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The Effect of the Rest of Crystal on the Electronic Structure of $Ti_xO_y^{-n}$ Clusters

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Electronic structures of the titanium oxide clusters with different surroundings have been calculated and the effect of the rest of the crystal on the electronic structure has been discussed. As far as the eigenvalue spectra are concerned, a constant potential surface is a good approximation for the rest of the crystal, that is, the eigenvalue spectra of the clusters are insensitive to their surroundings, which is discussed on the basis of the charge compensation and energy cancellation principle.

1. INTRODUCTION

Understanding of the electronic structure of solid materials is always pursued by both theoreticians and experimentalists because the knowledge of the electronic structure of solid materials is indispensible for explaining XPS and UPS results. Ideally, the electronic structure of solid materials should be determined for the whole crystal. However, it is impossible to include the whole crystal in calculations without introducing approximations; because of the overwhelming CPU time and at the moment, no computer is sufficiently large to finish this task. The difficulty facing theoreticians is how to construct a calculational model as close as possible to the real system. In order to solve this problem, Siegbahn *et al.* (1) proposed to use an array of point charges to approximate the rest of the crystal, so that the calculation is performed only on a cluster. Considering the charge distribution in the real system, some researchers suggest using the wave function instead of the point charge array in calculation (2). In order to imitate the rest of the crystals, Watson (3) used a charged sphere around the cluster and usually obtained results comparable to experimental results. Victor Luana and L. Pueyo (4) developed the TES (Theory of Electronic Separability) method and their systematic works demonstrate that the TES method can describe the transition metal ions in an ionic crystal very well. Among these different schemes, the point charge model is frequently used due to its simplicity. Until now, many papers have been published based on the point charge model (5–6). However, according to our knowledge, still no universal approximation schemes have been developed to meet the needs of calculation in different systems. For example, the point charge approach is only valid for some completely ionic compounds; nobody gives a strict verification that the point charge model can be extended to the other incomplete ionic systems, such as TiO_2 (rutile). The purpose of this paper is to study the effect of the rest of the crystal on the electronic structure of the isolated titanium oxide cluster.

2. CALCULATION METHOD

(i) Ab Initio calculations were performed with the Gaussian 90 program developed by Pople *et al.* (7) on Convex. In our calculation, we adopt Willard R. Wadts' scheme for Ti and Morris Kraus's (8–11) for O; namely, we replace the chemically inert core electrons with effective potentials and hence reduce the calculation to a computationally more feasible and chemically more important valence electron problem. Starting with the basis sets they proposed, we adequately enlarge the Ti 3*d* and O 2*p* primitive sets (but removed the polarization function from the original basis set for O) and optimized these basis sets until the best description was reached for the electronic structure of the TiO_6^{-8} cluster in its singlet ground state for which much theoretical and experimental data can be found from the literature (the controlled parameters in optimization are energy gap, valence, and conduction band compositions).

The geometric parameters are obtained from experimental results for the rutile TiO_2 structure. The cluster charge is determined as the summation of the formal charge: +4 for Ti and −2 for O.

(ii) The Xα method (12–13) is used to calculate the radial distribution of the atomic charge density for free Ti, Ti^{+4}, O, and O^{-2} or Ti^{+4} and O^{-2} enclosed in the Watson

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sphere, using the spin restricted scheme. In these calculations, we do not consider relativistic corrections.

(iii) The Madelung potential calculation (14) is performed by summing the contribution from each point charge, supposing +4 for Ti and −2 for O.

3. RESULTS AND DISCUSSION

3.1. *Ab Initio Calculation on a Series of Titanium Oxide Clusters*

a. Systematic study of the electronic structures of a series of free clusters for TiO_4^{-4}, TiO_5^{-6}, $Ti_3O_{15}^{-18}$, $Ti_4O_{16}^{-16}$, $Ti_4O_{18}^{-18}$, *and* $Ti_7O_{24}^{-20}$. According to our knowledge, most work is performed on the cluster isolated from the massive materials. Consistency between the theoretical and experimental results encourages researchers to explain their experimental data based on the theoretical calculation. Tsukada *et al.* calculate the electronic structures of MgO (15) and TiO_2 (5), using a point charge array to approximate the rest of the crystal and their result is in accordance with the UPS measurement. For MgO, most people believe it is a pure ionic compound, therefore, the point charge approximation does not introduce significant error in calculation. However, the validity for TiO_2 is in doubt because it is generally believed that the Ti–O bond has some covalent character (16); therefore, we must know the effective charge on each ion in the real crystalline. Some people suggest we solve this problem by self-consistent charge calculation. In fact, if we can determine the trend of the DOS variation with size of clusters, we can draw some information about the whole crystal by extrapolation. Based on this idea, we calculated the DOS spectra of TiO_4^{-4}, TiO_5^{-6}, TiO_6^{-8}, $Ti_3O_{15}^{-18}$, $Ti_4O_{18}^{-18}$, and $Ti_7O_{24}^{-20}$ (see Figs. 1 and 2). It is obvious that from the DOS of $Ti_3O_{15}^{-18}$ on qualitatively similar DOS are obtained; It is concluded, therefore, that the DOS of $Ti_3O_{15}^{-18}$ already reproduce the electronic structure of the whole crystal quite well. Perhaps the positional order of some states in each band can be changed due to neglecting the rest of the crystal, as in the case of MgO observed by Tsukada *et al.* (15), but this has no influence on our conclusion above because this situation does not occur between the different bands. Comparing the DOS of the TiO_2 cluster to those of experimental and theoretical results published in the literature, our results describe the electronic structure of bulk titanium oxide qualitatively well except that the valence band is broadened (ca. 10 eV in our case but 6 eV determined by the UPS for the bulk TiO_2 (17)). The wider valence band is due to the boundary effect, which we will discuss further in the following paragraph. These facts told us that, as in the case of the ionic MgO, the main role of the rest of the crystal is to shift the spectra as a whole and it does not change the DOS spectra too much.

