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Review Article

Ab Initio Method for Estimating the Theoretical Hardness of Covalent Crystals with a Cubic Structure

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Abstract

A method for predicting the limiting (theoretical) hardness of covalent (diamond-like materials) from first principles was presented. The proposed method takes into account that hardness is a property of the surface layer of the material. The influence of the outer surface of the material on the internal energy states of the electron-ion system is taken into account. The hardness of the material at different recesses from the outer surface is estimated. There was an agreement between the calculated and experimental data.

Key words: Surface energy, electron-ion system energy, theoretical compressive strength, heas, tensile strength, pseudopotential method, mechanical characteristics

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

From the mechanical characteristics, the theoretical strength, Young's modulus and thermal expansion coefficient, as well as their temperature dependence can be calculated from first principles for different materials (borides, carbides, silicides, covalent crystals, multi-element metal alloys and eutectic composites, etc.)¹⁻⁷. In these works, the method of a priori pseudopotential (author's development) presented was used^{8,9}.

Hardness is a complex character of material since it depends on the yield strength of the substance, elastic stiffness and plasticity. The theoretical methods used are semi-empirical models that make it possible to evaluate the hardness of crystalline compounds based on their structural data¹⁰⁻¹⁶. Such models are used to predict mechanical properties when creating new materials.

In the proposed models (mainly for refractory materials, borides and carbides), the authors use different physical characteristics to describe hardness, such as shear moduli, elastic moduli, band gap energy, interatomic interaction potential, etc. But at the same time, in all these models there is an adjustable parameter for matching the calculated results with the experiment.

In^{17,18}, an adjustable parameter was used to estimate the solid solution hardening hardness and its temperature dependence on metal HEAs, diborides and carbides.

Purpose of the work: For materials that deform and fail elastically, calculate the hardness from the first principles. The investigated materials were diamond, BN and SiC with a cubic structure. Calculations are carried out using the method of pseudopotentials.

By definition, hardness is the ability of materials to resist deformation in the surface layer. For the studied class of materials hardness, as well as the strength of crystalline materials, depends on the interatomic interaction, the size and packing of atoms in the elementary lattice and the number of valence electrons. The difference between the two characteristics is that strength is a property of the entire material and hardness is only for a surface layer.

The choice of covalent crystals with a cubic structure was due to the following factors:

- These crystals are brittle and under external influences are deformed and destroyed elastically, which makes it possible to compare compressive strength and hardness, given that the applied stress in the second case will not lead to destruction and will act only in the surface layers

- Reliability of the method is determined by comparison with verified experimental data (if available). Diamond-like materials with a cubic structure are most experimentally studied

RESULTS AND DISCUSSION

To assess the physical characteristics of the surface layer, it is proposed to solve the following problems:

- **Task 1:** Calculate the theoretical strength of diamond-like materials through the interaction energies of close-packed atomic planes

To describe the process of destruction of diamond-like materials under uniaxial loading, we use the value of the interaction energy between atomic planes (perpendicular to the loading axis). This differs significantly from the generally accepted approach, where the value of the total energy per atom in the unit cell is used to calculate the strength characteristics at the micro level¹⁹⁻²².

Due to the anisotropy of the single crystal, some crystallographic directions are easily deformed. For diamond, boron nitride and silicon carbide having a cubic structure, such directions are the spatial diagonals of the cubic lattice and the atomic planes perpendicular to the diagonals are close-packed. When solving such problems, it is more convenient to describe the diamond-like structure in hexagonal axes (Fig. 1).

The interaction energy between atomic planes was calculated using interatomic potentials⁵.

The unit cell of diamond-like materials in hexagonal axes contains 6 atoms, which are located on parallel planes (AA*BB*CC*). The structure of diamond and diamond-like materials in hexagonal axes will be described by a three-layer alternation of (001) planes. The distance between two densely packed atomic planes will be $c/4$ and $c/12$ (c is the spatial diagonal of the cubic lattice). In the first case, the atoms in adjacent planes are in an identical position, in the second case there is a displacement.

If an atom on plane A is taken as the origin of coordinates, then the radii-vectors of the remaining 5 atoms in the unit cell will be (Fig. 1):

$$\vec{r}_1 = \frac{1}{4} \vec{c}$$

$$\vec{r}_2 = \frac{2}{3} \vec{a} + \frac{1}{3} \vec{b} + \frac{1}{3} \vec{c}$$

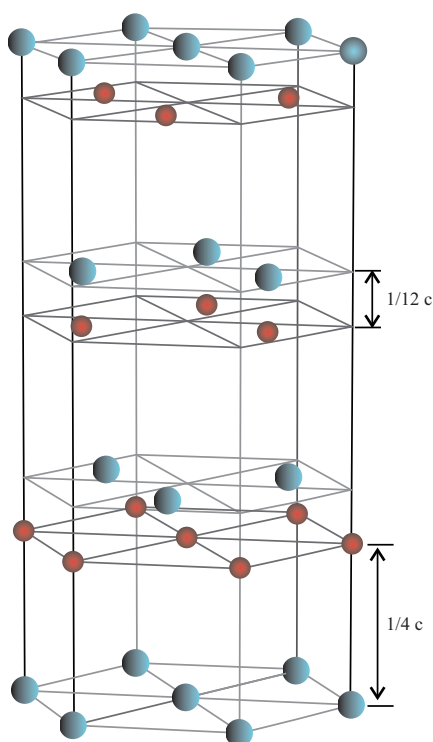


Fig. 1: Description of the structure of diamond-like materials in hexagonal axes. The spatial diagonal of the cube (111) is chosen as the c-axis ($c = 1.732 a_0$, a_0 is the cubic lattice parameter). On the basic close-packed planes (111) there are atoms of the same type in the case of BN or SiC

