Surface, Size and Thermal Effects in Alkali Metal with Core-Electron Binding-Energy Shifts

Wen-huan Zhu\textsuperscript{a}, Zhong-kai Huang\textsuperscript{b,c,d,*}, Mao-lin Bo\textsuperscript{c,*}, Jin Huang\textsuperscript{d}, Cheng Peng\textsuperscript{c}, Hai Liu\textsuperscript{e,*}

\textsuperscript{a} National Key Laboratory of Science and Technology on Micro/Nano Fabrication, Shanghai Jiao Tong University, Shanghai 200240, China
\textsuperscript{b} Key Laboratory of Inorganic Special Functional Materials of Chongqing, Yangtze Normal University, Chongqing 408100, China
\textsuperscript{c} Key Laboratory of Extraordinary Bond Engineering and Advanced Materials Technology of Chongqing, Yangtze Normal University, Chongqing 408100, China
\textsuperscript{d} School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China
\textsuperscript{e} Key Laboratory of Advanced Display and System Applications of Ministry of Education, Shanghai University, Shanghai 200072, China

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Consistency between density functional theory calculations and X-ray photoelectron spectroscopy measurements confirms our predictions on the undercoordination-induced local bond relaxation and core level shift of alkali metal, which determine the surface, size and thermal properties of materials. Zone-resolved photoelectron spectroscopy analysis method and bond order-length-strength theory can be utilized to quantify the physical parameters regarding bonding identities and electronic property of metal surfaces, which allows for the study of the core-electron binding-energy shifts in alkali metals. By employing these methods and first principle calculation in this work, we can obtain the information of bond and atomic cohesive energy of under-coordinated atoms at the alkali metal surface. In addition, the effect of size and temperature towards the binding-energy in the surface region can be seen from the viewpoint of Hamiltonian perturbation by atomic relaxation with atomic bonding.

Key words: Alkali metal, First principle calculation, Metal surface, Binding-energy, Size effect, Thermal effect

I. INTRODUCTION

As we know, the alkali metals lie in Group 1 of the periodic table, including lithium (Li), sodium (Na), potassium (K), rubidium (Rb), Cesium (Cs) and francium (Fr) \cite{1–7}. In the complete electron configuration of the alkali metal in period \textit{n}, the sub-outer shell has 8 electrons with a shell electron configuration of \((n-1)s^2(n-1)p^6\) (except that Li has only two electrons in the shell of 1s\(^2\)) and is similar to the outmost shell of the inert gas element in period \((n-1)\). Thus, the outer shell of the alkali metal contains only one electron in the valence shell of ns\(^1\). This valence electron is loosely bound to the nuclei with the lowest nuclear charge in period \textit{n}, where the alkali metal performs the largest atomic radii and the highest reactivity. However, the alkali metals have low ionization energies \cite{8} and electronegativity \cite{9}. Due to their outstanding chemical ac-

\*Authors to whom correspondence should be addressed.
E-mail: zhongkaihuang@yznu.edu.cn, bmlwd@yznu.edu.cn, hliu5@shu.edu.cn
tivity and reducing abilities, they can easily react with most non-metal elements to synthesize the ionic compounds. The oxides or hydroxides derived from this element category are readily soluble in water and highly alkaline. The alkali metals are widely applied in the superconductivity, chemical physics, atomic energy industry, metallurgy, photovoltaic cells, chemical batteries, and so on [10–13].

In recent decades, the alkali metals have been measured by X-ray photoelectron spectroscopy (XPS), which is a powerful technique to detect elemental compositions of the surface of the material and determine the related chemical states [14–22]. To be specific, the XPS or ultraviolet photoelectron spectroscopy has been used to obtain electronic binding energy (BE) from the alkali metal surfaces at different emission angles [23, 24], sizes [25–27], and temperatures [28–30]. Even though considerable experimental XPS measurements and theoretical analysis have been performed over alkali metal surfaces, the underlying physics of local atomic bonding and electrons interaction at the surface of the alkali metals have not been insightfully understood. Therefore, it is highly desirable to achieve understanding at atomic scale of the influence of atomic bonding, size, emission angle and temperature on the energy shift of alkali metal surfaces by employing a method, which could be capable of obtaining photoelectron spectral information in the outermost one or two atomic layers of the metal surface.

