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Structural Stabilities of Ordered Arrays of Nb₄ Clusters on NaCl(100) Surface *WANG Xiao-Chun(王晓春)^{1,2}, ZHANG Jian-Hua(张建华)¹, WEN Yu-Hua(文玉华)¹,
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Adsorption of ordered (2 × 2) arrays of Nb₄ clusters on the insulating surface of NaCl(100) is studied by the first-principles calculations within the density functional theory. The calculations on the relaxed geometries and cohesive energies show that both the tetrahedron and quadrangle-Nb₄ can be stably adsorbed on this substrate, which may have important applications. The adsorption of quadrangle-Nb₄ on the NaCl(100) surface is more stable than that of tetrahedron-Nb₄. Both the Nb₄ clusters studied and a single Nb atom prefer the top site of the Cl atom in the NaCl(100) surface. Electronic structure analysis suggests that the interactions between the Nb₄ clusters and the substrate are weak.

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The fabrication and understanding of nanostructures has become an exciting area of research. In particular, clustering on surfaces by nucleation and growth during atom deposition has been an important subject in the basic and applied science for decades.^[1] The epitaxial growth of nanostructures on surfaces is of both scientific interest and technological importance. The surprising size uniformity of three-dimensional (3D) islands achieved in the growth of both elemental and compound semiconductor thin films^[2–7] has shown great promise for their use as quantum dots. These experiments have stimulated extensive theoretical studies, which have progressively advanced our understanding of the epitaxial growth of nanostructures on surfaces. In particular, the structural stabilities and electronic structures of periodical arrays of clusters on the surfaces have been intensively investigated in order to understand the basic physics of these systems.^[8–10]

In contrast to semiconductor or metal surfaces, less study has been reported for the periodical arrays of metal clusters on the insulating surface. Recently, theoretical studies have been carried out on the adsorption of Cu, Ag, Au,^[11] and Na₈^[12] on the typical ionic crystal NaCl(100), which is an insulating surface. For the adsorption of single metal atom, it is found that adsorption takes place preferentially on Na sites. No stabilization was found for the metal on anionic positions. The binding energies are small (about 0.1 eV) and the metal–surface distances are larger than 3 Å.^[11] For the study of Na₈ on NaCl(100), the *ab initio* molecular dynamics study shows that the concept of a magic Na_{*n*} cluster is not meaningful without reference to the electronic environment to which the cluster is exposed.^[12] Experimentally, the Fe cluster arrays with a very good size uniformity on the NaCl(100) surface

has also been achieved.^[13] These investigations show that the systems of the metal cluster arrays and single metal adatom on the NaCl surface are very important. However, as far as we know, the structural stabilities and electronic properties of periodical arrays of transition metal Nb₄ clusters on the insulating surfaces have not yet been explored. The magic cluster Nb₄, with both electronically and atomically closed shell structures, is highly stable.^[14] The ground state of Nb₄ was shown to be a regular tetrahedron with side 2.53 Å and zero spin.^[15] The structural stabilities and electronic structures of 2-D arrays of Nb₄ clusters on the metal Cu(111) surface and semiconductor GaN(0001) surface have been reported.^[9,10] In this Letter, we present our first-principles calculations for a nanostructure system with ordered Nb₄ arrays on the insulating NaCl(100) surface. Such a study should be helpful for comparing adsorption properties of the same metal cluster on different substrates.

The present calculations have been performed using the Vienna *ab initio* simulation package (VASP), which is based on the density functional theory and the projector augmented wave (PAW) representation.^[16–18] A generalized gradient-corrected exchange-correlation functional (GGA) given by Perdew and Wang is used.^[19,20] The plane wave kinetic energy cutoff employed is 25.1 Ry. These choices produce a lattice constant of 5.67 Å for bulk NaCl, compared to the experimental value of 5.63 Å.^[21] Periodically repeated slab geometry, with three NaCl layers and a vacuum spacing about 22 Å between the slabs, is employed. Nb₄ clusters are adsorbed on both sides of the slab. In our calculations, the p(2 × 2) surface cells of NaCl(100) are used and the 4 × 4 × 1 Monkhorst–Pack *k*-point meshes,^[22] which corresponds to 4 special points in the irreducible two-

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dimensional Brillouin zone (BZ), are employed for the BZ integration. Optimizations of the atomic structures were performed by the conjugate-gradient technique, using the calculated Hellmann–Feynman forces as a guide.^[23] All the atoms in the unit cell are fully

relaxed except for the central NaCl layer, which are fixed at their respective bulk positions. Energy convergence is reached when the forces on the relaxed atoms are less than $0.01 \text{ eV}/\text{\AA}$.

