Layer and orientation resolved bond relaxation and quantum entrapment of charge and energy at Be surfaces

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The chemistry and physics of under-coordination at a surface, which determines the process of catalytic reactions and growth nucleation, is indeed fascinating. However, extracting quantitative information regarding the coordination-resolved surface relaxation, binding energy, and the energetic behavior of electrons localized in the surface skin from photoelectron emission has long been a great challenge, although the surface-induced core level shifts of materials have been intensively investigated. Here we show that a combination of the theories of tight binding and bond order-length-strength (BOLS) correlation [C. Q. Sun, Prog. Solid State Chem., 2007, 35, 1–159], and X-ray photoelectron spectroscopy (XPS) has enabled us to derive quantitative information, by analyzing the Be 1s energy shift of Be(0001), (1010), and (1120) surfaces, for demonstration, regarding: (i) the 1s energy level of an isolated Be atom (106.416 ± 0.004 eV) and its bulk shift (4.694 eV); (ii) the layer- and orientation-resolved effective atomic coordination (3.5, 3.1, 2.98 for the first layer of the three respective orientations), local bond strain (up to 19%), charge density (133%), quantum trap depth (110%), binding energy density (230%), and atomic cohesive energy (70%) of Be surface skins up to four atomic layers in depth. It is affirmed that the shorter and stronger bonds between under-coordinated atoms perturb the Hamiltonian and hence the fascinating localization and densification of surface electrons. The developed approach can be applied to other low-dimensional systems containing a high fraction of under-coordinated atoms such as adatoms, atomic defects, terrace edges, and nanostructures to gain quantitative information and deeper insight into their properties and processes due to the effect of coordination imperfection.

I. Introduction

Interaction between under-coordinated atoms is key to the fascinating behavior of low-dimensional systems such as adatoms, atomic defects, atomic chains, tubes, cavities, and surfaces of bulky solids. The shorter and stronger bonds between under-coordinated atoms cause local strain and potential well depression, also called quantum entrapment. The locally densely trapped energy provides a perturbation in the Hamiltonian, binding energy density, electroaffinity, and atomic cohesive energy, which determine the mechanical, thermal, electronic, optic, magnetic, dielectric, catalytic, and chemical properties that are completely different from those of the bulk interior. The under-coordinated atoms also serve as activation centers for many processes such as chemical reactions and growth nucleation. Although the chemistry and physics of materials at these sites have been intensively investigated, determination of the underlying mechanism still remains a great challenge. Therefore, the elucidation of the electronic structure and the electronic binding energy at sites surrounding the under-coordinated atoms is of great importance, since its clarification can improve our understanding of the origination of the novel physical properties of surfaces and nanostructures. From the spectra of X-ray photoelectron spectroscopy (XPS), the binding energies (BE), being a superposition of the intra-atomic trapping and the interatomic binding (crystal potential) contributions, of various elements can be determined but the discrimination of the two identities from each other is infrequent and indirect due to the lack of suitable guidelines from the perspective of the intrinsic Hamiltonian perturbation. One often takes the bulk component as the reference with zero shift in energy as the determination of the actual bulk shift from the energy level of an isolated atom is hardly possible. Such a zero-bulk-shift assumption annihilates plenty of useful information such as the energy level of an isolated atom and its bulk shift which is non-zero according to energy band theory.

The Be 1s core level shift (CLS) of the hcp(0001), (1120), and (1010) surfaces of Be(1s22s2) has been intensively investigated experimentally using XPS and theoretically based on a density functional premise and in terms of the “initial-final states”
convention in the past decades. Using synchrotron radiation, Johansson et al. measured the Be(0001) surface 1s CLS and identified three distinct components of shifts with energies of $-825 \pm 30$ (S1), $-570 \pm 25$ (S2), and $-265 \pm 20$ (S3) meV with respect to the low energy (large absolute value) component at 111.835 (B) eV. For the Be(110) surface, three components were identified to shift by $-700$ (S1), $-500$ (S2), and $-220$ (S3) meV but two components would suffice for the (1120) surface. These CLS were assigned as negative shifts according to the “initial-final states” convention, i.e., the surface layers add states at higher energies (smaller absolute values) than the bulk component. This assignment is in contrast with the mixed add states at higher energies (smaller absolute values) than the correlation. Using a combination of the tight binding model, the higher energy component corresponds to the B component, therefore collect more bulk information. From this perspective, the higher energy component corresponds to the B component, instead.

