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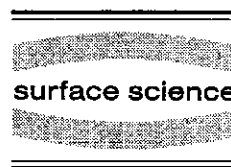
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Abstract

Using a two-dimensional polarizable point-ion shell model and the effective plane-wise summation technique for evaluations of two-dimensional Madelung potentials, the NiO (001) surface structure, in which a two-dimensional translation operation is possible, has been calculated. The calculations result in a rumpling of the surface layer; anions at the top layer move outwards along the direction normal to (001) surface relative to cations. The general features obtained by EELFS and LEED experiments are interpretable in terms of the results calculated, though there are some deviations from the experimental results. Such deviations are accounted for by the electronic polarizability of O^{2-} ion on the top layer, which is expected to be larger than bulk value 1.98 \AA^3 .

Keywords: Computer simulations; Construction and use of effective interatomic interactions

1. Introduction

We have constructed a two-dimensional polarizable point-ion shell model which is applicable to the crystal structures in which lattice periodicities are preserved even after relaxations take place [1]. The surface structures are one of the typical two-dimensional periodic lattices. The shell model is applied to crystals of high ionicities. As for NiO, the ionicity is 0.887 [2] and reliable experimental results on (001) surface structure are available [3,4]. Yikegaki et al. [3] carried out the EELFS measurements which yield nearest-neighbour distances of $\sim 2.00 \text{ \AA}$, slightly shorter than the spacing of the $Ni^{2+}-O^{2-}$ pair normal to the (001) plane in the bulk [5], i.e., $4.1684/2$

$\cong 2.08 \text{ \AA}$, while Welton-Cook and Prutton observed [4], using the LEED method, that the real NiO(001) free surface is slightly contracted towards the inside (about -1.9% of the bulk lattice constant). Both experiments are indicative of a reduction of ionic spacings normal to the (001) surface by 1.9–3.8% of the bulk value. Since these results enable us to compare the calculated results with experiments, it is important to carry out a theoretical construction of NiO (001) surface using the two-dimensional shell model and to investigate the factors which govern the surface structure.

2. Theory

The NiO crystal is considered as a stack of planes parallel to the (001) plane. Lattice energies in rigid

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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 [6,7]. Based upon a fully ionic model [2], the lattice energy per NiO formula unit, E_L , has the form of the summation of Madelung energy (E_M), the short-range repulsive energy (E_R), and the van der Waals energy (E_{vdW}) in the following way:

$$E_L = \frac{1}{2} \sum_i \left[q_i e V_i + \sum_{j \neq i} \left(A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \right) \right], \quad (1)$$

where V_i is the site potential of the i th ion with the charge $q_i e$, e being the electronic charge, r_{ij} is the spacing between ions i and j , A_{ij} and B_{ij} are the Born–Mayer constants of the repulsive interaction, and C_{ij} represents the van der Waals constant between the particular ion pair. 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 i th 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, $\mathbf{c} \parallel z$ axis, and a_0 is the lattice constant, 4.1684 Å [5]. A two-dimensional unit cell contains two Ni^{2+} ions and two O^{2-} ions at the l th 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 also the same relation holds also for the O^{2-} ions.

The theoretical parameters required in energy calculations on NiO were already obtained, and the appropriateness of these parameters was also justified [8,9]. 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 between the l th and $(l+1)$ th layers as $a_l/2$, as illustrated in Fig. 1, the energy-minimum condition of the rigid ion model calculation based upon Eq. (1) yields the combination $\{a_1/2 = 3.9535/2 \text{ Å}, a_2/2 = 3.8929/2 \text{ Å}, a_3/2 = 3.8863/2$

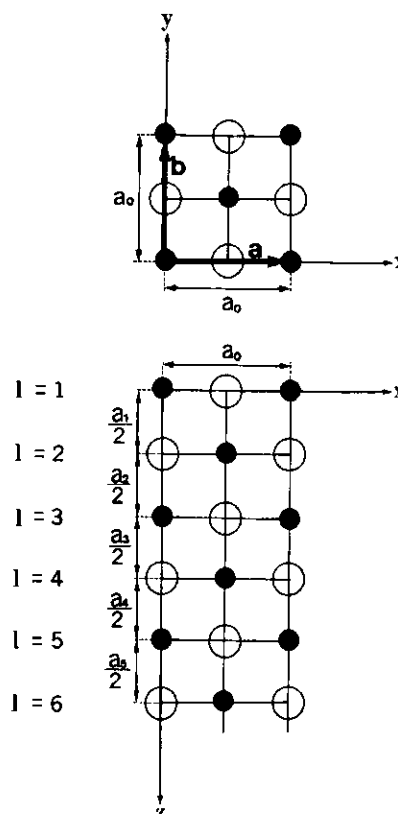


Fig. 1. The unit cell of NiO (001) surface in rigid and unpolarized NiO. The primitive translation vectors \mathbf{a} and \mathbf{b} are on the (001) surface with the lattice constant, $a_0 = 4.1684 \text{ Å}$ and another vector \mathbf{c} is normal to the (001) surface plane, but $|\mathbf{c}| = \infty$.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

Å, $a_4/2 = 3.9016/2 \text{ Å}$ and $a_l/2 = 4.1684/2 \text{ Å}$ ($l \geq 5$)). Between $a_4/2$ and $a_5/2$, there is still a discontinuity. In principle, a huge calculation could result in a continuous change in the lattice constant but, practically, it is impossible.