Recently, zone-resolved photoelectron spectroscopy (ZPS) analysis method [31] is developed by using collected XPS data to purify coordination-resolved knowledge of electronic BE of under-coordinated atoms, such as atoms around defects or at solid surfaces. The advanced ZPS technique can interpret the physical and chemical processes at the surfaces or interfaces in a static or dynamic manner. Required ZPS data can be collected after performing XPS measurements for an edge of electronic BE of under-coordinated atoms, such as atoms around defects or at solid surfaces. The theoretical analysis have been performed over alkali metal surfaces by employing a method, which facilitates the reproduction of thermal and size trend of energy changes, but also clarifies the physical origin of their core-electron BE shifts in alkali metals. It has resulted in the clarification of the atomic bonding with the quantification of essential physical quantities, such as the atomic bond energy, atomic cohesive energy, and atomic coordination number.

II. PRINCIPLES

A. Tight-binding approximation

By applying the band theory, we can describe the Hamiltonian of an electron that transfers in the \( \nu \)-th atomic orbit of the atom in the nanostructure as follows,

\[
\hat{H} = \left[ -\frac{\hbar^2 \nabla^2}{2m} + \hat{V}_{\text{atom}}(r) \right] + \hat{V}_{\text{cry}}(r)(1 + \Delta_H) \quad (1)
\]

where \( -\frac{\hbar^2 \nabla^2}{2m} \) represents the kinetic energy of an isolated atom, \( \hat{V}_{\text{atom}}(r) \) denotes the intra-atomic trapping potential of the atom, \( \hat{V}_{\text{cry}}(r) = \hat{V}_{\text{cry}}(r + R) \) is the crystal potential, and \( \Delta_H \) illustrates perturbations to \( \hat{V}_{\text{cry}}(r) \) at the equilibrium condition. In addition, \( \hat{V}_{\text{cry}}(r) \) includes all the inter-atomic interaction from the surroundings of the atom. Both \( \hat{V}_{\text{atom}}(r) \) and \( \hat{V}_{\text{cry}}(r) \) keep the periodicity with a spatial period of the lattice constant \( R \).

The eigen wave function of the electron can be expressed as \( \phi_{\nu, i} = \langle \nu, i | \rangle e^{ikr} \equiv | \nu, i \rangle \). The modulation prefactor \( e^{ikr} \) in the Bloch function can be omitted in the core-electron wave function for its strong localization. Assuming that \( \Delta_H \) insignificantly affects the core-electrons and their wave function, \( | \nu, i \rangle \), can approximate the wave function of the core-electron of an isolated atom, yielding the following equation,

\[
\langle \nu, i | \nu, j \rangle = \delta_{i,j} = \begin{cases} 
1 & (i = j) \\
0 & (i \neq j)
\end{cases}
\]
in which \( i \) and \( j \) indicate the \( i \)-th and \( j \)-th atomic site, respectively.

In order to study the core-electron BE shift, several types of energies are considered. The \( \nu \)-th atomic core level energy of the isolated atom, \( E_{\nu}(0) \), is ruled by the interplay between the electron and the ion-core within the atom. The core level shift energy, \( \Delta E_{\nu}(z) \), results from the crystal potential and the added perturbations. In detail, they can be respectively expressed as,

\[
E_{\nu}(0) = -\langle \nu, i | \hat{V}_{\text{atom}}(r) | \nu, i \rangle
\]

and

\[
\Delta E_{\nu}(z) \equiv E_{\nu}(1 + \Delta H) \left[ 1 + \left( \frac{z \beta}{\alpha} \right) \right]
\]

\[
E_{\nu} = -\langle \nu, i | \hat{V}_{\text{cry}}(r) | \nu, i \rangle
\]

\[
\alpha = -\langle \nu, i | \hat{V}_{\text{cry}}(r)(1 + \Delta H) | \nu, i \rangle
\]

\[
\beta = -\langle \nu, i | \hat{V}_{\text{cry}}(r)(1 + \Delta H) | \nu, j \rangle
\]

where \( E_{\nu} \) is the energy dispersion of the electron in an ideal solid, \( \alpha \) depicts the exchange integral, \( \beta \) gives the overlap integral, and \( z \) denotes the effective atomic coordination number. Normally, \( E_{\nu} \) plays a dominant role as the first-order approximation in the core-level shift, and \( z \beta / \alpha \) is smaller than 3%.

