SOLID STATE PHYSICS

COMPUTER SIMULATIONS OF THE BAND STRUCTURE AND DENSITY OF STATES OF THE LINEAR CHAINS OF NaCl IONS

L.N. Myasnikova[1], A.S. Istlyaup[1], D.M. Sergeyev[1,2], N.N. Zhanturina[1],
K.Sh. Shunkeyev[1], A.I. Popov[3]

[1]Zhubanov Aktobe Regional State University, 34 A.Moldagulova Ave., Aktobe,
030000, KAZAKHSTAN
[2]Begeldinov Military Institute of Air Defence Forces, 39 Moldagulova Ave.,
Aktobe, 030012, KAZAKHSTAN
[3] Institute of Solid State Physics, University of Latvia, 8 Ķengaraga Str., LV-1063
LATVIA
e-mail: myasnikova_ln@mail.ru, popov@latnet.lv

The paper presents the results of first-principles computer simulations of the band structure, the density of states, and the total energy of NaCl (NaCl, Na_2Cl_2, Na_3Cl_3, Na_4Cl_4, Na_6Cl_6) linear chains of atoms. Modelling of the specified characteristics is realised in the computer code Atomistix ToolKit combined with Virtual NanoLab. The total energy depends on the number of ions in the nanoobject under study, but practically does not depend on the geometric arrangement of ions.

Keywords: *NaCl, band structure, computer simulations, density of states, total energy*

1. INTRODUCTION

Alkali halides are the simplest and most representative ionic crystals. The alkali halides NaF, NaCl, NaBr, and NaI crystallize in the rock salt (B1) structure at ambient conditions. They have many interesting physical properties such as high melting point, strong miscibility, and large band gaps. Due to the fact that in these materials the effective exciton mechanism [1]–[10] of the formation of radiation defects is implemented, they are widely used as radiation detectors, such as scintillators [11]–[15] and a storage phosphors for image plate detectors and optically stimulated dosimeters [16]–[20]. Moreover, alkali halides are used as infrared (IR) optical windows and optoelectronic devices [21], [22].

Nowadays, the properties of alkali halide nanocrystals have attracted great

attention of experts in chemistry, physics, and engineering. Structural, electronic, dynamic, and chemical characteristics of materials depend primarily on the state (phase) and the degree (size) of aggregation. Atomic chains containing 3–500 particles exhibit unique physical and chemical phenomena, which are of both fundamental and technological significance, and provide ways and means to explore the "transition" from molecular to condensed-matter systems [23]. They are simultaneously regarded as fundamental objects, in which the molecular and solid properties are reflected [24]–[29]. There are three main areas of application: first, nanocrystalline structures represent the ultimate in miniaturization of solid-state materials. Second, many nanocrystal properties are dominated by their surfaces because a large fraction of the atoms lies in the outermost layer. Third, the finite size and number of atoms in a nanocrystal, which is often less than 10^3, mean that systems having the structures of bulk crystalline matter can be calculated with a precision typically reserved for atoms and molecules, using modern methods [30], [31].

In the last decade, many papers were published about the properties of alkali halide nanocrystals. They include results on the cohesion, bonding, and structures; crystallinity phenomena including cleaving and melting; molecular adsorption reactions; halide-transfer reactions; electron substitution, solvation, and spectroscopy; surface electron states; electronic excitations and photochemistry; multiple charging; and other subtle effects in nanolattices [23], [32]. However, some major issues remain open, such as the reliability of structural calculations, based on first-principles methods. With these calculations, most experimental results could be interpreted.

A deep understanding of the optical properties of solids is impossible without a detailed knowledge of their electronic structure. The electronic processes in ionic crystals are considered on the basis of the approximate quantum-mechanical theory where the motion of electrons and nuclei is separated based on adiabatic Born-Oppenheimer approximation [33], [34]. One of the characteristics of the reflecting property of a nano-objects is the electronic density of states: the number of allowed electron (or hole) states per volume for a given energy [31].

