

SURFACE POTENTIAL OF MgO SEMIBOUNDED CRYSTALS

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Surface properties of MgO semibounded crystals are studied within the polarization model. Electrostatic and dipole potentials of the MgO (001) surface are calculated. The values of induced dipole moments show a strong dependence on the atom remoteness from the boundary of the crystal. Our calculations indicate that the near-surface region with the properties differing from the bulk ones contains three layers of atoms.

The physical and chemical properties of surface layers and their geometric and electronic structure determine most applications of insulating surfaces. The modern methods of electron spectroscopy (photoemission and Auger spectroscopy, high-resolution electron-energy-loss spectroscopy) allow one to clearly recognize and analyze the structure of surface films. A more precise interpretation of experimental spectra is provided by the use of quantum mechanical and other theoretical methods.

Magnesium oxide is the well-known high-temperature ceramic material. It is intensively studied experimentally and theoretically, which makes it possible to perform a detailed comparison of experimental and computational results. Therefore, theoretical approaches are often tested on magnesium oxide. This oxide is used as a model one in the investigations of alkaline-earth oxides which possess a very simple crystal structure and are close to purely ionic crystals by their properties [1–4]. Magnesium oxide is also one of the most fundamental materials for industrial science due to its wide applications ranging from chemical engineering to microelectronics.

Effective ion charges on the constituents in a MgO crystal are known to approach the values of $\pm 2e$. Different quantum mechanical calculations give values of $\pm 1.85e$ and more [5–7]. In the present study, we use the effective charges of $\pm 1.96e$ [6] and perform calculations within the frames of the polarization model proposed by us earlier [8]. The MgO lattice constant a is assumed to be equal to 4.22\AA . The values of a estimated by a number of computational techniques lie in the range of 4.160--

4.259\AA (see [3] for details). The experimental value is 4.20\AA [9].

The surface potential of a semibounded MgO crystal contains the Coulomb, short-range, and polarization parts. The short-range contribution is usually calculated in the nearest-neighbour approximation for a sufficiently large cluster of $N \times N \times M$ ions, and the Coulomb and polarization parts are found by summing all the charge and dipole centers of a semibounded crystal.

Let's find the Coulomb potential for MgO (001) surface. The Poisson equation defines the potential for a system of charges:

$$\Delta\psi(x, y, z) = -4\pi\rho(x, y, z), \quad (1)$$

where $\psi(x, y, z)$ is the electrostatic potential of all ions, and $\rho(x, y, z)$ is the charge density.

MgO (001) surface comprises the charges located on the XY planes at the distance of $a/2$ from one another. The distance between the charges of the same sign on the XY plane equals a . The distance between planes is $a/2$ (Fig. 1).

The charge density for this surface is given by

$$\begin{aligned} \rho(x, y, z) = q\delta(z) & \left\{ \sum_{n=-M}^M \sum_{k=-M}^M \delta(x - na)\delta(y - ka) + \right. \\ & + \sum_{n=-M}^M \sum_{k=-M}^M \delta(x + \frac{a}{2} - na)\delta(y + \frac{a}{2} - ka) - \\ & - \sum_{n=-M}^M \sum_{k=-M}^M \delta(x - na)\delta(y + \frac{a}{2} - ka) - \\ & \left. - \sum_{n=-M}^M \sum_{k=-M}^M \delta(x + \frac{a}{2} - na)\delta(y - ka) \right\}. \quad (2) \end{aligned}$$

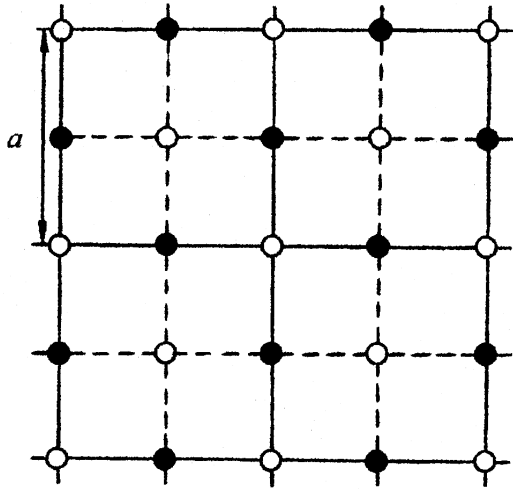


Fig. 1. The structure of MgO (001) surface. Open and black circles represent, respectively, the oxygen and magnesium ions.

where $\delta(x)$ is the Dirac delta-function, and $M \rightarrow \infty$ for the infinite planar lattice.