**B. BOLS correlation**

As the lattice periodicity is terminated at the surface, the coordination number of atoms in the outer atomic layers is reduced, according to the BOLS correlation [33]. One part of the bonds is broken while the other part of bonds among the undercoordinated atoms is shortened and stiffened. After the bond relaxation, the anisotropic bond contraction coefficient, \( C_{z} \), is revealed to depend on the effective coordination number \( z \) of an atom in the \( i \)-th atomic layer, \( z_{i} \), where the index \( i \) counts from the outermost layer of the skin inward up to three. The dependence can be expressed as

\[
C_{z} = \frac{d_{z}}{d_{b}} = \frac{2}{1 + \exp\left((12 - z_{i})/8z_{i}\right)}
\]

where \( d_{z} \) and \( d_{b} \) represent the bond lengths among the uncoordinated atoms and the bulk, respectively. Besides, the single-bond energy \( E_{z} \) can be described as \( E_{z} = C_{z}^{-m} E_{b} \), where \( m \) is the bond nature indicator and verifies the correlation between the bond energy and the bond length. In this work, \( m=1 \), which is used for most metals [33].

In general, the coordination number imperfection can emerge due to surface effect, size effect, thermal effect, and many other factors, such as mechanical modulation, electron-phonon coupling, magnetic fields, etc. This work focuses on the aforementioned first three effects. By combining the TB approximations and the BOLS notations, i.e. the BOLS-TB method, the coordination number-imperfection induced perturbation term in the Hamiltonian (see Eq.(1)) can be given in the following,

\[
\Delta_{H} = \begin{cases}
C_{z}^{-m} - 1 = \frac{E_{z}}{E_{b}} - 1 & \text{(surface effect)} \\
\tau K^{-1} \sum_{i \leq 3} C_{i}(C_{i}^{-m} - 1) & \text{(size effect)} \\
\int_{0}^{T} \eta(T) dt \frac{E_{z}}{E_{b}} & \text{(thermal effect)}
\end{cases}
\]

where \( \tau \) denotes the shape factor of the nanostructure, \( K \) indicates the size dimension, and \( \eta(T) \) is the specific heat per coordinate.

Importing the XPS data, the core level energy of an isolated atom, \( E_{\nu}(0) \), and the core level shift energy, \( E_{\nu}(z) - E_{\nu}(0) \), can be given as follows,

\[
E_{\nu}(0) = \frac{C_{z}}{C_{z} - C_{z}^{-1}} \left( C_{z} - C_{z}^{-1} \right) \left( C_{z}^{-m} - 1 \right)
\]

\[
E_{\nu}(z) - E_{\nu}(0) = (E_{\nu}(12) - E_{\nu}(0)) \times C_{z}^{-m} \quad \text{(2)}
\]

where \( z=0 \) and 12 label the coordination number of the isolated atom and that of an atom in the solid, respectively.

**C. DFT calculation**

In this work, first principle calculations are performed to verify results from the BOLS-TB approach. In the framework of DFT, the geometry optimizations of Li, Na, K and Rb clusters with varied structures are performed and the corresponding electronic structures are calculated by utilizing Vienna \emph{ab initio} Simulation Package [34, 35]. Herein we uses 15 Å vacuum spaces along the \( x, y, \) and \( z \) directions for all the calculated structures, and the initial alkali metal clusters are modeled by the glue potential devised by Ercolessi and Doye [36, 37], so that the initial structure has the lowest en-
ergy. The exchange-correlation functional effects are investigated by using the generalized gradient approximation of Perdew-Burke-Emzerhof [38]. The energy cutoff is set to be 400 eV. A $1 \times 1 \times 1$ Monkhorst-Pack grid is used for sampling the Brillouin zone. By using the conjugate gradient method, full geometry optimizations and self-consistent electronic calculations are guaranteed for each system employing a convergence criterion for the total energy of 0.01 meV. Actually, our calculation results can be verified through experiments, and the related experimental methods can refer to studies by Riffe et al. [20, 28, 29]. In the work, the alkali-metal samples were prepared by condensation of alkali-metal vapor onto a Ni(100) substrate cooled to 78 K, and the photoemission data on the alkali metals were obtained from tests conducted by 6 m toroidal-grating monochromator beamline at Synchrotron Light Source. The photoelectron-energy distributions were measured with a 100 mm vacuum science workshop hemispherical analyzer, which was operated with a pass energy of 2 eV for Na, K, and Rb and 5 eV for Li. More details about the experimental procedures can be found in Ref.[28].

III. RESULTS AND DISCUSSION

A. Surface effect

Macroscopic properties of the alkali metals at the surfaces differ from those of the bulk, and the surface effect is emphasized in this subsection. In our work, radioactive francium (Fr) is not considered.

