Bond relaxation in length and energy of Li atomic clusters

Maolin Bo,^a Yan Wang,^b Yonghui Liu,^a Can Li,^c Yongli Huang,^{a*} Chang Q Sun^{d*}

^a Key Laboratory of Low-Dimensional Materials and Application Technologies (MOE), Hunan Provincial Key Laboratory of Thin Film Materials and Devices, and School of Materials Science and Engineering, Xiangtan University, Hunan 411105, China

^b School of Information and Electronic Engineering, Hunan University of Science and Technology, Hunan 411201, China

^c Institute of Coordination Bond Metrology and Engineering, School of Materials Science and Engineering, China Jiliang University, Hangzhou 330018, China

^d NOVITAS, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

*E-mail: huangyongli@xtu.edu.cn; ecqsun@ntu.edu.sg.

Abstract

A combination of the photoelectron spectrometry and density functional theory calculations has confirmed bond-order-length-strength (BOLS) predictions on the atomic undercoordination induced local bond contraction, charge densification and bond energy entrapment of Lithium (Li) atomic clusters and Layer-resolved Li(110) skins. Analysis also derives the energy level of an isolated Li atom and its shift upon bulk and skin formation, which is beyond the scope of currently available approaches.

Keywords: Li solid skins and atom clusters, XPS, DFT, Binding energy

1. Introduction

Atomic clusters can be seen as polyatomic aggregates between isolated atoms and bulk solids, in which a considerable part of the atoms are located in skins of low coordination numbers[1-4]. The nature and distribution of these atomic sites vary with cluster size, and many of the most interesting properties[5,6] of clusters are intimately connected to this interplay between the size-dependent geometry shapes [7-10] and the electronic structure[11-14]. This also makes clusters interesting for applications where the tuning of various physical and chemical properties could be achieved by cluster size selection[15-20]. However, nanoscale materials have a variety of possible geometrical shapes and structures[21-23]. Predictions the size-dependency of the atom coordination number (CN), skin-to-volume ratio, local bond strain, energy density, atomic cohesive energy, and electron binding energy (BE) with different geometrical shapes and structure nanoclusters are considerably challenging.

Basically, local bond strain and energy density originates from the presence of broken bonds, the so-called dangling bonds, localized on the skin atoms. To understand the bonding and electronic dynamic characteristics, we show that the Li solid skins[24-26] and atom clusters[27,28] follow consistently the predictions of the bond-order-length-strength (BOLS) notion[29], the tight-binding (TB) theory[30], photoelectron spectroscopy (XPS), and the density functional theory (DFT).

2. Principles and calculation methods

An extension of the atomic coordination-radius premise of Pauling[31] and Goldschmidt[32] has resulted in the BOLS notion, which uses the following expressions:

$$\begin{cases}
C_{z_i} = d_{z_i} / d_b = 2 / \{1 + \exp[(12 - z_i) / 8z_i]\} & \text{(bond contraction coefficient)} \\
E_{z_i} = C_{z_i}^{-m} E_b & \text{(bond strengthening)} \\
E_c(z) = z_i E_{z_i} & \text{(atomic cohesive energy)} \\
E_d(z) = E_{z_i} / d_{z_i}^\lambda & \text{(binding energy density)}
\end{cases} \quad (1)$$

where d is the bond length, E is the bond energy, and C_{z_i} is the coefficient of bond contraction with z_i being the effective coordination of an atom in the i th atomic layer. The value i is counted from the outermost layer inward, up to a value of three. For $i > 3$, the atomic bonds are assumed to be set sufficiently deep in the bulk of the solid such that they do not experience significant deficiencies in atomic CN(z), unlike those at and near the skin. The bond-nature indicator m correlates the bond energy with the bond length. For most metals, $m = 1$. The CN, i.e., $z = 0$ and $z = 12$, represent an isolated atom and an atom in the ideal bulk, respectively. $\lambda = 1$ defines a monoatomic chain, $\lambda = 2$ defines the monoatomic sheets or single walled nanotube, and $\lambda = 3$ is the general case of a three-dimensional solid. The core idea of the bond order-length-strength (BOLS) correlation mechanism is that if one bond breaks, the neighboring ones become shorter and stiffer. Consequently, local strain and quantum trapping are formed immediately nearby the potential barrier at sites surrounding the broken bonds.

