

ELECTRONIC STRUCTURE OF SODALITE: A COMPUTATIONAL STUDY

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Quantum-chemical semi-empirical modified INDO and ab-initio Density-Functional techniques have been applied to study the electronic structure of natural sodalite. The emphasis has been made on the reproduction of the ground electronic state of the material. Density of electronic states and effective charges on the constituent ions have been obtained using both methods and compared.

1. Introduction

Sodalites belong to a wide class of tectosilicates, the primary building unit of which is a tetrahedron with a Si or an Al atom in the centre and four oxygen atoms at its apices; each oxygen atom is shared by two adjacent tetrahedra. The tetrahedra build up the framework of the material in the form of the periodic array of truncated polyhedra (β -cages) inscribed into cubic unit cells. Each unit cell of the sodalite crystal comprises 12 tetrahedral sites, and in all naturally occurring sodalites the Si/Al ratio is close to unity [1, 2]. Usual synthetic samples exhibit the same composition; however, there was also reported a way of producing a pure silica sodalite from nonaqueous solutions [3].

The introduction of aluminium into tetrahedral sites necessitates charge compensation by extraframework species situated within the sodalite cages. This is the basis for unusual optical, electrical and other properties of sodalites. The stabilising of highly reactive metal and semiconductor clusters, neutral and charged, by the framework generates ideal conditions for electron solution, confinement and quantum-size effects. Nonstoichiometric halogen sodalites are used as cathodochromic media for memory devices [4]. Moreover, there has been reported the newly developed sodalite semiconductor containing quantum supralattices based on sodium matrices with a quarter of the sodium substituted for silver [5].

The sodalite framework in the case of the aluminosilicate includes 3 Al atoms per one β -cage which should be balanced by counterions of total charge +3. This can be realised by 3 Na ions giving rise to dry sodalite. But the latter is rather an unusual material, as in tetrahedrally organised lattice the sites of multiplicity 4 are occupied with a greater ease. To accommodate an additional sodium ion per cage a univalent anion is introduced, as a rule situated in the cage centre. It may be a halogen Cl^- , Br^- , I^- (halosodalites), a hydroxyl group (basic sodalites), and sulphur based complex anions such as SO_4^{2-} , S_2^- , S_3^- (ultramarines); the nature of the latter is still in question. The molecular form of the anions often violates the lattice symmetry; the variable amount of neutral water molecules dissolved by the material has the same effect. Thus sodalites present an interesting example of disordering in framework materials (such as zeolites): a relatively strict periodicity of the framework is contrasted by a loose pattern in the composition and location of the extraframework species.

In recent years electronic structure of sodalites has attracted the interest due to their unique optical properties. Depending on the composition of extraframework species, the width of optical gap in sodalites can vary from ~8 eV and down field, reaching even into the infrared region (the dry sodalite oversaturated by sodium is black).

Denks *et al* [6] have assigned the major contributions to the absorption spectra of halo- and basic sodalites, in particular. The absorption bands, whose edge was below 8 eV, were considered to have the local character with excitation of extraframework anions, whereas the bands of higher energy were attributed to aluminosilicate framework and localised oxygen excitons. Well resolved thermo- and photoluminescence bands were also observed and interpreted in terms of structural and electron-hole defects of

the extraframework lattice (the colour centres in sodalites). Effects resulting from solvation of electrons on sodium clusters in sodalites were studied in [3, 7] by means of both electron spin resonance and optical spectroscopies.

The structure of the valence band for a number of silicates has been scrutinised in a series of works by Barr *et al* [8] using methods of the electron surface spectroscopy. The work included sodalites, in particular. The general conclusions of the work were 1) the electronic structure of all silica materials such as alpha-quartz and siliceous sodalite is very similar, and 2) the introduction of aluminium into the framework can be considered in terms of the admixture of NaAlO₂ structural units into the silica for more siliceous materials or of the admixture of SiO₂ units into NaAlO₂ for silicates with the high content of Al. The authors observed the shift down field of the leading edge of the valence band upon introducing Al into the framework and simultaneous decrease in the width of the valence band. Unfortunately, these studies did not include the halo-sodalites and the structure of their valence band and the rôle of extraframework anions are still not clarified.

