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Hardness of Covalent and Ionic Crystals: First-Principle Calculations

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A new concept, the strength of bond, and a new form expressing the hardness of covalent and ionic crystals are presented. Hardness is expressed by means of quantities inherently coupled to the atomistic structure of matter, and, therefore, hardness can be determined by first-principles calculations. Good agreement between theory and experiment is observed in the range of 2 orders of magnitude. It is shown that a lower coordination number of atoms results in higher hardness, contrary to common opinion presented in general literature.

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Hardness, in general, is understood as the extent to which a given solid resists both elastic and plastic deformations. Experimentally, its value is defined by pressing an indenter into the surface of a material and measuring the size of the impression. The reproducible relationship of a load to the area or depth of indentation is a measure of hardness, such as found in Brinell, Rockwell, Vickers, or Knoop hardness testers [1].

The hardness measured by a diamond indenter that is shaped as an inverted pyramid is known as Vicker's or Knoop's microhardness. Because Knoop's scale uses a sharper diamond wedge, its values may be lower than Vicker's scale values for the same load.

In principle, hardness should be related to crystal orientation. However, during the indentation, the force of the diamond wedge is diverted sideways, so the sample is subjected to a combination of stresses—compression, shear, and tension in various directions. Consequently, the anisotropic effects are reduced. Additionally, the strength of shear or tension of a sample is highly dependent on the presence of defects in the sample. As a result, experimental values of hardness can vary by more than 10% for the same sample [2].

It is obvious that the hardness characterized above is a complex quantity and, therefore, for theoretical study, we need another appropriate definition. Recently, Gao *et al.* [3] calculated the hardness of an overly covalent crystal using the expression

$$H(\mathrm{GPa}) = 350[(N_e)^{2/3} e^{-1.191 f_i}]/d^{2.5}, \quad (1)$$

where N_e is the electron density expressed in the number of valence electrons per cubic angstrom, d is the bond length in angstroms, and f_i is the ionicity of the chemical bond in a crystal scaled by Phillips [4]. First, this method was employed for calculating the hardness of typical covalent and polar covalent crystals [3] and, later, complex oxide materials [5] and nitride spinels [6].

In this work, for the first time to our knowledge, the *ab initio* method for the calculation of the hardness of single crystals is presented. The new concepts introduced here, the strength of a bond S_{ij} and the reference energy e_i, independent of particular bond type, are inherently coupled to the atomistic structure of matter and to quantities accessible by first-principles techniques, which forms the major advance over the previous methods.

The e_i quantities that will be essential for further considerations play a key role in the correlations between bulk moduli and core-level shifts in transition-metal carbides and nitrides [7]. Even though hardness is different from bulk or shear moduli, the bulk modulus is the best indicator of the hardness for materials with diamondlike structure [2]. Bulk properties are expected to be related with hardness because, from the microscopic point of view, not only the surface but the finite volume of the sample interacts with the indenter. Accordingly, atomic bonds in volume have to be taken into account.

We introduce bond strength S_{ij} between atoms i, j

$$S_{ij} = \sqrt{e_i e_j}/(d_{ij} n_{ij}), \quad (2)$$

where the reference energy $e_i = Z_i/R_i$, Z_i is the valence electron number of the atom i, and n_{ij} is the number of bonds between atom i and its neighboring atoms j at the nearest neighbor distance d_{ij}.

The radius R_i is determined for each atom in a crystal in the following way: For a given atom i within a solid, we choose a sphere centered at the atom i, the radius R_i of which is found out so that the sphere contains exactly the electronic valence charge Z_i. In other words, the radius is chosen so that the sphere is electrically neutral as a whole.

In brief, the bond strength S_{ij} is determined by the valence electron numbers Z_i, Z_j of the atoms i, j in the bond, the crystal valence electron density, the number of bonds n_{ij}, and the bond length d_{ij} between atoms i, j. The reference energy e_i of the atom i is the potential of the individual atom i to attract the crystal valence charge.

Using this concept of bond strength, we set up our theory on the following statement: The hardness of the ideal single crystal is proportional to the bond strengths S_{ij} and to their number in the unit cell of the crystal.