In the TB theory, the Hamiltonian and wave function describing an electron moving in the v th orbit of an atom in the bulk solid is as follows:

$$H = \left[-\frac{\hbar^2 \nabla^2}{2m} + V_{atom}(r) \right] + V_{cry}(r)(1 + \Delta_H),$$

where $V_{atom}(r)$ is the intra-atomic potential due the atom at the origin and $V_{cry}(r)$ is the crystal potential due to all other atoms. This determines the v th core level energy, $E_v(0)$, of an isolated atom, and determines the core level shift (CLS), $\Delta E_v(z)$. These parameters use the following relations:

$$E_v(0) = \langle v, i | V_{atom}(r) | v, i \rangle$$

$$\Delta E_v(z) = \langle v, i | V_{cry}(r)(1 + \Delta_H) | v, i \rangle \left[1 + \frac{z \langle v, i | V_{cry}(r)(1 + \Delta_H) | v, j \rangle}{\langle v, i | V_{cry}(r)(1 + \Delta_H) | v, i \rangle} \right]$$

$$\cong E_b(1 + \Delta_H)(1 + \left(\frac{z\beta}{\alpha} < 3\% \right)) = E_{z_i} \quad (2)$$

E_b represents the single bond energy in the ideal bulk, and any perturbation to the bond energy E_b will accordingly shift the core level. $|v, i\rangle$ is the eigenwave function at the i th atomic site with z neighbors, because $\langle v, i | v, j \rangle = \delta_{ij}$, with the Kronig function δ_{ij} (if $i = j$, $\delta_{ij} = 1$; otherwise, $\delta_{ij} = 0$). The parameter $\alpha = \langle v, i | V_{cry}(r)(1 + \Delta_H) | v, i \rangle \propto \langle E_b \rangle$ (exchange integral) is the energy interaction between the crystal potential and the specific core electron at site i . $\beta = \langle v, j | V_{cry}(r)(1 + \Delta_H) | v, j \rangle \propto \langle E_b \rangle$ (the overlap integral) is the energy of the exchange interaction between the crystal potential and the overlapping neighboring electrons. Unlike the valence band, which shows charge intermixing upon alloy or compound formation and that valence electrons are very sensitive to chemical or physical treatment, the core band distribution and BE shift result from the overlap and exchange integrals of the interatomic potential and the specific eigenwave function of the core electrons.

Incorporating the BOLS into the TB approximation yields $\Delta E_v(z)$, which dominates the shift of BE and can be reorganized as follows:

$$\Delta E_v(z) = E_v(z) - E_v(0) = \Delta E_v(12)(1 + \Delta_N) = (E_v(12) - E_v(0))(1 + \Delta_i)$$

and

$$\begin{cases} \Delta_N = \sum_{i \leq 3} \gamma_i \Delta_i = \tau K^{-1} \sum_{i \leq 3} C_{z_i} \Delta_i = \tau K^{-1} \sum_{i \leq 3} C_{z_i} (C_{z_i}^{-m} - 1) & (\text{Nanocluster}) \\ \Delta_i = \frac{E_z}{E_b} - 1 = C_{z_i}^{-m} - 1 & (\text{Solid skins}) \end{cases} \quad (3)$$

$\gamma_i = V_i / V = \tau C_{z_i} K^{-1}$ is the skin-to-volume ratio, proportional to τ ($\tau = 1, 2$, and

3 corresponds to the dimensionality of a thin plate, a cylindrical rod, and a spherical dot, respectively) and inversely proportional to the dimensionless size K . **The skin is the outermost three atomic layers of the surface.**

For the skin CLS, we have the following relation:

$$E_v(z) - E_v(0) = [E_v(12) - E_v(0)] \times C_{z_i}^{-m}$$

$$\frac{E_v(z) - E_v(0)}{E_v(z') - E_v(0)} = \frac{C_z^{-m}}{C_{z'}^{-m}} \quad (z' \neq z) \quad \text{or} \quad E_v(0) = \frac{C_{z'}^m E_v(z') - C_z^m E_v(z)}{C_{z'}^m - C_z^m} \quad (z' \neq z)$$
(4)

With the derived $E_v(12)$, $E_v(0)$, the bond-nature indicator m , and the given z values for the outermost three atomic layers, we are able to decompose the measured XPS spectra into the corresponding skin and bulk components.