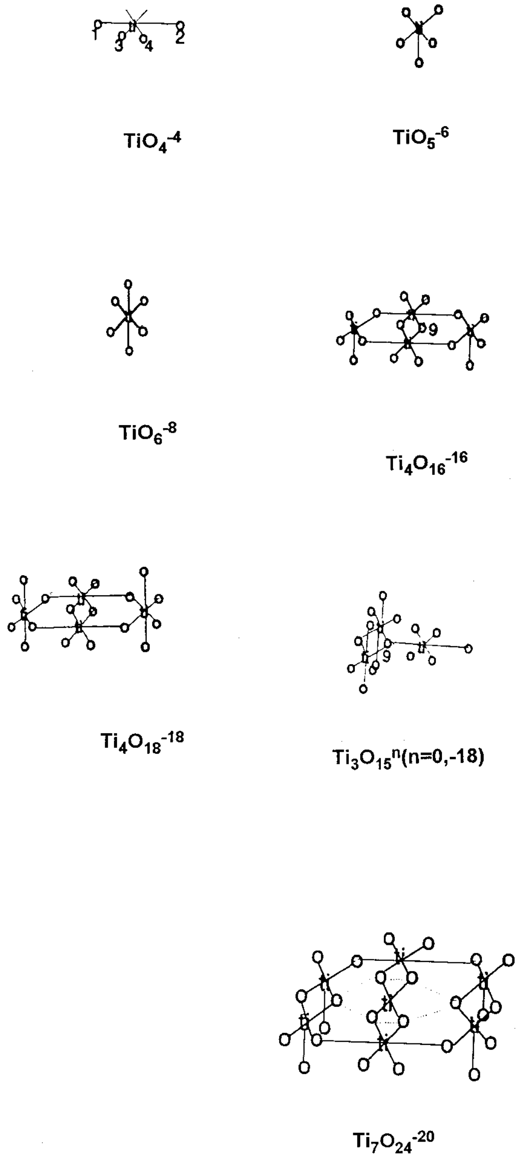

FIG. 1. The geometries for the $Ti_xO_y^{-n}$ clusters.

b. Influence of the different surroundings on the electronic structure of TiO_6^{-8}. In the literature, researchers have used different approximations for the rest of the crystal in their calculations, such as the Watson sphere model (3), the proton saturation model (that is, using protons to reduce the cluster charge or hydrogen atoms to eliminate the dangling bond), and the point charge model (1). Here we select TiO_6^{-8} as a calculational model and calculate its electronic structures using the above three surroundings. Tables 1 and 2 list the total atomic charge and gross orbital populations. There exist some common characteristics in Tables 1 and 2. The first is that the atomic charges are much lower than +4 for Ti and −2 for O and this conclusion seems independent of the surroundings. The second

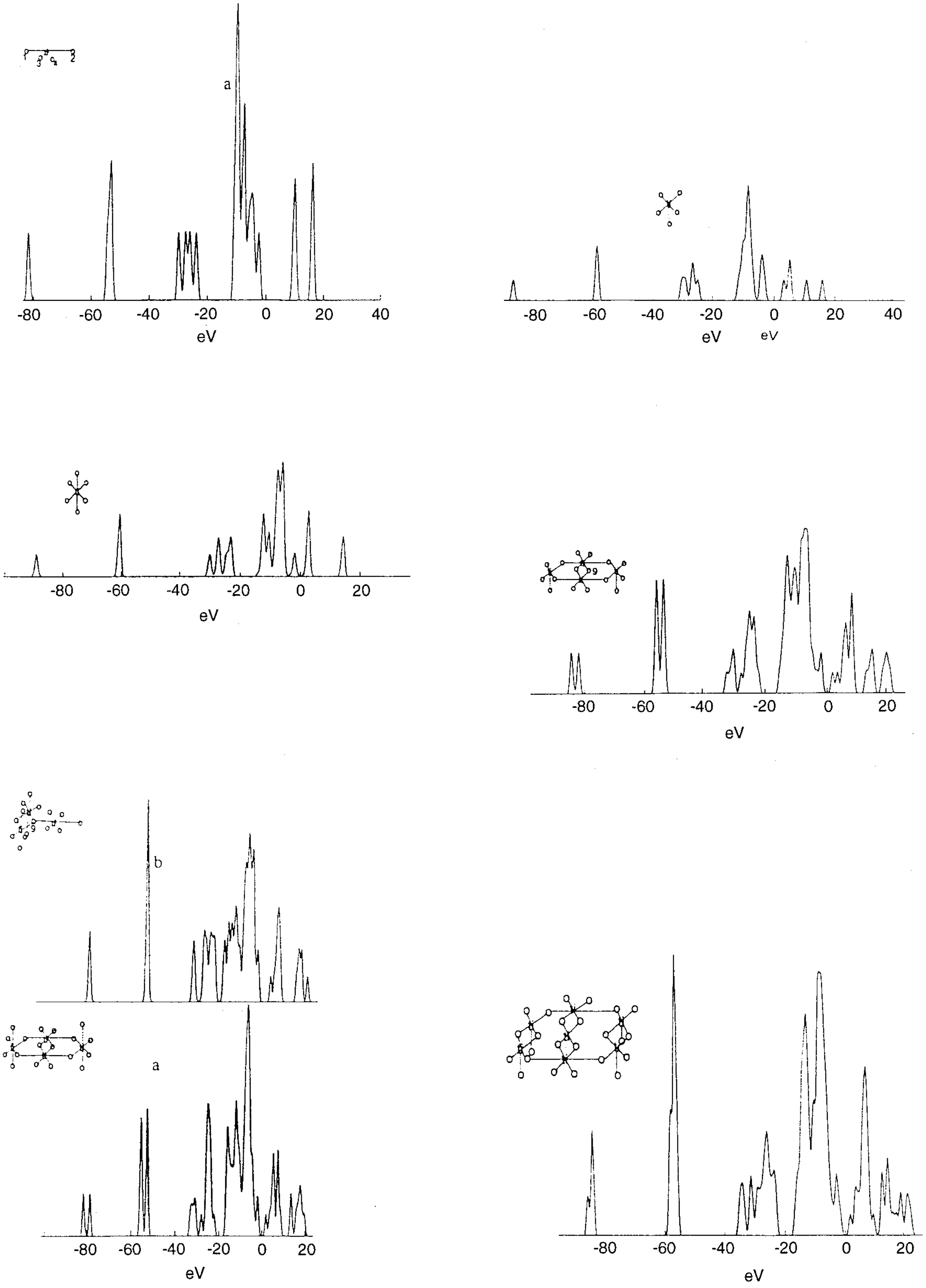

FIG. 2. The DOS spectra of the $Ti_xO_y^{-n}$ clusters.

TABLE 1
Atomic Charge (a.u.)