A low-temperature scanning tunneling microscopy (STM) investigation revealed that the Fermi contour of the Be(110) surface state is located at the boundary of the surface Brillouin zone, and the surface-state electrons provide the main part of the charge density near the Fermi energy. Highly anisotropic standing waves of the surface charge density were observed on Be(110) near the step edges and the point defects, which is consistent with STM observations from Au–Au chain ends, Au island edges, and graphene edges. It is our opinion that the standing waves correspond to the edge states due to charge localization, polarization and densification induced by the densely and deeply trapped core electrons. On the other hand, in a theoretical calculation, found a 25% inward surface relaxation of the Be(110) surface, which is attributed to the pronounced surface states close to the Fermi energy.

Although the physics of materials at defects and surfaces has been extensively investigated, the laws governing the energetic behavior of electrons and the property change of materials in the surface region remain unclear. In order to understand the physical origin of the unusual behavior of surface electrons and to derive quantitative information regarding the structure relaxation, binding energy and the quantum trap depth, we have analyzed the XPS characteristics of Be(0001), Be(110), and Be(1120) surfaces from the perspective of chemical bond–crystal potential–energy band correlation. Using a combination of the tight binding approximation and the bond order-length-strength (BOLS) correlation algorithm, we have been able to derive quantitative information from measurements regarding: (i) the energy level of an isolated Be atom and its bulk shift; (ii) the layer and orientation resolved local strain and quantum entrapment and (iii) the relative binding energy density and the relative atomic cohesive energy at the surfaces. Recent progress and the current work affirmed that the shorter and stronger bonds between under-coordinated atoms provide perturbation in the Hamiltonian that globally defines the positive core-level shift.

II. Principles

2.1 Bond–potential–band correlation

Interatomic bonding plays a pivotal role in differentiating the behavior of a bulk solid as opposed to that of individually-isolated constituent atoms. For instance, the energy levels of an isolated atom evolve into bands that shift downward in energy upon bulk formation; phase transition can only happen to the bulk rather than to single atom; an isolated atom does not have a detectable melting point or mechanical strength as the bulk counterparts do. Without interatomic bonding, neither solid nor liquid could form. Therefore, the performance of a material is determined uniquely by the constituent atoms and the interactions among them.

The interatomic bonding at site $r$ in an extended bulk solid is represented by the periodic crystal potential, $V_{cr}(r,B)$, a resultant of attraction and repulsion of many-body effects. Electrons in different orbits of the constituent atoms will experience the $V_{cr}(r,B)$ but the value of $V_{cr}(r,B)$ varies for electrons in different orbits or energy levels because of the screening effect. The $V_{cr}(r,B)$ for electrons in the inner shells is much weaker. Normally, the $V_{cr}(r,B)$ has a magnitude of several eVs, much weaker than the intra-atomic trapping, $V_{atom}(r)$, of the inner electrons up to the $10^3$ eV level in the deepest level. Under the equilibrium conditions of a bulk, the maximum value of $V_{cr}(r,B) \approx E_B$, the cohesive energy per bond. The coupling of the $V_{cr}(r,B)$ with the relevant Bloch wave functions determines the entire band structure and related properties of a specimen such as the band gap, core level shift, band width, and the dispersion relations and the allowed energy states in the valence band and below, as well as the dielectrics and electroaffinity according to energy band theory.