Together with increases in computational power and method development, first-principles DFT calculations has gained more applicability for directly calculating the binding energies or at least the chemical shifts of desired atomic configurations. We conducted first-principle DFT calculations of the optimal Li_N clusters, as shown in **Fig. 1**. The calculations were focused on the change of the bond and electronic characteristics of under-coordinated atoms, as well as the geometric structures, size dependence, and energy distribution of the core band. The relativistic DFT calculations were conducted using the Vienna *Ab initio* simulation package (VASP) **5.2.2 version**. The DFT exchange-correlation potential utilized the **projector-augmented wave (PAW) generalized gradient approximation (GGA)[33] Li-sv** functional for geometric and electronic structures. The plane wave cutoff was 400 eV, and thus, for refined structures, final and accurate energy values were computed by the same code using a precise cutoff energy of 400 eV in all the cases. **The cell size is $25 \times 25 \times 25 \text{ \AA}$. The Brillouin zone was sampled at the G-point only. In calculations, All atoms were fully relaxed that the energy converges to 10^{-4} and the force on each atom converges to be less than $0.001 \text{ eV/\AA}$.**

3 . Results and Discussion

Fig. 2 shows a decomposition of the measured XPS 1s spectrum collected from a

solid Li(110) skin[26]. The spectrum from the skin of the Li(110) specimen was, respectively, decomposed into three components corresponding to the bulk (B) and the skin skins S_2 and S_1 from higher (smaller absolute value) to lower BE. These components follow the constraints of Eq. (4) and use the parameters given in **Table 1**. Then we can find the average $\langle E_{1s}(0) \rangle = \sum_N \langle E_{1s_i}(0) \rangle / N$ with standard deviation σ of $E_{1s}(0)$ calculated using a least root-mean-square method. A fine tuning of the CN values of the components will minimize σ and improve the accuracy of the effective CN for each sublayers. To minimize the error in the envelope and experimental spectra, the BE of an isolated atom is optimized to be 50.567 eV with a respective bulk shift of 54.906 eV. Based on these criteria, we obtain the following z -resolved CLS for Li: $E_{1s}(z) = \langle E_{1s}(0) \rangle \pm \sigma + \Delta E_{1s}(12) C_{z_i}^{-m} = 50.673 \pm 0.001 + 4.233 C_{z_i}^{-1}$ (eV).

Fig. 3a shows DFT calculations of the 1s-orbit DOS for Li of $C_{2v}14$, $C_{2v}19$, $D_{2h}24$, $C_{2v}25$, C_s26 , $C_{1v}34$, C_s35 , $D_{3h}38$, and $C_{1v}57$ clusters. DFT calculations showed that the peaks of BE shifted toward higher BEs as the cluster size was reduced. Using the sum rule of the core-shell structure while considering the skin-to-volume ratio ($\gamma_i = \tau C_{z_i} K^{-1}$), we can deduce the size dependence of the v th energy level of cluster, $E_v(0)$, and its bulk shift, $\Delta E_v(12)$, as follows:

$$E_v(K) = E_v(12) + [E_v(12) - E_v(0)] \tau K^{-1} \sum_{i \leq 3} C_{z_i} (C_{z_i}^{-m} - 1) \quad (5)$$

For a cluster that is approximately spherical, we need to consider the interaction between the specific central atom and its surrounding neighbors within the critical volume, and the number of atoms N is related to its radius K as follows[34]:

$$K^{-1} = (3N / 4\pi)^{-1/3} = 1.61 N^{-1/3} \quad (6)$$

The incorporation of Eq. (6) into Eq. (5) yields the N -dependence of the core level BE:

$$E_v(N) = E_v(12) + \Delta E_v(12) \left[1.61\tau N^{-1/3} \sum_{i \leq 3} C_{z_i} (C_{z_i}^{-m} - 1) \right]. \quad (7)$$

Based on the BOLS concept, the CN of the outmost layer of an atomic cluster is $z_1 = 2.60$ (average CN of cluster from 14 to 57) and those of the second and inner layer are $z_2 = z_1 + 2 = 4.60$ and $z_3 = 12$, respectively. From the relationship shown in Eq (1), we can calculate the bond-contraction coefficient of the outmost, second, and inner layers to be $C_1 = 0.778$, $C_2 = 0.900$ and $C_3 = 1$, respectively. With the value of $\Delta E_{1s}(12) = 4.233$ eV derived from the skin analysis, we can calculate the BE shift:

$$E_{1s}(N) = E_{1s}(12) + 2.194\tau N^{-1/3} (\text{eV}) \quad (8)$$

Fig. 3b shows that the 1s core band CLS of the size-selected free Li_N nanoclusters linearly increases with $N^{-1/3}$ and shape factor $\tau = 1.695$. According to the slope and intercept derived from size-induced BE shifts and Eq. (7),

