

Discussion on Surface Characterization by DV-X α Method

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Understanding of surface characters is very important for material design such as adsorbent and ultra fine particles. DV-X α method, which is one of quantum chemical method, can be applied to surface state. However, there are few reports on characterization of surface properties such as a surface structure and surface energy. In this study, the rumpling surface structure and surface energy of alkaline earth metal oxides and LiF (rock-salt structure) compounds have been discussed on basis of the calculated results using DV-X α method. Displacement of atoms in surface layer (first layer) represented relaxed structure. The optimal displacement obtained from bond strength between the first and second layer corresponded with the values experimentally obtained in reference. The bond in the surface layer was stronger than that of the inner-layer. Increments of bond strength correlate with surface energy for alkaline earth metal oxides. Surface properties were acceptably explained by DV-X α method.

Key words: Surface relaxation, Surface energy, Quantum chemical calculation, DV-X α method, Overlap population, Alkaline earth metal oxides

1. INTRODUCTION

Every substance has surface, which has character differed from a bulk state. There are many materials using surface characteristics such as adsorbent, catalyst and gas censor.

For the fine-particle materials, a surface character becomes remarkable because of increasing of specific surface area. The reactions concerned with solid phase such as sintering and dissolution phenomenon of substances start from a surface, the surface property is very important. It is indispensable for the development of the new material to analyze the surface characteristics.

On the other hand, DV-X α method, which is one of calculation method for quantum chemistry, had many results in the field of inorganic chemistry due to development of computer. For example, DV-X α method was applied to solubility of atom to solid

state,¹⁾ mechanochemical reaction,²⁾ dielectric substance³⁾ and adsorption phenomenon of molecules^{4,5)} and so on. However, there are few reports on application to surface characterization.

In this study, DV-X α method was applied to alkaline earth metal oxides (MgO, CaO, SrO and BaO) and LiF with rock-salt type structure to discuss (1) magnitude of surface relaxation and (2) surface energy as surface characteristics.

2. CALCULATION METHOD

2.1 Surface relaxation

The magnitude of surface relaxation of MgO and LiF were calculated using model cluster (Mg₃₈O₃₇)²⁺ and (Li₃₈F₃₇)²⁺, respectively (Fig. 1). The "inter-layer" and "intra-layer" represent perpendicular and parallel bond to surface, respectively. The 2000 point charges were distributed at virtual atomic site around the

Table I Surface relaxation of MgO and LiF ⁶⁾

	Surface relaxation (SR)** / %	Rumple (R)*** / %	Ratio of surface relaxation* / %	
			ϵ^+	ϵ^-
MgO	-3	5	-5.5	-0.5
LiF	-11	12	-17	-5

* ϵ^+ and ϵ^- represent the ratio of surface relaxation for cation and anion, respectively. The ratio of surface relaxation is shown as formula $\epsilon = (a_s - a_b)/a_b$. a_s : distance between first and second layer, a_b : distance between cation and anion at bulk.

** The surface relaxation(SR) is represented as average of the ratio of surface relaxation for cation and anion. The formula is shown as $SR = (\epsilon^+ + \epsilon^-)/2$.

*** The rumple(R) is represented as difference of the ratio of surface relaxation for anion and cation. The formula is shown as $R = \epsilon^- - \epsilon^+$.

model cluster to represent the bulk state. The total charge of the model cluster is neutral.

For the bulk state, the validity of model cluster was judged by comparing the calculated band gap with that of literature. The surface state was calculated without point charges above the surface of (100) plane. The magnitude of relaxation (displacement of atom) of the relaxed surface was determined by the value in reference (Table I ⁶⁾). The states of surface were calculated with surface relaxation of -1, -3, -5 and -7 % for MgO, and -9, -11, -13 and -15 % for LiF (Fig.1). In addition, rumple, representing asperity of surface atom was constant at 5 and 12 % for MgO and LiF, respectively.

2.2 Surface energy

The surface energy of alkaline earth metal oxides, MgO, CaO, SrO and BaO were calculated using model cluster ($M_{14}O_{13}$)²⁺ (M: alkaline earth metal) to discuss relation between bonding state at the surface and surface energy. The point charges were placed in a similar manner as mentioned in 2.1. The ideal surface without relaxation was used to simplify the surface model. The calculated surface was (100) plane.