In the crystallite-imperfect regions such as at sites surrounding defects, adatoms, edges, surfaces and the skins of nanomaterials, the single-body Hamiltonian is perturbed because of the bond strain, bond nature alteration and the associated bond energy gain, also called quantum entrapment. We can introduce the perturbation coefficient, $\Delta \mu = \gamma(z) - 1$, with $\gamma(z) = c(z)^{-\alpha}$ being the bond energy enhancement coefficient, to the Hamiltonian of an extended bulk,

$$H(\gamma) = \left[-\frac{\hbar^2 \nabla^2}{2m} + V_{atom}(r)\right] + \gamma(z)V_{cr}(r,B)$$

The terms in the brackets correspond to the Hamiltonian of an isolated atom. $V_{atom}(r)$ is the potential of the intra-atomic trapping that determines the $\alpha$th atomic energy level of an isolated atom, $E_{\alpha}(0) = \langle \phi_{\alpha}(r) | V_{atom}(r) | \phi_{\alpha}(r) \rangle$, from which the core level shifts when the crystal potential is involved, $\phi_{\alpha}(r)$ is the specific Bloch wave function for the tightly-binding core electron at site $r$, which satisfies $\langle \phi_{\alpha}(r) | \phi_{\alpha}(r) \rangle = \rho \delta_{ij}$, where $\delta_{ij}$ is the Kronecker delta function and $\rho$ the charge density.
According to the tight-binding approximation, the non-zero shift of a particular $i$th level, $\Delta E_i(A)$, from the $E_i(0)$, is determined by the exchange and overlap integrals,

$$\begin{align*}
\Delta E_i(\gamma) &= \gamma \Delta E_i(B) = \gamma (\beta + 2z) \gamma E_b \\
\gamma &= -\langle\phi_n(r_i)\rangle |V_{cr}(r_i) + 1 + \Delta H|\phi_n(r_i)\rangle \gamma E_b \quad \text{(Overlap Integral)} \\
\gamma &= -\langle\phi_n(r_i)\rangle |V_{cr}(r_i) + 1 + \Delta H|\phi_n(r_i)\rangle \gamma E_b \quad \text{(Exchange Integral)}
\end{align*}$$

(Core level shift)

Since the wave functions of the tight binding electrons in the inner shells are not overlapped, $x$ is much smaller than $\beta$. From the XPS spectrum bulk component whose maximal width is $2x = (0.1-1.0) \text{ eV level}$, one can estimate that $x$ is of the order of $10^{-2}-10^{-1} \text{ eV}$. $z$ is the atomic coordination number (CN). $\beta$ is at the $10^9 \text{ eV level}$. Therefore, the BE shift is dominated by $\beta$ and proportional to the bond energy. Hence, the chemical bond, potential well, and the core level shift can thus be correlated.

2.2 Surface local strain and quantum entrapment

According to the BOLS correlation theory, bonds between under-coordinated surface atoms are shorter and stronger. The potential well becomes deeper; an additional potential trap is added to the under-coordinated atoms and hence the energy levels of these atoms will drop correspondingly. If nonbonding electrons exist such as the otherwise conduction electrons in the half-filled s-orbits, polarization of the nonbonding electrons by the densely trapped bonding electrons may take place. Such occurrence of surface polarization may add density-of-states to the upper edges of both the valence15 and the core band, such as those identified from Rh(5s$^1$).21 The polarization is responsible for the observed Be(1010) edge13 and Au chain end and edge states as well.

Because of the local bond strain, densification of charge, and mass will occur at the local sites. Thus, the broken-bond-induced local strain and quantum entrapment provides perturbation to the Hamiltonian in the $n$th atomic layer region characterized by an effective atomic CN of $z_n$.

$$\begin{align*}
\Delta H &= \Delta(z) = \gamma(z) - 1 = c(z) - c(z) \gamma^{m-1} & \text{(Hamiltonian perturbation)} \\
c(z) &= 2/[1 + \exp((12 - z_i)/(8z_i))] & \text{(Bond strain coefficient)} \\
c(z) &= E_i(z_i)/E_0 & \text{(QT depth or bond energy gain)}
\end{align*}$$