Firstly, the XPS spectra of bcc(110) surfaces are shown in FIG. 1 for the Li 1s, Na 2p, K 3p, Rb 4p and Cs 5p energy levels, which are the sub-outer shells of the alkali metal atoms. The profiles are decomposed using three components of first atomic layers ($S_1$), second atomic layers ($S_2$), and bulk, with related atomic coordination number values of 3.95, 5.85, and 12, respectively. For each alkali metal, the binding energy increases along the inside bulk to the outmost atomic layer. In the Group 1 of the periodic table, the binding energy decreases as the coordination number grows.

Secondly, the BE shifts induced by the surface effects are analyzed in a quantitative manner. Three components ($l=3$) for the alkali metal surfaces indicate $N=C_l^2=3$ possible values for $E_\nu(0)$. The distribution has an average atomic $\nu$-th level of $\langle E_\nu(0) \rangle$ and a standard deviation of $\sigma$.

$$E_\nu(0) = \frac{1}{N} \sum_{n} \frac{E_{\nu n}(0)}{N}$$

$$\sigma = \sqrt{\frac{1}{N} \sum_{n} (E_{\nu n}(0) - \langle E_\nu(0) \rangle)^2}$$

$\langle E_\nu(0) \rangle$ can be treated as an inherently constant,

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Quantitatively, as the period increases in Group 1 of the periodic table, an obvious drop is found in the BE of the sub-outer shell of the alkali metal atoms, as shown in Table I. The previous experiments reported that the BE shifts in alkali metals for Li 1s [30], Na 2p [42], K 3p [42], Rb 4p [27], and Cs 5p [39] are about 0.51 eV, 0.23 eV, 0.32 eV, 0.18 eV, and 0.23 eV, respectively. The corresponding BE shifts as shown in Table I are 0.51 eV (Li 1s), 0.34 eV (Na 2p), 0.404 eV (K 3p), 0.187 eV (Rb 4p), and 0.223 eV (Cs 5p). By comparison, it can be found that our calculated BE shifts for Li 1s, Na 2p, and K 3p are about 0.1 eV larger than the experimental results [30, 42], while for Rb 4p and Cs 5p, the calculated and experimental results [27, 39] are plausibly consistent, which can be attributed to different experimental conditions, such as vacuum level.

Thirdly, the ZPS analysis method is adopted to distinguish changes in certain energy regions of the spectral band. As shown in FIG. 2(a), the ZPS profile of Rb(3d_{5/2}) is obtained based on the XPS spectra from Rb(3d_{5/2}) on graphite [23] at emission angles of 0° and 70°. FIG. 2(b) displays the spectra from Cs(3d_{5/2}) on graphite [24]. In each plot, the intensities of the normalized XPS spectra collected at large emission angles are generally weakened due to the scattering loss. In order to well treat the background influence, Shirley

TABLE I The effective coordination number (z), bond strain ε_{z}=(C_{z}−1), relative core level shift ΔE_{ν}(i)=E_{ν}(i)−E_{ν}(B), relative atomic cohesive energy δE_{C}=E_{C}(z)/E_{C}(12)−1=(z_{ν}C_{z}^{−m}−1), and the relative energy density δE_{D}=E_{D}(z)/E_{D}(12)=(C_{z}^{−m}+δ−1) in various registries of alkali metal surfaces.