	TiO_6^{-8} (free)	TiO_6^{-8} +6 point charge	TiO_6^{-8} +Watson sphere	TiO_6^{-8} +6 proton		
Ti	0.4477	0.2036	0.2408	0.2670	1H	−0.0534
1O	−1.4694	−1.3390	−1.3056	−0.3154	2H	−0.0534
2O	−1.4694	−1.3390	−1.3032	−0.3154	3H	−0.0557
3O	−1.3772	−1.3569	−1.3166	−0.3154	4H	−0.0557
4O	−1.3772	−1.3569	−1.3168	−0.3154	5H	−0.0534
5O	−1.3772	−1.4059	−1.5353	−0.3402	6H	−0.0534
6O	−1.3772	−1.4059	−1.4631	−0.3402		

is that the surroundings mainly cause redistribution of the valence electrons but nearly no effect on the core electron populations. The third is that ignoring the rest of the crystal causes a more negative charge on the O atom. This can be understood by comparing the total atomic charge of clusters (column 1–3 in Table 1) to that with proton surroundings (column 4 in Table 1). This implies that if we use the wave function instead of point charges to represent the rest of the crystal in a cluster calculation, the atomic charges on Ti and O will be reduced further and, consequently, the real potential surface between atoms in the crystal is much flattened. In order to study the effect of the different surroundings on the eigenvalues, we give the eigenvalue spectra in Fig. 3. It is noticed that they are actually the same except for being shifted by a different constant value. (If we removed the proton contribution from the eigenvalue spectrum of the cluster with proton surrounding, the eigenvalue spectrum of this cluster becomes more similar to the others in Fig. 3.) This result reveals that the surroundings of the cluster play a role as a constant potential in the eigenvalue spectra. Figure 4 shows the DOS of TiO_6^{-8} with different surroundings. In order to make comparisons, we draw the sub-DOS of TiO_6^{-8} from $\mathrm{Ti}_7\mathrm{O}_{24}^{-20}$ as a reference because this subcluster is surrounded by other O^{-2} and Ti^{+4} in $\mathrm{Ti}_7\mathrm{O}_{24}^{-20}$ and should be closer to the real crystal. It is noticed that the similarity appeared among the DOS spectra of the free TiO_6^{-8}, TiO_6^{-8} with the Watson sphere, and the subcluster TiO_6^{-8} in $\mathrm{Ti}_7\mathrm{O}_{24}^{-20}$. This means that the effect of the rest of the crystal on the electronic structure looks more like that of the Watson sphere with opposite charge (the charge neutral requirement) or that of a constant potential surface. It is known that the point charge model sometimes can give a result consistent with that of the experiment. The reason is that the electronic structure of a cluster

TABLE 2
Gross Orbital Population

	TiO_6^{-8} (free)	TiO_6^{-8} +6 point charge	TiO_6^{-8} +Watson sphere	TiO_6^{-8} +6 proton	
Ti 1*s*	1.9971	1.9998	1.9987	1.9998	1H 1*s* 0.7099
2*s*	0.2629	0.2278	0.2618	0.2111	2*s* 0.3435
3*px*	2.0000	2.0000	2.0000	2.0001	2H same as 1H
3*py*	2.0000	2.0000	2.0000	2.0001	3H 1*s* 0.7115
3*pz*	2.0000	2.0000	2.0000	2.0001	2*s* 0.3442
4*d*0	0.5643	0.8487	0.8746	0.6637	4H same as 3H
4*d* + 1	0.9151	0.6156	0.5299	0.7276	5H 1*s* 0.7100
4*d* − 1	0.4658	0.6306	0.5081	0.7496	2*s* 0.3435
4*d* + 2	0.8640	0.8435	0.8910	0.6623	6H same as 5H
4*d* − 2	0.4831	0.6304	0.6950	0.7184	
1O 1*s*	1.7768	1.8137	1.7885	1.3968	
1*Px*	1.9365	1.8391	1.8479	1.8536	
1*Py*	1.8555	1.8623	1.8586	1.2279	
1*Pz*	1.9006	1.8238	1.8106	1.8372	
2O	same as 1O	same as 1O	same as 1O	same as 1O	
3O 1*s*	1.7700	1.8154	1.7879	same as 1O	
1*Px*	1.8509	1.8646	1.8440		
1*Py*	1.8442	1.8507	1.8674		
1*Pz*	1.9121	1.8262	1.8175		
4O	same as 3O	same as 3O	same as 3O	same as 1O	
5O 1*s*	same as 3O	1.8261	1.7976	1.4006	
1*Px*		1.8623	1.9401	1.8531	
1*Py*		1.8647	1.9363	1.8553	
1*Pz*		1.8529	1.8609	1.2313	
6O	same as 3O	same as 5O	same as 5O	same as 5O	

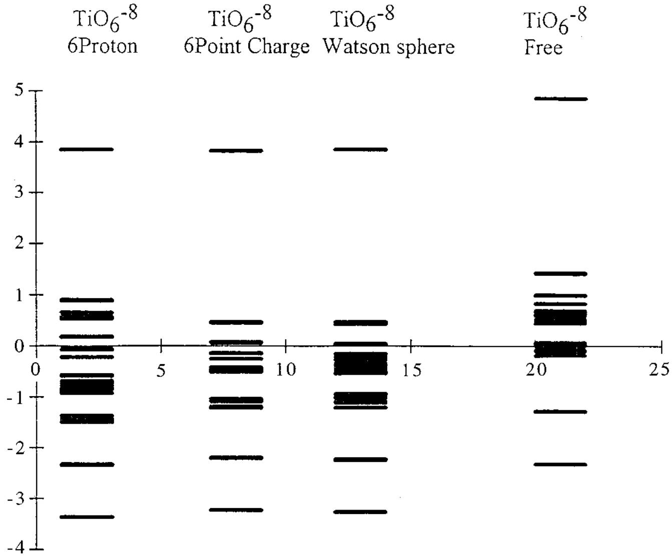

FIG. 3. Eigenvalue spectra for TiO_6^{-8} cluster with different surroundings.

is insensitive to the potential surface and to most extent determined by the nearest surroundings. In fact, when we try to minimize the error due to dropping of the rest of the crystal by using point charge array, another error is introduced because of the unknown quantities of the charge on each ion in crystalline, even though some people suggest that the atomic charge be determined by the self-consistent method. Since the Watson sphere only offers a homogeneous potential within the sphere of the cluster, which is equivalent to a constant potential, we therefore can set this constant potential equal to zero after finishing calculation, and then shift the whole spectra according to the Fermi energy. Following this procedure we should get qualitatively correct DOS of the whole crystal at least as accurate as that of the point charge model.