Computational approach has become a major technique in materials physics and chemistry [9]. Recently, the rapid progress in computer resources has allowed one to study at the *ab initio* or semi-empirical level crystal systems even as large as sodalites. Both molecular and periodical models were applied to model siliceous, alumino-silicate and alumino-phosphate sodalites [10, 11]. The one-electron models with empirical pseudopotentials [3, 12] have been derived to reproduce transition energies in dry sodalites and related systems. A number of studies concentrated on the catalytic properties of sodalite framework and the reproduction of the geometry of chemically active sites using the Hartree-Fock [13] and the Density Functional [14] based techniques.

However, the rôle of extraframework anion (chlorine in our case) in the formation of the electronic bands has not been investigated. Moreover, the electronic transitions on the extraframework complexes were not studied self-consistently within a coherent approach which would include the interaction with the framework. We present here the first study of the ground electronic state of chloro-sodalite. The work is meant to be first in the cycle of studies on the electronic structure and transitions in sodalites based on the self-consistent methods.

2. Methodical notes

Two basic approaches have been accepted in the present study *vis.* the Hartree-Fock method in the semi-empirical form (a modified INDO scheme [15]) and the Density Functional method using numerical basis sets and frozen core approximation [16]. The periodical Large Unit Cell (LUC) model is the common basis of both approaches which facilitates a direct comparison of the results. The main approximation introduced by this model is that only one point, the centre of the Brillouin zone, is taken into account.

We note here that the first method, as implemented in the program SYMSYM [17], exploits the system symmetry which allowed us to build unit cells of large size and thus effectively take into account significantly greater number of **k**-points. Another advantage of the method, as compared to the *ab initio* DFT program DSOLID [18], is the correct procedure of summation of the exchange integrals. The second program uses an arbitrary cut-off radius which corresponds to a wrong representation of the density matrix: its elements are unknown, in fact, when one of the orbitals is centred within the central LUC and another outside (see discussion in [15]). On the other hand, the advantage of Dsolid is the *ab initio* character of the method implemented and a consistent account of the correlation effects in the system. The latter, of course, is true only for the ground state, but this is exactly the aim of the present study.

The semi-empirical parameters used in this work have been fitted to reproduce geometry and electronic structure of such crystalline systems as alpha-quartz, corundum and rock salt, which allowed us successfully predict corresponding properties for a number of ternary compounds. This work where the method is applied to the system of so complex a chemical composition is a test for the method which essentially based on taking into account only two-centre interactions (the three- and four-centre integrals are neglected).

As the geometry optimisation is the crucial time-demanding step in the electronic structure investigation, in the present study we have chosen the compromise and performed the full optimisation procedure only at the semi-empirical level and then used the ion positions and the lattice parameters in both semi-empirical and density functional calculations. The small size of the unit cell affordable in the density functional calculation has limited our corresponding semi-empirical modelling by the LUC of 1x1x1 size in the problem of geometry optimisation. However, we used the LUC of 2x2x2 size studying the electronic

structure of sodalite in the final single-point calculation so that to obtain a better representation of the density matrix.

The version of the program DSolid we have used in our DFT studies does not produce the density of electronic states, whereas the program SYMSYM allowed us to obtain the corresponding plot using the tetrahedra method. (The electronic spectra in all \mathbf{k} -points are calculated using the interpolation and perturbation method [19].) To make these two results comparable, we have represented the lines in the DFT spectrum by gaussians with the dispersion 0.3 eV; at the same time the semiempirical spectrum has been broadened using the convolution with the gaussian of the same dispersion.

Finally, neither of the two programs produces projected densities of states or population analysis for molecular (crystal) orbitals. Therefore we were able only indicate the most important atomic contributions to the electronic bands analysing the molecular orbitals in the atomic orbitals representation.

3. Results of calculations and analysis

Geometry optimisation of the LUC of size 1x1x1 using the INDO method has led to the results presented in Table 1.

