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Application of a polarizable point-ion shell model to a two-dimensional periodic structure: The NiO (001) surface

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A two-dimensional polarizable point-ion shell model developed from the original model of Dienes *et al.* was constructed, using the effective plane-wise summation technique for evaluation of two-dimensional Madelung potentials, and then applied to the NiO (001) surface in which a two-dimensional translation operation is possible, in order to assess the validity of the shell model constructed. Displacements of ions around an imperfection such as a surface plane are obtained by solving the equilibrium equations which contain displacements as unknowns, as in the original model. The two-dimensional shell model treats a crystal which contains a small number of displacements because of the two-dimensional periodicity which is invariably preserved even after a relaxation takes place. The experimental results relevant to the NiO (100) surface obtained in low-energy electron-diffraction and electron energy-loss fine-structure measurements, which are indicative of a reduction of ionic spacings normal to the (001) planes very near to the free surface by 1.9–3.8 % of the bulk lattice constant, were interpreted in terms of the calculations with the two-dimensional polarizable point-ion shell model, using the parameters determined in the bulk, although there were some slight deviations from the experiments. The surface effects upon the parameters were investigated and the relaxation in the surface structure was found to be very sensitive to the electronic polarizability of the O^{2-} ion at the top layer. A comparison between the theoretical predictions and the experiments indicated some increment to the polarizability of the O^{2-} ion on the surface plane from the bulk value.

I. INTRODUCTION

The polarizable point-ion shell model constructed by Dienes *et al.*[1] is one of the strongest and the most reliable means of calculating energy changes induced by an imperfection which breaks the three-dimensional periodicity in an ionic crystal. This model is essentially based upon the following framework. When an imperfection is formed in a perfect ionic crystal, the electrical field from this imperfection results in displacements of outer shells, in particular ions around the imperfection, so as to minimize the energy of the crystal; that is, a relaxation takes place. A determination of displacements enables a calculation of the relaxation energy. This model uses a spherical crystal region in which the displacements are calculated by matrix techniques, while the displacements outside the sphere are evaluated by the approximate method of Mott and Littleton.[2] These treatments are rationalized because the three-dimensional periodicity is broken. In fact, previous energy calculations on polarons and point defects prove the legitimacy of the shell model used.[1,3–7]

We applied this shell model to the lattice-energy calculations of crystals containing ordered arrays of crystallographic shear planes in which three-dimensional periodicities are preserved even after relaxations take place.[8,9] In such calculations, spherical crystal regions were also used rather than using the three-dimensional periodicities because a theoretical treatment in a periodic structure was not yet established. The situation in the two-dimensional structure is similar, as shown in energy calculations on grain boundaries in TiO_2 (Ref. 10).

The primary aim in this paper is, therefore, to construct a theoretical method developed from a polarizable point-ion shell model, which is applicable in periodic structures. The illustrative example treated here is the (001) surface of NiO, which crystallizes with rock-salt structure because of the following reasons: (i) the NiO(001) surface structure has a two-dimensional periodicity; (ii) a two-dimensional periodic structure is expected to be treated theoretically much more easily than a three-dimensional one; (iii) some experimental results on the NiO(001) surface are available;[11,12] (iv) the effective plane-wise summation technique developed by Parry now enables us to calculate two-dimensional Madelung potentials;[13,14] (v) the ionicity of NiO is so high,[15] i.e., $f=0.887$, that a polarizable point-ion shell model can be applied; and (vi) the parameters required in energy calculations of NiO have already been obtained.[5,6]

As for NiO(001) surface, Yikegaki *et al.*[12] carried out the electron energy-loss fine-structure (EELFS) measurements which yield nearest neighbor distances of ~ 2.00 Å, slightly shorter than the spacing of the Ni^{2+}-O^{2-} pair normal to the (001) plane in the bulk,[16] i.e., $4.1684/2 \cong 2.08$ Å. Before Yikegaki *et al.*, Welton-Cook and Prutton observed,[11] using the low-energy electron-diffraction (LEED) method, that the real NiO(001) free surface is slightly contracted (of $\simeq 1.9\%$ of the bulk lattice constant, i.e., $\simeq 0.04$ Å) toward the inside. Both experiments are indicative of a reduction of ionic spacings normal to the (001) surface by 1.9–3.8% of the bulk value. These results are very important in the assessment

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of the validity of the theoretical method to be constructed in this paper.

The construction of the theoretical method developed from the shell model, which is applicable in periodic structures, is of great importance in investigations of physical and chemical properties of ionic crystals. There is much previous literature[17–25] on theoretical studies of surfaces of rock-salt-structured ionic crystals.[17–25] Sawada and Nakamura[24] have even succeeded in estimating temperature dependences of ionic displacements in sodium halide crystals, applying the Einstein model to the Verway model. Though the equilibrium ionic positions calculated here are static ones, it is of interest to compare the results obtained in this paper with theirs, calculated by a theoretical method quite different from ours. The theoretical knowledge obtained by computer simulations of two-dimensional grain boundaries in NiO by Duffy and Tasker[26,27] is also of much help in the present work.

The parametrization of numerical values employed in the present calculations was made in the bulk, as will be described in Sec. III. Though the two-dimensional theoretical treatment is simpler than the three-dimensional one, a crystal surface presents some difficulties in the parameters required in calculations. Tasker[25] argued that serious question should be given to the validity of applying the numerical parameters determined in the bulk to a crystal surface where the environment is very different to the bulk. One of the most important differences between a surface and the bulk must be the polarizabilities of ions. Tasker[25] suggests that anions are more polarizable at the surface than in the bulk, whereas cations show negligible differences in polarizability. In this paper, calculations using bulk numerical parameters will be carried out as the first trial and, then, surface effects on the parameters will be considered in discussion.