It should be pointed out that, in optimizing the geometry structure of cluster, the effect of the rest of the crystal must be considered because the existence of a small gradient in the potential surface will lead to totally different geometry structure in the iteration process (4). For this purpose, the more accurate calculation method should be used.

c. Effect of charge of cluster on the electronic structure of titanium oxide cluster. Walch and Ellis (18) calculated the neutral cluster of MgO and their result fits the experimental data fairly well. Matsumura *et al.* (19) studied hydrogen adsorption onto the surface of LiF. In their calculation, they used the neutral clusters of $(LiF)_9$ and $(LiF)_8$ to imitate the real crystal. They got a result consistent with experiment. In order to distinguish the two irregular sites of MgO surfaces as candidates for the H_2–D_2 exchange reaction, the same group took the neutral MgO cluster as a calculational model. Comparable results with experimental data have been obtained. Therefore, they concluded that the Madelung potential does not affect significantly the relative energy diagram of neutral clusters. Here we calculated the neutral and charged clusters of TiO_6^n ($n = 0, -8$) and $Ti_3O_{15}^m$ ($m = 0, -18$) and verified that there are no obvious differences in the DOS spectra between the neutral and charged clusters (we only show the DOS spectra of $Ti_3O_{15}^m$ ($m = 0, -18$) in Fig. 5). In Section 3.1b, we demonstrated that the surroundings of the cluster have some effect on the atomic charge distribution in clusters. However, according to the DOS of $Ti_3O_{15}^m$ ($m = 0, -18$), this atomic charge redistribution has almost no effect on the DOS pattern. This means that the effect of the rest of the crystal on the pattern of the DOS of titanium oxide cluster is not so large as we expected; namely, the DOS of titanium oxide cluster seems insensitive to the potential well selected. In fact, according to the result of Citrin and Thomas (20), the valence band position of the ion in the crystal is almost the same as that of the free neutral atom. In this sense, the position of the electronic state in the neutral cluster should be more similar to that of the ion in the crystal. Their conclusion is based on an ionic or nearly ionic compound, such as alkali metal halides. In our case, it is believed that covalency makes some contribution to the Ti–O bond. However, the similarity between the DOS of the neutral and charged titanium oxide cluster reveals that the rest of the crystal mainly makes a constant contribution to the DOS spectra (that is, it shifts the DOS spectra as a whole). Recio *et al.* (21) performed molecular orbital calculations on $(MgO)_n$ and $MgO)_n^+$ ($n = 1 - 13$) clusters and found almost the same relationship between dissociation energies and the cluster sizes for the neutral and charged clusters. In the next section, we explore the origin of this consistency of the DOS pattern based on the atomic charge distribution.

Some may argue about what differences in electronic structure exist between the cluster and bulk material. We say here that the free cluster usually cannot keep the same geometry as it has in the crystal and inevitable geometric distortion from crystalline form may take the main role in determining the DOS pattern of cluster. If this structural distortion does not exist, the DOS of the cluster should be similar to that of the massive material because of the localized properties of the electronic structure. This is the reason why one can use results from the cluster to correlate with experimental data obtained on the massive materials.

3.2. Radial Charge Distribution

Figure 6 shows that the radial charge density distributions ($(R(r)^2r^2 \sim r)$) of the free Ti, Ti^{+4}, O, and O^{-2} obtained by the $X\alpha$ method. It is noticed that Ti and Ti^{+4} have almost the same charge density in their inner regions and the maximum difference appears at the outer regions. The

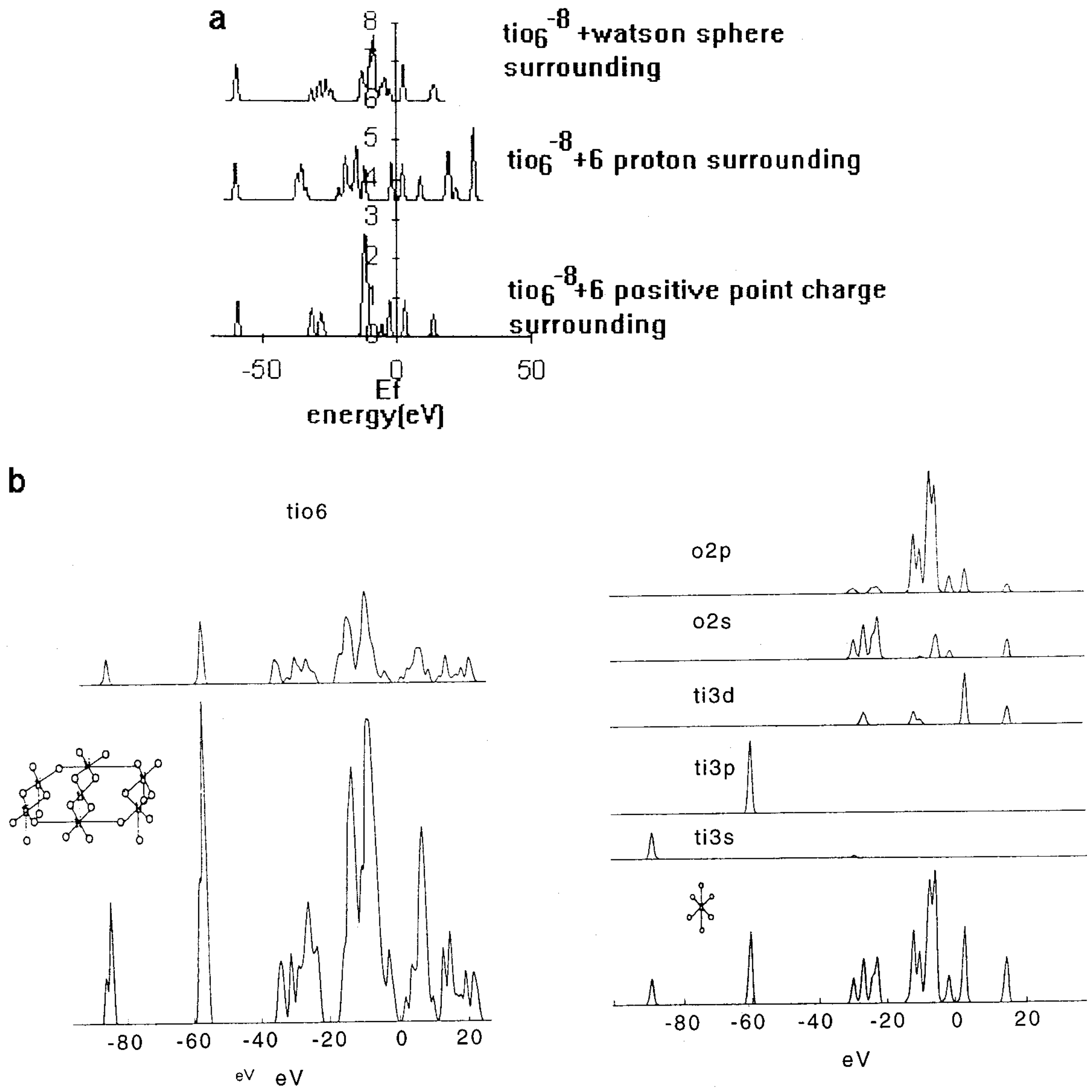

FIG. 4. (a) The DOS spectra of the TiO_6^{-8} with different surroundings. (b) The DOS spectra of the TiO_6^{-8} in the $Ti_7O_{24}^{-20}$ and free charged TiO_6^{-8}.

