

# ABORDARE TEORETICĂ CHIMICĂ A DURITĂȚII. 1 APLICAȚII LA STRUCTURI HOMODESMICE

## THEORETICAL CHEMICAL APPROACH OF HARDNESS. 1 APPLICATION TO HOMODESMIC STRUCTURES

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*Hardness is an important mechanical property of materials. It is defined as the resistance of a material to localized deformation. The ionicity of chemical bond plays a significant role in mechanical properties such as hardness, bulk modulus. Recent studies have shown that hardness, a complex property, can be calculated using very simple approaches or even analytical formulae. In these models, the theoretical hardness is described as a function of the bond density and bond strength. The bond strength may be characterized by energy gap, reference potential, electron-holding energy or Gibbs free energy, and different expressions of bond strength may lead to different hardness models. The chemical bond parameters and hardness values of crystals had been calculated based on our own model of ionicity derived from the dielectric theory of the chemical bondings. Part 1 of the paper deals with the correlation between bond length, unit cell parameters, ionicity, and hardness for some homodesmic inorganic compounds. The results of computation and comparison with experimental data are performed.*

*Duritatea este o importantă proprietate mecanică a materialelor. Ea este definită ca rezistența unui material la o deformare localizată. Ionicitatea legăturii chimice joacă un rol important pentru unele proprietăți mecanice cum ar fi duritatea, modulul de compresibilitate. Studii recente au arătat că duritatea, o proprietate complexă, poate fi calculată pe baza unor abordări simple sau chiar formule analitice. În aceste modele, duritatea teoretică este descrisă ca o funcție de densitatea electronică a legăturii și tăria legăturii. Tăria unei legături chimice poate fi caracterizată de structura de bandă, potențial de referință, energia electronică sau energia liberă Gibbs iar din acest motiv diversele expresii ale tăriei legăturii pot conduce la modele diferite ale durității. Parametrii legăturii chimice și valorile de duritate de material au fost calculate pe baza unui model propriu al ionicității, derivat din teoria dielectrică a legăturii chimice. Acest prim articol este dedicat conexiunii dintre lungimea legăturii, parametrii celulei elementară, ionicitate și duritate pentru oxizi cu structură homodesmică. Rezultatele calculelor comparate cu date experimentale indică o foarte bună concordanță.*

**Keywords:** hardness, ionicity, homodesmic structures

### 1. Introduction

Hardness is a measure of a material's resistance to being scratched or dented and is measured using various experimental techniques, including the Vicker's and Knoop tests. However, the values obtained often vary depending on the testing method, the Knoop diamond, for example, is sharper than the Vickers's and gives a lower hardness. Indeed, experimental values of hardness can vary by more than 10% for the same material. Scientists have therefore been keen to devise a theoretical technique for predicting the hardness of a material with more certainty.

When it comes to measuring the "hardness" of a material, most tests are distinctly low-tech and basically involve pressing a diamond tip into the surface and measuring the size of the dent

produced. Therefore, to predict the hardness of materials without going anywhere near a lab has become a very important task.

Several years ago, F.Gao and coworkers [1, 2] has made an important step towards this goal by developing a semi-empirical formula for the hardness of a material based on the length of the bonds between its components atoms, the number of electrons available for bonding, and the "ionicity", which is the degree to which each pair of atoms shares the electrons between bonds. (In "covalent" materials like silicon the electrons are shared equally, whereas in "ionic" materials one atom takes over its neighbor's electrons entirely; "polar covalent" materials lie in-between.). Recent developments in the field of microscopic hardness models have been reviewed. In these models, the theoretical hardness is described as a function of

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the bond density and bond strength. The bond strength may be characterized by energy gap, reference potential, electron-holding energy or Gibbs free energy, and different expressions of bond strength may lead to different hardness models. Present paper deals with a novel approach on theoretical ionicity / basicity based on electronic energy levels or band structure of solids. Our approach is based mostly on experimental data, available in literature, but with a better understanding of the physical-chemical meaning of the concept. The obtained results are similar to those reported in literature but computed with more sophisticated methods. A first test of our approach was performed on crystal structures exhibiting homodesmic chemical bondings.