A brief description on this model will be given because full details were published elsewhere [1]. The total energy of an ionic crystal containing a free surface, E_T , is given by

$$E_T = E_L + E_{\text{Relax}}, \quad (2)$$

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}) [1].

After a relaxation has taken place, the vector between the i th ion in the unit cell at the origin and the j th ion in the n th unit cell, changes from R_{ij} to the effective vector R'_{ij} which is given by

$$R'_{ij} = R_{ij} + \frac{\mu_i}{Q_i} - \frac{\mu_j}{Q_j}, \quad (3)$$

where μ_i and Q_i are the dipole moment and the shell parameter of the i th ion. Since the shell parameter is the product of the number of polarizable electrons and the electronic charge, μ_i/Q_i is the displacement of the i th ion. The two-dimensional translation operation yields the same magnitude for the dipole moment on the j th ion in every unit cell. In this scheme, the total energy E_T is a function of dipole moments. The equilibrium dipole moments are obtained by minimizing the total energy with respect to the components of individual dipole moments as follows:

$$\frac{\partial E_T}{\partial \mu_{il}} = 0, \quad l = x, y \text{ or } z, \quad (4)$$

where μ_{il} is the l component of the i th dipole moment.

3. Results and discussion

Table 1 summarizes ionic displacement along the z -axis, d_z . The nearest neighbour spacings normal to the free surface are evaluated from the displacements and summarized in Table 2, in which the spacing between Ni^{2+} in the l th layer and O^{2-} in the $(l+1)$ th layer and that between O^{2-} in the l th layer and Ni^{2+} in the $(l+1)$ th layer are denoted as $D(\text{Ni}-\text{O})$ and $D(\text{O}-\text{Ni})$.

The theoretical study predicts rumpled (001) surfaces in rock-salt structures [10]. In spite of this fact, the main structural conclusion obtained by Welton-Cook and Prutton [4] is that the real $\text{NiO}(001)$ free surface (i.e., the first layer) is slightly contracted (-1.9% of the bulk lattice constant) towards 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 2 shows that the mean nearest-neighbour distance in the top layer, i.e., D_{av} between the top and second layers, reduces to 2.063 \AA from the bulk value, 2.084 \AA (i.e., -1% of the bulk constant).

The mean magnitude of the spacings, $D(\text{O}-\text{Ni})$ between the first and second layers and that between the second and third layers dominates the experimental nearest-neighbour distance in the EELFS mea-

Table 1

Shell parameters, Q , and ionic displacements along the z -axis, d_z , at each $(\alpha_0^e)_S$; the results at $(\alpha_0^e)_S = \alpha_0^e = 1.98 \text{ \AA}^3$ represent the shell parameters and the displacements calculated by the use of the bulk parameters

	$(\alpha_0^e)_S = 1.98 (\text{\AA}^3)$		$(\alpha_0^e)_S = 2.35 (\text{\AA}^3)$		$(\alpha_0^e)_S = 2.40 (\text{\AA}^3)$		$(\alpha_0^e)_S = 2.45 (\text{\AA}^3)$		$(\alpha_0^e)_S = 2.50 (\text{\AA}^3)$	
	$Q(e)$	$d_z(\text{\AA})$	$Q(e)$	$d_z(\text{\AA})$	$Q(e)$	$d_z(\text{\AA})$	$Q(e)$	$d_z(\text{\AA})$	$Q(e)$	$d_z(\text{\AA})$
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

Table 2

The nearest neighbor spacings at each electronic polarizability of the O^{2-} ion at the top layer; the spacing along the z -axis between Ni^{2+} on the l th layer and O^{2-} on the $(l+1)$ th layer and that between O^{2-} on the l th 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_{av} ; the results at $(\alpha_0^e)_s = 1.98 \text{ \AA}^3$ represent the nearest neighbor spacings calculated by the use of the bulk parameters