similarity in the inner regions is the basis for the frozen core and effective core potential approximation. Suppose that there are two test charges moving from infinity toward the nuclei, in one case Ti and the other Ti^{+4}, respectively. Initially, two test charges see two different centers, one Ti and another Ti^{+4}. As they move closer, they still see two different nuclei, but with charges $+q_1$ and $+q_2$, respectively. When the test charges reach the inner regions, they see the same centers having equal charges. This fact reveals that how much the effective charge should be used in the point charge model depends on the bond length (22). In the core regions, the cation behaves like a free atom and therefore it can be replaced by the effective core potential or be frozen in the calculation. If the test charge is located in the outermost region where the charge density is zero, Ti^{+4} can be reasonably treated as +4 point charge. In the real crystal, the nearest ligand is usually located between the inner and outer regions, and therefore it will feel the different behaviors of the neutral Ti atom and Ti^{+4} cation. If we use a sphere, with radius equal to the Ti–O bond length in the TiO_2 crystal (rutile), to surround the nuclei of Ti and Ti^{+4}, the total charge in this sphere equals 15.90 and 15.40 a.u., respectively. The charge outside this sphere can be treated as the delocalized charge and homogeneously distributed in the whole crystal. If we define the difference in charge in this sphere between the Ti atom and Ti^{+4} cation as an effective charge, this value equals 0.5 for the Ti cation, much lower than +4. So a lower effective charge will lead to a much flattened potential surface. Based on a similar arguement, the effective charge

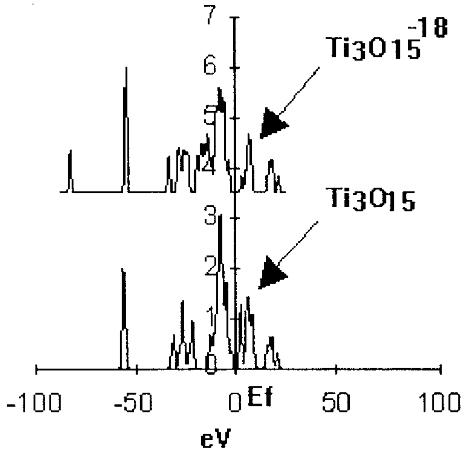

FIG. 5. The DOS spectra of $Ti_3O_{15}^n$ ($n = 0, -18$) clusters.

on the O ion in TiO_2 (rutile) is determined to be −0.75 a.u. Parry (23) calculated the atomic partial charge for lead oxide and found that the partial atomic charge ranges between −0.39 and −0.44 for O, whereas for Pb, the atomic partial charge ranges between 0.39 and 0.90. To our knowledge, no one has yet made a similar calculation on TiO_2 (rutile) except here. By the X-ray method, Vidal-Valat *et al.* (24) studied MgO, which is believed to be more ionic than TiO_2 (rutile), and found that the formal charge on Mg should be +1 rather than +2 as the ionic requirement. Other examples are BaO (25) and include the alkali metal halides (26). All these facts imply that our result about the atomic partial charge for TiO_2 (rutile) is reasonable even though a rough treatment is applied in our calculation.

The above discussion is based on the free atom and ion. In fact, the neighbor lattice site is always occupied by the counterion, which also has charge density distribution ($R(r)^2 \sim r$) around it. Supposing that the system is completely ionic, we can calculate the superpositioned charges of the Ti plus O and Ti^{+4} plus O^{-2} systems (27–28). Let x represent the radius of the anion O and change x from 0.0 to 3.66 a.u. We then calculate the charge in each sphere by integration and then sum, giving the result shown in Fig. 7. It is noticed that the total charge in the ionic system is almost the same as that obtained from the neutral Ti plus O. What is the basic principle involved in this result? From the radial charge density distribution we know that, although the charge density of Ti^{+4} is lower than that of the neutral Ti in the outer region, the difference is compensated for by the counter ion, in our case the anion O^{-2}, which has higher charge density than that of the neutral oxygen. We call this effect the charge compensation principle. One direct extension of this result is that in a crystal, the potential surface between lattice sites is very flattened; therefore, in most cases, the Watson sphere is a good approximation to the rest of the crystalline. Citrin and Thomas (20) calculated the eigenvalues for the free ion, the ion in the crystal, and the neutral atom. They concluded that the eigenvalues of the ion in the crystal is almost the same as that of the neutral atom instead of the free ion. Based on the theoretical calculation, Nicolaides (29) predicted that the 1s binding energy in the free negative O ion should be shifted by 16 eV compared to that of the free O. For O^{-2}, this energy shift should be at least doubled,