II. LATTICE ENERGIES IN RIGID TWO-DIMENSIONAL PERIODIC STRUCTURES

The NiO crystal is considered as a stack of planes, parallel to the (001) plane on which the two-dimensional translation operation is possible. Lattice energies in rigid and unpolarized two-dimensional periodic structures become rather easy to simulate theoretically because two-dimensional structures are exploited to simplify the calculation by the use of the effective plane-wise summation technique established by Parry.[13,14] Based upon a fully ionic model,[15] the lattice energy per NiO formula unit, E_L, has the form of the summation of Madelung energy (E_M is the long-range Coulombic energy), the short-range repulsive energy (E_R), the van der Waals energy (E_{vdW}) and the zero-point energy (E_0) in the following way:[28,29]

$$E_L=\tfrac{1}{2}\sum_i\left[q_ieV_i+\sum_{j\neq i}\left[A_{ij}\exp(-B_{ij}r_{ij})-\frac{C_{ij}}{r_{ij}^6}\right]\right]+\frac{9Nk_B\Theta_D}{8}\,, \qquad (1)$$

where V_i is the site potential of the ith ion with the charge q_ie, e being the electronic charge, which will be described below; r_{ij} is the spacing between ions i and j; A_{ij} and B_{ij} are the Born-Mayer constants of the repulsive interaction; C_{ij} represents the van der Waals constant between the particular ion pair, N is the number of ions per formula unit, Θ_D is the Debye temperature (317.4 K) (Ref. 30); and k_B is Boltzmann's constant. In Eq. (1), $\sum_i$ represents the summation of ions per unit cell and $\sum_{j\neq i}$ indicates the summation over all ions in a crystal except the ith ion.

As illustrated in Fig. 1, a two-dimensional periodic structure is characterized by primitive translation vectors $\mathbf{a}=a_0\mathbf{i}$, $\mathbf{b}=a_0\mathbf{j}$, and $\mathbf{c}\propto(\mathbf{a}\times\mathbf{b})$, but $|\mathbf{c}|=\infty$, where $\mathbf{i}$ and $\mathbf{j}$ are the unit vectors along x and y axes on (001) planes; consequently, $\mathbf{c}\|z$ axis, and a_0 is the lattice constant, 4.1684 Å (Ref. 16). A two-dimensional unit cell contains two Ni^{2+} ions and two O^{2-} ions at the lth layer (l is from 1 to ∞), where the (001) free surface is the first layer (i.e., l is 1). Because of the two-dimensional symmetry, these two Ni^{2+} ions are equivalent to one another, and the same relation holds also for the O^{2-} ions.

The site potential V_i is formulated by the effective plane-wise summation technique in the following form (Parry's potential):[13,14]

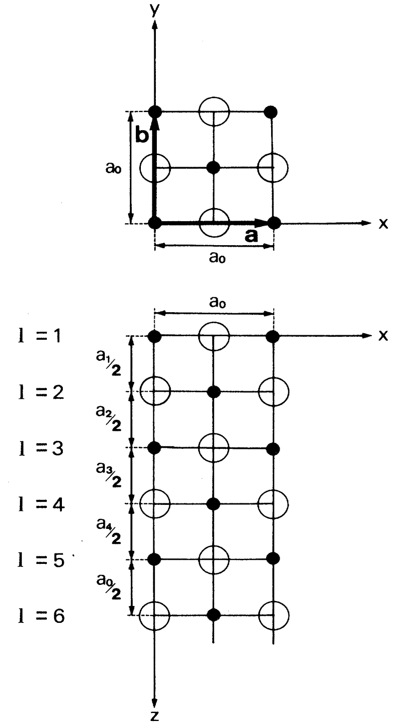

FIG. 1. The unit cell of the NiO(001) surface in rigid and unpolarized NiO. The primitive translation vectors **a** and **b** are on the (001) surface with the lattice constant $a_0=4.1684$ Å, and another vector **c** is normal to the (001) surface plane, except that $|\mathbf{c}|=\infty$. Each of the (001) planes parallel to the free surface is denoted as the lth layer, where the free surface is the first layer. The layer spacing between the lth and $(l+1)$th layers is denoted as $a_l/2$.

$$V_i=\sum_j q_j e M_{ij}\ ,$$

$$M_{ij}=\frac{\pi}{S}\left[\sum_{\mathbf{k}}\frac{e^{i\mathbf{k}\cdot\rho_{ij}}}{k}\left\{e^{ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}+\eta u_{ij}\right]+e^{-ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}-\eta u_{ij}\right]\right\}\right]+\left[\sum_{\mathbf{N}}\frac{\operatorname{erfc}(\eta R_{ij})}{R_{ij}}\right]-\frac{2\eta}{\sqrt{\pi}}\ , \qquad (2)$$

where

$$\lim_{k\to 0}\frac{e^{i\mathbf{k}\cdot\rho_{ij}}}{k}\left\{e^{ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}+\eta u_{ij}\right]+e^{-ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}-\eta u_{ij}\right]\right\}\longrightarrow -2u_{ij}\operatorname{erf}(\eta u_{ij})-2\frac{e^{-\eta^2u_{ij}^2}}{\sqrt{\pi}\eta}\ .$$

In this expression, $R_{ij}=|\mathbf{R}_{ij}|=|\mathbf{N}+\mathbf{r}_{ij}|=|n_x\mathbf{a}+n_y\mathbf{b}+\mathbf{r}_{ij}|$, where $\mathbf{r}_{ij}$ denotes the vector between ions i and j in the unit cell at the origin, and $\mathbf{N}$ is the two-dimensional lattice vector from the unit cell at the origin to the nth unit cell, where n_x and n_y are integers. $\mathbf{R}_{ij}$ is then the vector between the ith ion in the unit cell at the origin and the jth ion in the nth unit cell. The vector $\mathbf{r}_{ij}$ consists of two components: $\boldsymbol{\rho}_{ij}$ in planes parallel to the surface plane (i.e., $\perp z$ axis), and $\mathbf{u}_{ij}$ perpendicular to the surface (i.e., $\parallel z$ axis), u_{ij} being $|\mathbf{u}_{ij}|$. S is the unit area of the unit cell facing the surface, $\mathbf{k}$ is the two-dimensional reciprocal-lattice vector in planes parallel to the surface, and k represents $|\mathbf{k}|$. In Eq. (2), the summations, $\sum_{\mathbf{k}}$ and $\sum_{\mathbf{N}}$ include $\mathbf{k}=\mathbf{0}$ and $\mathbf{N}=\mathbf{0}$ terms, while $\sum_j$ indicates the summation over all ions in the crystal. However, $2\eta/\sqrt{\pi}$ is subtracted to remove the self-interaction term of the ith ion (i.e., $j=i$) included in the reciprocal summation, where η is the Gaussian width parameter that may be chosen to maximize the convergence of the summation (i.e., the convergence parameter).

TABLE I. The parameters of NiO employed in the calculations: Born-Mayer constants of the repulsive interaction, A and B; van der Waals constants C; free ion polarizabilities α^0; electronic polarizabilities α^e; and shell parameters Q. These parameters are quoted from Ref. 5, which determined these parameters in the bulk.

