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COMPUTER SIMULATION
OF THE DENSITY OF THE STATE
OF THE NAF NANOCRYSTAL

At present, various theoretical research methods are intensively used to interpret experimental results related to the study of the properties of defects in solids. Progress in this direction is possible thanks to the improvement of computer technology and the development of modern quantum chemical packages. The paper presents the results of computer simulation of the density of states and the total energy of an ideal NaF nanocrystal (Na₁₃F₁₄, Na₄F₅, Na₂₂F₂₃) and with the simplest point defects in various cluster compounds (Na₁₂F₁₃, Na₂₁F₂₂). Simulation of characteristics is implemented in the Atomistix ToolKit with Virtual NanoLab program in GGA (generalized gradient approximation) functionality. Objects studied are quantum dots. The results obtained may be useful in the study of nanocrystals.

Key word: NaF nanocrystal, density of states, band structure, total energy, computer simulation.

NaF нанокристалының құй тығыздығының
компьютерлік модедьеу

Қазіргі кезде қатты денелердең ақауылдарының қасиеттерін зерттеуге байланысты эксперименталды натижелерді түсіндіру ушін түрлі теориялық зерттеулер адісі бөлінеді. Бұл бағыттағы прогресс компьютерлік технологияның желілірі және заманауи құндылық қимиялық және кристалдық ағылшында мүмкін болады. Берілген жұмыста NaF (Na₁₃F₁₄, Na₄F₅, Na₂₂F₂₃) идеал нанокристалы мен қаралайық нүктелік ақаулары бар түрлі кластерлік косылыстың (Na₁₂F₁₃, Na₂₁F₂₂) күй тығыздығы мен тоқы энергиясының компьютерлік модельдегі көрсетілген. Сипаттағылған моделдені Atomistix ToolKit with Virtual NanoLab бағдарламасы негізінде GGA (generalized gradient approximation) функционалдығында жүзеге асырылды. Зерттелген объектілер құндылық нүктелерге жатқызылды. Алынған натижелерді нанокристалдарды зерттеуде пайдалану қажет мүмкін.

Түйін сөздер: NaF нанокристалы, құй тығыздығы, зоналық құрылыс, тоқы энергия, компьютерлік модельдегі.
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Компьютерное моделирование плотности состояния нанокристалла NaF

В настоящее время интенсивно применяются различные теоретические методы исследования для интерпретации экспериментальных результатов, связанных с изучением свойств дефектов в твердых телах. Прогресс в этом направлении возможен благодаря совершенствованию компьютерных технологий и разработке современных квантово-химических пакетов. В работе представлены результаты компьютерного моделирования плотности состояния и полной энергии идеального нанокристалла NaF (Na13F14, Na12F13, Na22F23) и с простейшими точечными дефектами в различных кластерных соединениях (Na12F13, Na21F22). Моделирование характеристики реализовано в программе Atomistix ToolKit с функциональностью GGA (generalized gradient approximation). Исследуемые объекты относятся к квантовым точкам. Полученные результаты могут быть полезны при исследовании нанокристаллов.

Ключевые слова: нанокристалл NaF, плотность состояний, зонная структура, полная энергия, компьютерное моделирование.
1s²2s²2p⁶3s¹, F° – 1s²2s²2p⁶. In the NaF matrix, the ions of the corresponding elements take on the following electron configuration – Na⁺ – 1s²2s²2p⁶, F⁻ – 1s²2s²2p⁶. As a result, the valence electron located on the outer shell of Na° completely goes to F°.

The Na13F14 cluster contains 27 ions, as shown in Figure 1a, is a negatively charged cube with indices (j, k, i) = (3, 3, 3) and with O₈ symmetry. The Na₁₂F₁₃ cluster is obtained by removing the Na⁺ and F⁻ ions from the central region of the nanooject (Figure 1b). The Na₄F₅ object contains 9 ions, as shown in Figure 1c, is a plane with indices (j, k, i) = (3, 3, 1). The Na₂₂F₂₃ cluster is a parallelepiped with indices (j, k, i) = (3, 3, 5), containing 45 ions (Figure 1d). The Na₂₁F₂₂ nanooject, shown in Figure 1f, was obtained by removing Na⁺ and F⁻ ions from the center of the penultimate layer [7]. The distance between the centers of the nearest ions in NaF is 2.31Å [22-23].