(3)

where $m$ is the bond nature indicator.20 For metals, $m = 1$. According to band theory and the BOLS correlation, the surface-induced energy shift of the $i$th level, $E_i(0)$, follows the relation:

$$E_i(i) - E_i(0) = [E_i(B) - E_i(0)] \times (1 + \Delta_i) \quad (4)$$

where $E_i(B) - E_i(0) = \Delta E_i(B)$, thus we have the relation

$$\frac{E_i(i) - E_i(0)}{E_i(f) - E_i(0)} = \frac{1 + \Delta_i}{1 + \Delta_f} = c(z_i)^{-1} \quad (i \neq i) \quad (5a)$$

If taking the XPS spectrum bulk component as a reference, we have

$$\frac{E_i(i) - E_i(B)}{E_i(f) - E_i(0)} = \frac{c(z_i)^{-1} - 1}{c(z_f)^{-1} - 1}, \quad (i \neq i) \quad (5b)$$

Given an XPS profile with clearly identified $E_i(i)$ and $E_i(B)$ components of a surface $(i = 1, 2, \ldots)$, one can easily calculate the atomic $E_i(0)$ and bulk $\Delta E_i(B)$ with the relations derived from eqn (5):

$$\begin{align*}
E_i(0) &= \frac{(1 + \Delta_i) E_i(i) - (1 + \Delta_f) E_i(f)}{\Delta_f - \Delta_i} = \frac{c(z_i)E_i(i) - c(z_f)E_i(f)}{c(z_i)^{-1} - c(z_f)^{-1}}, \quad (i \neq f) \\
\Delta E_i(B) &= E_i(B) - E_i(0)
\end{align*}$$

(6)

If a total of $l$ components are used to decompose a set of XPS spectra from different surfaces of a specimen, $E_i(0)$ should take the mean value of the $N = C(l, 2) = \binom{l}{2}$ possible combinations with a standard deviation $\sigma$. The minimal standard deviation may serve as a criterion for the accuracy of spectral decomposition which involves the peak energies and the corresponding effective CNs. The latter is the unique parameter for fitting. The intrinsic $E_i(0)$ and $\Delta E_i(B)$ values should not be affected by experimental conditions, chemical reactions, crystal size or orientation, or surface relaxation. However, crystal orientation may lead to a fluctuation of the component peak energies and the number of components because of the slight difference in the effective atomic CNs. Accuracy of the determination is strictly subject to the $z$-component peak energies and the number of components.

Fig. 1a illustrates the decomposition of the surface CLS with $P$, $B$, $S_1$ and $A$ components representing the states due to from high (small absolute value) to low, polarization, bulk,
index surfaces, \( i \) may be larger as demonstrated in the spectral decomposition. Fig. 1b shows anhcp crystal unit cell with the hcp(0001), (1010), and (1120) surfaces indicated.

2.3 Surface binding energy density and atomic cohesive energy

We have the expression for the coordination-resolved core level shift and local lattice strain:\(^{20}\)

\[
E_{i}(z) = E_{i}(0) + \Delta E_{i}(B)c_{i}^{-1} = c(z) - 1 = 2/[1 + \exp((12 - z)/(8z))] - 1
\]

(7)

As the detectable quantities can be directly connected to the binding energies such as bond nature, order, length, and strength,\(^{20}\) we are able to predict coordination dependence of the relative binding energy density, \(E_{d}(z) = E_{d}(z)/d^{3}\), and the relative cohesive energy per atom, \(E_{c}(z) = z_{i}E_{c}(z)\), in each atomic layer,\(^{27,31}\)

\[
E_{d}(z)/E_{c}(B) = c(z)^{-4}
\]

\[
E_{c}(z)/E_{c}(B) = z_{i}c(z)^{-1}
\]

(8)

with \(z_{i} = z/12\). Subscript \( i \) represents the atomic layers counted from the outermost inwards. The binding energy density and the atomic cohesive energy are related to the local elastic modulus\(^{31}\) and the local melting point\(^{27}\) at the specific atomic site, respectively. More details regarding the interdependence of various physical and chemical properties have formed the subjects of recent thematic reports.\(^{3,20}\)

III. Calculation algorithm

Based on the criteria established in section 2.2, we fit the XPS spectra by using Gaussian components with respect to the energy shifts given by Johansson et al.\(^{6-8,11}\) for Be, as listed in Table 1. For Be(0001), the initial four components are sufficient. An addition of the \( S_{i} \) component in the lower end of the spectrum is needed to represent the under-coordinated Be atom in the outermost Be(1010) layer. The effective CNs determined here are consistent with those for Rh(0001) and (1010) surfaces,\(^{25}\) indicating the reliability of this approach.