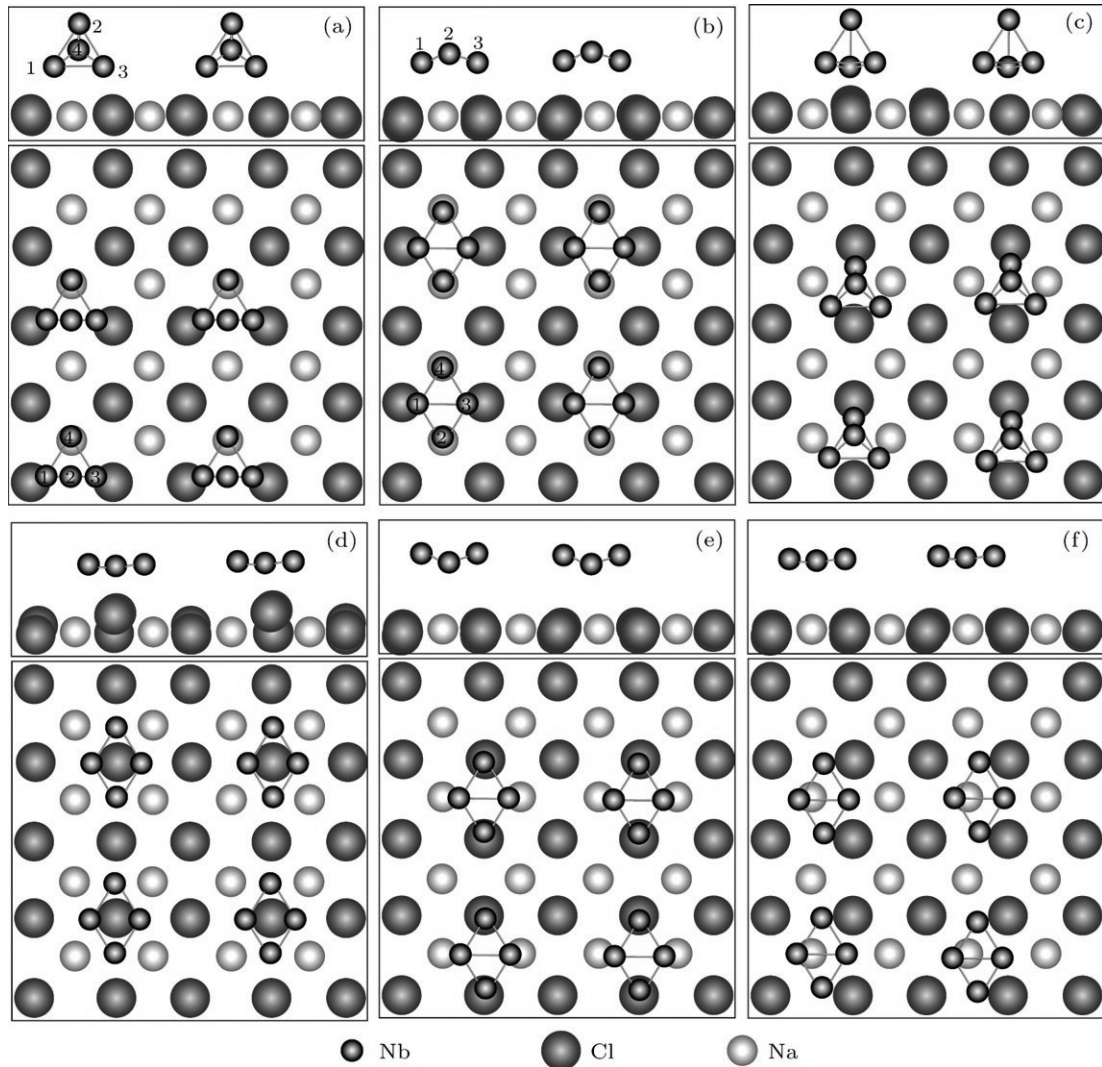


Fig. 1. Side (upper panel) and top (lower panel) views of the important adsorption configurations of Nb_4 clusters on the NaCl (100) surface. Here we take binding energy E_b in units of $\text{eV}/\text{Nb-atom}$ for Nb_4/NaCl (100), and the distance d between the lowest Nb atom of the Nb_4 clusters and the NaCl (100) surface, in units of \AA : (a) $E_b = 0.22$, $d = 2.57$, (b) $E_b = 0.29$, $d = 2.67$, (c) $E_b = 0.15$, $d = 2.51$, (d) $E_b = 0.17$, $d = 2.35$, (e) $E_b = 0.24$, $d = 2.75$, (f) $E_b = 0.16$, $d = 3.14$.

We first discuss the geometries of the tetrahedron- (i.e., 3D-Nb_4) and quadrangle- Nb_4 clusters (2D-Nb_4) adsorbed on the NaCl (100) surface. For the free Nb_4 clusters, we have presented the results in Ref. [9], which is in good agreement with the experimental and other theoretical data. The present calculations show that a single Nb atom would prefer the top site of Cl atoms. For the 3D- (tetrahedron) and 2D- (quadrangle) Nb_4 cluster arrays on the NaCl (100) surface, the important adsorption sites are summarized in Figs. 1(a)–1(f). The barycentres of the adsorbed Nb_4 clusters in Figs. 1(a), 1(b), 1(c) and 1(e) are located around the hollow sites of the NaCl (100)

surface, while the others are located around the top sites of the surface. According to our calculations, the adsorptions of the 3D-Nb_4 cluster arrays on the top and bridge sites of NaCl (100) surface are not stable (there is one bridge site and two top