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

\[ u_k(\vec{r}) \exp \left\{ -i \left( \frac{E}{\hbar} - \vec{k} \cdot \vec{r} \right) \right\}, \]

where the function \( u_k(\vec{r}) \) has translational lattice symmetry, \( E \) is energy, \( \vec{k} \) is the wave vector. For a face-centered alkali halide crystal, the first Brillouin zone is a fourteen-shape d truncated octahedron shape; six faces have the form of squares, eight – the form of regular hexagons. The \( \Gamma \) -point lies at the center of the Brillouin zone (point \( \Gamma \)), the X-point lies at the center of the square plane, the L-point is at the center of the hexagon. Along the [100] axis, the wave vector value 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 center of the Brillouin zone (point \( \Gamma \)). The upper hole zones are formed from the \( p \)-states of the halogen and have a negative dispersion typical of the \( p \)-zones. The bottom of the conduction band is \( s \)-character, the effective electron mass is isotropic and has a value of the order of \((0.5-1) m_0\).

Computer simulation of the objects of study was carried out within the framework of the density functional theory in the local density approximation.

When performing calculations, the exchange-correlation functional is approximated by a generalized gradient approximation (GGA):

\[ E^{GGA}_{xc}[\rho] = \int n(\vec{r}) e^{GGA}(\rho(\vec{r}), |\Delta n(\vec{r})|) n(\vec{r}) d\vec{r}, \]

Where \( n(\vec{r}) \) is the density of a non-degenerate ground state of a system of \( N \) electrons in a potential \( V(\vec{r}) \), corresponding to the ground state \( \Psi \) and energy \( E \), \( e^{GGA} \) is the universal functional GGA, \( e_{xc}(\rho) \) is exchange-correlation energy of a homogeneous gas with a density \( \rho \).

The main parameters of the computing resource are: Intel (R) Core (TM) i7-4790 CPU @ 3.6 GHz 8 core processor, 8 GB RAM, system type – 64-bit operating system, operating system – Windows 8.1.

The position of the electron is described by the wave function \( \psi(x, y, z) \). The probability of finding
an electron at a certain point \((x, y, z)\) is described by the expression \(|\psi(x, y, z)|^2\), where the total probability \(\int_{-\infty}^{\infty} |\psi(x, y, z)|^2 \, dx dy dz\) is normalized to one.

Electrons at the bottom of the conduction band behave like free particles (with an effective mass) trapped in a box. Consider the electrons of the conduction band, but the result for holes is similar.

For our parabolic conduction band:

\[
E = E_c - \frac{\hbar^2 k^2}{2m}.
\]

For electrons in a rectangular volume \(L_x\) through \(L_y\) through \(L_z\) with an infinite limiting potential \(U(x, y, z) = 0\) inside the box and outside \(\infty\), the electron wave function \(\psi\) should reach zero and take the form of a harmonic function inside the region. Wave function solution:

\[
\psi(x, y, z) = \sin(k_x x) \sin(k_y y) \sin(k_z z),
\]

where \(k_x, k_y, k_z\) are wave vectors for an electron in directions \(x, y\) and \(z\). The real wave function in a solid is more complex and periodic (with a crystal lattice), but this is a good approximation for parabolic regions near the edges of the zone.

Fulfillment of boundary conditions: when \(x, y\) or \(z = 0\), the sinusoidal functions vanish. On opposite boundaries of the rectangular region, \(\sin(k_x L_x) = 0, \sin(k_y L_y) = 0,\) and \(\sin(k_z L_z) = 0\), for directions \(x, y\) and \(z\). Allowed wave vectors satisfy:

\[
k_x L_x = \pi n_x, \quad k_y L_y = \pi n_y, \quad k_z L_z = \pi n_z,
\]

where \(n_x, n_y, n_z\) are whole numbers [24].

**Simulation results**

Using computer simulation, the density spectra of the states of the NaF nanocrystal were obtained in various cluster compounds (Na\textsubscript{1}F\textsubscript{1}, Na\textsubscript{1}F\textsubscript{2}, Na\textsubscript{2}F\textsubscript{3}, Na\textsubscript{4}F\textsubscript{5}, Na\textsubscript{2}F\textsubscript{23}, Na\textsubscript{2}F\textsubscript{22}) at a temperature of 1 K (Figure 2). The total and specific energy is calculated not only in the indicated objects, but also in their “positive” twins (Table 1).

