracture, deformation, and destruction of material, and a rigorous quantum mechanical description of these processes is extremely complicated. It is therefore very valuable to develop simple approximate methods that yield physical insight into the fundamental nature of hardness, elucidate the main features of the phenomenon in a semiquantitative way, and can help to identify materials that are hard or superhard.

Potential candidates for hard materials should meet the following conditions:¹⁵ a three-dimensional network composed of short bonds, highly directional bonding, and a high density of valence electrons in covalent bonds. These basic conditions were quantitatively included in a semiempirical model for the calculation of hardness of covalent and ionic crystals,¹⁶ and the atomistic point of view of the model, based on the concept of bond strength s_{ij} , was successfully tested on 30 binary compounds with the zinc blende and rocksalt structures. However, the laborious first-principles calculations and the application of the formulas presented in Ref. 16 limit the practical use of the model.

The purpose of this work is (i) to generalize the previous method and to present a different approach avoiding first-principles calculations, (ii) to explicitly demonstrate how to apply a simplified microscopic model of hardness even for complex structures, and (iii) to predict the hardness of recently studied materials.

First, let me generalize the basic quantities and equations of the model. For the crystals where atoms i and j have different coordination numbers, the bond strength s_{ij} of the individual bond between atoms i and j reads

$$s_{ij} = \sqrt{(e_i e_j)} / (n_i n_j d_{ij}), \quad (1)$$

$$e_i = Z_i / R_i, \quad (2)$$

where n_i and n_j are coordination numbers of atoms i and j , respectively, d_{ij} is the interatomic distance of atoms i and j , and Z_i is the valence electron number of the atom i . For each atom i , the radius R_i is chosen so that the sphere centered at

atom i in a crystal contains exactly the valence electronic charge Z_i . For the purpose of the determination of R_i , the standard total energy calculation within density functional theory was applied.

In the case of two atoms 1 and 2 forming one bond of strength s_{12} in a unit cell of volume Ω , the expression for hardness H has the form

$$H = (C/\Omega) b_{12} s_{12} e^{-\sigma f_2} \quad (3)$$

where

$$f_2 = \left(\frac{e_1 - e_2}{e_1 + e_2} \right)^2 = 1 - \left[2\sqrt{(e_1 e_2)} / (e_1 + e_2) \right]^2, \quad (4)$$

and the number b_{12} counts interatomic bonds between atoms 1 and 2 in the unit cell; C and σ are constants.

The essential physics of this model is in the bond strength s_{ij} , consisting of two terms [see Eq. (1)]. The first, the square root of $e_i e_j$ divided by the interatomic distance, is related to the intensity of the electrostatic field in the range of the first coordination sphere. The second, the reciprocal of $n_i n_j$, characterizes the sharing of the valence electrons in bonds. Shorter interatomic distances increase the intensity of the field, and a smaller number of nearest neighbors increases the valence electron density in bonds, and vice versa. Consequently, a three-dimensional network, short bonds, and a small number of nearest neighbors are the conditions for high hardness. It is obvious that the concept of bond strength can be applied only in cases where the bond charge lies between the atoms. In the case of a metallic bond it is meaningless.

From Eqs. (1)–(4) above we see that the calculation of hardness needs structural data and the radii R_i . In fact, the estimate of hardness does not need structure constants determined by first principles; the experimental data are more then satisfactory. The difficulty in practical use lies in the determination of the radii R_i .

First, let us look at the radii R_i hidden in the quantities e_i presented in Table I of Ref. 16 and compare the R_i of the same element in different compounds. All distances in this work are given in angstroms.

For example, the radius of carbon in diamond $R_i(C) = Z_i/e_i = 0.97$. In a similar way we obtain radii of carbon $R_i(C) = 1.02, 1.06, 1.07, 1.06, \text{ and } 1.07$ for SiC, VC, TiC, WC, and NbC, respectively. We see that all $R_i(C)$ of carbon

can be approximated by $R(C)=1.05$ with an accuracy of 3%. In the case of boron in BN, BP, and BAs we obtain $R_i(B)=1.02, 1.09,$ and $1.14,$ respectively, and $R(B)=1.08$.