## 2. Physical-chemical aspects of hardness

### 2.1. Hardness of simple compositional crystals

Previously, it was commonly accepted that the superhard materials, such as diamond, cubic boron nitride (c-BN), and carbon nitrides, are the strongly covalent bonded compounds formed by light elements [2, 3]. However, recently, it was reported that partially covalent heavy transition metal (TM) boride, carbide, nitride, and oxide are found to be good candidates for superhard materials, [4]. In order to design the new superhard materials [5,6], clarifying the nature of hardness is of utmost importance. In recent years many attempts to develop a physical definition of hardness have been made. Among the theories developed within the last years we shall focus on that of Gao et al. [1,2] and that seems to be more appropriate for understanding oxides behavior concerning hardness. It adopts the following form for polar crystals:

$$H_V(\text{GPa}) = 14(N_a \exp(-1.191 \cdot f_i)) E_h \quad (1)$$

$$N_a = \left( \sum \frac{n_i Z_i n_i Z_i}{2V} \right)^{2/3} \quad (2)$$

where  $n_i$  is the number of the  $i$ -th atom in the cell,  $Z_i$  is the valence electron number of the  $i$ th atom,  $N_a$  the covalent bond number per unit area,  $f_i$  the ionicity of bonds, and  $N_e$  the electron density expressed in the number of valence electrons per cubic angstrom. Also  $E_h$  is the covalent gap which characterizes the strength of the covalent bond.

Also, equation (1) can be expressed as:

$$H_V(\text{GPa}) = 8.82(N_e^{2/3} \cdot \exp(-1.191 \cdot f_i)) E_h = 556 \frac{N_a \exp(-1.191 \cdot f_i)}{d^{2.5}} = 350 \frac{N_e^{2/3} \exp(-1.191 \cdot f_i)}{d^{2.5}} \quad (3)$$

In most cases the nature of the chemical bondings involved in determination of theoretical hardness is described including the ionicity parameter  $f_i$ . Unfortunately, it is still not very clear the "physical-chemical" image of this parameter, despite many existing theories, starting with Pauling's classical approach [7] up to the modern view provided by dielectric theory of chemical bonding of Phillips and van Vechten [8,9].

The approach to be presented in present paper tries to revive the fruitful concept of ionicity of the chemical bonding without considering an explicit atomic parameter as electronegativity, starting from Phillips-van Vechten theory.

## 3. Ionicity approach

The starting point of our approach is based on ionicity of crystalline solids. The concept of crystal ionicity has proved to be a useful unifying concept for understanding chemical trends in diverse problems in solid state physics and chemistry. In particular, the dielectric description of ionicity developed by Phillips [8] and van Vechten [9,10] has been successfully employed in a variety of areas [11]. Originally, these ideas have been developed for binary  $ANB^{8-N}$  compounds but it has been shown by various authors [12,13] that this ionicity concept can be generalized to include multibond crystals and complex crystal structures. These aspects will be considered in a future paper.

The reason for using initially the crystal ionicity for a potential description of glass basicity is related to the fact that for a crystalline structure (a homodesmic one) the bond ionicity is identical with the so-called bulk ionicity, so that even individual oxides within a glass can be described by the bond ionicity.

The ionicity parameter

$$f_i = \frac{C^2}{E_g^2} = \frac{C^2}{E_h^2 + C^2} \cdot f_c = \frac{E_h^2}{E_g^2} = \frac{E_h^2}{E_h^2 + C^2} \quad (5)$$

of the dielectric theory of the chemical bonding [8-10], the homopolar part

$$E_h \propto d^{-2.48} \quad (6)$$

( $d$  nearest-neighbor distance) and the heteropolar part

$$C \propto \left( \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right) \exp\left( -k_{TF} \frac{r_A + r_B}{2} \right) \quad (7)$$

( $Z_i$ ,  $r_i$  valences and radii of the constituents of a compound AB, respectively;  $k_{TF}$  is the wave number of the Thomas – Fermi screening) of the mean bonding–antibonding  $E_g = (E_h^2 + C^2)^{1/2}$  of the electronic band structure are fitted in such way that they reproduce through the Penn model [14] for the static dielectric constant.

Levine's [12,15] modifications introduced for the calculation of (6) and (7) have improved the results obtained for various crystal structures. Also, Zhang's [16] ideas of improving Levine's approach allowed the decomposition of complex multibond crystals into a sum of binary crystals.

Unfortunately, as one can see from relation (7) there are still some ambiguous quantities such  $r_A$ ,  $r_B$ ,  $Z_A$ ,  $Z_B$ , that always generated various values for the same property of a solid (e.g. different sets of radii, different valence charges, etc.).