Ion pair	A (eV)	B (Å^{-1})	C (eV Å^6)
Ni^{2+}-O^{2-}	550.96	2.815	13.16
O^{2-}-O^{2-}	22 764.3	6.711	23.52
Ion	α^0 (Å^3)	α^e (Å^3)	$Q(e)$
Ni^{2+}	0.36	0.68	6.49
O^{2-}	3.88	1.98	1.71

This plane-wise summation method is, however, subject to the condition that the layer cell has a nonzero z component of dipole moments.[13,14,31] In certain crystal directions such as the (111) direction in NiO, the planes are charged; for example, they may consist of either just anions or cations. Such orientations are associated with infinite surface energies,[25] and the surfaces cannot generally exist without restructuring, in which case Parry's potential cannot be applicable. The NiO(001) surface, however, consists of a stack of neutral charged planes, and Madelung potentials are to be calculated by this method.

III. (001) SURFACE STRUCTURE OF UNPOLARIZED AND RIGID NiO

As described in Sec. I, the theoretical parameters required in energy calculations on NiO were already obtained, and the appropriateness of these parameters was also justified.[5,6] They are collected in Table I, but the Born-Mayer constant A of the Ni^{2+}-O^{2-} pair is modified slightly from the previous value, 556.43 eV, to 550.96 eV, which yields the theoretical lattice constant in the bulk equal to the experimental value $a_0=4.1684$ Å, because the ionic spacings near the surface, with which the lattice constant participates directly, are to be the criteria in the assessment of the two-dimensional shell model which will be constructed in this paper. This change, however, results in a slight decrease of less than 0.1% of the lattice energy per unit cell in the bulk.

Near the surface, one expects that spacings between layers parallel to the surface differ from the bulk value even in rigid and unpolarized NiO. Denote the spacing

TABLE II. The combination of layer spacings near the free (001) surface plane $\{a_1/2,a_2/2,a_3/2,a_4/2\}$ for several values of the electronic polarizability of the O^{2-} ion at the top layer, $(\alpha_O^e)_S$. To investigate the surface effect on the parameters, $(\alpha_O^e)_S$ is varied from 2.35 to 2.50 Å^3, and $(\alpha_O^e)_S=1.98$ Å^3 (i.e., the bulk polarizability).

$(\alpha_O^e)_S$ (Å^3)	$a_1/2$ (Å)	$a_2/2$ (Å)	$a_3/2$ (Å)	$a_4/2$ (Å)
1.98	3.9535/2	3.8929/2	3.8863/2	3.9016/2
2.35	3.9034/2	3.8895/2	3.8861/2	3.9030/2
2.40	3.8953/2	3.8887/2	3.8861/2	3.9033/2
2.45	3.8871/2	3.8878/2	3.8857/2	3.9031/2
2.50	3.8789/2	3.8869/2	3.8857/2	3.9029/2

TABLE III. The monopole field along the z axis, ϵ_z, acting on each ion at each value of $(\alpha_O^e)_S$. The monopole field on Ni(l) has the negative value of O(l) and vice versa, where Ni(l) and O(l) are Ni^{2+} and O^{2-} ions at the lth layer. The results at $(\alpha_O^e)_S = 1.98$ Å^3 represent the monopole fields calculated by the use of the bulk parameters. The x and y components of the monopole field on every ion are zero at any magnitude for $(\alpha_O^e)_S$.

$(\alpha_O^e)_S$	ϵ_z (eV/Å) 1.98 (Å^3)	ϵ_z (eV/Å) 2.35 (Å^3)	ϵ_z (eV/Å) 2.40 (Å^3)	ϵ_z (eV/Å) 2.45 (Å^3)	ϵ_z (eV/Å) 2.50 (Å^3)
O(1)	−0.6871	−0.7247	−0.7310	−0.7374	−0.7439
Ni(2)	0.0583	0.0243	0.0188	0.0133	0.0077
O(3)	−0.0063	−0.0029	−0.0022	−0.0016	−0.0008
Ni(4)	−0.0161	−0.0174	−0.0177	−0.0179	−0.0177
O(5)	0.1819	0.1808	0.1806	0.1807	0.1809
Ni(6)	−0.0030	−0.0030	−0.0030	−0.0030	−0.0030

between the lth and $(l+1)$th layers as $a_l/2$, as illustrated in Fig. 1; then the optimum condition for the total lattice energy at $a_l/2 = a_0/2 = 4.1684/2$ Å $(l \geq 4)$ is $\partial E_L/\partial a_1 = \partial E_L/\partial a_2 = 0$ when $a_3/2$ is treated as a variable parameter, while the lattice constant on (001) planes is $a_0 = 4.1684$ Å. This condition determines magnitudes for $a_1/2$ and $a_2/2$, and then the lattice energy E_L is calculated by Eq. (1) at each value for $a_3/2$. By changing the value for $a_3/2$, the combination of layer spacings $\{a_1/2 = 3.9573/2$ Å, $a_2/2 = 3.8950/2$ Å, $a_3/2 = 3.9045/2$ Å, and $a_l/2 = 4.1684/2$ Å $(l \geq 4)\}$ yields the minimum lattice energy. Though this combination would indeed be one of the candidates for the rigid and unpolarized surface structure, the discontinuity between $a_3/2$ and $a_4/2$ requires another iteration. By treating $a_3/2$ and $a_4/2$ as independent variable parameters with $a_l/2 = 4.1684/2$ Å $(l \geq 5)$ then the similar treatment leads to the combination $\{a_1/2 = 3.9535/2$ Å, $a_2/2 = 3.8929/2$ Å, $a_3/2 = 3.8863/2$ Å, $a_4/2 = 3.9016/2$ Å, and $a_l/2 = 4.1684/2$ Å $(l \geq 5)\}$, as tabulated in Table II. Between $a_4/2$ and $a_5/2$, there is still a discontinuity. Further iterations are theoretically possible but impractical.