In the simplest case of the crystal of an element (e.g., silicon, two Si atoms in the unit cell), the hardness equals

$$H[\text{strength/volume}] = (C/\Omega)\sqrt{e_i e_i}/(d_{ii} n_{ii}). \qquad (3)$$

For two atoms in the volume Ω, one bond strength S_{ii} counts interatomic Si-Si bonds only once. The proportionality constant C is chosen so that it couples calculated values with experimental values if all distances (i.e., R_i, d_i, and for Ω) are measured in angstroms. Since the experimental value of hardness of any chosen element determines the value of C, the hardness of other crystal elements can test the validity of Eq. (3). For typical covalent diamond and silicon crystals $n_{ii} = 4$, and for a good agreement with experimental values, the constant C should be at about $C = 1550$.

The definition of hardness based on the bond strengths implies that the crystal lattice is supported by bonds in all directions, and, consequently, $n_{ij} \geq 4$ for all atoms in the crystal. If the coordination number of the atom in a crystal is lower than fourfold, then the mechanism for plastic deformation or the volume change under pressure of the indenter prefers bending or rotation rather than breaking the bonds of the crystal framework. The concept of breaking bonds loses its meaning also in metals where the electron gas is just a sort of negatively charged glue for the packing of the positive ions. In such cases, the hardness of material is obviously lower than the value predicted by Eq. (3).

When there are differences in the e_i, e_j potentials of the atoms in the bond, it is evident that the trend of breaking the bonds increases by the presence of the "weaker partner" in the bond. The effect of the difference between e_i and e_j is phenomenologically described by the exponential factor $\exp(-\sigma f_e)$, where

$$f_e = \left[\frac{e_i - e_j}{e_i + e_j}\right]^2 = 1 - [2\sqrt{(e_i e_j)}/(e_i + e_j)]^2. \qquad (4)$$

The far right side has been rearranged to see that $f_e = 1 - [(\text{geometrical average})/(\text{arithmetic average})]^2$, which is a suitable form with respect to generalization for more e_x components.

Then the expression for hardness of the binary compound with two different atoms (atom a and b in the volume Ω) has the form

$$H[\text{strength/volume}] = (C/\Omega)\sqrt{(e_a e_b)}/(d_{ab} n_{ab}) e^{-\sigma f_e}. \qquad (5)$$

The constant σ should approach 4, supposing that it is chosen so that the calculated hardness fits experimental values for NaCl and KCl crystals having the highest f_e values of all the compounds studied in this work.

We do not optimize the fit of C and σ to experimental data taking into account their variations [2]. We use the values $C = 1550$ and $\sigma = 4$ throughout this work. All other quantities in Eqs. (4) and (5) are material dependent and determined from standard *ab initio* calculations.

To test our theory, at first we calculated the hardness of several binary compounds using Eq. (5). Performing a standard total energy calculation within density functional theory (DFT) in the local density approximation (LDA), we obtained equilibrium lattice constants, crystal charge density, and corresponding radii R_i, R_j that determine the e_i and e_j. The LDA plane-wave all-electron pseudopotential method [8] was used; however, any other computational technique producing reliable crystal charge density can be applied. In Table I, the results of our LDA calculations, and, on the right side, the experimental data of hardness and results of Gao's equation [3] based on experimental bond length d_{expt} and ionicities f_i [4] are given.

The *ab initio* results on the left side of Table I are in good accordance with Gao's results [3] and experimental data for all A^{III}-B^{V} compounds. For A^{II}-B^{VI} ZnS, ZnSe, and ZnTe, our results are closer to experiment than the results of Gao's theory. Compared to experimental data, hardness of the transition-metal carbides and nitrides and ionic NaCl and KCl are also in reasonable agreement with experiment. It is interesting to note that the e_i quantities for the same atom in different bonds (e.g., carbon in tetrahedral diamond or in SiC and in octahedral WC, TiC, or VC) differ by no more than 10%. These similarities can be observed in Table I also for N, Cl, or "cations" Ga, Al, or Zn. It seems plausible to transfer these values to other compounds with a similar bonding to get a qualitative prediction of the hardness of more complex materials.

For more complex crystals than binary compounds, we at first generalize Eq. (5). Following Refs. [3,5,6,10], the hardness of multicomponent compound systems is expected as a geometrical sum of the values of hardness of all binary systems in the solid. For a system with n different binary systems described by bond strengths S_{ij} derived from the energies e_i, e_j, the generalized form of Eq. (5) is

$$H = \frac{C}{\Omega} n \left[\prod_{i,j=1}^{n} N_{ij} S_{ij}\right]^{1/n} e^{-\sigma f_e},$$
$$f_e = 1 - \left[k\left(\prod_{i=1}^{k} e_i\right)^{1/k} \Big/ \sum_{i=1}^{k} e_i\right]^2, \qquad (6)$$

where N_{ij} is the number—or multiplicity—of the binary system ij, and k corresponds to the number of different atoms in the system.