Our approach starts from the same relation (5) of defining ionicity, but considering the homopolar (covalent) and the heteropolar (ionic) fractions as described in Figure 1 [17,18]

It is interesting to note that one can define ionicity ( $f_i$ ) or covalency ( $f_c$ ) of a chemical bonding in a *symmetrical* way, a feature that is not fulfilled by any other definition of ionic – covalent

character, i.e.  $f_i = \frac{C^2}{E_g^2}$  (ionicity) or  $f_c = \frac{E_h^2}{E_g^2}$

(covalency), and obviously  $f_i + f_c = 1$  with no other additional condition. This pictorial view allows one to consider directly the ionic fraction as the energy difference between the fundamental energy levels of the two partners involved in the chemical bonding that can be calculated or taken tabulated values.

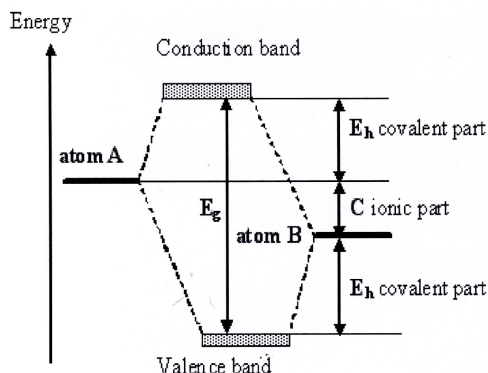


Fig. 1 – Ionic – covalent character of chemical bonding in solids / Caracterul ionic-covalent a legăturilor chimice în solide.

Consequently, in this way the energy contribution (in eV) to  $E_g$  of each part (homopolar and heteropolar) is to be considered as presented in Figure 2.

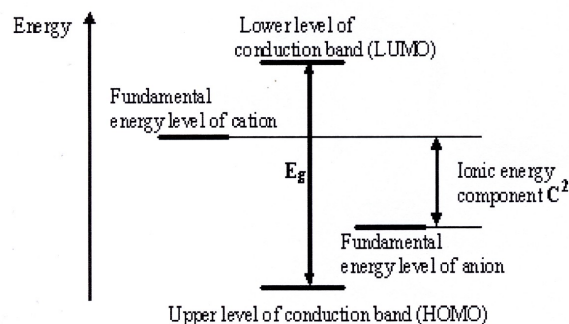


Fig. 2 – Direct definition of ionic fractions for solids (LUMO – lowest unoccupied molecular orbital; HOMO – highest occupied molecular orbital) / Definiția directă a fracției ionice a legăturii chimice din solide. LUMO- cel mai jos orbital molecular neocupat cu electroni; HOMO- cel mai înalt orbital molecular ocupat cu electroni.

in this way, it is possible to avoid the alteration of the calculated values when using different sets of radii or values for valence charge for the involved atoms in the chemical bondings.

Our approach to define ionicity leads to some interesting consequences considering inherently several known results but which proofs were rather intuitively than rigorous. Hence, our model takes into account the characteristic atomic features through their fundamental energy levels that are considered in a natural way with the collective (molecular) features of multibond solids and not through adjustable empirical parameters that makes possible to distinguish the different ionic character of the same chemical bonding among the polymorphs for a given composition. This approach is not possible when using traditional models based on electronegativity of elements. These aspects have been discussed extensively in a previous paper [17].

One of the most important consequences, in our opinion, is the variation of ionicity with structural parameters of a solid phase. This variation is mainly due to the sensitivity of the band electronic structure even to any of as small change of the network (crystalline or vitreous). Also, the band gap depends on many other factors such as: defects, growth method, crystal structure, temperature, oxidation state of cations, etc. This aspect will be further discussed in the paper.

It is important to emphasize an aspect provided by our model. If we agree with representation from Fig.2, the fundamental energy levels are fixed for any atom according to the position within the Periodic Table. Then one can observe that the heteropolar part C is constant ( $C^2 = const.$ ). Hence, it follows that ionicity depends directly on the amount of homopolar part and on the value of  $E_g$ , where  $E_g$  can be obtained

experimentally via spectroscopic methods or calculated using quantum chemistry techniques. In this way, any alteration of  $E_h$  values change the ionicity. As according to relation (2),  $E_h$  depends only on  $d$  (distance between the nearest neighboring atoms or internuclear distance), it is possible to use this measurable parameter for estimating ionicity. Any change within the structure will affect the value of  $E_g$  and, implicitly the value of  $E_h$  (as  $C$  is constant according to the proposed scheme). Using this ionicity approach it is no longer necessary to estimate any dependence of the ionicity on other structural parameter as coordination number, oxidation number, ionization potential, etc., while this is fulfilled *sine die* when  $E_g$  changes with any type of modification within the structure, since the energy gap value is the resultant of all interactions occurring between the atoms.