$$E_{1s}(N) = 46.417 + 3.721N^{-1/3} (\text{eV})$$

Owing to large skin-to-volume ratio and novel electronic structures, clusters usually show a lower melting temperature[35], a higher magnetic moment[36], and better catalysis[37] than their bulk counterparts. Purpose to probe the skin-to-volume ratio of clusters, an extended range of cluster size $N^{-1/3}$ has to be taken into account in order to probe their dependence. **Fig. 4** show calculate BE shifts of structure of Li Oh(13,55) and FCC(13,55). We compared Oh and FCC structures with the same atom number, as is shown in **Table 2**. We found different shapes geometrical and structure with different BE shifts. Therefore, it should be discriminate skin-to- volume ratio (γ_{ratio}) of different geometrical shapes and structures of clusters. Here, we have the relations of skin-to- volume ratio from Eq. (4) and Eq. (6):

$$\left\{ \begin{array}{l} C_z = \frac{\Delta E_{1s}(12)}{\Delta E_{1s}(N) + \Delta E_{1s}(12)} \quad (\text{bond contraction coefficient}) \\ \varepsilon_z = C_z - 1 \quad (\text{local bond strain}) \\ \gamma_{ratio} = \tau C_z K^{-1} = 1.61\tau C_z N^{-1/3} \quad (\text{skin-to-volume ratio}) \end{array} \right. \quad (9)$$

$\Delta E_{1s}(N) = E_{1s}(z) - E_{1s}(12)$ is the CLSs of an atom in the ideal bulk. From Eq. (9), we found the skin-to-volume ratio is dependent on BE shifts and cluster size $N^{1/3}$. On the other hand, BE shifts with the nanocluster size because of the variation in the skin-to-volume ratio. With the shape factor $\tau = 1.695$ and $E_{1s}(B) = 4.233$ eV, we calculate the skin-to-volume ratio of Li nanocluster using Eq. (9), as is shown in **Table 3**. We found the γ_{ratio} of Oh structures is larger than that of FCC structures, the skin of BE FCC structures is higher than that of Oh structures, and the increase bond strain ε_z induces nanocluster to shrink.

To obtain the N imperfection z , δE_d , δE_c of the Li nanoclusters, we use the relations from Eq. (1), Eq. (4), and Eq. (7):

$$\left\{ \begin{array}{l} z = 12 / \left\{ 8 \ln \left(2 \times 1.61 \tau \Delta'_H N^{-1/3} + 1 \right) + 1 \right\} \quad (\text{cluster CN}) \\ \delta E_c(z) = z_i E_{z_i} / z_b E_b = z_{ib} C_z^{-m} \quad (\text{relative atomic cohesive energy}) \\ \delta E_d(z) = (E_{z_i} / d_{z_i}^3) / (E_b / d_b^3) - 1 = C_z^{-(m+3)} - 1 \quad (\text{relative binding energy density}) \end{array} \right. \quad (10)$$

Where $z_{ib} = z / 12$ is the reduced CN, $z = 12$ is the bulk value and $m = 1$ for metal.

Given the shape factor τ , Δ'_H , and $\Delta E_{1s}(12)$ of and Eq. (9) and Eq. (10), we have

$$\left\{ \begin{array}{l} z = 12 / \{8 \ln(2 \times 0.879 N^{-1/3} + 1) + 1\} \\ \varepsilon_z = \frac{4.233}{3.721 N^{-1/3} + 4.233} - 1 \\ \gamma_{ratio} = 2.729 \times \frac{4.233 N^{-1/3}}{\Delta E_{1s}(N) + 4.233} \\ \delta E_c(z) = \frac{z}{12} \times \frac{4.233}{3.721 N^{-1/3} + 4.233} \\ \delta E_d(z) = \left(\frac{4.233}{3.721 N^{-1/3} + 4.233} \right)^{-4} - 1 \end{array} \right. \quad (11)$$

Therefore, we can calculate the z , ε_z , δE_d , δE_c , γ_{ratio} of the Li_N clusters using Eq. (11)(see **Fig. 5** and **Table 3**). The under-coordination atom induced strain and bond energy gain results in excessive energy on the surface of skin depth, and therefore, higher stress and tension exists on the skin than those in the bulk interior. The atom BE density E_d and local bond strain ε_z determine the processes and phenomena at the nanoclusters, including structural reconstruction and relaxation. The nanocluster skins are often harder and more elastic than the bulk interior, but the skin melts easier. On the other hand, the atom cohesive energy E_c of an under-coordinated skin atom is generally lower than that of the bulk.