To simplify the solution of Eq. (1) with density (2), let's consider the lattice with a charge distribution density in the following form:

$$\rho_0(x, y, z) = q\delta(z) \times \left\{ \sum_{n=-M}^M \sum_{k=-M}^M \delta(x - na)\delta(y - ka) - \frac{1}{a^2} \right\}. \quad (3)$$

The last term in (3) corresponds to a uniformly distributed compensatory charge. It is introduced in order to avoid the divergence of the series in the solution of (1). As follows from (3), the charge distribution density (2) can be written as

$$\rho(x, y, z) = \rho_0(x, y, z) + \rho_0(x + \frac{a}{2}, y + \frac{a}{2}, z) - \rho_0(x, y + \frac{a}{2}, z) - \rho_0(x + \frac{a}{2}, y, z). \quad (4)$$

Due to the symmetry of a MgO crystal, the potential of the system and its charge density can be expressed by periodic functions. Let's expand the functions $\psi_0(x, y, z)$ and $\rho_0(x, y, z)$ in the Fourier series:

$$\psi_0(x, y, z) = \sum_{k,n} \psi_{kn}(z) e^{2\pi i \frac{kx+ny}{a}}, \quad (5)$$

$$\rho_0(x, y, z) = \sum_{k,n} \rho_{kn}(z) e^{2\pi i \frac{kx+ny}{a}}. \quad (6)$$

After the substitution of (5) and (6) into (1), we obtain the equation

$$\frac{\partial^2 \psi_{kn}(z)}{\partial z^2} - \frac{4\pi^2}{a^2} (k^2 + n^2) \psi_{kn}(z) = -4\pi \rho_{kn}(z), \quad (7)$$

where $\psi_{kn}(z) \rightarrow 0$ for $z \rightarrow \pm\infty$.

The coefficients of expansion (6) can be found from (3) and the δ -function representation in the form of a Fourier integral

$$\rho_{kn}(z) = \frac{1}{(2Ma)^2} \int_{-Ma}^{Ma} dx \int_{-Ma}^{Ma} dy \rho_0(x, y, z) e^{-2\pi i \frac{kx+ny}{a}}. \quad (8)$$

Relation (8) yields

$$\rho_{kn}(z) = \frac{q}{a^2} \delta(z) [1 - \delta_{k,0} \delta_{n,0}], \quad (9)$$

where $\delta_{k,n}$ is the Kronecker symbol.

Consequently, after the substitution of (9) into (7), we get the final form of the equation, which allows one to find the coefficients of the Fourier series

$$\frac{\partial^2 \psi_{kn}(z)}{\partial z^2} - \frac{4\pi^2}{a^2} (k^2 + n^2) \psi_{kn}(z) = -\frac{4\pi q}{a^2} (1 - \delta_{k,0} \delta_{n,0}). \quad (10)$$

and ψ_{00} is equal to 0 for $k=0$ and $n=0$.

When $k \neq 0$ and $n \neq 0$, the function ψ_{kn} is chosen in the form of a Fourier integral:

$$\psi_{kn}(z) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \varphi(\tau) e^{i\tau z} d\tau. \quad (11)$$

The substitution of (11) into (10) yields

$$\left[\tau^2 + \frac{4\pi^2}{a^2} (k^2 + n^2) \right] \varphi(\tau) = \frac{4\pi q}{a^2}. \quad (12)$$

The solution of this equation is

$$\varphi(\tau) = \frac{4\pi q}{a^2} \frac{1}{\tau^2 + \frac{4\pi^2}{a^2} (k^2 + n^2)}. \quad (13)$$

Now, let's replace $\varphi(\tau)$ in (11) by its above expression:

$$\psi_{kn}(z) = \frac{2q}{a^2} \int_{-\infty}^{+\infty} \frac{e^{i\tau z}}{(\tau - i\frac{2\pi}{a} \sqrt{k^2 + n^2})(\tau + i\frac{2\pi}{a} \sqrt{k^2 + n^2})} d\tau. \quad (14)$$