| Item | State | z | E_{ν}(i) | ΔE_{ν}(i) | -ε_{z}/% | -δE_{C}/% | δE_{D}/% |
|------|-------|---|---------|-----------|--------|----------|--------|
| Li 1s (110) | Bulk | 12 | 54.906 | 0 | 0 | 0 | 0 |
| | S2 | 5.83 | 55.205 | 0.299 | 6.61 | 47.98 | 31.43 |
| | S1 | 3.95 | 55.520 | 0.614 | 12.67 | 62.31 | 71.92 |
| Na 2p (110) | Bulk | 12 | 30.595 | 0 | 0 | 0 | 0 |
| | S2 | 5.83 | 30.764 | 0.169 | 6.61 | 47.98 | 31.43 |
| | S1 | 3.95 | 30.943 | 0.348 | 12.67 | 62.31 | 71.92 |
| K 3p (110) | Bulk | 12 | 18.354 | 0 | 0 | 0 | 0 |
| | S2 | 5.81 | 18.551 | 0.197 | 6.67 | 48.12 | 31.81 |
| | S1 | 3.93 | 18.757 | 0.404 | 12.76 | 62.46 | 72.67 |
| Rb 4p (110) | Bulk | 12 | 14.940 | 0 | 0 | 0 | 0 |
| | S2 | 5.83 | 15.029 | 0.089 | 6.61 | 47.98 | 31.43 |
| | S1 | 3.95 | 15.127 | 0.187 | 12.67 | 62.31 | 71.92 |
| Cs 5p (110) | Bulk | 12 | 11.830 | 0 | 0 | 0 | 0 |
| | S2 | 5.83 | 11.940 | 0.110 | 6.61 | 47.98 | 31.43 |
| | S1 | 3.95 | 12.053 | 0.223 | 12.67 | 62.31 | 71.92 |
background correction and spectral peak area conservation are used to regulate these spectra. Compared to the XPS data of the zero emission angle, more information is introduced in those regarding surfaces with different emission angles, which can improve the ZPS analysis by distilling the interference information due to surface effects. The valleys of Rb at 110.93 eV in FIG. 2(a) and Cs at 726.68 eV in FIG. 2(b) are the subtracted Rb and Cs bulk and the mixture of bulk and surface ingredients. At the surface, quantum entrapment leads to deepening of the core band through the shrink of the atomic coordination number. The positive BE shift results in the emergence of the Ts component, in agreement with the Goldschmidt-Pauling-Feibelman prediction [43, 44] and the BOLS theory. In addition, the ZPS analysis for the sub-outer shell of the alkali metals can provide the information, including the z-resolved bond strain $\varepsilon_z$, the BE shift $\delta E_z$, the relative atomic cohesive energy $\delta E_C$, and relative energy density $\delta E_D$ of alkali metals, as shown in the Table I. The obtained variables are of great significance in learning the surface features of the alkali metals, since the macroscopic properties of the skins are mediated by the under-coordination resolved energetics.

B. Size effect

Recently, theoretical and experiment investigations of the Si [45], Se [46], Sb [19], Pb [47], Mo [48], and Au [49] size-selected clusters revealed a linear dependence of the energy shifts of the core band on the inverse of the particle size. Kooser et al. [46] proposed that the $ab initio$ calculation of dissociation and appearance energies combined with PEPICO technique was a very useful tool for the size-selective exploration of the electronic structure of Se microcluster and its fragmentation dynamics. In our previous work [47], taking advantage of the consistency between the density functional theory calculations and photoelectron spectroscopy measurements, we have clarified that shorter and stronger bonds between the undercoordinated Pb atoms can cause the local densification and entrapment of core electrons, which, in turn, polarize the other conducting electrons in the skins and edges, resulting in the respective electron binding energy shift. The nanoclusters of the alkali metals possess excellent physical and chemical properties based on their large surface-to-volume ratio, and their according binding energy shifts due to the size effect studied in this subsection.

The tendency of size dependence is ruled by the surface-to-volume ratio, $\gamma_i = \pi C_{z_i} K^{-1}$. If the nanocluster is approximated as a sphere, it is necessary to take the interplay between the inner atoms and surrounding atoms inside the critical range into account [47]. The corresponding number of atoms $N$ can be described as

$$N = 4\pi K^3/3,$$

and the radius $K$ can be given as,

$$K^{-1} \approx 1.61 N^{-1/3}$$

(3)

This relation indicates that a term of the cluster size $N^{-1/3}$ needs to be considered when probing the surface-to-volume ratio.

According to the BOLS correlation, the BE shifts in the nanocluster can be deduced as follows,

$$E_p(K) = (E_p(12) - E_p(0)) \pi K^{-1} \sum_{i \leq 3} C_{z_i} (C_{z_i}^{-m} - 1) + E_p(12)$$

(4)
BE shifts of the sub-outer shell of the alkali metal atoms in the nanocluster are listed as follows,

\[
\begin{align*}
E_{1s}(N) &= 3.721N^{-1/3} + 46.417 \text{ (Li 1s calculation)} \\
E_{2p}(N) &= 3.007N^{-1/3} + 30.595 \text{ (Na 2p experiment)} \\
E_{2p}(N) &= 3.007N^{-1/3} + 24.196 \text{ (Na 2p calculation)} \\
E_{3p}(N) &= 1.853N^{-1/3} + 20.620 \text{ (K 3p experiment)} \\
E_{3p}(N) &= 1.853N^{-1/3} + 15.595 \text{ (K 3p calculation)} \\
E_{4p}(N) &= 1.397N^{-1/3} + 14.940 \text{ (Rb 4p experiment)} \\
E_{4p}(N) &= 1.397N^{-1/3} + 12.620 \text{ (Rb 4p calculation)}
\end{align*}
\]

After analyzing DFT calculation data, we found that the change of \(\Delta E_{\nu}(N)\) was mainly induced by the size effect, which was consistent with the trend of experimental results [25–27].