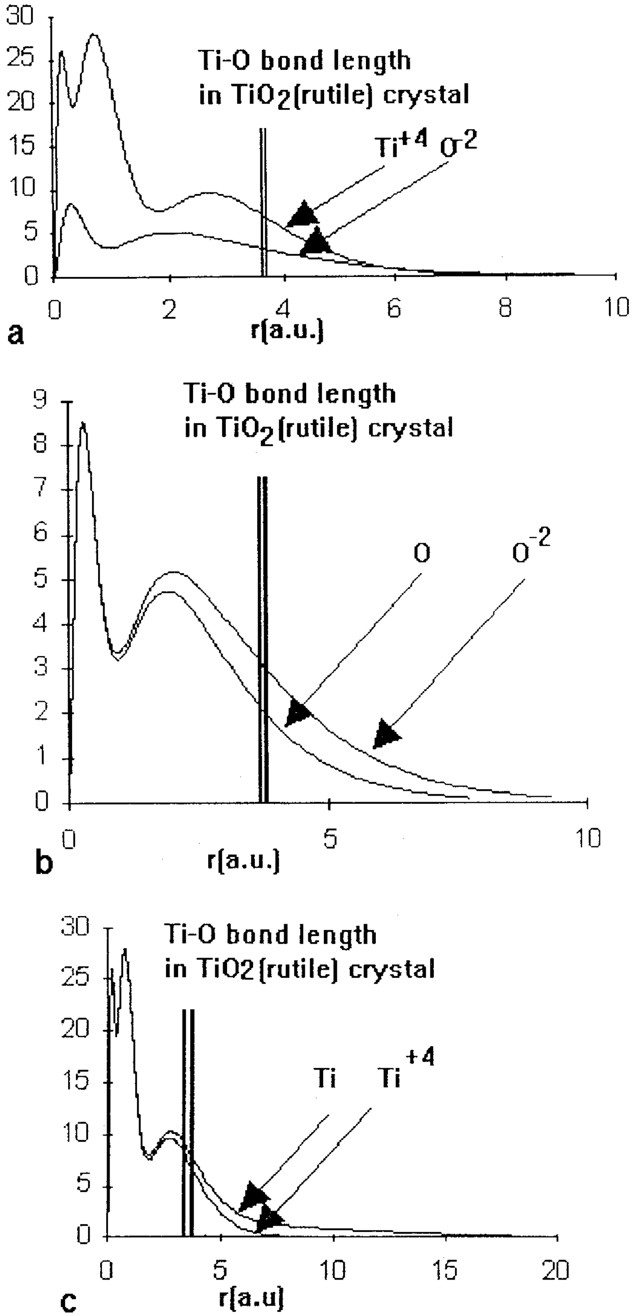

FIG. 6. The charge density distributions for (a) Ti^{+4} and O^{-2}, (b) O and O^{-2}, and (c) Ti and Ti^{+4}.

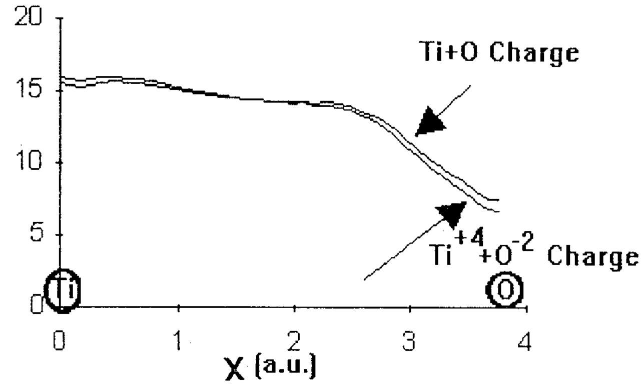

FIG. 7. The variations of the total charge for Ti + O and Ti^{+4} + O^{-2} systems with x values.

whereas in the crystal, the experimental value is much smaller than this value. Most attributed these effects to the Madelung potential. Nevertheless, according to the charge compensation discussed above, it is easy to understand the binding energy shift in these processes. For the free ion, the charge compensation effect does not exist; therefore, the eigenvalue is lower (for the free anion) or higher (for the free cation) than that in the crystal. We calculate the radial charge distributions of the free Ti, Ti^{+4}, O, and O^{-2} and sum in the real space regions between Ti (Ti^{+4}) and O (O^{-2}) (see Fig. 8). It is verified again that, except in the core region, the charge distribution is very similar to that of the neutral Ti plus O system. In the core region, the cancellation principle (30–32) takes effect and, therefore, our conclusion is still valid. This means that in TiO_2 (rutile), the electron binding energies should be the same as those of the free Ti and O atoms. This point is discussed in more detail below. It should be stressed here that even though the discussion above is based on the ionic model, our conclusion is still valid for the covalent compound because, in this case, less charge transfer takes place during the bond formation and the charge distribution should be much closer to that of the neutral system.

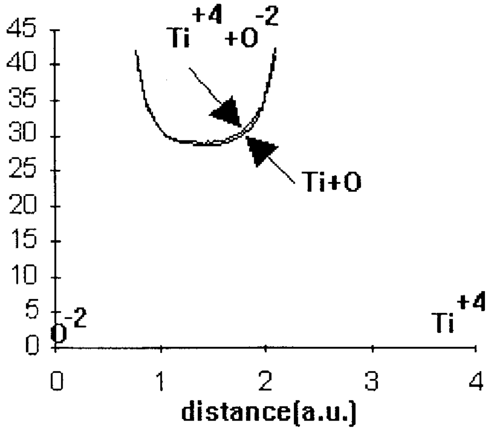

FIG. 8. The radial charge distributions for Ti^{+4} + O^{-2} and Ti + O systems.

From the discussion above, we know that charge compensation should be generally valid but we do not give a strict demonstration. It is impossible to check the validity of the charge compensation principle by calculating the superpositioned radial charge density system by system. But here we discuss the same thing in another way (20). Removal or addition of the outer electrons to an atom makes the binding energy shift by approximately qe^2/r, where q is the change in charge and r is the average radius from which the electrons are removed (or to which they are added). Putting this ion into a crystal makes the electron binding energy shift in the opposite direction and this change results from the electronic-static interaction between an electron on the ion of interest and other ions in crystal, which are treated as point charges for simplicity. There are additional corrections due to polarizability and compressibility. Including all these terms, the shift in binding energy of an electron on the jth ion in crystal is given by the expression

$$e^2 \sum{}' q_i/R_{ij} - E_{\mathrm{rep}} - E_{\mathrm{pol}}, \qquad [1]$$

where the prime indicates summation over all the ions except the one of interest. The symbol q_i represents the charge (in units of e) on the ith ion and R_{ij} is the distance between the ith and jth ions. E_{pol} and E_{rep} represent polarization and repulsive effects. The first term can be simplified in terms of the nearest cation–anion separation R, namely,

$$e^2/R \sum{}' q_i/R_{ij}/R = e^2/R\varphi_j, \qquad [2]$$

where φ_j is the reduced Madelung constant.

Now, the absolute binding energy can be expressed as

$$E_x \cong E_x^{\mathrm{pc}} = E_{\mathrm{fa}} + qe^2/r + \varphi e^2/R - E_{\mathrm{rep}} - E_{\mathrm{pol}}, \qquad [3]$$

where E_x, E_x^{pc}, and E_{fa} represent the absolute binding energy for the ion in the real crystal, binding energy for the ion embedded in the point charge array, and binding energy for the free atoms, respectively.

If cancellation between qe^2/r and $\varphi e^2/R$ and cancellation between E_{rep} and E_{pol} are complete, E_x and E_{fa} should be the same. A convenient way to check this conclusion is directly to compare the experimental binding energy with that of the free atoms (see Table 3).

