

## CALCULATION OF ELECTRON STRUCTURE OF TALC BY SEMIEMPIRICAL METHODS OF QUANTUM CHEMISTRY

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The electron structure of the isolated layer of the ideal structure of talc was computed using semiempirical quantum-chemical method INDO/2. The computation was aimed at finding a cluster modelling electron properties of an infinite plane with sufficient accuracy. The cluster fulfilling the above requirements consists of 298 atoms. Electron densities on individual atoms and bond orders were obtained by the computation. The used method and the chosen size of the cluster enable to distinguish unambiguously the existence of two types of Mg (M1 and M2 type) in the structure. Simultaneously, apical oxygens forming hydroxyl groups differ clearly from apical oxygens non-bonded to hydrogen atoms. A significant difference of atomic net charges on the basal and apical oxygens was obtained.

## INTRODUCTION

All phyllosilicates have structures based on two-dimensional silicate layers. The talc -  $Mg_3Si_4O_{10}(OH)_2$  was chosen as a model of the very important group of such minerals (2:1 trioctahedral minerals) [Fig. 1]. With the respect to its structure and physical properties, this system is a suitable model for situations when the layers or the particles interacting with the surface layer are bonded predom-

inantly by long-range electrostatic forces and interaction by chemical bonding plays only negligible role. The first step for the study of the interactions of this kind must be the calculation of the electron structure of an isolated layer giving sufficiently realistic description of the properties of the layer. Some papers devoted to such computations have appeared in the last years [1-3]. The papers mentioned use different modifications of EHT methods; it is a well known fact that these methods overestimate the magnitudes of atomic charges and give inadequately polar bonds. These papers use different models of the studied minerals; in the work [1] a small cluster model was used, works [2, 3] are utilising translational periodicity of studied systems and they consider the layer as two-dimensional infinite system. All these works are aimed to the study of the influence of isomorphous substitutions on the electron structure.

The goal of this work is to obtain the electron structure of the isolated, idealized layer (symmetry of the tetrahedral sheet is  $p6mm$ ) of talc which can serve as a reference model for the study of the influence of geometrical changes (rotating, tilting and deformation of the structural units of the layer - the tetrahedra and octahedra) and the influence of the isomorphous substitutions.

This is the reason for the choice of such quantum-chemical method which could give more reliable picture of the electron structure than EHT or IEHT methods. The resulting choice of the method is a compromise between our requirement and the possibilities of the individual methods.

Ab initio crystal-orbital (CO) methods [4] would be an ideal solution with respect to the accuracy of the method as well as with regard to the use of realistic model system. Unfortunately, the size of the unit cell of our system does not allow to realize such computation using the basis set of sufficiently good

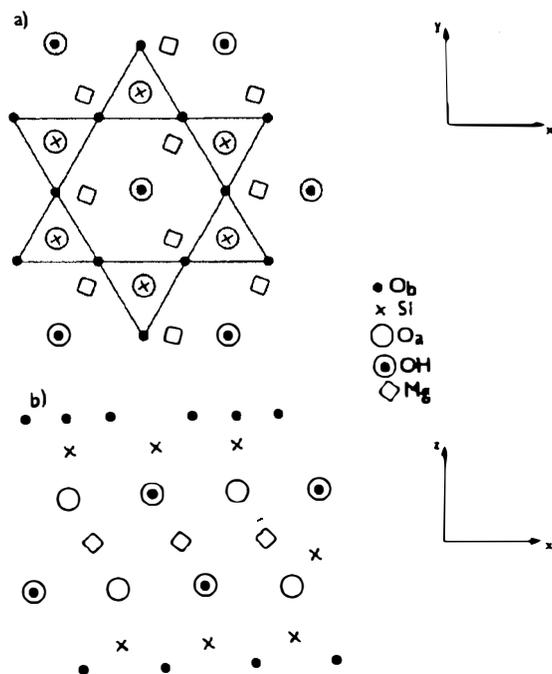


Fig. 1. Structure of idealized layer of talc - a)  $xy$  projection (for clarity only the upper tetrahedral sheet is drawn); b)  $xz$  projection.

quality even for the idealised structure of the talc. Moreover, the interpretation of the obtained results in direct space is much more simple and illustrative for the chemist. Therefore, the cluster model of the studied system was used. With the respect to the expected size of the cluster the quantum-chemical INDO/2 method [5] was chosen as the method for calculation of the electron structure. By experience of the authors, this choice represents a reasonable compromise between the exactness of the method of calculation and the reality of the studied model.