The work function can be read in the following,

\[
\begin{align*}
\Phi_1 &= \Phi_{\nu}^{\text{Fermi}}(12) - \Phi_{\nu}^{\text{Fermi}}(12) \\
\Phi_2 &= \Phi_{\nu}^{\text{vacuum}}(12) - \Phi_{\nu}^{\text{Fermi}}(12) \\
\Phi &= \Phi_1 + \Phi_2 = \Phi_{\nu}^{\text{vacuum}}(12) - \Phi_{\nu}^{(12)}
\end{align*}
\]

where \(\Phi_{\nu}^{\text{Fermi}}\) and \(\Phi_{\nu}^{\text{vacuum}}\) are the BEs of the \(\nu\)-th electrons in the solid condition and isolated atoms, respectively. The ground state energy of \(\Phi_{\nu}^{\text{vacuum}}(12)\) is determined by the DFT calculations, excited state \(\Phi_{\nu}^{(12)}\) is obtained in the experiments, and \(\Phi\) denotes the difference between them. Due to the large surface-to-volume ratio and induced electronic structures, the melting point is expected to be lower in the cluster than that in the bulk.

### C. Thermal effect

The mechanical and electronic properties of alkali metals will be altered due to the thermal instability. In this subsection, we investigate the thermal effect on the alkali metals.

As the temperature increases, the bond length and strength will change accordingly. Following the BOLS correlation, the thermal effect will be modulated by the atomic coordination number for uncoordinated atoms. On the basis of the local bond average approach, the bond energy, \(E(z,T)\), and the bond length, \(d(z,T)\), can be described as follows,

\[
\begin{align*}
E(z,T) &= E_b \left[ 1 + \frac{(C_{z}^{m} - 1) - \int_{T_0}^{T} \eta(T)dT}{E_b} \right] \\
d(z,T) &= d_b \left[ 1 + (C_{z} - 1) \left( 1 + \int_{T_0}^{T} \alpha(T)dT \right) \right]
\end{align*}
\]
TABLE II The average effective coordination number (z), local bond strain $\varepsilon_z$, BE density $\delta E_D$, atomic cohesive energy $\delta E_C$, and relative core-level shifts $\Delta E'_c(N)$ from various registries of the alkali metal nanoclusters.