$$\vec{r}_3 = \frac{2}{3} \vec{a} + \frac{1}{3} \vec{b} + \frac{7}{12} \vec{c}$$

$$\vec{r}_4 = \frac{1}{3} \vec{a} + \frac{2}{3} \vec{b} + \frac{2}{3} \vec{c}$$

$$\vec{r}_5 = \frac{1}{3} \vec{a} + \frac{2}{3} \vec{b} + \frac{11}{12} \vec{c}$$

where, \vec{a} and \vec{b} are vectors of the hexagonal lattice on the basal plane and \vec{c} is a vector perpendicular to the basal plane.

The pseudopotential of ions, taking into account the structure of materials in hexagonal axes, can be represented as:

$$V(\mathbf{q}) = \frac{1}{6} \left\{ \begin{aligned} &V_A(1 + \exp(-i\vec{q}\vec{r}_2) + \exp(i\vec{q}\vec{r}_4)) + \\ &V_B(\exp(-i\vec{q}\vec{r}_1) + \exp(-i\vec{q}\vec{r}_3) + \exp(-i\vec{q}\vec{r}_5)) \end{aligned} \right\} \quad (1)$$

where, V_A and V_B are the pseudopotentials of the components (for diamond $V_A = V_B$) and \mathbf{q} is the reciprocal lattice vector^{5,6}.

Within the framework of the pseudopotential method, based on the form of pseudopotential (1), For ideal structures, the interaction energy $\Phi(h, \rho)$ per unit atomic area was calculated between close-packed atomic planes, located at a distance h , where the atoms on neighbouring planes are shifted by the vector ρ ⁵.

Calculations show that the interaction energy of atomic planes with interplanar spacings $c/12$ and $c/4$ differ by almost an order of magnitude, the latter being much weaker related⁵.

That is, under the action of external loads, atomic planes with interplanar distances $c/4$ are subjected to deformation, in contrast to the "structural units", which consist of atomic planes with interplanar distance $c/12$.

For known values of the interaction energy of the layers, the stress is determined from the relationship:

$$\sigma_c = \frac{1}{h} \frac{\partial \Phi(h, \rho)}{\partial e_c} \quad (2)$$

where, e_c is e_{111} - is the relative strain in the direction of the space diagonal c .

The values of the lattice parameter and deformation are presented and the strengths are calculated through the interaction energies between structural units at $h = c/4$. For comparison, the results of calculations by other authors are also given. There was an agreement between the calculated data both with the experiment and with the data of other authors as shown in Table 1.

- **Task2:** Estimation of the energy of the outer surface and its influence on the internal states of the electron-ion system

Because close-packed atomic planes with an interplanar spacing of $c/12$ are strongly interconnected compared to atomic planes located at distances of $c/4$, they form a structural unit that does not undergo deformation when the material is loaded i.e., it could be considered, that the material consists of parallel structural units spaced from each other at a distance of $c/4$. The energy of interaction between structural units is equal to Φ_0 .

Let the sample under study be semi-infinite, with a free surface coinciding with a close-packed atomic plane. It is assumed that the outer surface of the material has half the energy of interaction with the missing atomic plane – $\Phi_0/2$.

Table 1: Lattice parameter c, theoretical strength (σ_{1max} and σ_{2max}) and corresponding strain (e^{*111} , e^{**111}) under compression and tension

	c (nm)		Compression		Stretching	
	Calculated	Experimental	σ_{1max} (GPa)	$-e^{*111}$	σ_{2max} (GPa)	e^{**111}
C	0,6351	0,6274	137,02	0,153 (0,151) ²²	105,82 (95) ¹⁹	0,139
BN	0,6424	0,6348	103,06	0,155	88,56	0,143
SiC	0,7602	0,7527	59,24	0,158	47,98 (50,8) ²¹	0,14 (0,135) ²¹

Note that the energy of the outer surface of the material is positive compared to the energy of internal electrons and ions. The energy between structural units in a semi-infinite sample differs from the energy Φ_0 . To find it, it is necessary to redistribute the energy of the outer surface over the layers. For this purpose, the simplest method is proposed for averaging the energy values over two adjacent layers, taking into account the energy of the outer surface.