3. RESULTS AND DISCUSSION

3.1 Surface relaxation and bond strength

(a) The bulk state

The calculated band gap for model clusters ($Mg_{14}O_{13}$)²⁺ and ($Li_{13}F_{17}$)²⁺ agreed with those in reference^{7, 8)} as shown in Table II. Furthermore, the characteristic of ionic compounds clearly appeared in

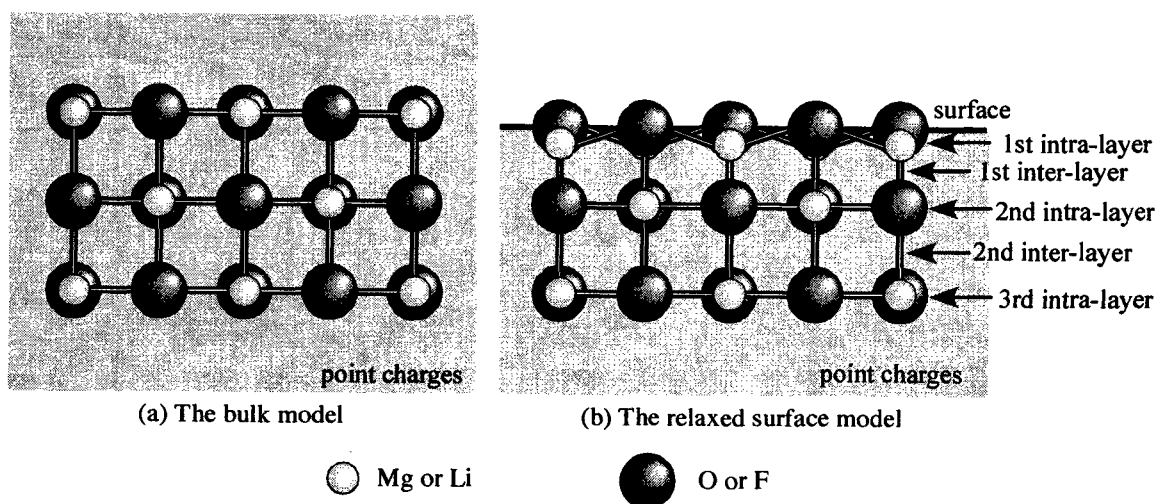
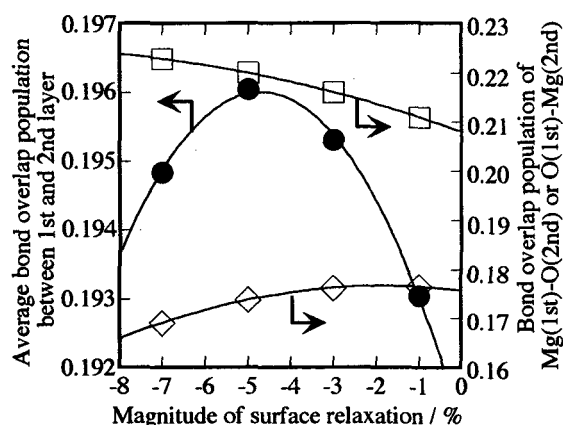
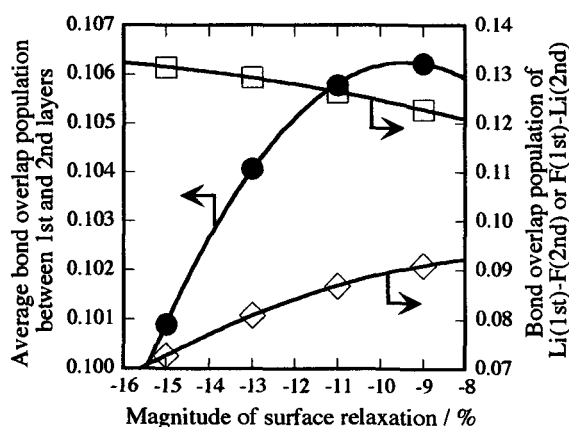


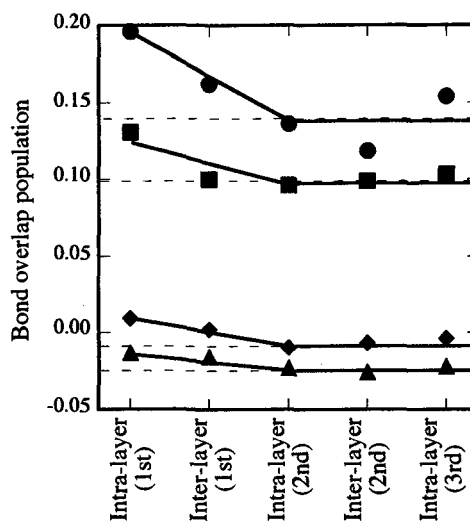
Fig.1 The bulk model and the relaxed surface model used in the calculation. The composition of model clusters is ($Mg_{14}O_{13}$)²⁺ and ($Li_{13}F_{17}$)²⁺ for MgO and LiF, respectively.