In this paper, an attempt was made to determine the band structure, the density of states, and the total energy of NaCl linear chains with different number of ions using the computer simulations of Atomistix ToolKit combined with Virtual NanoLab [35].

2. DESCRIPTION OF THE OBJECT AND METHODS OF RESEARCH

The isolated atoms of the alkali metal Na and the halogen Cl have the following electronic configuration: $Na^0 – 1s^2 2s^2 2p^6 3s^1$, $Cl^0 – 1s^2 2s^2 2p^6 3s^2 3p^5$. In NaCl matrix, the ions of the corresponding elements assume the following electronic configuration – $Na^+ – 1s^2 2s^2 2p^6$, $Cl^- – 1s^2 2s^2 2p^6 3s^2 3p^6$. As a result, the valence electron located on the outer shell of Na^0 completely passes to Cl^0.

We divided the studied NaCl objects into three categories: one-dimensional, two-dimensional and three-dimensional. The dimensional NaCl built chain of 2, 4, 6 and 12, alternating between a Na^+ ions and Cl^-. Plane of 4, 6, 8 and 12 ions are

constructed in the two-dimensional NaCl. Three-dimensional NaCl consists of 8 and 12 ions. The distance between the centres of the nearest ions in NaCl is 2.82 Å [36].

In the adiabatic approximation, the solution of the Schrödinger equation shows that the states of an excess electron in a crystal with a periodic field are described by the Bloch wave functions [37]

$$u_k\left(\vec{r}\right)\exp\left\{-i\left(\frac{E}{h}t-\vec{k}\vec{r}\right)\right\},$$

where the function $u_k\left(\vec{r}\right)$ has the translational symmetry of the lattice, E – energy, $\vec{k}$ – wave vector. For a face-centered alkali halide crystal, the first Brillouin zone is a fourteen-tetrahedron in the form of a truncated octahedron; six faces have the form of squares, eight – the form of regular hexagons. The Γ-point lies in the centre of the first Brillouin zone (k =0), the X-point lies in the centre of the square plane, the L-point is at the centre of the hexagon. Along the [100] axis, the value of the wave vector varies from 0 to k_x, along the [111] direction from 0 to k_L. In all alkali halide crystals, the maximum of the valence band and the minimum of the conduction band are located in the centre of the Brillouin zone (Γ point). The upper hole zones are formed from the p-states of the halogen and have a negative dispersion typical of the p-bands. The bottom of the conduction band has an s-character, the effective mass of the electron is isotropic and has a value of the order of (0.5-1) m_0.

Computer modelling was carried out within the framework of the density functional theory (DFT) in the local density approximation [38].

3. RESULTS AND DISCUSSION

The calculated band structure of one-dimensional NaCl is shown in Fig. 1. The calculated band gap for a chain of two ions is 10.25 eV, of four ions – 11.4 eV, of six – 8.45 eV and of twelve – 10.46 eV. Note that in the first case, the energy minimum is observed at the Γ point of the Brillouin zone. The upper valence band in alkali halide crystals is associated with p-states of halogen. Function $E\left(k\right)$ has a maximum at the Γ-point. Due to the spin-orbit interaction for the p-hole at the Γ-point, the zone is split into two components. For the upper component, the orbital and spin moments of the p-hole are parallel and $j^+ = 3/2$. For the lower component, the orbital and spin moments are antiparallel and $j^+=1/2$. At the Γ-point, the upper component can degenerate. At the X- and L-points of the Brillouin zone, the valence band splits into three components. The lowest valence band occurs mainly from the s-orbit of Cl halogen, while the chlorine p-orbit is very weakly bound to the p-state of Na, as can be seen from the density of states (Fig. 2). In Fig. 2a, we observe two peaks responsible for s-orbits. The peak near -12 eV is connected with the halogen Cl, and the peak in the vicinity of zero energy is connected with Na. Figure 2b presents p-states of NaCl.
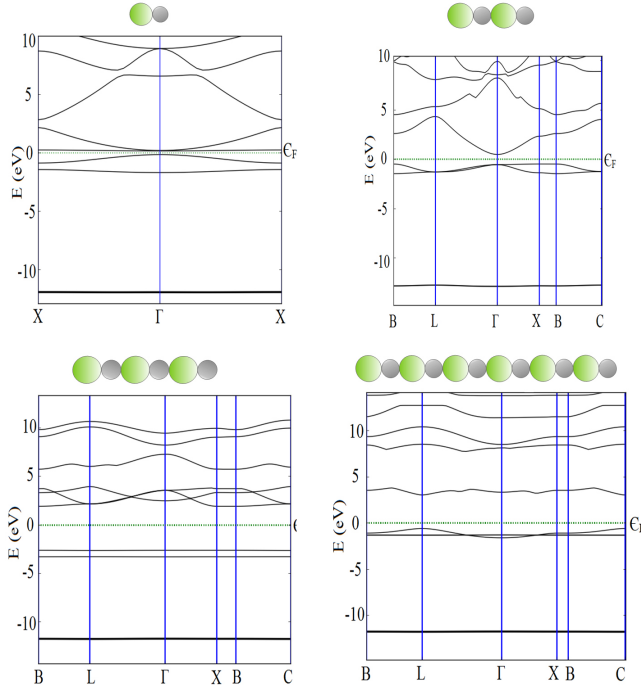
Fig. 1. Band structure of one-dimensional NaCl.
(Grey balls are sodium ions, green balls are chlorine ions)