Considering experimental error, the agreement is very good. (It is noted that the binding energies for cation and

TABLE 3
The Binding Energies for Ion in Crystal and Free Atoms (eV)

	TiO_2(110) (rutile)[a]			Free Ti	Free O
Ti 2*p*1/2	465.0			465	
Ti 2*p*3/2	459.4			459	
Ti 3*s*	60.0–62.0			64	
Ti 3*p*	39.0–41.0			39.0	
O 1*s*	530.7				538
O 2*s*	24.2–28.4				28.4
	MgO[b]			Free Mg	Free O
Mg 1*s*	1305.3 (1308)[c]			1308	
Mg 2*s*	90.6 (93.3)			92	
Mg 2*p*	51.7 (54.4)			54	
O 1*s*	532.2 (534.9)				538
O 2*s*	23.7 (26.4)				28.4
O 2*p*	6–10.5 (8.7–13.2)				13.6
	Pb_3O_4[d]	β-PbO_2[d]	PbO_{rh}[d]	Free Pb	Free O
Pb 4*f*/5/2	142.3 (148)[c]	142.0 (148)	143.7 (148)	148	
Pb 4*f*/7/2	137.5 (143.2)	137.3 (143.3)	138.8 (143.1)	144	
O 1*s*	529.1 (534.8)	528.9 (534.9)	529.9 (534.2)		538

[a] Ref. (17).
[b] Ref. (15).
[c] The values in parentheses have been shifted by a constant.
[d] Ref. (33).

anion in MgO (15), Pb_3O_4, rhombic PbO, and β-PbO_2 (33) are systematically lower than those of the free atoms, but the difference is constant for the same compound. Therefore we can reasonably attribute this difference to the charging effect on the sample during the experiment or the contact potential between the sample and the spectrometer.) More examples can be found from the work of Citrin and Thomas (20). This fact verifies again that charge compensation is a generally valid principle.

It is very interesting that the charge of the Watson sphere affects the eigenvalues of the free Ti^{+4} ion. As the charge of the Watson sphere changes from 0 to −3 (the radius of the Watson sphere is 3.66 a.u. which is equal to the Ti–O bond length in TiO_2 (rutile)), we found that all eigenvalues are shifted in the same direction but the splittings between them are constant (see Fig. 9). This phenomenon is also observed by Citrin and Thomas (20). They found that even though the absolute eigenvalues of the free ion are different from those in the crystal, the splittings between eigenvalues are the same. This fact in turn verifies that the rest of the crystal affects the electronic structure of the cluster just like the Watson sphere (see Fig. 9). Luana and Pueyo (4) studied the free $(CrF_6)^{-4}$ cluster and this cluster embedded in $KCrF_3$ crystalline by TES method and found that the spacings between eigenvalues in the free cluster are the same as that in the embedded cluster; this conclusion is independent of the parameters in their calculation. This means that we can obtain the eigenvalue spectra of the embedded $(CrF_6)^{-4}$ in $KCrF_3$ crystalline by shifting that of the free $(CrF_6)^{-4}$ cluster as a whole by a constant value. The consistency between different methods can easily be understood by Eq. [3] above and the charge compensation principle.

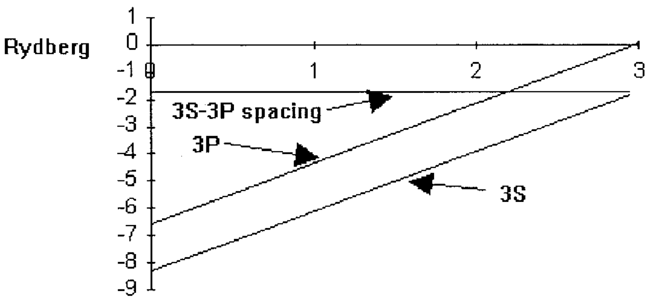

FIG. 9. The effect of the Watson sphere charge on the eigenvalues of the Ti^{+4}.

3.3. Madelung Potential Based on the Point Charge Model

Now, we consider the contribution of the potential energy from the rest of the crystal to each ion site in the cluster (12). For the large cluster, there are large differences in potential energy among the lattice sites if we take the formal charge +4 for Ti and −2 for O. At the bridge oxygen site, this energy difference is more than 10 eV. If the point charge model is a good approximation for TiO_2 (rutile), the bridge oxygen on the surface should be unsta-

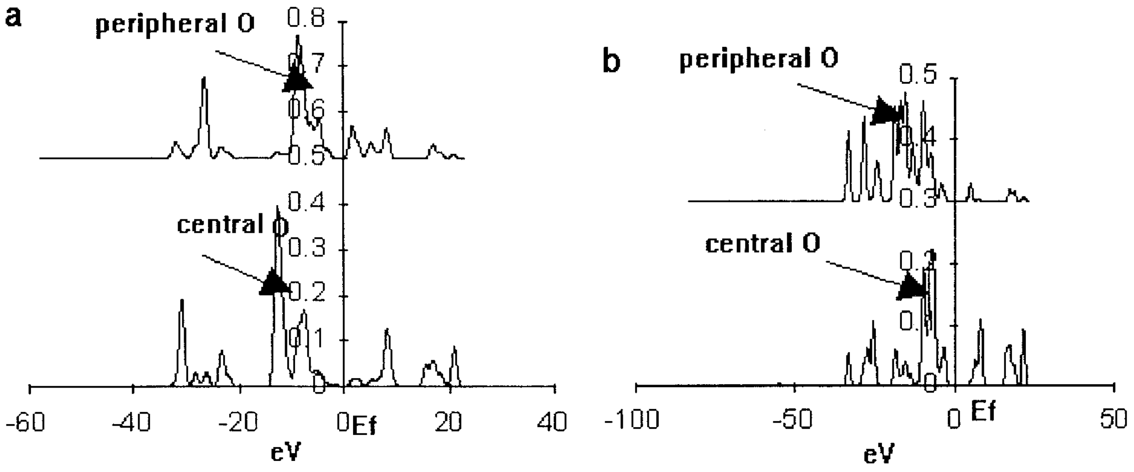

FIG. 10. The subDOS spectra of the O with different surroundings in the (a) neutral Ti_3O_{15} cluster and the (b) $Ti_3O_{15}^{-18}$ cluster.