TABLE 1. Results of crystal structure optimisation of chloro-sodalite using modified INDO periodical model. Extension of the LUC used is 2x2x2.

Parameter	Experiment	Theory
a	8.91 Å	9.20 Å
Na: x=y=z	0.175	0.171
O: x	0.150	0.150
y	0.135	0.135
z	0.440	0.452

The overestimation of the lattice parameters and of the volume of the corresponding unit cell is a common feature of the crystal calculations in which a LUC of small size is used. It is apparently caused by the fact that the exchange interaction (having the attractive character) in this model is cut off at the LUC boundary.

The crystal lattice of chloro-sodalite has the $P\bar{4}3n$ space group. Positions of the Si, Al, and Cl atoms are fixed by the symmetry. The Na atoms are fixed on the principal diagonals of the cubic unit cell, whereas the oxygen atoms are in the general crystallographical positions. This leaves altogether five geometrical parameters for optimisation: that is the lattice parameter \mathbf{a} and four fractional coordinates. As seen from Table 1, the optimised fractional coordinates are quite close to experiment. The deviations can be interpreted in terms of a slight shortening of the Na-Cl bond and a widening of the Si-O-Al angle. Results of the calculation of the electronic structure are summarised in Table 2 and Figure 1. As mentioned above we make a major emphasis on the reproduction of the ground state, hence the main object of interest here is the valence band and the effective charge distribution.

TABLE 2. Parameters of the electronic structure of chloro-sodalite. Since the INDO LUC model exploits minimal basis sets, the $Cl\ 4s$ states are not accounted for. Therefore, to compare results of INDO and DFT calculations, the E_g value in the first line is corrected omitting the $Cl\ 4s$ states.

	INDO	DFT
Effective charge: Si	2.77	1.45
Al	2.56	1.06
O	-1.57	-0.85
Na	0.92	0.87
Cl	-0.85	-0.84
E_w , eV	7.9	7.5
E_g , eV		
omitting $Cl\ 4s$ peak	11.4	5.9
accounting for $Cl\ 4s$	-	3.8

Both the INDO and the DFT calculations give similar widths and structural features of the valence band, however the positions of the Cl 3p states according to the DFT method are in the middle of the upper sub-band. But the INDO method predicts the formation of a separate, uppermost sub-band due to the Cl 3p

states. It can be concluded in general that all the states are somewhat compressed and shifted upfield in the DFT calculation.