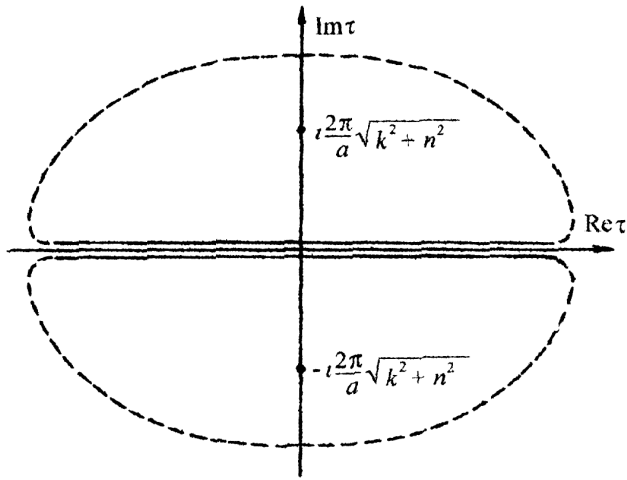


Fig. 2. The poles and integration contour for the calculation of integral (15)

The calculation of integral (14) is done along the closed integration contour in the complex plane (see Fig. 2). For $z > 0$, the integrand in (14) tends to zero in the upper part of the plane, whereas this function tends to zero in the lower part of the plane for $z < 0$. Here, the Cauchy formula can be used as [10]

$$\oint \frac{f(z)}{z - z_0} dz = 2\pi i f(z_0). \quad (15)$$

According to (15),

$$\psi_{kn}(z) = \frac{q}{a} \frac{e^{-2\pi\sqrt{k^2+n^2}\frac{|z|}{a}}}{\sqrt{k^2+n^2}}. \quad (16)$$

After the substitution of (16) into (5), the formula for the potential plane with the charge density (3) can be written as follows:

$$\psi_0(x, y, z) = \frac{q}{a} \sum_{k,n=-\infty}^{+\infty} \frac{e^{2\pi i \frac{kx+ny}{a}}}{\sqrt{k^2+n^2}} \times e^{-2\pi\sqrt{k^2+n^2}\frac{|z|}{a}}, \quad (17)$$

where $k \neq 0$ and $n \neq 0$ simultaneously.

With the use of (4), the MgO (001) surface potential (Fig. 1) is defined by

$$\psi_q^s(x, y, z) = \frac{q}{a} \sum_{k,n=-\infty}^{+\infty} \frac{[1 - (-1)^k][1 - (-1)^n]}{\sqrt{k^2+n^2}} \times e^{2\pi i \frac{kx+ny}{a}} \times e^{-2\pi\sqrt{k^2+n^2}\frac{|z|}{a}}. \quad (18)$$

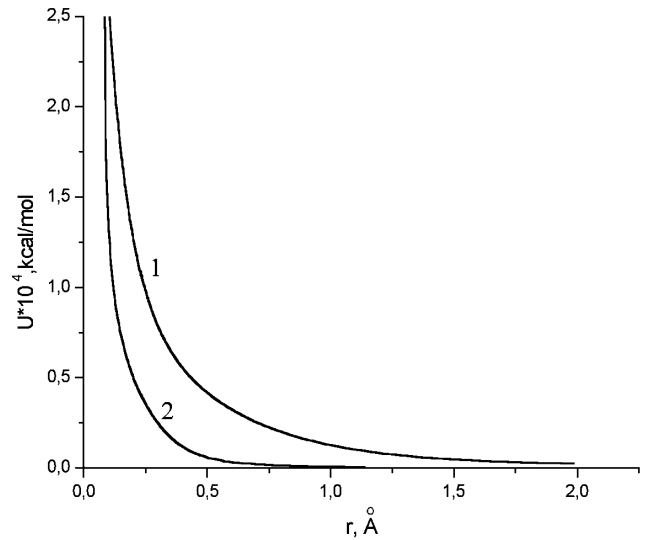


Fig. 3. Coulomb (1) and dipole (2) potential of MgO (001) surface. r is the distance from the surface

Then, the summation is taken over the planes along the z -axis, and the following expression is obtained for the Coulomb surface potential of a semibounded MgO crystal:

$$\begin{aligned} \psi_C(x, y, z) = & \\ = & \frac{q}{a} \sum_{m=0}^{\infty} (-1)^m \sum_{k,n=1}^{\infty} \frac{[1 - (-1)^k][1 - (-1)^n]}{\sqrt{k^2+n^2}} \times \\ & \times e^{2\pi i \frac{kx+ny}{a}} \times e^{-2\pi\sqrt{k^2+n^2}\left|\frac{z}{a} + \frac{m}{2}\right|}. \end{aligned} \quad (19)$$

This surface Coulomb potential is shown in Fig. 3 (curve 1).