| Item      | Method     | $N$ | $E_p(N)$ | $\Delta E'_c(N)$ | z  | $-\varepsilon_z/\%$ | $\delta E_D/\%$ | $-\delta E_C/\%$ |
|-----------|------------|-----|----------|------------------|----|---------------------|----------------|----------------|
| Li 1s cluster | DFT        | 14  | 47.911   | 1.494            | 2.28 | 26.09              | 235.05         | 74.313         |
|           |            | 19  | 47.759   | 1.342            | 2.43 | 24.07              | 200.88         | 73.310         |
|           |            | 24  | 47.691   | 1.274            | 2.52 | 23.13              | 186.46         | 72.696         |
|           |            | 25  | 47.666   | 1.249            | 2.55 | 22.78              | 181.30         | 72.490         |
|           |            | 26  | 47.659   | 1.242            | 2.56 | 22.69              | 179.86         | 72.421         |
|           |            | 34  | 47.616   | 1.199            | 2.61 | 22.07              | 171.17         | 72.075         |
|           |            | 35  | 47.551   | 1.134            | 2.71 | 21.13              | 158.42         | 71.376         |
|           |            | 38  | 47.534   | 1.117            | 2.73 | 20.88              | 155.17         | 71.235         |
|           |            | 57  | 47.362   | 0.945            | 3.03 | 18.26              | 123.97         | 69.096         |
| Bulk      |            | 46.417 | 0        | 12               | 0   | 0                  |                |                |
| Na 2p cluster | DFT        | 13  | 25.421   | 1.225            | 1.81 | 33.80              | 420.765        | 77.215         |
|           |            | 25  | 25.214   | 1.018            | 2.02 | 29.93              | 314.910        | 75.975         |
|           |            | 30  | 25.157   | 0.961            | 2.10 | 28.64              | 285.644        | 75.476         |
|           |            | 32  | 25.124   | 0.928            | 2.14 | 28.02              | 272.65         | 75.222         |
|           |            | 53  | 24.979   | 0.783            | 2.39 | 24.61              | 209.638        | 73.580         |
| Na 2p     | Experiment at $\Phi_2=9.154$ eV | 3000 | 24.436   | 0.240            | 4.88 | 9.09              | 46.42          | 55.265         |
|           |            | 5000 | 24.396   | 0.200            | 5.37 | 7.70              | 37.79          | 51.516         |
| Bulk      |            | 24.196 | 0        | 12               | 0   | 0                  |                |                |
| K 3p cluster | DFT        | 13  | 15.850   | 0.730            | 2.728 | 20.299            | 155.815        | 71.250         |
|           |            | 24  | 15.800   | 0.680            | 2.852 | 19.783            | 141.50         | 70.372         |
|           |            | 25  | 15.763   | 0.643            | 2.955 | 18.901            | 131.170        | 69.636         |
|           |            | 47  | 15.718   | 0.598            | 3.092 | 17.814            | 119.18         | 68.648         |
|           |            | 54  | 15.620   | 0.500            | 3.451 | 15.360            | 94.85          | 66.023         |
|           |            | 55  | 15.603   | 0.483            | 3.529 | 14.89            | 90.5           | 65.446         |
| K 3p cluster | Experiment at $\Phi_2=5.501$ eV | 90   | 15.570   | 0.450            | 3.682 | 14.026            | 83.036         | 64.31          |
|           |            | 650  | 15.400   | 0.280            | 4.841 | 9.216            | 47.221         | 55.56          |
|           |            | 1900 | 15.310   | 0.190            | 5.904 | 6.444            | 30.532         | 47.411         |
|           |            | 3800 | 15.260   | 0.140            | 6.766 | 4.831            | 21.904         | 40.754         |
| Bulk      |            | 15.120 | 0        | 12               | 0   | 0                  |                |                |
| Rb 4p cluster | DFT        | 13  | 13.224   | 0.604            | 1.924 | 31.604            | 356.964        | 76.554         |
|           |            | 28  | 13.127   | 0.507            | 2.256 | 26.352            | 239.897        | 74.468         |
|           |            | 36  | 13.125   | 0.505            | 2.378 | 24.758            | 212.008        | 73.658         |
|           |            | 53  | 13.033   | 0.413            | 2.580 | 22.435            | 176.278        | 72.285         |
|           |            | 55  | 12.988   | 0.368            | 2.600 | 22.221            | 173.248        | 72.145         |
| Rb 4p     | Experiment at $\Phi_2=9.154$ eV | 40  | 13.090   | 0.470            | 2.355 | 25.052            | 216.933        | 73.815         |
|           |            | 90  | 12.980   | 0.360            | 2.836 | 19.926            | 143.234        | 70.485         |
|           |            | 110 | 12.960   | 0.340            | 2.953 | 18.917            | 131.359        | 69.650         |
|           |            | 170 | 12.910   | 0.290            | 3.308 | 16.276            | 103.519        | 67.074         |
| Bulk      |            | 12.620 | 0        | 12               | 0   | 0                  |                |                |

where $T_0$ denotes the ambient temperature as a reference. $\eta(T)$ and $\alpha(T)$ are the specific heat per bond and thermal expansion coefficient, respectively. Both terms are temperature dependent. $\eta(T)=C_v(T)/\theta_D$ is regulated in the Debye model for the z-coordinated atoms, where $\theta_D$ is the Debye temperature. To be specific, though the thermal detection is usually treated as an isobaric process, the difference between $C_p$ and $C_v$...
can be negligible for the condensed phase [32], and thus it is reasonable to describe \( \eta(T) \) by a function of \( C_v \).

For \( T > \theta_D \), the bond energy performs a linear dependence on the temperature as \( E_i = \eta_1 T_m + \eta_2 \), in which \( \eta_1 \) is the constant specific heat per bond, \( \eta_2 \) is the fold 1/\( z_b \) of heat of atomization for an atom in the molten state, and \( T_m \) is the melting temperature of the bulk alkali metal. The melting temperature at \( T > \theta_D \) is taken as \( T_{mi} \times z_i E_i \), where \( E_i \) is the atomic cohesive energy. By comparing \( T_m \) and \( T_{mi} \), it can be deduced that \( T_{mi}/T_m = z_i E_i/(z_i E_b) = z_b C_i^{-m} = 1 + \Delta T \), where \( \Delta T \) indicates the perturbation to the atomic coherency.

The normalized atomic coordination is obtained by \( z_{ib} = z_i / z_b \), in which \( z_b = 12 \) refers to the standard coordination number value of the fully coordinated system. Therefore, we can have \( T_{mi}/T_m = z_{ib} C_i^{-m} = T_m(1 + \Delta T) \) and \( E_i = \eta_1 T_{mi} + \eta_2 = C_i^{-m} E_b = C_i^{-m} (\eta_1 T_m + \eta_2) \) [50].