### METHOD

The basic cluster used for modelling of infinite plane of one ideal layer of talc was constructed in the way preserving the electroneutrality and the symmetry of the whole layer [Fig. 1]. The used structural parameters of the idealized structure of talc are the following: Si-O bond length  $1.622 \times 10^{-10}$  m and Mg-O bond length  $2.162 \times 10^{-10}$  m [6]. Unsaturated valencies of frontier atoms of the cluster were completed by hydrogen atoms.

The quantum-chemical computations were realized for this cluster and then it was stepwise enlarged in manner preserving the symmetry. This process was stopped when the charges of atoms forming the central part of the cluster were equal in all symmetry equivalent positions. The resulting cluster consisted of 298 atoms [Fig. 2]. We suggested that the atoms in the central part of the cluster represent the bulk atoms of the two-dimensional infinite plane. Moreover, we found that the equality of atomic charges was

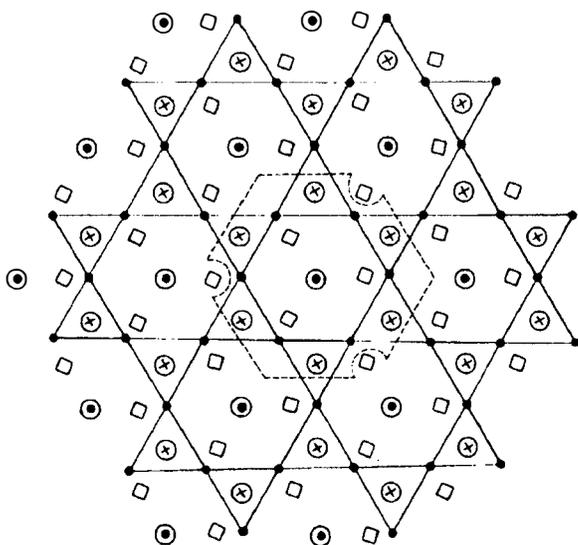


Fig. 2. The 298 atomic cluster of idealized layer of talc. The central part of the cluster is also drawn (---). The meaning of the symbols is as in Fig. 1. (for clarity only the upper tetrahedral sheet is drawn.)

Table I

Atomic populations and gross atomic charges in idealized, isolated talc layer (layer group symmetry  $p6mm$ )

Atom	Atomic population	Atomic charge
O <sub>b</sub> (basal)	6.7814	-0.7814
Si	2.3077	1.6923
H (OH group)	0.9025	0.0975
O <sub>a</sub> (OH, apical)	6.5968	-0.5968
O <sub>a</sub> (apical)	6.6725	-0.6725
Mg (M1)	1.4687	0.5313
Mg (M2)	1.4550	0.5450

Table II

Wiberg indices of bonds in idealized, isolated talc layer

Bond	Wiberg index
Si - O <sub>b</sub>	0.7787
Si - O <sub>a</sub>	0.7136
O <sub>a</sub> - H	0.9514
Mg(M1) - O <sub>a</sub>	0.2110
Mg(M1) - O <sub>a</sub> (OH)	0.1651
Mg(M2) - O <sub>a</sub>	0.1815, 0.2135
Mg(M2) - O <sub>a</sub> (OH)	0.1741

reached not only for the symmetry equivalent atoms in the central part but to the satisfactory degree of accuracy for all the symmetry equivalent atoms in the whole cluster except the frontier atoms.

### RESULTS AND DISCUSSION

The cluster [Fig. 2] obtained by the above described method consists of 298 atoms. Table I shows atomic charges of the atoms from the central part of the cluster. One can see a clear difference of charges of the basal and apical oxygens. The basal oxygen atoms are significantly more negative. The least negative is the apical oxygen atom forming the hydroxyl group. Very small positive charge of the hydrogen in the hydroxyl group indicates the low acidity of the OH groups of talc. The charges of the magnesium atoms in the two non-equivalent positions M1 and M2 are clearly different. The magnesium atom in the position M1 has higher positive charge than in the position M2.