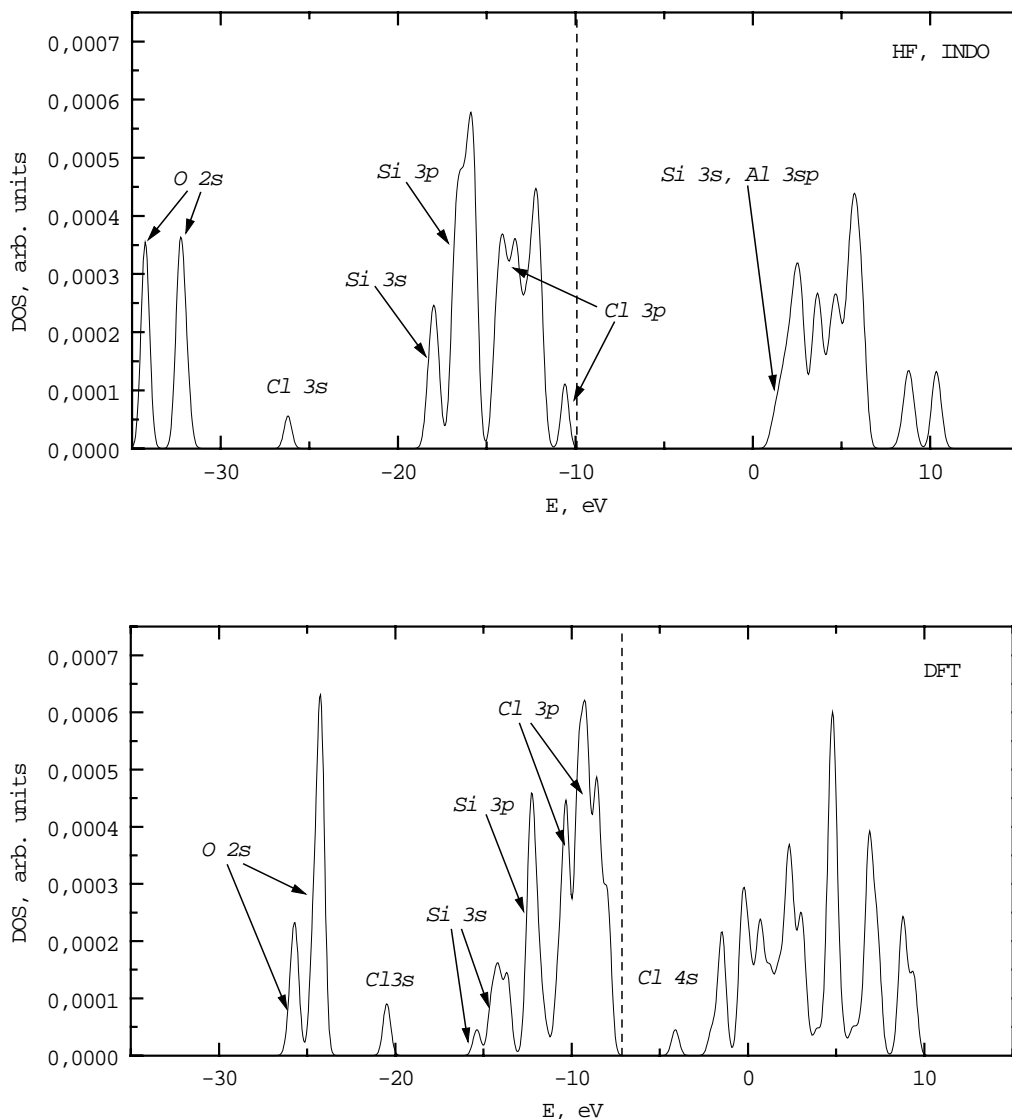


Figure 1. Density of electronic states of chloro-sodalite. Two graphs represent results of *ab initio* DFT and semiempirical INDO HF calculations. Dashed lines indicate the top of the upper valence band. The major contribution to the upper valence band is due to $O\ 2p$ states in both DFT and INDO calculations. Details of the calculations are given in the text.

Since the INDO computational scheme is based on the minimal basis sets we could not reproduce the localised excitations on the Cl atoms that correspond to a transition from Cl 3p to Cl 4s states. As a result, the Cl 4s unoccupied states are not present on the corresponding graph of the density of states for the INDO method. Therefore we have excluded the Cl 4s peak from an estimate for the one-electron optical gap in the DFT calculation (see Table 2). As a result we obtained the value of 5.9 eV which is a reasonable guess as compared with the Hartree-Fock (in the semi-empirical form) value of 11.4 eV. We note here that the DFT method tends to greatly underestimate the optical gap value whereas the Hartree-Fock overestimates. Thus we should expect that the optical gap should lie somewhere in the middle, at about 8-9 eV which is in good agreement with experiment (for a wide class of aluminosilicate materials).

The effective charges given by the INDO method as expected describe the system as highly ionic. This is in contrast to the DFT results that emphasise the partial covalent character of the bonding in the

material. However, the latter should be treated cautiously, It is a well known fact that the Mulliken analysis (used by DSolid) systematically underestimates effective charges in ionic crystals.

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Conclusions

Our modelling evidences that the semi-empirical INDO and *ab initio* DFT approaches well complement each other in reproduction and prediction of the electronic properties of so complex a material as sodalite. The DFT calculation confirmed that the localised optical transition on Cl extraframework anions determine the absorption edge in chloro-sodalite as proposed in [6]. Both INDO and DFT calculations demonstrated that the bottom of the upper valence band in sodalites is fixed by the Si 3s states similarly to other silicates.

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