We need to point out that the quantities of \( E_{i}(0) \) and \( E_{i}(B) \) are intrinsic constant values for a given material disregarding surface layers, and adatoms. The number of \( S_{i} \) components for a specific surface is subject to the atomic number and the interlayer spacing. For heavy metals such as Cu, Ag, W and Pd, \( i = 2 \) would suffice. For the light Be atom and the hcp high

Table 1 Atomic-layer and crystal-orientation resolved effective CN (\( z \)), local strain (\( c(z) - 1 \)), relative binding energy density (\( c(z)^{-4} \)), and relative atomic cohesive energy (\( z_{i}c(z) \)) with \( z_{i} = z/12 \) determined from the measured XPS profiles of Be(0001), (1010), and (1120) surfaces under the established approach and the criteria. The energy shift \( E_{i}(i) - E_{i}(B) \) for each component is the input and the effective CNs are the adjustable parameters. The 1s core level of 106.416 ± 0.004 eV and the B component at 111.11 eV should be identical for all the surfaces. The coordination dependence of the Be 1s core level shift is expressed as \( E_{i}(z) = E_{i}(0) + \Delta E_{i}(B)c_{i}^{-1} = 106.416 ± 0.004 + 4.694/c(z) \) eV where \( c(z) = 2/[1 + \exp((12 - z)/(8z))] \).

<table>
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<th>( i )</th>
<th>( E_{i}(i)/eV )</th>
<th>( z )</th>
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the orientation. Therefore, we can refer the energy shifts of all surface components to the $E_n(B)$ before knowing the $E_n(0)$. According to the tight binding and BOLS theories, a positive shift is preferred. The given energy shifts enable us to determine the effective atomic CN as the unique variable in the present exercise for each component and the $E_n(0)$ using eqn (5) and (6). It is emphasized that the effective CN is different from the apparent CN.$^1$ Incorporating the BOLS correlation mechanism into the measured surface relaxations,$^{32,33}$ the effective CN for the fcc(001) outermost surface is four instead of six.

IV. Results and discussion

Fig. 2 shows the XPS decomposition of the Be(0001), (10\(\overline{1}\)0), and (1120) surfaces. The intensities of the atomic-layer and crystal-orientation resolved components also change with the incident beam energy. Including the B component that was counted only once, there are a total of $l = 12$ components for the Be surfaces considered, as shown in Table 1. There will be a combination of $C(12,2) = 12!(12 - 2)!/2! = 66 = j$ values of $E_n(0)$. Using the least-root-mean-square approach, we can find the average of $\langle E_n(0) \rangle = \sum_n E_n(0)/j$ and the standard deviation, $\sigma = (\sum_{2j}(E_n(0) - \langle E_n(0) \rangle)^2/(j(j - 1)))^{1/2}$. A fine tuning of the CN values will minimize the $\sigma$ value and hence improve the accuracy of the effective CNs, the local strain, the binding energy density and the cohesive energy per discrete atom in differently oriented surface layers.

According to the decomposition criteria, the B component must exist in all the surfaces. The invisibility of the B component in the Be(1120) surface spectrum indicates that the high-mass density of the low-index Be(1120) surface prevents the incident beam from penetrating into the bulk underneath the first four atomic layers. The fitting indicates that the Be surface skin is formed by at most four surface atomic layers because of the lower atomic cross section and the packing density. For a Ni surface$^{34}$ and a 3.5 nm sized gold cluster,$^{35}$ the surface is only two interatomic spacings thick. The lack of bulk information in the Be(1120) spectrum also indicates the penetration depth of the 135 eV X-ray beams is limited to the outermost three atomic layers.