Now, let's consider the polarization term of the surface potential. As a result of oxygen ion polarization and non-compensated ion surroundings, the polarization dipole moments are induced on oxygen ions in the crystal surface layers. Their values are the largest in the first surface layer and decrease rapidly when moving inside the crystal. The field of dipoles makes an essential contribution to the crystal surface potential.

The procedure similar to that described above is used to find the dipole surface potential. Two planes with the distance of λ between them are considered. One plane contains positive charges and the other – negative ones. For $\lambda \rightarrow 0$, we have the point dipole ($\varepsilon\lambda = \mu$, ε is the point charge in the system, μ is the value of the dipole moment). As in the previous case, the potential for the

system of charges is defined by the Poisson equation, and the charge density in the limits of the plane is represented by the sum of sublattices of the opposite-charged ions. For MgO (001) surface, we get

$$\rho(x, y, z) = \rho_0(x, y, z - \lambda) + \rho_0(x + \frac{a}{2}, y + \frac{a}{2}, z - \lambda) - \rho_0(x, y, z) - \rho_0(x + \frac{a}{2}, y + \frac{a}{2}, z). \quad (20)$$

The potential for the system of charges with such a density is found with the help of (17):

$$\psi_d(x, y, z) = \frac{q}{a} \sum_{k,n=1}^{\infty} \frac{[1 + (-1)^{n+k}]}{\sqrt{k^2 + n^2}} \times e^{2\pi i \frac{kx+ny}{a}} \times \times \left[e^{-2\pi\sqrt{k^2+n^2}|\frac{z-\lambda}{a}|} - e^{-2\pi\sqrt{k^2+n^2}|\frac{z}{a}|} \right]. \quad (21)$$

A more convenient form for computations is

$$\psi_d(x, y, z) = \frac{q}{a} \sum_{k,n=1}^{\infty} \frac{[1 + (-1)^{n+k}]}{\sqrt{k^2 + n^2}} \times e^{2\pi i \frac{kx+ny}{a}} \times \times e^{-2\pi\sqrt{k^2+n^2}|\frac{z}{a}|} \times \left[e^{-\frac{2\pi\sqrt{k^2+n^2}}{a}(|z-\lambda|-|z|)} - 1 \right]. \quad (22)$$

Let's introduce the function

$$f(z) = |z - \lambda| - |z| = \begin{cases} -\lambda, & z > \lambda, \\ -2z + \lambda, & 0 < z < \lambda, \\ \lambda, & z < 0. \end{cases} \quad (23)$$

It follows from (23) that, for $\lambda \rightarrow 0$, (22) can be written as

$$\psi_d(x, y, z) = \frac{2\pi}{a^2} \sum_{k,n=1}^{\infty} [1 + (-1)^{n+k}] \times e^{2\pi i \frac{kx+ny}{a}} \times \times e^{-2\pi\sqrt{k^2+n^2}|\frac{z}{a}|} [-qf(z)]. \quad (24)$$

Here, $-qf(z) \xrightarrow{\lambda \rightarrow 0} \mu \cdot \text{sign}(z)$, where $\mu=ql$ is the dipole moment.