The resultant monopole field acting on each ion in the perfect NiO crystal (bulk) is zero because monopole fields from all other ions counteract each other. In the case of the (001) surface, however, effective monopole fields act on ions in layers near the surface because the point symmetry is lower than that of the bulk. The monopole field acting on the ith ion ϵ_i is given by way of the site potential V_i:

$$\epsilon_i = -\mathrm{grad}\, V_i = \sum_j q_j e(-\mathrm{grad} M_{ij}) . \tag{3}$$

Because of the two-dimensional symmetry, x and y components of the monopole field acting on every ion are zero, while the z component on Ni(l) has the negative value of that on O(l), and vice versa, where Ni(l) and O(l) are Ni^{2+} and O^{2-} ions at the lth layer. Table III tabulates the monopole fields in a stack of up to six planes $(l=6)$. Ions inside the seventh layer have the bulk crystal monopole fields, i.e., $\epsilon = 0$. One expects, then, that such monopole fields would induce dipole moments only along the z axis in layers near the free surface. This prediction will be rationalized theoretically in Sec. IV. Most of the theoretical studies on rock-salt structures are based upon ionic displacements perpendicular to the free surface, as well.

IV. TWO-DIMENSIONAL POLARIZABLE POINT-ION SHELL MODEL

The fundamental principle of a two-dimensional polarizable point-ion shell model is similar to the one constructed by Dienes *et al.*,[1] except for several points. A brief description of the framework of the two-dimensional shell model will be given in this section, because full details as to the original model were published elsewhere.[1,4] The total energy of an ionic crystal containing a free surface, E_T, is given by

$$E_T = E_L + E_{\mathrm{Relax}} , \tag{4}$$

where E_{Relax} represents the relaxation energy which consists of the changes in Madelung, repulsive, and van der Waals energies, i.e., ΔE_M, ΔE_R, and ΔE_{vdW}, and the polarization energy E_p consisting of three components, i.e., the interaction between the dipole moment and the monopole field (E_{p1}), the dipole-dipole interaction energy (E_{p2}), and the dipole self-energy (E_{p3}), which includes free ion polarizabilities α^0 in Table I (Refs. 1 and 4).

After a relaxation has taken place, the vector between the ith ion in the unit cell at the origin and the jth ion in the nth unit cell changes from $\mathbf{R}_{ij}$ to the effective vector $\mathbf{R}'_{ij}$ which is given by

$$\mathbf{R}'_{ij} = \mathbf{R}_{ij} + \frac{\boldsymbol{\mu}_i}{Q_i} - \frac{\boldsymbol{\mu}_j}{Q_j} = n_x \mathbf{a} + n_y \mathbf{b} + \boldsymbol{\rho}_{ij} + \mathbf{u}_{ij} + \frac{\boldsymbol{\mu}_i}{Q_i} - \frac{\boldsymbol{\mu}_j}{Q_j} , \tag{5}$$

where $\boldsymbol{\mu}_i$ and Q_i are the dipole moment and the shell parameter of the ith ion. The shell parameter is the product of the number of polarizable electrons and the electronic charge. The two-dimensional translation operation yields the same magnitude for the dipole moment on the jth ion in every unit cell. In this scheme, the total energy E_T is a function of the dipole moments. The equilibrium dipole moments are obtained by minimizing the total energy with respect to the components of individual dipole moments as follows:

$$\frac{\partial E_T}{\partial \mu_{il}} = 0, \quad l = x, y, \text{ or } z , \tag{6}$$

where μ_{il} is the l component of the ith dipole moment. A stack of up to ten planes from the free surface comprises the block whose energy in the unit cell at the origin is calculated. It should then be emphasized that the two-dimensional translation operation reduces the number of unknowns to 3×20, i.e., μ_{ix}, μ_{iy}, and μ_{iz} $(i = 1-20)$. Equation (6) leads to the following expression:

$$
\begin{aligned}
&\sum_{k} A_{ii}^{lk}\mu_{ik}+\sum_{j\neq i}\sum_{k} A_{ij}^{lk}\mu_{jk}=C_i^l,\quad k=x,y\ \text{ or } z,\quad i\ \text{ and } j=1\sim 20\ ,\\
&A_{ii}^{lk}=\frac{\delta_{kl}}{\alpha_i^0}+\sum_{j\neq i}\left\{\sum_{\mathbf{N}}\left[\frac{(e_{ij})_k(e_{ij})_l B_{ij}^2 A_{ij}\exp(-B_{ij}R_{ij})}{Q_i^2}-\frac{42}{Q_i^2}\frac{(e_{ij})_k(e_{ij})_l C_{ij}}{R_{ij}^8}\right]+\frac{q_i q_j e^2 I_{ij}^{lk}}{Q_i^2}\right\},\\
&A_{ij}^{lk}=\sum_{j\neq i}\sum_{\mathbf{N}}\left[-\frac{(e_{ij})_k(e_{ij})_l B_{ij}^2 A_{ij}\exp(-B_{ij}R_{ij})}{Q_iQ_j}-\frac{3(e_{ij})_k(e_{ij})_l-\delta_{kl}}{R_{ij}^3}+\frac{42}{Q_iQ_j}\frac{(e_{ij})_k(e_{ij})_l C_{ij}}{R_{ij}^8}\right]-\sum_{j\neq i}\frac{q_i q_j e^2 I_{ij}^{lk}}{Q_iQ_j}\ ,\\
&I_{ij}^{lk}=\frac{\pi}{S}\delta_{kz}(1-\delta_{lz})\sum_{\mathbf{k}\neq 0} e^{i\mathbf{k}\cdot\rho_{ij}}k_l\left\{e^{ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}+\eta u_{ij}\right]-e^{-ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}-\eta u_{ij}\right]\right\}\\
&\qquad+\frac{\pi}{S}\delta_{kz}\delta_{lz}\sum_{\mathbf{k}\neq 0} e^{i\mathbf{k}\cdot\rho_{ij}}k\left\{e^{ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}+\eta u_{ij}\right]+e^{-ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}-\eta u_{ij}\right]\right\}\\
&\qquad+\sum_{\mathbf{N}}(e_{ij})_k(e_{ij})_l\left\{2\frac{\operatorname{erfc}(\eta R_{ij})}{R_{ij}^3}+\left[2\eta^2+\frac{1}{R_{ij}^2}\right]\frac{2\eta}{\sqrt{\pi}}e^{-\eta^2R_{ij}^2}\right\},\\
&C_i^l=\epsilon_{il}\left[1+\frac{q_ie}{Q_i}\right]+\sum_{j\neq i}\sum_{\mathbf{N}}\left[\frac{(e_{ij})_l B_{ij}A_{ij}\exp(-B_{ij}R_{ij})}{Q_i}-\frac{6(e_{ij})_l C_{ij}}{Q_iR_{ij}^7}\right],\\
&\mathbf{e}_{ij}=\frac{\mathbf{R}_{ij}}{R_{ij}}=\left[\frac{(\rho_{ij})_x+n_xa_0}{R_{ij}}\right]\mathbf{i}+\left[\frac{(\rho_{ij})_y+n_ya_0}{R_{ij}}\right]\mathbf{j}+\left[\frac{u_{ij}}{R_{ij}}\right]\mathbf{k}=(e_{ij})_x\mathbf{i}+(e_{ij})_y\mathbf{j}+(e_{ij})_z\mathbf{k}\ ,
\end{aligned}
\tag{7}
$$