sites, i.e., the top of Na and Cl atoms). Among the adsorption geometries in Figs. 1(a)–1(f), the most stable adsorption site is shown in Fig. 1(b), i.e. the $2\text{D-Nb}_4/\text{NaCl}$ (100). Similarly, on the Cu (111) surface the adsorption of 2D-Nb_4 clusters is more stable than that of 3D-Nb_4 .^[9] The binding energy is $0.29 \text{ eV}/\text{Nb-atom}$ for this most stable adsorption geometry. All the other adsorptions are metastable as

compared to Fig. 1(b), for example, the adsorption site in Fig. 1(a) is metastable, with a binding energy of 0.22 eV/Nb-atom which is lower than the most stable adsorption by 0.07 eV/Nb-atom. The binding energy is defined as the energy required to separate a single Nb₄ cluster from the NaCl (100) surface, i.e. $E_{\text{binding}} = (E_{\text{total}} - E_{\text{free-Nb}_4} - E_{\text{clean-NaCl}(100)})/8$, where E_{total} is the total energy of the adsorbed system, $E_{\text{free-Nb}_4}$ is the total energy of an independent free Nb₄ cluster, $E_{\text{clean-NaCl}(100)}$ is the total energy of clean NaCl (100) surface (with atomic positions relaxed), and the number 8 is the total number of Nb atoms in one supercell. The binding energies for various adsorption sites. The binding energies suggest that the interactions between the Nb₄ clusters and the NaCl(100) surface are relatively weak, as compared to the systems of Nb₄/Cu(111)^[9] and Nb₄/GaN(0001),^[10] where the binding energies are of orders of about 2.0 and 2.2 eV/Nb-atom, respectively.