4. Summary

The combination of the BOLS-TB premise with the DFT calculations and XPS measurements has led to a consistent insight into the physical origin of the localized edge states of the Li solid and cluster.

- (i) Defects, skins, and various shapes of cluster are correlated by atomic under-coordination. The interaction between the under-coordinated atoms and the electronic distribution is the origin of the unusual performance of such under-coordinated systems.
- (ii) The analyzes of the XPS spectrum of the Li(110) skin has resulted in the determination of the BE of an isolated atom as 50.673 eV and its bulk shift as

4.233 eV.

- (iii) A reproduction of the photoelectron spectroscopic measurements and DFT calculations leads to the following observations: local bond strain ε up to 26.09%, BE density E_d increase by 235.05%, atomic cohesive energy E_c drops to 25.66%, skin-to-volume ratio up to 83.69% for under-coordinated Li atoms.

With the BOLS–DFT strategy, one is able to gain quantitative information on the local bond length and energy, charge distribution in various bands, BE density, and atomic cohesive energy, which form the key to mediating the macroscopic properties of a substance at the atomic scale in a way of bond-by-bond, and electron-by-electron engineering.

Acknowledgment

We acknowledge the financial support from NSF (Nos. 11172254 and 11402086).

Figure and Table captions:

Fig. 1 Geometrically optimized (a) $C_{2v}14$, $C_{2v}19$, $D_{2h} 24$, $C_{2v}25$, C_s26 , C_134 , C_s35 , $D_{3h}38$ and C_157 (b)FCC 13, $I_{oh}13$, FCC 55 and $I_{oh} 55$ structures of Li_N nanoclusters[38].

Fig. 2 Decomposed XPS spectra of the Li(110)[26] skin probed with different incident beam energies with three Gaussian components representing the bulk B and the second S_2 and the top S_1 sublayer of the skin. Peak intensity I_1/I_2 ratio difference evidences that high energy x-ray collect's more information from the bulk component. **Table 1** shows the derived information.

Fig. 3 (a) Cluster size-induced quantum entrapment of Li_N clusters. (b) BE shift of size-selected free Li_N clusters versus $N^{-1/3}$. The related derived information is listed in **Table 3**.

Fig. 4 DFT derived DOS of FCC and Oh structures (a) Li_{13} and (b) Li_{55} clusters.

Fig. 5 Atom number N resolved (a) local bond strain ε_z and atomic cohesive energy δE_c , (b) skin-to-volume ratio γ_{ratio} and BE density δE_d . The related derived information is listed in **Table 3**.

Table 1 The effective CN(z), relative core-level shifts ($\Delta E_{1s}(z) = E_{1s}(z) - E_{1s}(12)$), in various registries of the Li(110) skin [26].

	i	$E_{1s}(z)$	z	$\Delta E_{1s}(z)$
Li(110)	Atom	50.673	0	---
	B	54.906	12	0
	S ₂	55.205	5.83	0.299
	S ₁	55.520	3.95	0.614

Table 2 The local bond strain $\varepsilon_z = C_z - 1$, skin-to-volume ratio γ_{ratio} , BE and relative core-level shifts $\Delta E'_{1s}(z)$ from various registries of Li_N nanoclusters.

N	$E_{1s}(N)$	$\Delta E_{1s}(N)$	ε_z (%)	γ_{ratio} (%)
Oh13	47.652	1.235	22.59	89.85
FCC13	47.713	1.296	23.44	88.86
Oh55	47.571	1.154	21.44	56.39
FCC55	47.620	1.203	22.14	55.88
Bulk	46.417	0	1	0

Table 3 The average effective CN(z), local bond strain ε_z , BE density δE_d , atomic cohesive energy δE_c , skin-to-volume ratio γ_{ratio} , and relative core-level shifts $\Delta E'_{1s}(z)$ from various registries of Li_N nanoclusters.