where k_l is the l component of the two-dimensional reciprocal-lattice vector $\mathbf{k}$, $(\rho_{ij})_x$ and $(\rho_{ij})_y$ are x and y components of ρ_{ij} on the (001) planes, and $\sum_{j\neq i}\sum_{\mathbf{N}}$ indicates the summations over all ions in the crystal except the ith ion in every unit cell because the two-dimensional periodicity does not change the ionic spacing between the ith ion in the unit cell at the origin and that in the nth cell even if the relaxation takes place. The last terms in A_{ii}^{lk} and A_{ij}^{lk}, i.e., $\sum_{j\neq i}q_iq_je^2I_{ij}^{lk}/Q_i^2$ and $\sum_{j\neq i}q_iq_je^2I_{ij}^{lk}/Q_iQ_j$, and $\epsilon_{il}q_ie/Q_i$ in C_i^l come from the minimum condition of the Madelung energy, i.e., $\partial E_M/\partial\mu_{il}=\partial\sum_i q_ieV_i/\partial\mu_{il}=0$.

In a two-dimensional periodic structure, Eq. (7) becomes rather simple in comparison with the equilibrium equations in Refs. 1 and 4 because every coefficient A_{ii}^{lk}, A_{ij}^{lk} or C_i^l, disappears unless $k=l=z$. This is due to the fact that the summations, including $(e_{ij})_x$, $(e_{ij})_y$, or $(e_{ij})_x(e_{ij})_y$ become zero. The two-dimensional symmetry and monopole fields in Table III result in $C_i^x=C_i^y=0$ but $C_i^z\neq 0$. Then both x and y components of every dipole moment are zero, i.e., $\mu_{ix}=\mu_{iy}=0$, as predicted before. The number of unknowns, consequently, reduces moreover to 20.

Every term in A_{ii}^{zz}, A_{ij}^{zz}, and C_i^z is a necessary prerequisite to the calculations of dipole moments, i.e., μ_{iz}. All of them converge rapidly except $\sum_{\mathbf{N}}[3(e_{ij})_k(e_{ij})_l-\delta_{kl}]/R_{ij}^3$ in A_{ij}^{lk}, which is calculated by the Fourier transformation technique, using Ewald's method,[32] as shown in Eq. (8):

$$
\begin{aligned}
&-\sum_{\mathbf{N}}\frac{3(e_{ij})_k(e_{ij})_l-\delta_{kl}}{R_{ij}^3}\\
&\quad=-\frac{\pi(1-\delta_{kz})(1-\delta_{lz})}{S}\sum_{\mathbf{k}\neq 0}\frac{k_kk_l}{k}e^{i\mathbf{k}\cdot\rho_{ij}}\left\{e^{ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}+\eta u_{ij}\right]+e^{-ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}-\eta u_{ij}\right]\right\}\\
&\qquad-\frac{\pi\delta_{kz}\delta_{lz}}{S}\sum_{\mathbf{k}\neq 0}e^{i\mathbf{k}\cdot\rho_{ij}}\left\{ke^{ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}+\eta u_{ij}\right]+ke^{-ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}-\eta u_{ij}\right]-\frac{4\eta}{\sqrt{\pi}}e^{-[(k^2/4\eta^2)+\eta^2u_{ij}^2]}\right\}\\
&\qquad+\frac{\pi\delta_{kz}\delta_{lz}}{S}\frac{4\eta}{\sqrt{\pi}}e^{-\eta^2u_{ij}^2}-\frac{\pi(1-\delta_{kz}\delta_{lz})}{S}\sum_{\mathbf{k}\neq 0}(\delta_{kz}k_l+\delta_{lz}k_k)e^{i\mathbf{k}\cdot\rho_{ij}}\left\{e^{ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}+\eta u_{ij}\right]-e^{-ku_{ij}}\operatorname{erfc}\left[\frac{k}{2\eta}-\eta u_{ij}\right]\right\}\\
&\qquad+\sum_{\mathbf{N}}\left\{-\left[\frac{3(e_{ij})_k(e_{ij})_l-\delta_{kl}}{R_{ij}^3}\right]\operatorname{erfc}(\eta R_{ij})+\frac{2\eta}{\sqrt{\pi}}\left[\frac{1}{R_{ij}^2}-\left[2\eta^2+\frac{(4+\sqrt{\pi})}{2R_{ij}^2}\right](e_{ij})_k(e_{ij})_l\right]e^{-\eta^2R_{ij}^2}\right\}-\frac{4}{3}\frac{\eta^3}{\sqrt{\pi}}\delta_{kl}\ .
\end{aligned}
\tag{8}
$$

Then, the z component of each dipole moment can be solved from Eq.(7) by the matrix technique.

V. RESULTS AND DISCUSSION

A. (001) surface structure

Though Welton-Cook and Prutton concluded,[11] in 1980, that an extension of the calculation of the surface ionic configurations based on their shell model to the NiO(001) surface was impossible, mainly due to the absence of suitable data, such a calculation is now possible if the two-dimensional polarizable point-ion shell model is employed. In addition, the numerical parameters for NiO required in their shell model are now available.[5]