The calculated band gap for NaCl, constructed on a plane of four ions, is 11.83 eV, of six – 11.46 eV, of eight – 11.55 eV and of twelve – 12.09 eV (Fig. 3). Note that the same for the bulk NaCl constructed from eight ions is 11.92 eV and from twelve to 11.12 eV (Fig. 3). Note that the experimental band gap energy for lowest-energy direct transition in crystalline NaCl was estimated to be 8.97±0.07 eV at 77°K [39].
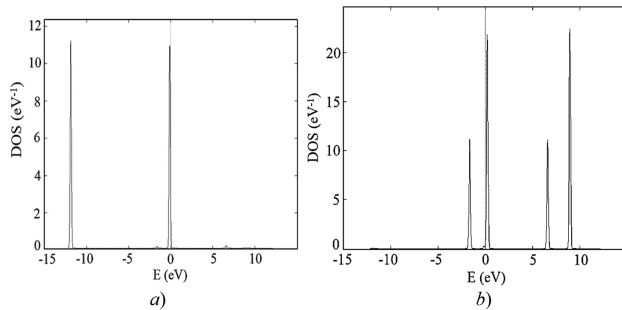

Fig. 2. Density of s (a), p (b) states of NaCl, consisting of one sodium ion and one chloride ion.

Table 1 shows the total energy of NaCl in 1-, 2- and 3- dimensions. We note that the value of the total energy depends on the number of ions in the object under study, but practically does not depend on the geometric arrangement of ions in space. At the same time, the values of the total energy vary in a narrow range, from -2815.15010 to -466.49970 eV. As we see from Table 1, with the increase in the

number of ions, the total energy decreases. For comparison, in Na_4Cl_3 cluster the total energy is higher to one order [31].