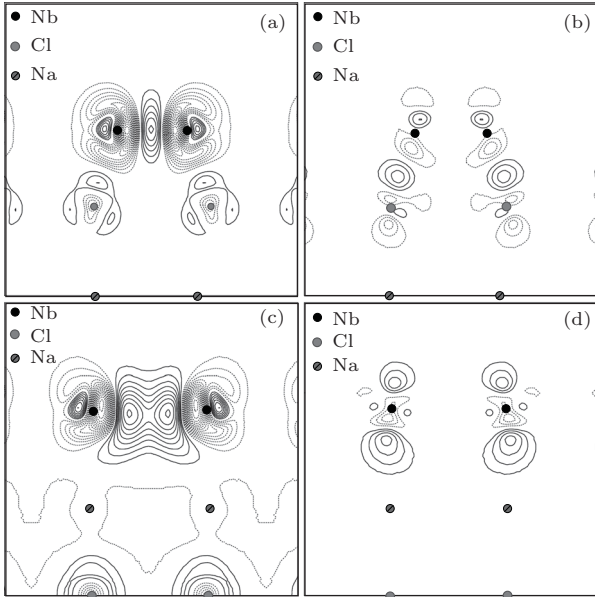


Fig. 2. Contour plots of two kinds of charge density differences (see text for their definitions) for the most stable configuration of Nb₄/NaCl(100) [Fig. 1(b)]. (a) For $\Delta\rho_1(\mathbf{r})$, the plotted plane is vertical to the NaCl surface and passing atoms Nb₁ and Nb₃; (b) the same as (a) but for $\Delta\rho_2(\mathbf{r})$; (c) for $\Delta\rho_1(\mathbf{r})$, the plotted plane is vertical to the NaCl surface and passing atoms Nb₂ and Nb₄; (d) the same as (c) but for $\Delta\rho_2(\mathbf{r})$. Solid and dashed lines correspond to $\Delta\rho > 0$ and $\Delta\rho < 0$, respectively.

The distances between the lowest Nb atom of the Nb₄ cluster and the NaCl (100) surface are also presented. Among all the six important adsorption sites of the Nb₄-clusters, the most stable configuration is shown in Fig. 1(b), as mentioned previously. The relaxed configuration of Fig. 1(b) shows that the atoms Nb₁ and Nb₃ locate near the top sites of the Cl atoms, and the atoms Nb₂ and Nb₄ locate on the top sites of the Na atoms. The two Cl atoms in Fig. 1(b) which are beneath the Nb₁ and Nb₃ atoms

shift up by 0.33 Å, whereas the Nb₂ and Nb₄ atoms shift up by 0.24 Å. The adsorption configuration of Fig. 1(e) is very similar to that of Fig. 1(b). The position of 2D-Nb₄ cluster relative to the surface in Fig. 1(e) is higher than Fig. 1(b) by 0.08 Å, indicating a lower binding energy and a weaker interaction with the surface. For the metastable configuration such as Fig. 1(a), although the distance between the lowest Nb atom and the substrate (2.57 Å) is shorter than that (2.67 Å) of Fig. 1(b), the binding energy, however, is lower than that of Fig. 1(b) since there are more atoms in Fig. 1(b), which are directly interacted with the substrate.

The nature of interactions between the adsorbed Nb₄ clusters and the NaCl(100) surface can be displayed by the contour plots of the charge density differences, as shown in Fig. 2. One of the charge density differences, which are helpful for visualizing the characteristics of bonding, is defined as the differences between the adsorbed Nb₄/NaCl(100) system and the superposition of atomic charge densities, i.e., $\Delta\rho_1(\mathbf{r}) = \rho[\text{Nb}_4/\text{NaCl}(100)] - \sum_{\mu} \rho_{\text{atom}}(\mathbf{r} - \vec{R}_{\mu})$. These contour plots for the 2D-Nb₄ cluster arrays on the NaCl(100) as in Fig. 1(b) are presented in Figs. 2(a) and 2(c). For Fig. 2(a), the plotted plane is vertical to the NaCl(100) surface and passing atoms Nb₁ and Nb₃, and for Fig. 2(c), the plotted plane is again vertical to the NaCl(100) surface but passing atoms Nb₂ and Nb₄. The present plots show that there is a weak bonding (slightly charge density increase) between the adsorbed Nb₄ clusters and the Cl atoms of the NaCl(100) surface, however, little bonding can be found between the Nb₄ clusters and the Na atoms. Figures 2(a) and 2(c) also show that the strong covalent bonding between the Nb atoms inside the Nb₄ cluster keeps unchanged upon adsorption on the NaCl(100) surface, the same as the case of Nb₄/Cu(111).^[9] Another contour plot for the charge density differences, which will help to visualize the charge transfers between the adsorbates and the substrate, is defined as the difference between the Nb₄/NaCl(100) and the two-dimensional sheet of the adsorbed Nb₄ and the clean NaCl(100) surface, i.e., $\Delta\rho_2(\mathbf{r}) = \rho[\text{Nb}_4/\text{NaCl}(100)] - \rho[\text{Nb}_4\text{sheet}] - \rho[\text{NaCl}(100)]$. Such contours for the 2D-Nb₄/NaCl(100) as shown in Fig. 1(b) are plotted in Figs. 2(b) and 2(d), where the plotting planes are the same as Figs. 2(a) and 2(c), respectively. Figures 2(b) and 2(d) show that there are more charge redistributions between the 2D-Nb₄ clusters and the Cl atoms than those between the Nb₄ clusters and the Na atoms, however, in both the cases the charge redistributions are not significant, indicating a relatively weak bonding between the adsorbed Nb₄ and the substrate. Both the charge redistribution and charge transfer plots indicate that the interactions between the adsorbates and the substrate should be relatively