The simulation of the (001) surface structure of rigid and unpolarized NiO yields the combination of layer spacings, $\{a_1/2=3.9535/2$ Å, $a_2/2=3.8929/2$ Å, $a_3/2=3.8863/2$ Å, $a_4/2=3.9016/2$ Å, and $a_l/2=4.1684/2$ Å $(l \geq 5)\}$, which contains the discontinuity between $a_4/2$ and $a_5/2$. A higher degree of accuracy using the method described above requires more iterations which, however, become difficult in practice. Alternatively, we have employed another approach. In the two-dimensional unit cell defined in this paper (see Fig. 1), three-dimensional pseudounit cells with the primitive translation vectors **a**, **b**, and $\mathbf{c}'=a_z\mathbf{k}$, which are in a form similar to the unit cell in the bulk, are assumed to be piled up normal to the free surface, **k** being the unit vector along the z axis. The mean lattice constant along the z axis, a_z, is evaluated to be 3.8837 Å by the condition of $\partial E_L/\partial a_z=0$ in the stack of up to 40 planes from the free surface. Then the repeat of the treatment described in Sec. III yields the combination of $\{a_1/2=3.9534/2$ Å, $a_2/2=3.8927/2$ Å, $a_3/2=3.8845/2$ Å, and $a_l/2=3.8837/2$ Å $(40 \geq l \geq 4)\}$ with a good continuity from $a_3/2$ to $a_4/2$. These results indicate that surface structures cannot be as simple as expected. It is very significant, however, that quite different theoretical treatments yield nearly the same magnitudes for $a_1/2$ and $a_2/2$, respectively, the differences being negligibly small. Thus $a_1/2$ and $a_2/2$ obtained in this way can be used as reliable parameters in a check of the validity of the two-dimensional polarizable point-ion shell model.

After the relaxation has taken place, the displacement of the ith ion, $\boldsymbol{\mu}_i/Q_i$, is obtained by solving Eq. (7) with the numerical parameters in Table I, the monopole fields in Table III, and the combination of layer spacings. Table IV summarizes values of the ionic displacements along the z axis, d_z. Ions inside the eighth layer do not relax. The nearest-neighbor spacings normal to the free surface are evaluated from the displacements and summarized in Table V, in which the spacing between Ni^{2+} in the lth layer and O^{2-} in the $(l+1)$th layer and that between O^{2-} in the lth layer and Ni^{2+} in the $(l+1)$th layer are denoted as D(Ni-O) and D(O-Ni).

These results contain several important features. Our calculations result in a rumpling of the surface layer; that is, anions at the top layer move outwards along the z axis relative to cations. Such a phenomenon is common in the results obtained by the previous theoretical studies,[17–24] despite the use of models different from ours. The behavior of ions on the fifth layer is a little abnormal because of the discontinuity in the layer spacings from $a_4/2$ to $a_5/2$. The different forces acting on the two species of ions cause the surface rumpling mainly due to the different magnitudes of the induced polarizations of these ions.[21] In the shell model employed here, the induced dipole moments are undoubtedly important, but the monopole field acting on each ion is one of the factors which determines the magnitudes of dipole moments. In the theoretical model proposed by Sawada *et al.*,[24] the monopole field acting on the anion sublayer on the free surface induces moments of anions outwards which dis-

TABLE IV. Shell parameters Q, and ionic displacements along the z axis, d_z, for various values of $(\alpha_O^e)_S$. The results for $(\alpha_O^e)_S=\alpha_O^e=1.98$ Å^3 represent the shell parameters and displacements calculated by the use of the bulk parameters.

	1.98 (Å^3)		2.35 (Å^3)		2.40 (Å^3)		2.45 (Å^3)		2.50 (Å^3)	
$(\alpha_O^e)_S$	$Q(e)$	d_z (Å)	$Q(e)$	d_z (Å)	$Q(e)$	d_z (Å)	$Q(e)$	d_z (Å)	$Q(e)$	d_z (Å)
O(1)	1.71	0.1965	1.86	0.1965	1.88	0.1969	1.90	0.1974	1.92	0.1979
Ni(2)	6.48	0.0015	6.54	0.0031	6.54	0.0034	6.54	0.0036	6.54	0.0039
O(3)	1.71	0.0021	1.70	0.0024	1.70	0.0024	1.70	0.0025	1.70	0.0024
Ni(4)	6.48	−0.0005	6.54	−0.0004	6.54	−0.0004	6.54	−0.0004	6.54	−0.0004
O(5)	1.71	−0.0564	1.71	−0.0557	1.71	−0.0557	1.71	−0.0557	1.71	−0.0558
Ni(6)	6.48	−0.0005	6.48	−0.0005	6.48	−0.0005	6.48	−0.0005	6.48	−0.0005
O(7)	1.71	−0.0002	1.71	−0.0002	1.71	−0.0002	1.71	−0.0002	1.71	−0.0002
Ni(1)	6.48	−0.0193	6.41	−0.0211	6.41	−0.0214	6.41	−0.0216	6.41	−0.0219
O(2)	1.71	0.0023	1.70	−0.0132	1.70	−0.0156	1.70	−0.0179	1.70	−0.0203
Ni(3)	6.48	−0.0002	6.55	−0.0004	6.55	−0.0004	6.55	−0.0004	6.55	−0.0005
O(4)	1.71	−0.0004	1.70	−0.0006	1.70	−0.0007	1.70	−0.0008	1.70	−0.0008
Ni(5)	6.48	0.0052	6.51	0.0051	6.51	0.0051	6.51	0.0051	6.51	0.0051
O(6)	1.71	0.0011	1.71	0.0011	1.71	0.0011	1.71	0.0011	1.71	0.0011
Ni(7)	6.48	0.0000	6.48	0.0000	6.48	0.0000	6.48	0.0000	6.48	0.0000

place the anions outwards, while a coupling between the charges of cations and the induced moments of the surface anions yields an inward displacement of cation sublayer at the free surface. In the shell model employed here, however, the displacements of both the anion and cation sublayers take place at the same time, by a mechanism similar to that for the displacement of the anion sublayer in their model. In addition, as shown in Eq. (7), the z components of Coulombic and repulsive interactions are also important factors which determine dipole moments, though Sawada and Nakamura[24] suggest that both Coulombic and repulsive interactions do not contribute to the surface rumpling in their model. It is very interesting that, in spite of the difference in the models employed, the results obtained contain the common features that the displacement of anions is outward relative to cations, resulting in a rumpled structure, and a mean surface plane is pulled inwards.

B. Comparison between experiments and calculated results

Most previous theories treat only the top layer, but the shell model constructed here simulates ionic configurations inside the surface plane, as indicated in Table IV. Every theoretical study predicts rumpled (001) surfaces in rock-salt structures.[17–24] In spite of this fact, the main structural conclusion obtained by Welton-Cook and Pruton[11] is that the real NiO(001) free surface (i.e., the first layer) is slightly contracted (of $\simeq 1.9\%$ of the bulk lattice constant, i.e., -0.04 Å) toward the inside and is not rumpled on a scale detectable by LEED analysis. Though the discrepancy between their experiments and the theoretical predictions for rumpled surfaces puzzles us very much, Table V shows that the mean nearest-neighbor distance in the top layer, i.e., $D_{\rm av}$ between the top and second layers, reduces to 2.063 Å from the bulk value 2.084 Å, by -0.021 Å (i.e., -1%).