In an analogous way we obtain the radii R_i and approximate values R for nitrogen: in BN, AlN, GaN, TiN, and NbN, the $R_i(N)$ are 0.95, 0.99, 1.01, 1.02, and 1.02; $R(N)=0.99$. For aluminum: in AlN, AlP, and AlAs the $R_i(Al)$ are 1.38, 1.53, and 1.55; $R(Al)=1.47$. For silicon: in Si and SiC the $R_i(Si)$ are 1.475 and 1.360; $R(Si)=1.42$. For phosphorus: in BP, GaP, and AlP we have $R_i(P)$ of 1.37, 1.46, and 1.44; $R(P)=1.42$. For gallium: in GaP, GaAs, and GaSb the $R_i(Ga)$ are 1.48, 1.51, and 1.54; $R(Ga)=1.51$; and finally for arsenic: in BAs, GaAs, and AlAs the $R_i(As)$ are 1.46, 1.54, and 1.52; $R(As)=1.50$.

We observe that the radii R_i are not very sensitive to (i) the partner atom in the covalent bond, or (ii) the interatomic distance. Therefore, we can approximate the radii R_i by an average value R that differs from the corresponding first-principles value usually by less than 5%. In this way, a list of the radii R could be obtained and applied; nevertheless, even such a simplified calculation is still beyond the reach of a pocket calculator.

Second, let us compare the radii R listed above with the atomic radii r of the elements¹⁷ published also in Kittel's¹⁸ textbook and presented here in parentheses:

$$R(B) = 1.08 (0.98), \quad R(C) = 1.05 (0.92),$$

$$R(N) = 0.99 (0.88),$$

$$R(Al) = 1.47 (1.43), \quad R(Si) = 1.42 (1.32),$$

$$R(P) = 1.42 (1.28),$$

$$R(Ga) = 1.51 (1.41), \quad R(Ge) = 1.52 (1.37),$$

$$R(As) = 1.50 (1.39).$$

Of course, the numerical values differ; however, we see that the radii R are about 4–14 % larger than the atomic radii r of the elements. Therefore, it is very tempting to apply the atomic radii r published in the textbook instead of the averages R obtained from first-principles calculations.

If we use quantitatively different values for the atomic radii r taken from Pearson's¹⁷ or Kittel's¹⁸ tables, the two constants C and σ in Eq. (3), previously determined for the R_i calculated from first principles, have to be changed to new values. First, the new value for the constant C is determined so that the calculated hardnesses of covalent silicon and diamond are close to experimental values; the exponential factor in Eq. (3) equals 1 identically and $C=1400$ is found. Then the value of the constant σ is chosen so that the calculated hardness fits the experimental value for KCl.

The usual method to get the experimental value of the hardness is to measure the depth or area of an indentation left by an indenter of a specific shape, with a specific force applied for a specific time. Different loads, different shapes of indenters, the orientational effect of the crystal, etc., do not provide the same experimental numerical data. The experi-

mental value of hardness is the result of a defined measurement procedure; therefore, any comparison with the theoretical values is limited in principle. In light of the variations of experimental data there is no sense in optimizing the fit of C and σ to obtain a better accordance between theory and experiment; for the purpose of the estimate of hardness, this simple determination of the constants C and σ is sufficient. In the rest of the paper, the values $C=1450$, $\sigma=2.8$, and the atomic radii of elements from Kittel's textbook¹⁸ or the original source¹⁹ are used; the structural data and interatomic distances are taken from Ref. 20. The resulting values of hardness are in the units of gigapascals.

First, however, we should test this atomic radii method, by comparison with the results of first-principles calculations.¹⁶

The hardness of crystals having one bond strength s_{ij} in the unit cell Ω is given by Eqs. (1) and (4).

(a) The zinc blende structure, ZnS arrangement, contains four molecules in its conventional unit cell, i.e., a fcc cube; each atom has around it four equally distant atoms. The structural parameters in Eqs. (1) and (3) are: $b_{12}=16$, $n_1(\text{Zn})=4$, and $n_2(\text{S})=4$.

Using the atomic radii for $r(B)=0.98$, $r(C)=0.92$, $r(N)=0.88$, $r(Al)=1.43$, $r(Si)=1.32$, $r(P)=1.28$, $r(Ga)=1.41$, and $r(As)=1.39$, we get the following hardness values:

$$H(\text{dia}) = 90.4 (95.4), \quad H(\text{BN}) = 63.6 (63.2),$$

$$H(\text{SiC}) = 31.1 (31.1), \quad H(\text{BP}) = 26.2 (26.0),$$

$$H(\text{BAs}) = 21.0 (19.9), \quad H(\text{AlN}) = 17.6 (17.6),$$

$$H(\text{Si}) = 11.7 (11.3), \quad H(\text{GaAs}) = 7.4 (7.4).$$

The first-principles results¹⁶ are given in parentheses.