In Figure 2, a certain amount of energy levels in the energy range from -20 eV to 20 eV are clearly visible. In this case, in all spectra (Fig. 2 a – f), the first pronounced narrow energy level is located in the region of \(-18\) eV. The main relatively wide energy level is observed in the region \(-1.5 \div -2\) eV to \(0.5\) eV. Then a series of narrow energy levels is recorded in the energy range from \(3\) eV to \(16 \div 20\) eV. The characteristic form of energy levels in the density spectra of states indicates that a NaF nanocrystal in various cluster compounds (Na\textsubscript{1}F\textsubscript{1}, Na\textsubscript{1}F\textsubscript{2}, Na\textsubscript{4}F\textsubscript{5}, Na\textsubscript{2}F\textsubscript{23}, Na\textsubscript{2}F\textsubscript{22}) at 1 K can be attributed to quantum dots.

### Table 1 – Full and specific energy of NaF nanocrystal

| Object   | Total energy, eV | Specific energy, eV | Object   | Total energy, eV | Specific energy, eV |
|----------|------------------|--------------------|----------|------------------|--------------------|
| Na\textsubscript{1}F\textsubscript{14} | -9140,61667       | -338,5413581       | Na\textsubscript{4}F\textsubscript{13} | -8510,59120        | -315,2070815       |
| Na\textsubscript{1}F\textsubscript{13} | -8480,54235       | -339,221694        | Na\textsubscript{1}F\textsubscript{12} | -7852,99247        | -314,1196988       |
| Na\textsubscript{2}F\textsubscript{5}  | -3251,71604       | -361,307822        | Na\textsubscript{4}F\textsubscript{4}  | -2620,11205        | -291,1235611       |
| Na\textsubscript{2}F\textsubscript{23} | -15030,90457      | -334,0201016       | Na\textsubscript{3}F\textsubscript{22} | -14400,23120       | -320,0051378       |
| Na\textsubscript{2}F\textsubscript{22} | -14368,42587      | -334,1494388       | Na\textsubscript{2}F\textsubscript{21} | -13742,51906       | -319,5934665       |
Computer simulation of the density of the state of the NaF nanocrystal

Figure 2 – Density of states of NaF nanocrystal in various cluster compounds (Na_{14}F_{13}, Na_{13}F_{12}, Na_{5}F_{4}, Na_{22}F_{23}, Na_{21}F_{22})

When plotting the dependence of the total energy on the number of elements in the negatively charged clusters Na_{13}F_{14}, Na_{12}F_{13}, Na_{2}F_{5}, Na_{22}F_{23}, Na_{21}F_{22}, we observe that the points lie along a straight line (Figure 3). A similar qualitative result is obtained with positively charged clusters of Na_{14}F_{13}, Na_{13}F_{12}, Na_{5}F_{4}, Na_{22}F_{23}, Na_{22}F_{21}.

According to the table, the total energy in negatively charged clusters of Na_{14}F_{13}, Na_{13}F_{12}, Na_{5}F_{4}, Na_{22}F_{23}, Na_{21}F_{22} varies from -3251.71604 eV to -15030.90457 eV. However, the specific energy for the Na_{13}F_{14}, Na_{12}F_{13}, Na_{22}F_{23}, Na_{21}F_{22} clusters has a narrower interval in the region from -334.0201016 eV to -339.22161694 eV. At the same time, for the Na_{4}F_{5} crystal, the specific energy is the smallest value of -361.3017822 eV.

The total energy in positively charged clusters of Na_{14}F_{13}, Na_{13}F_{12}, Na_{5}F_{4}, Na_{22}F_{23}, Na_{22}F_{21} varies from -2620.11205 eV to -14400.23120 eV. However, the specific energy for Na_{14}F_{13}, Na_{13}F_{12}, Na_{22}F_{23}, Na_{22}F_{21} clusters also has a narrow interval in the range from -314.1196988 eV to -320.0051378 eV. At the same time, for the Na_{3}F_{4} crystal, the specific energy is the highest value of -291.1235611 eV.
Figure 3 – Dependence of total energy on the number of elements in NaF clusters

Conclusion

Thus, in this work, in the framework of the density functional theory, the density of states and the total energy of the NaF nanocrystal are calculated, and the results of computer simulation of the band structure in various cluster compounds (Na$_{13}$F$_{14}$, Na$_{12}$F$_{13}$, Na$_{9}$F$_{5}$, Na$_{22}$F$_{23}$, Na$_{21}$F$_{22}$) are presented at a temperature of 1 K. Simulation of characteristics implemented in the program Atomistix ToolKit with Virtual NanoLab. The characteristic form of the density of states suggests that these objects can be attributed to quantum dots.

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