In this way, it is also established the role of homopolar part of energy gap,  $E_h$ , within the formulas describing hardness.

Preliminary calculations have shown a very good agreement with the values computed for hardness using more sophisticated approaches and where the physical-chemical nature is not that easy to be understood. Further research must be done in order to complete the view upon the nature of hardness of complex compositional compounds.

#### 4. Results and discussions

In the case of simple crystals having homodesmic chemical bondings the calculation of hardness is quite straight. The atomic energy levels values were taken from [19]. A first case to be analyzed is that of  $\text{SiO}_2$  polymorphs as a primary test of our approach. Ionicity of  $\text{SiO}_2$  polymorphic forms have been calculated according to our approach as presented in [17]. The Vickers hardness was calculated according to formula (3). The values of interatomic distances (bond lengths) were taken from literature [20] as well as the electron density expressed in the number of valence electrons per cubic angstrom ( $N_e$ ).

The results are given in Table 1.

Data on  $\text{SiO}_2$  experimental hardness values were available only for  $\alpha$ - quartz but even in this case the agreement is very good. As expected the calculated values for the other polymorphic forms of silica are in a narrow range as one could expect.

Another example of homodesmic crystals is that of alkaline-earth oxides having rock-salt structure, where the calculation of hardness is also easy to perform. The results of calculations are given in Table 2.

The only experimental values found in literature are in good agreement with the calculated ones.

Table 1

Calculated hardness of  $\text{SiO}_2$  polymorphic forms / Durtăți calculate pentru formele polimorfe ale  $\text{SiO}_2$

$\text{SiO}_2$ polymorphs	ionicity ( $f_i$ )	d (Si – O) (Å) experimental [21]	Hv (GPa) calculated	Hv (GPa) experimental
$\alpha$ - quartz	0.57	1.607	10.845	11 [22]
$\beta$ - quartz	0.6	1.58	10.92	-
$\beta$ - tridymite	0.59	1.54	11.78	-
$\alpha$ - cristobalite	0.575	1.605	10.82	-
$\beta$ - cristobalite	0.61	1.55	11.32	-
Coesite	0.53	1.61	11.32	-
Keatite	0.59	1.59	10.88	-
Stihovite	0.41	1.77	10.31	-

Table 2

Calculated hardness values for alkaline-earth oxides / Durtăți calculate pentru oxizii alcalino-teroși

MO oxides	$E_n$ (eV)	$C$ (eV)	ionicity ( $f_i$ )	d (M – O) (Å) experimental [20]	Hv (GPa) calculated	Hv (GPa) experimental
MgO	6.269	13.821	0.823	2.089	15.6	15-16.5 [23]
CaO	4.507	13.063	0.891	2.468	9.5	-
SrO	3.788	13.242	0.922	2.56	2.23	-
BaO	3.177	13.434	0.931	2.76	1.82	-

## 5. Conclusions

The simplicity of the approach allows a broader class of researchers to access the method easily and to calculate the hardness of materials even using only a hand-calculator.

Finally, the correlation between bond length and hardness in oxide crystals has been studied. The physical-chemical nature of the hardness of ionic crystals (mostly oxides) has been further discussed and the role of homopolar component of the chemical bonding of oxides was questioned.

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## ANIVERSĂRI



### 20 septembrie (1459) – Ziua oraşului Bucureşti

La această dată se împlinesc 558 de ani de la prima atestare documentară a existenţei Oraşului Bucureşti, într-un hrisov emis de cancelaria voievodului Vlad Ţepeş. În ordine cronologică, oraşul Bucureşti a devenit treptat, în secolele următoare, cea de a patra capitală a Ţării Româneşti a Munteniei (dupa Câmpulung, Curtea de Argeş şi Târgovişte) şi prima capitală a României Mari după Războiul de Întregire Naţională din 1916 – 1918

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