Finally, we get the following result for the sublattice of dipoles:

$$\psi_d(x, y, z) = \frac{2\pi\mu}{a^2} \text{sign}(z) \sum_{k,n=1}^{\infty} [1 + (-1)^{n+k}] \times$$

$$\times e^{2\pi i \frac{kx+ny}{a}} \times e^{-2\pi\sqrt{k^2+n^2}|\frac{z}{a}|}. \quad (25)$$

Summing up over all layers of the semibounded crystal gives such expression for the surface dipole potential:

$$\psi_d^s(x, y, z) = \frac{2\pi}{a^2} \sum_{m=0}^{\infty} \mu_m \text{sign}\left(\frac{z}{a} + \frac{m}{2}\right) \sum_{k,n=1}^{\infty} (-1)^m \times \times [1 + (-1)^{n+k}] \times e^{2\pi i \frac{kx+ny}{a}} \times e^{-2\pi\sqrt{k^2+n^2}|\frac{z}{a} + \frac{m}{2}|}. \quad (26)$$

The expression for the electrical field may be obtained on the base of (19), (26), and the well-known relation

$$\vec{E} = -\nabla\psi. \quad (27)$$

Let's rewrite (19) in the form

$$\psi_C(x, y, z) = \frac{16q}{a} \sum_{m=0}^{\infty} (-1)^m \times \times \sum_{k,n=1}^{\infty} \frac{\cos 2\pi(2k-1)\frac{x}{a} \cos 2\pi(2n-1)\frac{y}{a}}{\sqrt{(2k-1)^2 + (2n-1)^2}} \times \times e^{-2\pi\sqrt{(2k-1)^2 + (2n-1)^2}|\frac{z}{a} + \frac{m}{2}|}. \quad (28)$$

Substituting (28) into (27), we obtain

$$E_C^x(x, y, z) = \frac{32\pi q}{a^2} \sum_{m=0}^{\infty} (-1)^m \times \times \sum_{k,n=1}^{\infty} (2k-1) \sin 2\pi(2k-1)\frac{x}{a} \times \times \cos 2\pi(2n-1)\frac{y}{a} \times e^{-2\pi\sqrt{(2k-1)^2 + (2n-1)^2}|\frac{z}{a} + \frac{m}{2}|},$$

$$E_C^y(x, y, z) = \frac{32\pi q}{a^2} \sum_{m=0}^{\infty} (-1)^m \times$$

$$\times \sum_{k,n=1}^{\infty} (2n-1) \sin 2\pi(2k-1)\frac{x}{a} \times$$

$$\begin{aligned}
 & \times \sin 2\pi(2n-1)\frac{y}{a} \times e^{-2\pi\sqrt{(2k-1)^2+(2n-1)^2}\left|\frac{z}{a}+\frac{m}{2}\right|}, \\
 E_C^z(x, y, z) &= \frac{32\pi q}{a^2} \sum_{m=0}^{\infty} (-1)^m \text{sign}\left(\frac{z}{a} + \frac{m}{2}\right) \times \\
 & \times \sum_{k,n=1}^{\infty} \cos 2\pi(2k-1)\frac{x}{a} \cos 2\pi(2n-1)\frac{y}{a} \times \\
 & \times e^{-2\pi\sqrt{(2k-1)^2+(2n-1)^2}\left|\frac{z}{a} + \frac{m}{2}\right|}. \quad (29)
 \end{aligned}$$

Now we can find the values of dipole moments. The dipole moments on the oxygen ions lying in one layer are identical due to the symmetry of the system. As follows from (29), the field of charges applied to the chosen oxygen ions from one layer equals

$$\begin{aligned}
 E_l^z(0, 0, \frac{l}{2}a) &= \frac{32\pi q}{a^2} \sum_{m=2l+1}^{\infty} (-1)^m e^{-\pi\sqrt{(2k-1)^2+(2n-1)^2}m}, \\
 E_l^x(0, 0, \frac{l}{2}a) &= E_l^y(0, 0, \frac{l}{2}a) = 0, l = 0, 1, 2... \quad (30)
 \end{aligned}$$

In the case of the sublattice of dipoles,

$$\begin{aligned}
 E_d^z(0, 0, \frac{l}{2}a) &= \frac{32\pi^2}{a^3} \times \\
 & \times \sum_{\substack{m=0 \\ m \neq l}}^{\infty} \mu_m \left\{ 2 \cdot \frac{2 - e^{-2\pi m}}{(1 - e^{-2\pi m})^2} \times e^{-2\pi m} + \right. \\
 & + 2 \sum_{\substack{k=1 \\ n=1}}^{\infty} \sqrt{k^2 + n^2} \times e^{-2\pi\sqrt{k^2+n^2}m} + \\
 & + (-1)^m \sum_{\substack{k=1 \\ n=1}}^{\infty} \sqrt{(2k-1)^2 + (2n-1)^2} \times \\
 & \left. e^{-2\pi\sqrt{(2k-1)^2+(2n-1)^2}m} \right\}, \\
 E_d^x(0, 0, \frac{l}{2}a) &= E_d^y(0, 0, \frac{l}{2}a) = 0, l = 0, 1, 2... \quad (31)
 \end{aligned}$$