(b) The rock salt structure, NaCl arrangement, contains four molecules in its conventional unit cell, i.e., a fcc cube; each atom has around it six equally distant atoms. The structural parameters in Eqs. (1) and (3) are: $b_{12}=24$, $n_1(\text{Na})=6$, and $n_2(\text{Cl})=6$. Using the atomic radii $r(V)=1.35$ and $r(\text{Ti})=1.46$, we get the following hardness values:

$$H(\text{VC}) = 25.0 (27.2), \quad H(\text{TiN}) = 16.8 (18.7),$$

$$H(\text{TiC}) = 16.6 (18.8).$$

As above, the first-principles results¹⁶ are given in parentheses.

The atomic radii results are in reasonable accordance with the first-principles calculations; however, the most important outcome of this test is the ability of this atomic radii method to clearly distinguish soft, hard, or superhard crystals. In fact, this is the preeminent knowledge for materials scientists in the quest for new superhard compounds.

To demonstrate the practicality of this approach by explicit numerical examples, the hardness of the currently investigated materials is calculated. Available experimental data that I know of are presented in parentheses.

(i) PtN, OsC, and OsN crystals in the rocksalt structure were studied by Patil *et al.*¹ (PtN), and Zheng² (OsC and

OsN). Using their theoretical values for lattice constants, $a_0(\text{PtN})=4.40$, $a_0(\text{OsC})=4.33$, $a_0(\text{OsN})=4.34$, and the atomic radii $r(\text{Os})=1.353$, $r(\text{Pt})=1.387$, $r(\text{N})=0.88$, Eqs. (1)–(4) yield $H(\text{PtN})=24.3$, $H(\text{OsC})=24.1$, and $H(\text{OsN})=26.3$.

(ii) The cubic fluorite structure, CaF_2 arrangement, contains four molecules in its conventional unit cell, i.e., a fcc cube. Each Ca atom is at the center of eight F atoms; each F atom has around it a tetrahedron of Ca atoms. The structural parameters in Eqs. (1) and (3) are: $b_{12}=32$, $n_1(\text{Ca})=8$, and $n_2(\text{F})=4$. For example, for OsN_2 studied by Fan *et al.*,³ we have: $r_1(\text{Os})=1.35$, $Z_1(\text{Os})=6$, $Z_2(\text{N})=5$, and $d_{12}=2.09$. The value $Z_1=6$ corresponds to the valency given by Pearson,¹⁷ and leads to $H(\text{OsN}_2)=29.8$; however, the value $Z_1=8$, which correlates with the position of osmium in the periodic table, yields $H(\text{OsN}_2)=35.9$. The hardness in Eq. (3) is a result of two counteracting factors, the bond strength s_{12} and the exponential factor. With increase of Z_1 , s_{12} increases; however, the exponential factor decreases. Consequently, hardness is not very sensitive to the value of Z_1 in this case. This insensitivity is advantageous, taking into account that we do not know how many valence electrons of Os participate in the bonding, since some of them only screen the core charge. The same holds for the heavy transition metals Ru, Rh, Re, and Pt, forming carbides, borides, and nitrides. Therefore, in the following examples, we use the valencies Z from Pearson's work.¹⁷ For IrN_2 and PtN_2 studied by Yu *et al.*⁴ we have: $r_1(\text{Ir})=1.357$, $Z_1(\text{Ir})=6$, $Z_2(\text{N})=5$, $d_{12}=2.10$, and $H(\text{IrN}_2)=29.2$; and for PtN_2 $r_1(\text{Pt})=1.387$, $d_{12}=2.13$, and $H(\text{PtN}_2)=27.1$.

(iii) The tungsten carbide structure WC is hexagonal with a unimolecular cell. OsC and OsN crystals were studied theoretically by Zheng² and OsB by Gou *et al.*⁵ The structural parameters in Eqs. (1) and (3) are: $b_{12}=6$, $n_1(\text{W})=6$, $n_2(\text{C})=6$. The atomic radii and interatomic distances are $r_1(\text{W})=1.41$, $r_1(\text{Ru})=1.34$, $r_1(\text{Os})=1.35$, $d_{12}(\text{WC})=2.197$, $d_{12}(\text{RuC})=2.193$, $d_{12}(\text{OsB})=2.18$, $d_{12}(\text{OsC})=2.17$, and $d_{12}(\text{OsN})=2.22$. The resulting hardnesses are $H(\text{WC})=22.9$ [24.0 (Ref. 5)], $H(\text{RuC})=23.6$, $H(\text{OsB})=18.5$, $H(\text{OsC})=24.3$, and $H(\text{OsN})=25.9$.