ble and must go away due to the large repulsion between the bridge oxygen and the rest of crystal. It is obvious that this is not the true situation. We calculated the potential surface along the Ti–O bond and found that the potential surface was not so flattened as predicted above. The energy difference is more than 4 eV. For the surface cluster, this energy difference is more than 10 eV. If we use the effective charge determined in Section 3.2, namely, 0.5 for the Ti cation and −0.25 for the O (in order to keep the whole crystal neutral, we use −0.25 rather than −0.75 for the O anion), the energy difference between the bridge oxygen and the titanium on the surface is reduced to less than 0.6 eV. This value is reasonable because, according to the charge compensation, the bridge oxygen does not feel such strong repulsion from the rest of the crystal. Based on the discussion in Sections 3.1 and 3.2, the eigenvalues of ion in the crystal resemble those of the neutral atoms; therefore, the repulsion from the rest of crystal is not the main factor in the bond formation of the bridge oxygen with titanium on the (110) surface. Irle *et al.* (34) calculated the difference in charge density between an assemblage of free atoms and molecules and found that no large difference exists. Causa *et al.* (35) make a comparison between the experimental data and the theoretical result for MgO and do not observe a significant difference in the charge distribution. Compared with those of the Mg cation and O anion in the bulk, only a small deformation of the charge distribution occurs in the surface Mg and O. Therefore, it is concluded that the monolayer cluster of MgO is sufficient to reproduce the electronic structure of the MgO surface fairly well (36). These results can be interpreted with the charge compensation effect discussed above.

In order to understand this problem well, we compare the sub-DOS of the O with different surroundings. Figure 10 shows that the sub-DOS of oxygen surrounded by titanium is not influenced by whether the cluster is charged or neutral. The only difference between those of the neutral and charged clusters is that the spectrum as a whole is shifted by a constant value. This means that the approximation of the free charged model is good enough to qualitatively reproduce the electronic structure of the whole crystal.

In summary, as far as the electronic structure is concerned, it is justified to use the homogeneous potential surface to represent the rest of the crystal and a convenient way is to set this potential surface equal to zero; after finishing the calculation, the whole spectra should be shifted according to the Fermi level.

4. CONCLUDING REMARKS

For the calculation of the electronic structure of TiO_2 (rutile), as first order approximation, the free cluster model can describe the electronic structure of the whole crystal quantitatively well. It is obvious that charge compensation is valid in general for most materials even though we start our discussion with TiO_2 (rutile). Therefore, for incompletely ionic systems, we suggest using the free cluster model to approximate the whole crystal in the theoretical calculation.

REFERENCES

1. K. Siegbahn, C. Nordking, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg,'' ESCA-Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy.'' Almqvist & Wiksells, Uppsals, 1967.
2. W. H. Kleiner, *J. Chem. Phys.* **20**(11), 1784 (1952).
3. R. E. Watson, *Phys. Rev. B* **111,** 1108 (1958).
4. V. Luana and L. Pueyo, *Phys. Rev. B* **39**(15), 11039 (1989).
5. M. Tsukada, C. Satoko, and H. Adachi, *J. Phys. Soc. Jpn.* **47**(5), 1610 (1979).
6. K. M. Neyman and N. Roesh, *Chem. Phys.* **168,** 267 (1992).

7. J. A. Pople, Gaussian, Inc., Pittsburgh, PA.
8. W. J. Stevens, H. Basch, and M. Krauss, *J. Chem. Phys.* **81,** 6026 (1984).
9. P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82,** 270 (1985).
10. W. R. Wadt and P. J. Hay, *J. Chem. Phys.* **82,** 284 (1985).
11. P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82,** 299 (1985).
12. K. H. Johnson, *J. Chem. Phys.* **45,** 3085 (1966).
13. K. J. Johnson, J. G. Norman, Jr., and J. W. D. Connolly, ''Computational Methods for Large Molecules and Localized States in Solids,'' p. 161. Plenum, New York 1973.
14. H. M. Evjen, *Phys. Rev.* **39,** 675 (1932).
15. C. Satoko, M. Tsukada, and H. Adachi, *J. Phys. Soc. Jpn.* **45**(4), 1333 (1978).
16. A. H. Kahn and A. J. Leyendecker, *Phys. Rev.* **135**(5), 1321 (1964).
17. S. Fischer, Diploma Thesis, Tuebingen University, Germany, 1993.
18. P. F. Walch and D. E. Ellis, *Phys. Rev. B* **8**(12), 5920 (1973).
19. (a) K. Matsumura, A. Yamabe, Y. Yanagisawa, and R. Huzimura, *Surf. Sci.* **109,** 311 (1981); (b) H. Fujioka, S. Yamabe, Y. Yanagisawa, K. Matsumura, and R. Huzimura, *Surf. Sci.* **149,** L52 (1985).
20. P. H. Citrin and T. D. Thomas, *J. Chem. Phys.* **57**(10), 4446 (1972).
21. J. M. Recio, R. Pandey, A. Ayuela, and A. B. Kunz, *J. Chem. Phys.* **98**(6), 4783 (1993).
22. M. Springborg and O. E. Taurian, *J. Phys. C: Solid State Phys.* **19,** 6347 (1986).
23. D. E. Parry, *J. Chem. Soc., Faraday Trans. 2* **71,** 337 (1975).
24. G. Vidal-Valat, J. P. Vidal, and K. Kurki-Suonio, *Acta Crystallogr. Sect. A* **34,** 594 (1978).
25. G. K. Wertheim, *J. Electron Spectrosc. Relat. Phenom.* **34,** 309 (1984).
26. D. E. Parry and M. J. Tricker, *Chem. Phys. Lett.* **20**(1), 124 (1973).
27. J. Redinger and K. Schwarz, *J. Phys. B Condens. Matter* **40,** 269 (1981).
28. J. Yamashita and S. Asano, *J. Phys. Soc. Jpn.* **28**(5), 1143 (1970).
29. C. A. Nicolaides, *Chem. Phys. Lett.* **19**(1), 69 (1973).
30. J. C. Philips, *J. Phys. Chem. Solids* **11,** 226 (1959).
31. M. H. Cohen and V. Heine, *Phys. Rev.* **122**(6), 1821 (1961).
32. J. C. Philips and L. Kleinman, *Phys. Rev.* **116**(2), 287 (1959).
33. J. M. Thomas and M. J. Tricker, *J. Chem. Soc. Faraday Trans. 2* **71,** 329 (1975).
34. S. Irle, H. L. Lin, J. E. Niu, and W. H. E. Schwarz, *Ber. Bunsenges. Phys. Chem.* **96**(11), 1545 (1992).
35. M. Causa, R. Dovesi, C. Pisani, and C. Roetti, *Acta Crystallogr. Sect. B* **42,** 247 (1986).
36. U. Birkenheuer, J. C. Boettger, and N. Roesch, *J. Chem. Phys.* **100**(9), 6826 (1994).