The experimental principle of the EELFS measurements[12,33] implies that the mean magnitude of the spacings D(O-Ni) between the first and second layers and that between the second and third layers dominates the experimental nearest-neighbor distance. The corresponding value calculated is $(2.172+1.948)/2=2.060$ Å, which is a little longer than the EELFS result,[12] but decreases by -0.024 Å from the bulk value.

It should be emphasized that the layer spacings near the free (001) surface in Table V, which are comparable to the results of LEED and EELFS, are calculated on the basis of $a_1/2$ and $a_2/2$ in Table II. The experiments relevant to the NiO(001) surface are, therefore, interpretable in terms of theoretical values obtained by the two-dimensional polarizable point-ion shell model with the bulk parameters. The reduction of ionic spacings near the surface calculated here is, however, somewhat smaller than that in the experiments. This fact indicates the importance of the surface influence upon numerical parameters which are to be used in calculations, as described in Sec. I.

TABLE V. The nearest-neighbor spacings for various values of the electronic polarizability of the O^{2-} ion at the top layer. The spacing along the z axis between Ni^{2+} on the lth layer and O^{2-} on the $(l+1)$th layer and that between O^{2-} on the lth layer and Ni^{2+} on the $(l+1)$th layer are denoted as D(Ni-O) and D(O-Ni), respectively, and the meaning spacing of these is represented by $D_{\rm av}$. The results for $(\alpha_O^e)_S=\alpha_O^e=1.98$ Å^3 represent the nearest-neighbor spacings calculated by the use of the bulk parameters. D is in units of Å.

	$(\alpha_O^e)_S=1.98$ (Å^3)			$(\alpha_O^e)_S=2.35$ (Å^3)			$(\alpha_O^e)_S=2.40$ (Å^3)			$(\alpha_O^e)_S=2.45$ (Å^3)			$(\alpha_O^e)_S=2.50$ (Å^3)		
Layers	D(O-Ni)	D(Ni-O)	$D_{\rm av}$	D(O-Ni)	D(Ni-O)	$D_{\rm av}$	D(O-Ni)	D(Ni-O)	$D_{\rm av}$	D(O-Ni)	D(Ni-O)	$D_{\rm av}$	D(O-Ni)	D(Ni-O)	$D_{\rm av}$
1–2	2.1718	1.9551	2.0634	2.1451	1.9438	2.0444	2.1412	1.9419	2.0415	2.1373	1.9399	2.0386	2.1335	1.9379	2.0357
2–3	1.9490	1.9459	1.9474	1.9319	1.9454	1.9387	1.9292	1.9453	1.9373	1.9264	1.9451	1.9357	1.9236	1.9449	1.9342
3–4	1.9457	1.9433	1.9445	1.9459	1.9433	1.9446	1.9459	1.9434	1.9446	1.9457	1.9432	1.9445	1.9457	1.9432	1.9444
4–5	1.9452	2.0067	1.9760	1.9457	2.0068	1.9763	1.9458	2.0069	1.9764	1.9456	2.0069	1.9763	1.9456	2.0068	1.9762
5–6	2.0283	2.0883	2.0583	2.0289	2.0882	2.0586	2.0290	2.0882	2.0586	2.0290	2.0882	2.0586	2.0289	2.0882	2.0586
6–7	2.0853	2.0839	2.0846	2.0853	2.0839	2.0846	2.0853	2.0839	2.0846	2.0853	2.0839	2.0846	2.0853	2.0839	2.0846
7–8	2.0840	2.0842	2.0841	2.0840	2.0842	2.0841	2.0840	2.0842	2.0841	2.0840	2.0842	2.0841	2.0840	2.0842	2.0841
8–9	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842	2.0842

C. Surface effect on parameters

This section describes a trial to investigate the effect of different surface values for the model parameters. The most remarkable difference between the surface and the bulk must as suggested in Sec. I, be the polarizability of O^{2-} ions on the surface, which is expected to increase from the bulk value.[25] Electronic polarizabilities are involved in van der Waals constants,[34] while the shell parameters are determined by the method developed from the theory of Dick and Overhauser[35] by Shanker and Gupta,[36] using electronic polarizabilities. A change in a polarizability, therefore, varies magnitudes of van der Waals constants and shell parameters. Furthermore, our previous calculations[3,8] indicate that relaxations in crystals are very sensitive to magnitudes of shell parameters used.

According to Tasker's suggestion,[25] the electronic polarizability of the O^{2-} ion on the top layer, which is abbreviated as $(\alpha_O^e)_S$, is treated as a variable parameter, and then the van der Waals constants of the Ni^{2+}-O^{2-} and O^{2-}-O^{2-} pairs including this O^{2-} ion have corresponding values which involve the bulk polarizabilities except for $(\alpha_O^e)_S$. A combination of layer spacings in rigid and unpolarized NiO is obtained in the same way as before. Table III summarizes the combination of layer spacings $\{a_1/2,\ a_2/2,\ a_3/2,$ and $a_4/2\}$ at each magnitude for $(\alpha_O^e)_S$ in the range of 2.35–2.50 Å^3 along with the result obtained by the bulk value, i.e., $(\alpha_O^e)_S=\alpha_O^e=1.98$ Å^3. In every combination, $a_l/2=4.1684/2$ Å when $l\geq 5$.

The electronic polarizability of a cation is described with the Madelung potential of the cation in Ruffa's theory.[37] In the surface structure, however, Madelung potentials of cations deviate from the bulk value and vary as a function of the distance of a cation from the surface. The electronic polarizability of each cation is determined by Ruffa's theory, while that of each anion except $(\alpha_O^e)_S$ is estimated under the assumption that the simple additive rule[38] in the bulk holds at each (001) plane even near the free surface, i.e., $\alpha_{Ni}^e+\alpha_O^e=2.66$ Å^3. At the top layer, however, this rule does not hold. These polarizabilities yield recalculated van der Waals constants of particular ion pairs and shell parameters of ions. Using the modified parameters C_{ij} and Q, ionic displacements are evaluated by the two-dimensional shell model at each combination of layer spacings. In Table IV, shell parameters Q and ionic displacements along the z axis d_z at each $(\alpha_O^e)_S$ are tabulated along with the results obtained by the use of the bulk parameters. The corresponding nearest-neighbor distances are also summarized in Table V.