For illustration, we apply Eq. (6) to nitride spinel materials C_3N_4, Si_3N_4 studied in Refs. [6,11] and to cubic BC_2N studied in Ref. [3].

In nitride spinel materials, there are 8 structural units A_3N_4 ($A = \text{C, Si, Ge}$) in the unit cell: 8 A_α atoms have tetrahedral bonds with N atoms at the distance d_{tet}, and 16 A_β atoms have octahedral bonds with N atoms at the distance d_{oct}. 32 N atoms are bonded by A_α or A_β atoms in

TABLE I. Our *ab initio* results (first five columns) compared with experimental data and the results of Gao's [3] formula, Eq. (1).

	d_{theor}	e_1	e_2	f_e	H_{theor}	d_{expt}	f_i	H_{Gao}	H_{expt}
dia	1.527	4.121	4.121	0.000	95.4	1.554	0.000	93.6	96.0
Si	2.343	2.712	2.712	0.000	11.3	2.351	0.000	13.6	11.3[a]
Ge	2.418	2.631	2.631	0.000	9.7	2.449	0.000	11.7	8.8
SiC	1.887	2.941	3.910	0.020	31.1	1.887	0.177	30.3	31.0
BN	1.542	2.937	5.290	0.082	63.2	1.568	0.256	64.5	63.1
BP	1.938	2.737	3.663	0.021	26.0	1.966	0.006	31.2	33.0
BAs	2.052	2.632	3.433	0.017	19.9	2.052	0.002	26.0	19.0[a]
AlN	1.884	2.175	5.034	0.157	17.6	1.901	0.449	21.7	18.0
GaN	1.950	2.394	4.922	0.119	18.5	1.946	0.500	18.1	15.1
GaP	2.327	2.032	3.434	0.066	8.7	2.359	0.374	8.9	9.5[a]
AlP	2.353	1.967	3.476	0.077	7.9	2.365	0.307	9.6	9.4
InN	2.151	1.853	4.700	0.189	8.2	2.160	0.578	10.4	9.0
GaAs	2.422	1.987	3.251	0.058	7.4	2.456	0.310	8.0	7.5[a]
InP	2.534	1.778	3.350	0.094	5.1	2.542	0.421	6.0	5.4
AlAs	2.438	1.930	3.299	0.069	6.8	2.442	0.274	8.5	5.0[a]
GaSb	2.610	1.953	2.871	0.036	5.6	2.650	0.261	6.0	4.5[a]
AlSb	2.651	1.874	2.891	0.046	4.9	2.646	0.426	4.9	4.0[a]
InAs	2.615	1.749	3.193	0.085	4.5	2.619	0.357	5.7	3.8
InSb	2.790	1.720	2.825	0.059	3.6	2.806	0.321	4.3	2.2[a]
ZnS	2.334	1.192	4.189	0.310	2.7	2.347	0.623	6.8	1.8[a]
ZnSe	2.436	1.221	3.890	0.273	2.6	2.454	0.630	5.5	1.4[a]
ZnTe	2.620	1.253	3.440	0.217	2.3	2.637	0.609	4.1	1.0[a]
VC	2.049	3.659	3.774	0.000	27.2				29.0
TiC	2.130	2.815	3.725	0.019	18.8				24.7[a]
TiN	2.097	2.828	4.904	0.072	18.7				17.7[a]
WC	2.194	3.971	3.764	0.001	21.5	2.197	0.140	26.4	18.8[a]
NbC	2.219	3.272	3.723	0.004	18.3				18.0
NbN	2.187	3.296	4.906	0.039	19.5				17.0
NaCl	2.740	0.604	4.598	0.589	0.4	2.820	0.936	2.7	0.3
KCl	3.080	0.546	4.135	0.588	0.2	3.147	0.951	1.6	0.2

[a] Knoop hardness by Lide [9]; unless noted, all experimental data are taken from Ref. [3] and the references therein.