The optimal $\sigma$ value is 0.004–0.0042. The derived $E_{1s}(B) = 106.416 \pm 0.004$ eV and the bulk shift is $\Delta E_{1s}(B) = 4.694$ eV with three decimal places being sufficient with respect to the measurement precision. The derived effective CNs, the local strains, and the predicted trends of the local binding energy

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**Fig. 2** The decomposed XPS spectra for (a) the Be(0001), (b) (10\(\overline{1}\)0), and (c) (1120) surfaces with information derived as summarized in Table 1. The 1s core level of 106.416 ± 0.004 eV and the B component at 111.11 eV should be identical for all the surfaces of the same material.

**Fig. 3** Comparison of the BOLS prediction with the derived CN (layer-) and orientation-resolved values for (a) bond strain and the relative change of atomic cohesive energy ($E_c$), (b) potential trap depth and, (c) the relative energy density.
density and the atomic cohesive energy are given in Fig. 3 and Table 1. The derived bond cohesive energy is consistent with recent findings using a combination of molecular dynamics calculations, Pauling's correlation, and coherent electron diffraction, which revealed that individual Au nanocrystals of 3.5 nm in diameter demonstrate inhomogeneous relaxations occurring at the outermost two atomic layers. The undercoordination-induced bond contraction involves large out-of-plane bond length contractions for the edge atoms (≈0.02 nm, 7%), a significant contraction (≈0.013 nm, 4.5%) for {100} surface atoms, and a much smaller contraction (≈0.005 nm, 2%) for atoms in the middle of the {111} facets. In the current system the maximal contraction is around 19%, a value between the theory prediction for Be(100) and the measurement for Au.

Results show that the positive core-level shift assignment is more proper than the assignment of negative or mixed shift and hence the criteria established herewith are essentially true. The positive shift assignment allows us to derive the energy level of an isolated atom and its bulk shift. The derived fundamental factors are of great importance in determining the surface properties and surface processes.

Furthermore, the experimentally observed incident beam energy and emission angle trends provide evidence for the assignment of surface positive CLS, as the higher incident beam energies or smaller emission angles collect more information from the bulk than from the surface. Speranza and Minati reported that increasing the angle between the surface normal of graphite and the emission beam from 0 to 85°, decreases the penetration depth from 8.7 to 0.7 nm.

The surface-induced positive BE shift is consistent with a model of the surface interlayer relaxation mechanism. For Nb(001)-3d_{3/2} example, the first layer spacing contracts by 12% associated with a 0.50 eV core-level shift. A (10 ± 3)% contraction of the first layer spacing has caused the Ta(001)-4f_{5/2} level to shift by 0.75 eV. The assignment of a positive core-band shift has been elegantly favoured by XPS measurements revealing that the intensity of the low-energy bulk component often increases with the incident beam energy or with decreasing the angle between the incident beam and the surface normal in the measurement. Most strikingly, a recent X-ray absorption diffraction spectroscopic study revealed that the Ni 2p levels of the outermost three atomic layers shift positively to higher binding energies discretely, with the outermost atomic layer shifting the most.

Dominated by the under-coordinated atoms, the core-level features (both the main peak and the chemical satellites) of nanostructures move simultaneously towards lower binding energies and the size of the shifts depends on both the original core-level position of the components and the shape and size of the particle.

### V. Conclusion

We have systematically analyzed the Be 1s energy shift of Be(0001), (1010), and (1120) surfaces from the perspective of bond-potential–band correlation and elucidated information regarding: (i) the binding energy of an isolated Be atom, (ii) the bulk shift of Be 1s, (iii) the effective atomic CNs and the corresponding local strains, and (iv) prediction of the trends of coordination resolved binding energy density and cohesive energy per discrete atom in the surface of skin depth. The developed approach enhances the power of the conventional XPS technique for more quantitative information regarding surface processes and properties. The concepts of local strain and quantum entrapment may be essential for understanding the bonding and electronic behavior in the surface and atomic defect sites.

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### References


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