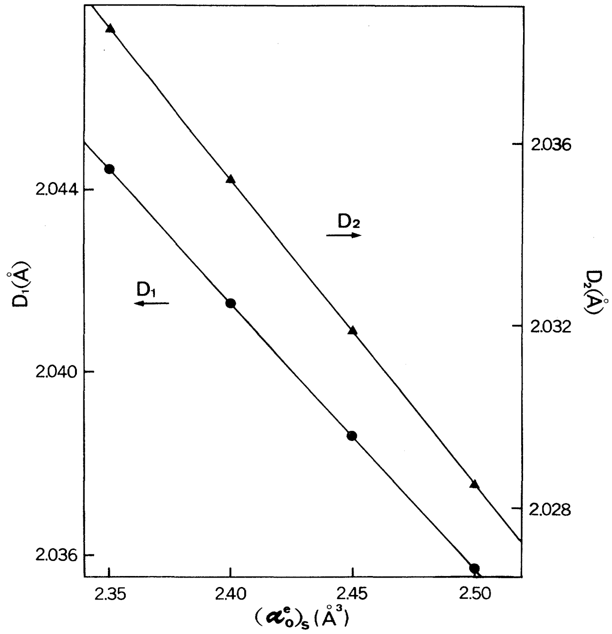

FIG. 2. The variation of the mean nearest-neighbor spacings D_1 and D_2, with the electronic polarizability of the O^{2-} ion at the top layer $(\alpha_O^e)_S$, in the range 2.35–2.50 Å^3. D_1 is the mean spacing of D(Ni-O) and D(O-Ni) between the first and second layers, and D_2 is the mean value of D(O-Ni) between the first and second layers and that between the second and third layers.

Figure 2 plots the mean value of the spacings D(O-Ni) and D(Ni-O) between the first and second layers against $(\alpha_O^e)_S$. This mean spacing is denoted as D_1 in Fig. 2. As $(\alpha_O^e)_S$ increases, D_1 decreases linearly and the best agreement with the LEED result[11] seems to be obtained at $(\alpha_O^e)_S\cong 2.43$ Å^3. Another mean value of D(O-Ni) between the first and second layers and that between the second and third layers, which is abbreviated as D_2, is also plotted in Fig. 2. As $(\alpha_O^e)_S$ increases, D_2 also decreases, but the extrapolation to the EELFS result ($\sim$2.00 Å) (Ref. 12) yields $(\alpha_O^e)_S\cong 2.93$ Å^3, which is extremely large in values compared with the bulk polarizability $\alpha_O^e=1.98$ Å^3. This fact suggests a possibility that D(Ni-O) between the first and second layers and also that between the second and third layers may contribute to the EELFS result to some extent. In fact, the mean value of D(O-Ni) and D(Ni-O) between the first and second layers and those between the second and third layers is in the range of 1.98–2.00 Å, even if $(\alpha_O^e)_S$ varies from 1.98 to 2.50 Å^3.

D. Energies of the NiO(001) surface

Though the energy per unit cell in the rigid and unpolarized surface structure is impossible to evaluate because a unit cell contains an infinite number of ions, the energy difference between the surface structure and the perfect crystal (i.e., bulk) can be calculated. Table VI tabulates the energy-difference, denoted as E_d, for various values of $(\alpha_O^e)_S$.

Determination of dipole moments by Eq. (7) yields the calculation of the relaxation energy E_{Relax}, which is the sum of ΔE_M, ΔE_R, ΔE_{VdW}, E_{p1}, E_{p2}, and E_{p3}, as described in Sec. IV. These calculated values are also summarized in Table VI. The summation of E_d and E_{Relax} corresponds to the surface energy E_S (Ref. 25). When $(\alpha_O^e)_S=1.98$ Å^3 (i.e., the bulk polarizability), E_d is large, but the magnitude of the relaxation energy $|E_{\mathrm{Relax}}|$ is

TABLE VI. The lattice-energy difference between the surface structure and the bulk, E_d, the relaxation energies E_{Relax}, which consist of ΔE_M, ΔE_R, ΔE_{vdW}, E_{p1}, E_{p2}, and E_{p3}; and the surface energy E_S, which is the sum of E_d and E_{Relax} at each $(\alpha_O^e)_S$. The results at $(\alpha_O^e)_S=\alpha_O^e=1.98$ Å^3 represent the energies calculated by the use of the bulk parameters. All measurements are in units of 10^{-2} eV/Å^2.

$(\alpha_O^e)_S$ (Å^3)	1.98	2.35	2.40	2.45	2.50
E_d	6.707	4.230	3.841	3.450	3.034
ΔE_M	19.660	20.051	20.189	20.345	20.509
ΔE_R	-12.404	-13.079	-13.146	-13.300	-13.451
ΔE_{vdW}	1.895	2.378	2.455	2.535	2.617
E_{p1}	-14.860	-16.817	-17.159	-17.518	-17.887
E_{p2}	-0.805	-1.234	-1.310	-1.390	-1.474
E_{p3}	6.507	7.623	7.818	8.024	8.236
E_{Relax}	-0.007	-1.007	-1.153	-1.301	-1.449
E_S	6.700	3.222	2.688	2.150	1.607

small. With increasing $(\alpha_O^e)_S$, E_d decreases, $|E_{\mathrm{Relax}}|$ increases, and, consequently, the surface energy decreases. These quantities are very sensitive to the electronic polarizability of the O^{2-} ion on the top layer. This fact implies that an increment in $(\alpha_O^e)_S$ surely enhances the relaxation in the surface structure considerably. A speculation about these results suggests that the value of $(\alpha_O^e)_S$ must be larger than the bulk polarizability. For further detailed discussions, however, more experiments relevant to the NiO(001) structure are required.

VI. CONCLUSIONS

In conclusion, a two-dimensional polarizable point-ion shell model was developed based upon the original model of Dienes *et al.*[1] This model was successfully applied to the NiO(001) surface structure, and the general features obtained by EELFS and LEED experiments[11,12] were interpretable in terms of the results calculated with this shell model, though there are some deviations from the experimental results. Such deviations are probably due to the use of bulk parameters employed at the surface in the calculations. The relaxation in the surface structure is found to be very sensitive to the magnitude of the electronic polarizability of the O^{2-} ion on the top layer, which is expected to be larger than the bulk value 1.98 Å^3.

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