distorted tetrahedrons. Since there are no N-N bonds (only 8 tetrahedral A_α-N and 16 octahedral A_β-N bonds), all bonds of 56 atoms in the unit cube can be described by A-N bonds. Therefore, the two binary systems ($n = 2$) in the unit cell, i.e., 8× (A_α-N) and 16× (A_β-N), can be characterized as $[d_{A_\alpha - \text{N}} = d_{\text{tet}}; e_{A_\alpha} e_{\text{N}}]$; $[d_{A_\beta - \text{N}} = d_{\text{oct}}; e_{A_\beta} e_{\text{N}}]$ for systems of atoms A_α and A_β, respectively. Equation (6) for the hardness then reads

$$H = \frac{C}{\Omega} 2 \left[8 \frac{\sqrt{e_{A_\alpha} e_{\text{N}}}}{4 d_{\text{tet}}} \times 16 \frac{\sqrt{e_{A_\beta} e_{\text{N}}}}{6 d_{\text{oct}}} \right]^{1/2} e^{-\sigma f_e},$$

$$f_e = 1 - [3(e_{A_\alpha} e_{A_\beta} e_{\text{N}})^{1/3} / (e_{A_\alpha} + e_{A_\beta} + e_{\text{N}})]^2.$$

Because this example serves as an illustration for using Eq. (6), instead of performing total energy calculations, we use distances d_{tet} and d_{oct} determined by DFT in LDA by Gao [6] or Mo [12], and we approximate the bond strengths with the "corresponding values" of e_{A_α}, e_{A_β}, and e_{N} from Table I. We obtain:

		Data	d_{tet}	d_{oct}	Ω	$\Rightarrow H$
C_3N_4:	$e_{\text{C}_\alpha} = 4.121$	[6]	1.51	1.63	296.7	70.1
	$e_{\text{C}_\beta} = e_{\text{C}\alpha}$	[12]	1.585	1.676	324.3	61.7
	$e_{\text{N}} = 5.29$					
Si_3N_4	$e_{\text{Si}_\alpha} = 2.94$	[6]	1.75	1.86	445.9	27.4
	$e_{\text{Si}_\beta} = e_{\text{Si}_\alpha}$	[12]	1.830	1.885	481.3	24.6
	$e_{\text{N}} = 5.03$					
Ge_3N_4:	$e_{\text{Ge}_\alpha} = 2.63$	[6]	1.85	1.95	519.7	19.1
	$e_{\text{Ge}_\beta} = e_{\text{Ge}_\alpha}$					
	$e_{\text{N}} = 4.92$					

The e_i values are taken from diamond and BN (for C_3N_4), from SiC and AlN (for Si_3N_4) and from Ge and GaN (for Ge_3N_4).

The values of hardness calculated by Gao [6] for C_3N_4, Si_3N_4, and Ge_3N_4 are 56.7, 30.9, and 24.3, respectively, with a reasonable agreement with our approximations.

In the ternary BC_2N compound, all atoms are tetrahedrally bonded. With respect to the nearest neighbors, two different carbon atoms C_α and C_β have to be made distinctive. In the tetragonal unit cell, there are eight atoms, each of the atoms B, C_α, C_β, and N 2 times. The nearest neighbors, the distances, and the corresponding products e_i of the bond strengths of four binary systems BN, BC_β, $C_\alpha C_\beta$, and $C_\alpha N$ can be written in the following way:

$$\begin{array}{lll} \mathrm{B}: & [d_{\mathrm{B}\text{-}\mathrm{N}} = 1.562; e_{\mathrm{B}} e_{\mathrm{N}}] & [d_{\mathrm{B}\text{-}\mathrm{C}_\beta} = 1.573; e_{\mathrm{B}} e_{\mathrm{C}_\beta}] \\ \mathrm{C}_\alpha: & [d_{\mathrm{C}_\alpha\text{-}\mathrm{C}_\beta} = 1.515; e_{\mathrm{C}_\alpha} e_{\mathrm{C}_\beta}] & [d_{\mathrm{C}_\alpha\text{-}\mathrm{N}} = 1.564; e_{\mathrm{C}_\alpha} e_{\mathrm{N}}] \\ \mathrm{C}_\beta: & [d_{\mathrm{C}_\beta\text{-}\mathrm{C}_\alpha} = 1.515; e_{\mathrm{C}_\beta} e_{\mathrm{C}_\alpha}] & [d_{\mathrm{C}_\beta\text{-}\mathrm{B}} = 1.573; e_{\mathrm{C}_\beta} e_{\mathrm{B}}] \\ \mathrm{N}: & [d_{\mathrm{N}\text{-}\mathrm{B}} = 1.562; e_{\mathrm{N}} e_{\mathrm{B}}] & [d_{\mathrm{N}\text{-}\mathrm{C}_\alpha} = 1.564; e_{\mathrm{N}} e_{\mathrm{C}_\alpha}]. \end{array}$$

For direct comparison with Gao's calculations, we use the lattice parameters $a = 3.576$, $b = 3.576$, $c = 3.608$ [Å] and the interatomic distances of Gao in Ref. [3].