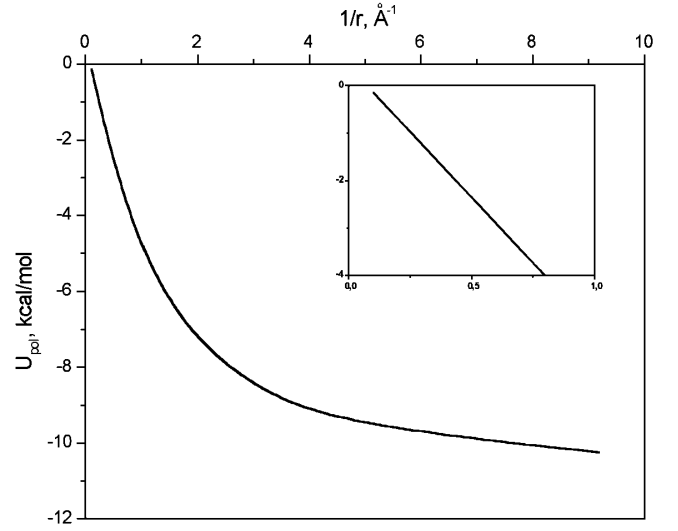


Fig. 4. Polarization energy of the proton – MgO (001) surface interaction.

Let's rewrite (31) in the simplified form:

$$E_d^z(0, 0, \frac{l}{2}a) = \sum_{\substack{m=0 \\ m \neq l}}^{\infty} \mu_m f_m. \quad (32)$$

With the use of the relation

$$\mu_l = \alpha \left[E_c^z(0, 0, \frac{a}{2}) + E_d^z(0, 0, \frac{a}{2}) \right], \quad (33)$$

where α is the scalar polarizability of oxygen ions ($\alpha = 1.44 \text{ \AA}^3$), we can obtain the equations that determine the dipole moments:

$$\begin{aligned}
 \alpha \sum_{m=0}^{l-1} \mu_m f_m - \mu_l + \alpha \sum_{m=l+1}^{\infty} \mu_m f_m &= -\alpha E_c^z(0, 0, \frac{l}{2}a), \\
 0 \leq l < \infty. \quad (34)
 \end{aligned}$$

The solutions of (34) are put into (25), and, as a result, we know the field created by the system of dipoles. The dipole moments of three upper surface layers of MgO (001) surface are: $\mu_1 = 0.231 \text{ a.u.}$, $\mu_2 = 0.208 \text{ a.u.}$, $\mu_3 = 0.0202 \text{ a.u.}$, respectively. The dipole moments of deeper layers are small enough and can be neglected. Curve 2 in Fig. 3 displays the dipole potential calculated according to (26).

The description of the ions' behavior on the boundary of solids is necessary for a number of problems of surface physics. Our model [8] was implemented to find the polarization energy in the proton – semibounded MgO crystal system (Fig. 4).

In summary, we present here a theoretical calculation of Coulomb and dipole potentials for MgO (001) surface within our polarization model. The influence of the ion remoteness from the boundary on the value of induced dipole moments has been discussed. This allows us to define the size of the near-surface region, namely, three layers of atoms, with the properties differing from the bulk ones.

This computational scheme can be used in the investigations of hydroxylation of oxide surfaces. The interaction of oxide surfaces with water molecules is one of the most important problems of surface physics that is studied by a great number of researchers [11–13].

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ПОТЕНЦІАЛ ПОВЕРХНІ НАПІВОбМЕЖЕНОГО КРИСТАЛА MgO

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Резюме

У межах поляризаційної моделі були досліджені поверхневі властивості напівобмеженого кристала MgO. Обчислено електростатичний та дипольний потенціали грані (001) кристала MgO. Виявлено залежність величини наведених дипольних моментів від розташування атомів відносно межі кристала. Наші розрахунки вказують на те, що розмір приповерхневої області із властивостями, відмінними від об'ємної фази, становить три шари атомів.