Table II The calculated and reference value of band gap for MgO and LiF

	Calculation / eV	Reference / eV
MgO	7.5	7.3 ⁷⁾
LiF	10.4	11 ⁸⁾

**Fig.2** Bond overlap population (BOP) of the first inter-layer for MgO. ●:average BOP of the first inter-layer, ◇:Mg(1st)-O(2nd) and □:O(1st)-Mg(2nd).**Fig.3** Bond overlap population (BOP) of the first inter-layer for LiF. ●:average BOP of the first inter-layer, ◇:Li(1st)-F(2nd) and □:F(1st)-Li(2nd).

the band structure, because main component of valence and conduction bands was O-2p orbital and Mg-3s orbital for MgO, respectively. The same result was obtained for LiF. From these results, it was found that these model clusters were available.

**Fig.4** Changes in bond overlap population (BOP) of M-O (M;alkaline earth metal) at each layer for the surface model cluster of MgO(●), CaO(■), SrO(◆) and BaO(▲). Broken lines show BOP of the bulk state for each compound.

(b) The bonding state at relaxed surface

The relationship between bond strength of the first “inter-layer” and magnitude of surface relaxation is shown in Fig.2 and Fig.3 for MgO and LiF, respectively. The “inter-layer” represents perpendicular bond to surface (cf. Fig.1). Bond overlap population (BOP) represents magnitude of covalent bond. For MgO, BOP was the largest value of 0.196 at magnitude of surface relaxation -4.7%. The magnitude of surface relaxation obtained by calculation was good corresponding with reference value of -3%. The bond strength (BOP) between Mg in the first layer and O in the second layer became weak with decrease of magnitude of the surface relaxation. On the other hand, that between O in the first layer and Mg in the second layer became strong with decrease of magnitude of the surface relaxation. Thus, the stable relaxation structure would be determined by balance of bond strength for Mg(1st)-O(2nd) and O(1st)-Mg(2nd). The same result was obtained for LiF, i.e. BOP was the largest value of 0.106 at magnitude of surface relaxation -9.4%. The magnitude of surface relaxation obtained by calculation was good corresponding with reference value of -11%.

The surface relaxation phenomenon of ionic compound such as MgO and LiF was influenced by bond strength of first “inter-layer”. Then, it was found

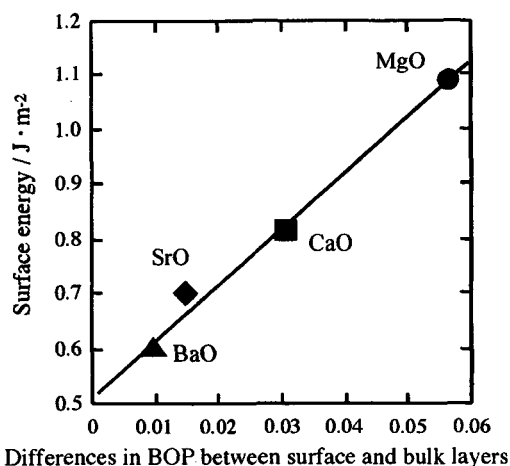


Fig.5 Relationship between the surface energy and the differences in BOP between the surface and the bulk layers.

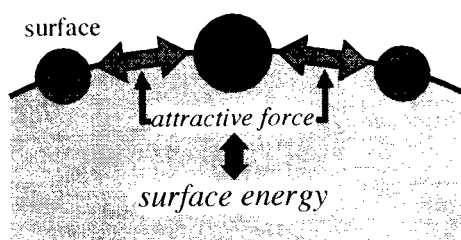


Fig.6 Schematic illustration for relation between the surface energy and the increment of bond strength at surface layer.

that the average bond strength of first “inter-layer” decided relaxed surface structure.

3.2 Surface energy and bond strength at surface

The validity for the application of DV-X α method to $(M_1O_{1.5})^{2+}$ (M: alkaline earth metal) model cluster was already confirmed in the past paper.⁹⁾

The ideal surface models were used to make simpler in the calculation. The bond strength of each layer is shown in Fig.4. The bond at first “intra-layer” was strengthened than that of inner layers every compound. The “intra-layer” represents parallel bond to surface. The relationship between the surface energy¹⁰⁾ at (100) and the difference of bond strength among the surface layer and bulk is shown in Fig.5. It was found that linear relationship exists between the surface layer reinforcement and surface energy. This result represents as following results (Fig.6). Surface area decreases to stabilize energy state, because

surface has higher energy state than inner. Then atoms at surface layer draw each other, and the bond at surface is strengthened. That is, surface bond reinforcement occurs due to surface tension, and relates with surface energy. Surface energy was explained well by DV-X α method.

4. CONCLUSION

DV-X α method was applied to surface properties of alkaline earth metal oxides and LiF with NaCl-type structure. The results are summarized as follows;

- 1) The displacement of atom in relaxed surface would be decided by average bond strength of the first “inter-layer”.
- 2) The bond of surface is stronger than that of bulk. This bond reinforcement relates with surface energy.
- 3) The surface properties were explained acceptably by DV-X α method. Therefore, this method is useful for design of materials used surface properties.

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