Let for the I-th and II-th layers the energy of interaction in the zeroth order is equal to Φ_0 and the free surface has the energy $-\Phi_0/2$. Let us define the interaction energy of the 1st layer as the arithmetic mean:

$$\Phi_I = (\Phi_0 + \Phi_0 - \Phi_0/2)/2 = \Phi_0 - \Phi_0/2^2 \quad (3)$$

For the second layer, the interaction energy is determined based on the refined value of the energy of the first layer:

$$\Phi_{II} = (\Phi_I + \Phi_0)/2 = \Phi_0 - \Phi_0/2^3 \quad (4)$$

and for the i - th layer:

$$\Phi_i = \Phi_0 - \Phi_0/2^{i+1} \quad (5)$$

As a result, the energy of interaction between the layers at different distances from the surface was obtained.

To determine the average value of the energy of the surface layer, summarize (5) over all layers and divide by the number of layers j.

As a result, the average value of the energy of interplanar interaction in the surface layer:

$$\Phi_d \approx \Phi_0 \left(1 - \frac{c}{6d}\right) \quad (6)$$

Here d is the distance from the outer surface deep into the material in the direction of the spatial diagonal.

Formula (6) takes into account the terms c/d in the first order, given that $c/d \ll 1$.

From Equation (6) it follows that the average energy of interplanar interaction for a semi-infinite sample is equal to Φ_0 and formula (2) is used to calculate the strength, where $\Phi(h, \rho) = \Phi_0$.

The theoretical strength, which is determined using Equation (2), has the same value throughout the crystal (taking into account the direction of deformation) and the hardness is determined only on the surface layer.

Comparing the accepted formulations for strength and hardness and can draw the following conclusions.

Strength and hardness: The characteristics of the material manifested under external influence. In the first case, the maximum stress that the material can withstand before failure is determined. In another case, withstand the stress until residual deformations appear.

In the case of covalent crystals, which are elastically deformed to failure, the difference between the concept of compressive strength and hardness is lost.

In addition, it should be taken into account that the force impact in determining the hardness and strength is applied in different ways. To determine the hardness, a local impact is used and for strength, the impact spreads over the entire surface of the material.

In the case of refractory borides, microhardness is mainly measured. The measurement accuracy depends on the number of measurements taken. If the total area of local influences of external forces tends to the surface area of the material, then an ideal variant of hardness measurement is obtained. To obtain an accurate hardness value, it is better to force the entire surface.

If in formula (2) the value of the energy of interplanar interaction in the surface layer (6) is used, then the function is obtained dependent on the theoretical hardness of the selected thickness of the material surface in the direction of the spatial diagonal of the cubic lattice:

$$H_d = \sigma_c \left(1 - \frac{c}{6d}\right) \quad (7)$$

The calculated values of the hardness of diamond-like materials for different selected thicknesses of the outer surface (Table 2).

A direct relationship has been obtained between strength and hardness with a proportionality factor depending on the hexagonal lattice parameter c and the thickness of the surface layer d.

Table 2: Theoretical hardness (H_d) of diamond-like materials depending on the thickness of the outer surface d (nm)

d (nm)	H_d (Gpa)		
	C (100)	BN (80-90)	SiC (30-50)
1	122,516	92,507	51,734
2	129,768	98,053	55,487
5	134,119	101,361	57,738
10	135,569	102,586	58,489
20	136,295	103,045	58,864
30	136,536	103,231	58,910

The known experimental average hardness values GPa were given in parentheses

All used semi-empirical hardness models show approximately the same values for the hardness of a diamond (~92 GPa), this is explained by the fact that all models are parametrized for the average hardness value in all crystallographic directions of a diamond.

In several experimental works, the measured diamond hardness varied from 140 to 170 GPa depending on the crystallographic orientation of the diamond surface²³ in the case of cubic boron nitride, the maximum $H_d = 108$ GPa, for silicon carbide $H_d = 72$ GPa.

The presented calculated values of theoretical hardness (Table 2) are minimal for diamond-like materials with a cubic structure and exceed the average value of the measured hardness of real materials (having structural defects), which is quite logical.

The presented method can be used to evaluate hardness for a limited class of materials that deform elastically or quasi-elastically. The presence of close-packed atomic planes in the structure facilitates the determination of the energy of the outer close-packed surface of the material and the assessment of its effect on the internal states of the electron-ion system. The method is acceptable for assessing the hardness of coatings, nanomaterials and thick films.

CONCLUSION

For the first time, a method for estimating hardness from first principles is presented. Theoretical hardness is a characteristic of the surface layer of a material. In the case of covalent crystals, the hardness is directly proportional to the compressive strength. The method for estimating the energy of the outer surface and taking into account its influence on the state of the electron-ion system in the surface layer makes it possible to determine the hardness at different distances from the free surface.

SIGNIFICANCE STATEMENT

Covalent crystals that deform and break elastically differ from other materials and to describe their hardness there is no need to take into account a set of characteristics

(elasticity, plasticity, viscosity, etc.) other than elastic ones. This makes it possible to calculate hardness from first principles, within the framework of this method, in contrast to the conventional approach, where it is believed that hardness cannot be directly calculated using atomistic modeling or first-principles calculations. For the first time, a physical interpretation of hardness for covalent crystals is given and a formula is obtained that describes the functional dependence of hardness on the distance to the surface.

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