Table II contains Wiberg indices [7] of important bonds from the central part. Bond orders Si-O vary in the range 0.71–0.78. This is in good accordance with

Si-O bond orders obtained using MNDO method for chemically different molecules containing Si-O bonds [8]. The high bond order of the O-H bond indicates very low acidity of the hydroxyl groups of talc. The bond orders between magnesium in position M2 and apical non-hydroxyl oxygen atoms show interesting behaviour. All bond lengths in this case are equal but the bond orders are different. On the contrary, the bond orders between Mg in position M1 and apical oxygens are equal for all non-hydroxyl oxygens. This fact can follow from different positions of two OH groups bonded to Mg at sites M1 and M2. Both are octahedrally coordinated, however, M2 site has the OH groups in cis-position and M1 site in trans-position. The lowest bond orders have bonds between magnesium atoms and oxygens of OH groups. This follows from the fact that apical oxygen atoms are coordinated by four other atoms. The low orders of these bonds can elucidate the fact that during acidic decomposition of phyllosilicates the Mg-O bonds are splitted preferentially [9].

### CONCLUSIONS

We can conclude that the cluster of 298 atoms obtained by the described procedure is large enough to have a central part which satisfactorily models the electron and bonding properties of two-dimensional infinite layer of talc. The used combination of semiempirical quantum-chemical method and the way of modelling of the layer enables to make conclusions about the electron and bond properties of atoms in non-equivalent positions in the structure and may be useful for elucidation of reaction mechanisms of decomposition of phyllosilicates. The atomic charges obtained by using this method are substantially lower than charges provided for similar systems by EHT methods [1-3]. This fact indicates both a good comprehension of covalency of the bonds in the studied system (e.g. calculated atomic charge of Si in talc layer is 1.7 e in this work and 2.38 e in [2]) and a more reliable description of the electron structure as well.

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## VÝPOČET ELEKTRÓNOVEJ ŠTRUKTÚRY MASTENCA POMOCOU SEMIEMPIRICKÝCH METÓD KVANTOVEJ CHÉMIE

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Práca je zameraná na výpočet elektrónovej štruktúry izolovanej idealizovanej vrstvy mastenca (symetria tetraedrickej siete  $p6mm$ ), ktorá môže slúžiť ako referenčný model pre štúdium vplyvu geometrických zmien (rotácie, vychýlenia a deformácie štruktúrnych jednotiek vrstvy - oktaédrov a tetraédrov) ako aj vplyvu izomorfných substitúcií centrálnych atómov.

Z metód štúdia tuhej fázy bol zvolený klastrový prístup, kde nekonečný periodický systém je nahradený konečným, dostatočne veľkým klastrom. Pre výpočet elektrónovej štruktúry bola zvolená kvantovo-chemická metóda INDO/2. Základný klastor bol navrhnutý tak, aby zachoval elektroneutralitu a symetriu celej vrstvy (Obr. 1). Tento základný klastor bol potom zväčšovaný až dovtedy, kým náboje na atómoch v centrálnej časti klastra (Obr. 2) boli rovnaké pre všetky symetricky ekvivalentné pozície. Výsledný klastor pozostáva z 298 atómov (Obr. 2). Možno predpokladať, že atómy centrálnej časti klastra reprezentujú atómy dvojrozmernej nekonečnej vrstvy. Získané náboje a atómové populácie pre jednotlivé typy atómov tvoriacich vrstvu ako aj poriadky väzieb sú uvedené v Tab. I a II.

Vypočítané nábojové hustoty na centrálnych atómoch oktaedrickej siete (Mg) potvrdzujú existenciu dvoch typov oktaédrov (M1 a M2). Tiež vrcholové atómy kyslíka tetraedrickej siete z hydroxylových skupín sa líšia od ostatných vrcholových atómov kyslíka. Vysoký poriadok väzby O-H znamená malú kyslosť OH skupiny. Naopak, nízky väzbový poriadok majú väzby Mg-O. Vyplýva to z toho, že vrcholové atómy kyslíka majú koordináciu 4. Nízky poriadok väzieb Mg-O môže tiež pomôcť vysvetliť mechanizmus kyselinového rozkladu fylosilikátov, pri ktorom sa najskôr narušujú práve väzby v oktaédroch.

*Obr. 1. Štruktúra idealizovanej vrstvy mastenca - a) xy projekcia (pre prehľadnosť len horná tetraedrická sieť je nakreslená), b) xz projekcia.*

*Obr. 2. 298 atómový klastor idealizovanej vrstvy mastenca. Centrálna časť klastra je tiež vyznačená (- - -). Význam symbolov je ako v Obr. 1. (pre prehľadnosť len horná tetraedrická sieť je nakreslená).*