weak. The strong covalent bonding inside the Nb₄ clusters accounts for the structural stability of the adsorption of Nb₄ on the NaCl(100) surface. The Nb₄ clusters tend to maintain their compactness structure on this surface and it is possible to well identify each cluster on the NaCl(100) surface. Furthermore, the density of Nb₄ clusters on the NaCl(100) surface can be extremely high, because in our (2 × 2) supercell calculations the charge density overlap between the neighbouring Nb₄ clusters are negligible.

In summary, the first-principles density functional calculations have been used to discuss the important adsorption sites, the structural stabilities and electronic properties of the periodical arrays of Nb₄ clusters on the NaCl(100) surface. The calculations show that the interactions between the adsorbed Nb₄ and the NaCl substrate are relatively weak. There are strong covalent bonding between Nb atoms inside a Nb₄, and the Nb₄ clusters tend to maintain the compactness configuration after adsorption on the NaCl(100) surface, for both the tetrahedron and quadrangle-Nb₄. Such stable clusters or quantum dot arrays on surfaces are potentially valuable for optical, electronic, and magnetic device applications.

References

- [1] Zinke-Allmang M, Feldman L C and Grabow M H 1992 *Surf. Sci. Rep.* **16** 377
- [2] Tersoff J, Teichert C and Lagally M G 1996 *Phys. Rev. Lett.* **76** 1675
- [3] Medeiros-Ribeiro G, Bratkovski A M, Kamins T I, Ohlberg D A and Williams R S 1998 *Science* **279** 353
- [4] Ross F M, Tersoff J and Tromp R M 1998 *Phys. Rev. Lett.* **80** 984
- [5] Floro J A, Sinclair M B, Chason E, Freund L B, Twisten R D, Hwang R Q and Lucadamo G A 2000 *Phys. Rev. Lett.* **84** 701
- [6] Leonard D, Krishnamurthy M, Reaves C M, Denbaars S P and Petroff P M 1993 *Appl. Phys. Lett.* **63** 3203
- [7] Xie Q, Madhukar A, Chen P and Kobayashi N P 1995 *Phys. Rev. Lett.* **75** 2542
- [8] Zhang L X, Zhang S B, Xue Q K, Jia J F and Wang E G 2005 *Phys. Rev. B* **72** 033315
- [9] Wang X C, Lin Q B, Li R Q and Zhu Z Z 2006 *Phys. Rev. B* **73** 245404
- [10] Wang X C, Zhu Z Z 2007 *Phys. Rev. B* **75** 245323
- [11] Mejias J A 1995 *Phys. Rev. B* **53** 10281
- [12] Häkkinen H and Manninen M 1995 *Phys. Rev. Lett.* **76** 1599
- [13] Gai Z, Wu B, Pierce J P, Farnan G A, Shu D, Wang M, Zhang Z and Shen J 2002 *Phys. Rev. Lett.* **89** 235502
- [14] Moro R, Xu X, Yin S and de Heer W A 2003 *Science* **300** 1256
- [15] Kumar V and Kawazoe Y 2002 *Phys. Rev. B* **65** 125403
- [16] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
- [17] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
- [18] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [19] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev. B* **46** 6671
- [20] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
- [21] Allouche A 1997 *Surf. Sci.* **374** 117
- [22] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [23] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045