Total and Specific Energy of NaCl

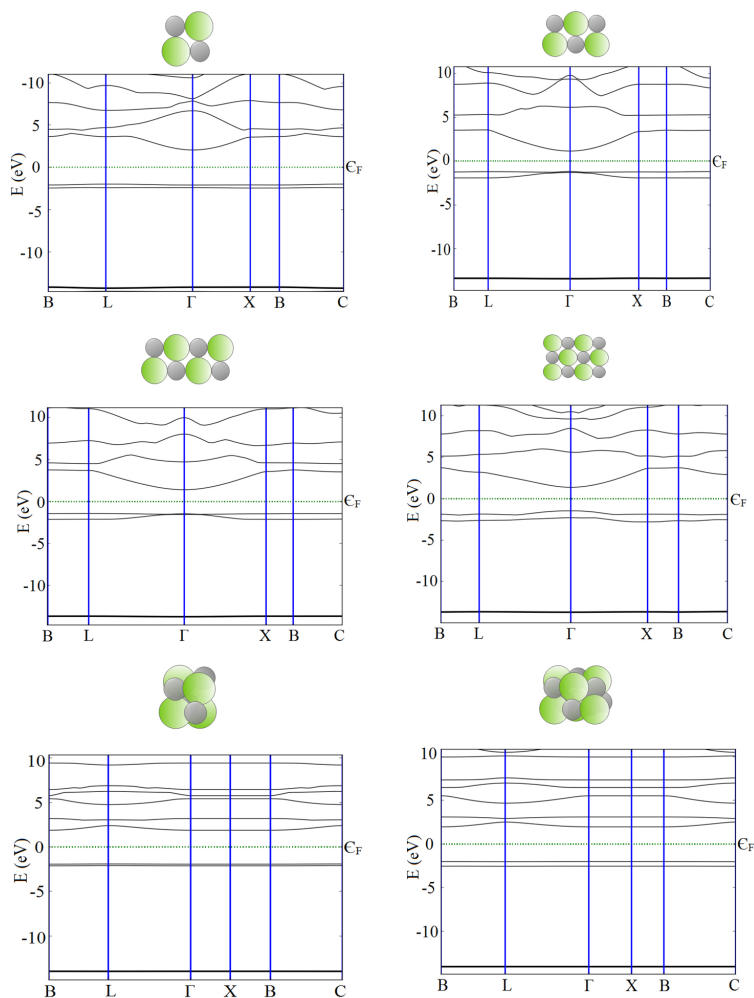| Object	Geometric location	Total energy, eV	Specific energy, eV
NaCl	1D	-466.49970	-233.24985
Na_2Cl_2	2D	-934.20591	-233.55148
Na_2Cl_2	1D	-934.68737	-233.67184
Na_3Cl_3	2D	-1398.40833	-233.06806
Na_3Cl_3	1D	-1398.79007	-233.13117
Na_4Cl_4	2D	-1864.85786	-233.10723
Na_4Cl_4	3D	-1876.45384	-234.55673
Na_6Cl_6	1D	-2754.87862	-229.57322
Na_6Cl_6	2D	-2795.56555	-232.96380
Na_6Cl_6	3D	-2815.15010	-234.59584

Fig. 3. Band structure of two-dimensional and three-dimensional NaCl.

4. CONCLUSIONS

In this paper, we presented the results of computer simulations of the band structure, the density of states, and the total energy of NaCl linear chains with different ion number (NaCl, Na_2Cl_2, Na_3Cl_3, Na_4Cl_4, Na_6Cl_6), depending on the geometric arrangement of ions.

Objects with a small number of atoms often exhibit thermodynamic, structural, energetic, dynamic, electronic, and chemical properties, which differ considerably from bulk materials, reflecting the finite-size of these systems. The simulation of the above-mentioned properties of NaCl chains may be useful for the calculation of energetical properties of alkali halide nanocrystals.

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ELEKTRONISKO JOSLU STRUKTŪRAS UN STĀVOKĻU BLĪVUMA DATORMODELĒŠANA NaCl JONU LINEĀRAJĀM ĶĒDĒM

L.N. Mjasņikova, A.S. Istļaup, D.M. Sergejevs, N.N. Žanturina,
K.Š. Šunkejevs, A.I. Popovs

Kopsavilkums

Pētījumā sniegtas NaCl (NaCl, Na_2Cl_2, Na_3Cl_3, Na_4Cl_4, Na_6Cl_6) lineāro atomu ķēdes elektroniskās joslas struktūras, stāvokļu blīvuma un pilnas enerģijas pirmo principu datormodelēšanas rezultāti. Norādīto īpašību modelēšana tiek realizēta ar datora kodu Atomistix ToolKit apvienojumā ar Virtual NanoLab. Kopējā enerģija ir atkarīga no pētāmā nanoobjekta jonu skaita, bet praktiski nav atkarīga no jonu ģeometriskā izkārtojuma.

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