(iv) In a hexagonal structure with the ZnO arrangement (two-molecule hexagonal unit) each atom has around it a tetrahedron of atoms of the opposite sort just as in a cubic ZnS arrangement: $n_1(\text{Zn})=4$, $n_2(\text{S})=4$; however, $b_{12}=8$. For aluminum nitride AlN we use $r_1(\text{Al})=1.43$, $r_2(\text{N})=0.88$, $d_{12}=1.90$, and $\Omega=41.7$; we get the hardness $H(\text{AlN})=17.4$. For SiC $r_1(\text{Si})=1.32$, $r_2(\text{C})=0.92$, $d_{12}=1.89$, and $\Omega=41.3$; $H(\text{SiC})=30.8$.

In the case of more than one bond strength s_{ij} , more than one $b_{ij}s_{ij}$ product has to be calculated. Then the hardness of a compound is calculated as the geometrical sum of all products $b_{ij}s_{ij}$, $b_{kl}s_{kl}$, etc. Therefore, the hardness of crystals having two different bond strengths in the unit cell Ω is given by the following expression:

$$H = (C/\Omega)2(b_{12}s_{12}b_{34}s_{34})^{1/2}e^{-\sigma f^4}, \quad (5)$$

$$f_4 = 1 - [4(e_1e_2e_3e_4)^{1/4}/(e_1 + e_2 + e_3 + e_4)]^2. \quad (6)$$

(i) Tetragonal hypothetical BC_3 has the diamondlike structure,^{6,7} where two atoms of carbon in the conventional fcc cube have been substituted by boron atoms. Each boron atom has four carbon neighbors; each carbon atom has four neighbors, three carbon and one boron atoms. The number of bonds in the fcc cube are: $b_{12}(\text{B-C})=8$, $b_{34}(\text{C-C})=8$, and $n_1(\text{B})=n_2(\text{C})=n_3(\text{C})=n_4(\text{C})=4$.

Using $r_1(\text{B})=0.98$, $r_2(\text{C})=0.92$, $d_{12}(\text{B-C})=1.63$, $d_{34}(\text{C-C})=1.52$, $\Omega=47.72$, $e_1=Z_1/r_1$, $e_2=Z_2/r_2$, and $e_4=e_3=e_2$, the hardness calculated by Eqs. (5) and (6) is $H(\text{BC}_3)=72.3$.

(ii) Nitride spinel materials, Si_3N_4 and C_3N_4 crystals,⁸ have $b_{12}(\text{Si-N})=32$, $b_{34}(\text{Si-N})=96$, $n_1(\text{Si})=4$, $n_2(\text{N})=4$, $n_3(\text{Si})=6$, and $n_4(\text{N})=4$.

For Si_3N_4 , $r_1(\text{Si})=1.32$, $r_2(\text{N})=0.88$, $r_3=r_1$, $r_4=r_2$, $d_{12}(\text{Si-N})=1.83$, $d_{34}(\text{Si-N})=1.88$, $\Omega=445.9$; and the hardness $H(\text{Si}_3\text{N}_4)=31.8$ [30.0 (Ref. 9)].

For C_3N_4 , $r_1(\text{C})=0.92$, $r_3=r_1$, $r_4=r_2$, $d_{12}=1.59$, $d_{34}=1.68$, $\Omega=324.3$; and $H(\text{C}_3\text{N}_4)=73.5$.

(iii) The aluminum boride structure, AlB_2 and TiB_2 crystals, is hexagonal with a unimolecular cell. The parameters for Eqs. (5) and (6) are $b_{12}(\text{Al-B})=12$, $b_{34}(\text{B-B})=3$, $n_1(\text{Al})=12$, $n_2(\text{B})=9$, $n_3(\text{B})=3$, and $n_4(\text{B})=3$.

For AlB_2 , $r_1(\text{Al})=1.43$, $r_2(\text{B})=0.98$, $e_4=e_3=e_2$, $d_{12}(\text{Al-B})=2.378$, $d_{34}(\text{B-B})=1.735$; and $H(\text{AlB}_2)=28.1$; the experimental value is 25.0.²¹

For TiB_2 , $r_1(\text{Ti})=1.46$, $r_2(\text{B})=0.98$, $d_{12}(\text{Ti-B})=2.379$, $d_{34}(\text{B-B})=1.748$; and $H(\text{TiB}_2)=31.6$ [33.7 (Ref. 21)].