If we denote $\Omega = 46.138$, and take into account $n = 4$ and all $N_n = 1$, then Eq. (6) is

$$H = \frac{C}{\Omega} 4 \left[\frac{\sqrt{e_{\mathrm{C}_\alpha} e_{\mathrm{C}_\beta}}}{4 d_{\mathrm{C}_\alpha \mathrm{C}_\beta}} \frac{\sqrt{e_{\mathrm{C}_\beta} e_{\mathrm{B}}}}{4 d_{\mathrm{C}_\beta \mathrm{B}}} \frac{\sqrt{e_{\mathrm{C}_\alpha} e_{\mathrm{N}}}}{4 d_{\mathrm{C}_\alpha \mathrm{N}}} \frac{\sqrt{e_{\mathrm{B}} e_{\mathrm{N}}}}{4 d_{\mathrm{BN}}} \right]^{1/4} e^{-\sigma f_e},$$

$$f_e = 1 - [4(e_{\mathrm{C}_\alpha} e_{\mathrm{C}_\beta} e_{\mathrm{B}} e_{\mathrm{N}})^{1/4} / (e_{\mathrm{C}_\alpha} + e_{\mathrm{C}_\beta} + e_{\mathrm{B}} + e_{\mathrm{N}})]^2.$$

The bond strengths e_i should be determined via R_i by total energy calculations. However, if we consider the structural similarity between BC_2N, and diamond and BN (tetrahedral bonding and interatomic distances), similarly as in the former case of nitride spinels, we can transfer the e_i values from diamond and BN from Table I to BC_2N. Approximating $e_{\mathrm{C}_\alpha} = e_{\mathrm{C}_\beta} = 4.121$, $e_{\mathrm{B}} = 2.937$, and $e_{\mathrm{N}} = 5.290$, we obtain a quantitative estimation of the hardness $H[\mathrm{BC_2N}] = 76.5$, in excellent agreement with Gao's [3] value 78 and experimental 76 ± 4 values.

The experimental value $a = 3.642$ Å [11] of the synthesized cubic phase BC_2N at ambient conditions gives, for all interatomic distances, the value 1.577 Å. With parameters, e_i above yields the value of hardness $H = 71.9$.

Finally, we note several general factors that can cause higher hardness of the crystal according to Eq. (5): (i) higher bond strengths S_{ij} and their density, i.e., a higher number of atoms in volume Ω (the case of small atoms) and, consequently, short interatomic distances. Notice that d_{ij} is in the denominator of S_{ij}; (ii) not too different e_i, e_j potentials of the atoms in the bond resulting in small factor f_e; (iii) a small number of nearest neighbors (coordination number C_N) because of n_{ij} in the denominator of S_{ij}.

The conditions in point (i) are generally accepted as conditions for high hardness [2]. Point (ii) is analogous to a small ionicity of the bond—see f_e and f_i in Table I. The small ionicity of the bond is again a well known factor increasing the hardness of covalent materials. On the other hand, it is traditionally accepted that the higher C_N of atoms results in the higher hardness of material [2]. The argument is that the high C_N, i.e., the large number of neighbors, supports each atom by more bonds. This "common sense" argument is in contradiction with point (iii) above: smaller C_N increases the bond strength ergo hardness. The physical reason in favor of smaller C_N follows from the meaning of the e_i, e_j quantities. Since e_i is the potential of an atom i to attract valence charge in the crystal, the division of $e_i e_j$ to more bonds creates weaker bonds and vice versa.

In summary, we present the first (to our knowledge) *ab initio* method for calculating the hardness of covalent and ionic crystals. We have shown that, even in the cases where Gao's [3] semiempirical method is applicable, the agreement with experiment is better for our *ab initio* method. By introducing new concepts, bond strengths, and their density, the present approach extends understanding the hardness on the structural and atomistic levels and explains why the lower coordination number of atoms results in higher hardness, contrary to the common sense opinion presented in general literature. Additionally, it was demonstrated that, by using the calculated e_i potentials in Table I as an approximation, a qualitative prediction of the hardness of complex materials can be obtained by means of the general expression of Eq. (6).

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