Using the Debye model, the thermal perturbation to the cohesive energy is given as the following,

\[
\Delta T = \int_0^T \frac{\eta(T) dt}{E_z} = \int_0^T \frac{C_v(T/\theta_D)}{z E_z} \frac{T}{\theta_D} dt = \frac{9 R}{E_{coh}} \left( \frac{T}{\theta_D} \right)^4 \int_0^T \int_0^{\theta_D} \frac{x^4 e^x}{(e^x - 1)^2} dx dt
\]

where \( E_{coh} = z E_z \) is the atom cohesive energy that needs to be estimated using the fitting method, and \( x_D = \theta_D / T \) [51]. XPS measurements [28] provide the initial thermal condition of \( T_0 \), and the perturbation term can be transformed into the following:

\[
\begin{align*}
\Delta T &= \int_0^{T_0} \frac{\eta(T) dt}{E_z} = \int_0^{T_0} \frac{C_v(T/\theta_D)}{z E_z} \frac{T}{\theta_D} dt \\
&= \int_0^{T_0} \frac{C_v(T/\theta_D)}{z E_z} \frac{T}{\theta_D} dt - \int_0^{T_0} \frac{C_v(T/\theta_D)}{z E_z} \frac{T}{\theta_D} dt \\
&= \int_0^{T_0} \frac{C_v(T/\theta_D)}{z E_z} \frac{T}{\theta_D} dt \\
\end{align*}
\]

 Assigning the XPS data and the BE shifts in the above equation, the Debye temperature \( \theta_D \) can be resolved. Under \( \theta_D \), the atmospheric pressure at 0 K and the bulk coordination number value of 12 serve as the inputs of numerical calculations [52, 53]. The outputs are presented in Table III, illustrating the properties such as the atomic cohesive energies.

As shown in FIG. 4, the dependence of theoretically calculated BE shifts on temperature is in accordance with that of measured results for the alkali metals. By the calculations, it is found that in the thermal range of \( T < \theta_D / 3 \), the slight change of the BE shifts induced by the small value of \( \int \eta(t) dt \) as \( \eta(t) \) is proportional to \( T^4 \). Within the range of \( T > \theta_D / 3 \), the specific heat at a constant volume, \( C_v \), reaches a certain value of 3R (R denotes the ideal gas constant) based on the Debye model as the temperature rises, and the dependence of the BE shifts on temperature consequently changes from nonlinear to linear. It can be indicated that the Debye temperature controls the shape of the curve in the low temperature region, and the term \( [z E_z(t)]^{-1} \) regulates the slope of the curve at the high temperatures.

According to the BOLS theory, the BE shift is related to the bond relaxation. In our study, the derivatives are sufficiently accurate since the consistency is approached in the effective coordination after the bond relaxation and corresponding energetics are induced by the sur-

| Item | \( \theta_D / K \) | \( T_0 / K \) | \( E_{coh} / eV \) | \( \Delta T_0 / eV \) |
|------|-----------------|--------------|-----------------|-----------|
| Li   | 344.0           | 80           | 0.82            | 0.003     |
| Na   | 156.0           | 83           | 1.10            | 0.009     |
| K    | 90.6            | 89           | 1.08            | 0.015     |
| Rb   | 55.6            | 78           | 1.09            | 0.010     |

FIG. 4 BE shift and fitting to the thermal shift with the known Debye temperature \( \theta_D \) [52, 53] as input parameters of alkali metals. The corresponding information is collected in Table III.
face, size and thermal effects. The three effects again demonstrate the BOLS correlation that the bonds between undercoordinated atoms get shorter but stronger than the coordinated ones, and the bond contraction leads to positive BE shifts.

IV. CONCLUSION

In this work, we studied the surface, size and thermal effects and energy level shift of alkali metals. The results demonstrate the ability of ZPS in quantifying the local atomic information at the alkali metal surface, including the energetics related to local bonds and the binding energy of electrons in under-coordinated atoms. The electron binding energies of Li 1s, Na 2p, K 3p, Rb 4p and Cs 5p levels are calculated using the BOLS-DFT methods. The relationship between the size of the nanocluster and associated electron binding energy is presented in the framework of the BOLS correlation. It is also found that the size effect is a superposition of the three-layer atomic effect of the surface. These concepts can shed light on the study of the relationship between size effects and surface effects. At last, the dependence of the BE shifts on temperature is illustrated for the alkali metals.

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