(iv) The rhenium diboride structure ReB_2 studied by Hao *et al.*¹⁰ is hexagonal, each rhenium atom has eight boron neighbors, $n_1(\text{Re})=8$, and each boron atom has four rhenium neighbors and three boron neighbors, $n_2(\text{B})=7$. The boron atoms are in puckered layers normal to the c_0 hexagonal axis with each boron atom 1.82 Å distant from three others, $n_3(\text{B})=n_4(\text{B})=3$. The bond strengths s_{12} and s_{34} correspond to Re-B and B-B bonds, respectively. The parameters in Eqs. (5) and (6) are $b_{12}=16$, $b_{34}=6$, $n_1=8$, $n_2=7$, $n_3=3$, $n_4=3$, $d_{12}=2.255$, $d_{34}=1.822$, $r_1(\text{Re})=1.375$, $r_2(\text{B})=0.98$, $Z_1(\text{Re})=6$, $Z_2(\text{B})=3$, $\Omega=54.5$, $e_1=Z_1/r_1$, $e_2=Z_2/r_2$, $e_4=e_3=e_2$; and $H(\text{ReB}_2)=35.8$.

(v) The osmium diboride structure, the OsB_2 crystal studied in Refs. 5, 11, and 12, is orthorhombic; however, the nearest neighbors give the same parameters as for the ReB_2 structure, i.e., $b_{12}=16$, $b_{34}=6$, $n_1=8$, $n_2=7$, $n_3=3$, $n_4=3$. In contrast to the ReB_2 structure, the osmium-boron distances are not the same, $d_{12}(\text{Os-B})=2.16-2.31$; the averaged bond lengths $d_{12}=2.23$ and $d_{34}(\text{B-B})=1.85$ are used. Applying $r_1(\text{Os})=1.35$, $r_2(\text{B})=0.98$, $Z_1(\text{Os})=6$, $Z_2(\text{B})=3$, $e_1=Z_1/r_1$, $e_2=Z_2/r_2$, $e_4=e_3=e_2$, and $\Omega=55.1$, we get $H(\text{OsB}_2)=35.2$. For the RuB_2 crystal studied by Chiodo *et al.*¹¹ with $d_{12}=2.22$, $d_{34}(\text{B-B})=1.84$, and $\Omega=54.0$, we get $H(\text{RuB}_2)=36.1$.

(vi) The osmium dinitride crystal OsN_2 , studied in various structural phases by Fan *et al.*,³ Young *et al.*,¹³ and Chen *et al.*,¹⁴ was shown to have a very large bulk modulus. In the pyrite structure, supposing interatomic distances $d_{12}(\text{Os-N})=2.142$ and $d_{34}(\text{N-N})=1.365$ and lattice constant $a_0=4.925$,³ the structural parameters are $b_{12}=24$, $b_{34}=4$, $n_1(\text{Os})=6$, $n_2(\text{N})=n_3(\text{N})=n_4(\text{N})=4$. Using the atomic data $r_1(\text{Os})$

$=1.35$, $r_2(\text{N})=0.88$, $Z_1(\text{Os})=6$, and $Z_2(\text{N})=5$, the hardness in this pyrite structure is $H(\text{OsN}_2)=36.7$. For the PtN_2 crystal with $d_{12}(\text{Pt-N})=2.09$, $d_{34}(\text{N-N})=1.42$, and $a_0=4.804$, we get $H(\text{PtN}_2)=38.8$.

The generalization of the equations for more than two different bond strengths follows from comparison of Eqs. (3) and (4) and Eqs. (5) and (6), respectively.

The results show that none of the transition metal borides, carbides, and nitrides calculated in this work are superhard, i.e., with hardness greater than 40 GPa. The intensity of the electric field of the atomic ions and the density of valence electrons, the essentials of hardness, crucially depend on the interatomic distances; very large transition metal atoms need more space for bonding compared to B-, C-, and N-based compounds. For example, let us hypothetically synthesize the NC_2 crystal in the ReB_2 , OsB_2 , or a similar structures. If such a crystal were stable, the calculation shows that its hardness could exceed the hardness of cubic boron nitride or even diamond.

In summary, a semiempirical microscopic model of hard-

ness is presented and applied to currently studied borides, carbides, and nitrides. It was found that none of the transition metal crystals studied here is superhard, i.e., with hardness greater than 40 GPa. It was demonstrated that (i) the hardness of covalent or polar covalent crystals can be estimated with considerable accuracy using only atomic radii and structural data of the crystal, and (ii) even for complex materials, the technique can be applied without laborious calculations. The simple computational method presented here clearly distinguishes soft, hard, and superhard crystals, which is an essential basis for materials scientists in the quest for new superhard materials.

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