Layers	$(\alpha_0^e)_s = 1.98 \text{ (\AA}^3)$			$(\alpha_0^e)_s = 2.35 \text{ (\AA}^3)$			$(\alpha_0^e)_s = 2.40 \text{ (\AA}^3)$			$(\alpha_0^e)_s = 2.45 \text{ (\AA}^3)$			$(\alpha_0^e)_s = 2.50 \text{ (\AA}^3)$		
	$D(O-Ni)$	$D(Ni-O)$	D_{av}	$D(O-Ni)$	$D(Ni-O)$	D_{av}	$D(O-Ni)$	$D(Ni-O)$	D_{av}	$D(O-Ni)$	$D(Ni-O)$	D_{av}	$D(O-Ni)$	$D(Ni-O)$	D_{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

D in units of \AA .

surements [3]. The corresponding value calculated is $(2.172 + 1.948)/2 = 2.060 \text{ \AA}$, which is a little longer than the EELFS result [3], but decreases by -1.2% of the bulk value. Such a deviation must be ascribed to the electronic polarizability of O^{2-} ions on the top layer which must be easily polarizable compared with O^{2-} in the bulk, as Tasker suggests [11].

Then, the electronic polarizability of the O^{2-} ion on the top layer, which is abbreviated as $(\alpha_{\text{O}}^e)_s$, is treated as a variable parameter. Accordingly, the van der Waals constants of $\text{Ni}^{2+}-\text{O}^{2-}$ and $\text{O}^{2-}-\text{O}^{2-}$ pairs including O^{2-} ions at the top layer have the corresponding values because these constants involve $(\alpha_{\text{O}}^e)_s$.

The electronic polarizability of each cation is determined by Ruffa's theory [12], while that of each anion except $(\alpha_{\text{O}}^e)_s$ is estimated under the assumption that the simple additive rule in the bulk holds at each (001) plane even near the free surface, i.e., $\alpha_{\text{Ni}}^e + \alpha_{\text{O}}^e = 2.66 \text{ \AA}^3$ [13]. 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. In Table 1, shell parameters Q , and ionic displacements along z -axis, d_z , at each $(\alpha_{\text{O}}^e)_s$ are tabulated. The corresponding nearest-neighbour distances are also summarized in Table 2.

Fig. 2 plots the mean value of the spacings, $D(\text{O}-\text{Ni})$ and $D(\text{Ni}-\text{O})$, between the first and second layers against $(\alpha_{\text{O}}^e)_s$. This mean spacing is denoted as D_1 in Fig. 2. As $(\alpha_{\text{O}}^e)_s$ increases, D_1 decreases linearly and the best agreement with the LEED result [4] seems to be obtained at $(\alpha_{\text{O}}^e)_s \cong 2.43 \text{ \AA}^3$. Another meaning value of $D(\text{O}-\text{Ni})$ 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 $(\alpha_{\text{O}}^e)_s$ increases, D_2 also decreases, but the extrapolation to the EELFS result ($\sim 2.00 \text{ \AA}$) [3] yields $(\alpha_{\text{O}}^e)_s \cong 2.93 \text{ \AA}^3$, which is extremely large in values compared with the bulk polarizability $\alpha_{\text{O}}^e = 1.98 \text{ \AA}^3$. This fact suggests a possibility that $D(\text{Ni}-\text{O})$ between the first and second layers and also that between the second and third layers may contribute to the EELFS result to some extent.

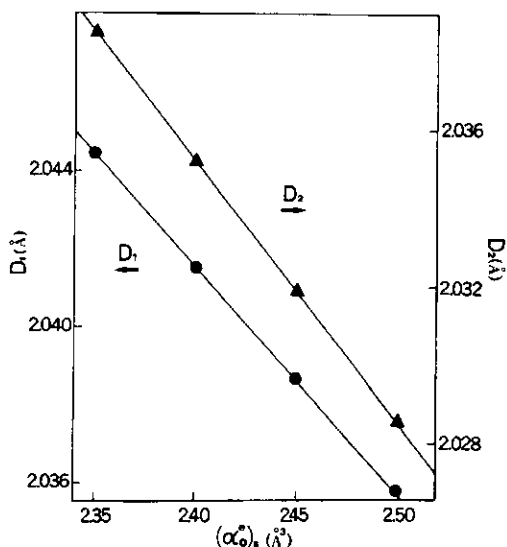


Fig. 2. The mean nearest neighbor spacings, D_1 and D_2 , against the electronic polarizability of the O^{2-} ion at the top layer, $(\alpha_{\text{O}}^e)_s$, in the range of 2.35 to 2.50 \AA^3 , D_1 ; the mean spacing of $D(\text{Ni}-\text{O})$ and $D(\text{O}-\text{Ni})$ between the first and second layers, and D_2 ; the mean value of $D(\text{O}-\text{Ni})$ between the first and second layers and that between the second and third layers.

4. Conclusions

A two-dimensional polarizable point-ion shell model was successfully applied to the results of EELFS and LEED [3,4], though there are some deviations from the experimental results. Such deviations depend upon the magnitude for the electronic polarizability of O^{2-} ions on the top layer, which is expected to be larger than the bulk value.

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