N	$E_{1s}(N)$	$\Delta E_{1s}(N)$	z	$-\varepsilon_z$ (%)	δE_d (%)	δE_c (%)	γ_{ratio} (%)
14	47.911	1.494	2.28	26.09	235.05	25.66	83.69
19	47.759	1.342	2.43	24.07	200.88	26.72	77.65
24	47.691	1.274	2.52	23.13	186.46	27.28	72.72
25	47.666	1.249	2.55	22.78	181.30	27.49	72.07
26	47.659	1.242	2.56	22.69	179.86	27.56	71.22
34	47.616	1.199	2.61	22.07	171.17	27.95	65.64
35	47.551	1.134	2.71	21.13	158.42	28.61	65.80
38	47.534	1.117	2.73	20.88	155.17	28.79	64.22
57	47.362	0.945	3.03	18.26	123.97	30.94	57.96
Bulk	46.417	0	12	0	0	100	0

References

- [1] R.E. Benfield, Faraday Transactions 88 (1992) 1107.
- [2] H.-G. Fritsche, R. Benfield, Z Phys D - Atoms, Molecules and Clusters 26 (1993) 15.
- [3] E.V. Carino, H.Y. Kim, G. Henkelman, R.M. Crooks, J. Am. Chem. Soc. 134 (2012) 4153.
- [4] Y. Wu, D. Wang, X. Chen, G. Zhou, R. Yu, Y. Li, J. Am. Chem. Soc. 135 (2013) 12220.
- [5] M. Jamet, W. Wernsdorfer, C. Thirion, V. Dupuis, P. Mélinon, A. Pérez, D. Mailly, Phys. Rev. B 69 (2004) 024401.
- [6] B. Lee, R.E. Rudd, Phys. Rev. B 75 (2007) 041305.
- [7] Z. Li, X. Peng, J. Am. Chem. Soc. 133 (2011) 6578.
- [8] R. Narayanan, M.A. El-Sayed, Nano Letters 4 (2004) 1343.
- [9] A.S. Barnard, X.M. Lin, L.A. Curtiss, J. Phys. Chem. B 109 (2005) 24465.
- [10] S. Mostafa, F. Behafarid, J.R. Croy, L.K. Ono, L. Li, J.C. Yang, A.I. Frenkel, B.R. Cuenya, J. Am. Chem. Soc. 132 (2010) 15714.
- [11] R. Agrawal, H.D. Espinosa, Nano Lett 11 (2011) 786.
- [12] I.V. Yudanov, A. Genest, S. Schauermaun, H.J. Freund, N. Rosch, Nano Lett 12 (2012) 2134.
- [13] J. Akola, M. Manninen, H. Häkkinen, U. Landman, X. Li, L.-S. Wang, Phys. Rev. B 62 (2000) 13216.
- [14] I.V. Yudanov, R. Sahnoun, K.M. Neyman, N. Rösch, J. Hoffmann, S. Schauermaun, V. Johánek, H. Unterhalt, G. Rupprechter, J. Libuda, H.-J. Freund, J. Phys. Chem. B 107 (2003) 255.
- [15] D. Alloyeau, C. Ricolleau, C. Mottet, T. Oikawa, C. Langlois, Y. Le Bouar, N. Braidly, A. Loiseau, Nature materials 8 (2009) 940.
- [16] I.M.L. Billas, A. Châtelain, W.A. de Heer, Science 265 (1994) 1682.
- [17] A.A. Herzing, C.J. Kiely, A.F. Carley, P. Landon, G.J. Hutchings, Science 321 (2008) 1331.
- [18] S. Hamed, Y. Chung-Kai, F.L.G. Johannes, B. Andre, S. Urs, J.F. Paddy, K. Fred van, J. Micromech. Microeng. 20 (2010) 064012.
- [19] E.M. Ronald, B.S. Vijay, Nanotechnology 11 (2000) 139.
- [20] D. Kong, G. Wang, Y. Pan, S. Hu, J. Hou, H. Pan, J. Zhu, J. Phys. Chem. C 115 (2011) 6715.
- [21] V. Komanicky, H. Iddir, K.-C. Chang, A. Menzel, G. Karapetrov, D. Hennessy, P. Zapol, H. You, J. Am. Chem. Soc. 131 (2009) 5732.
- [22] V.G. Grigoryan, M. Springborg, Physical Review B 70 (2004) 205415.
- [23] J.P. Chou, H.Y.T. Chen, C.R. Hsing, C.M. Chang, C. Cheng, C.M. Wei, Phys. Rev. B 80 (2009) 165412.
- [24] D.M. Riffe, G.K. Wertheim, Phys. Rev. B 61 (2000) 2302.
- [25] G. Wertheim, D. Riffe, P. Citrin, Phys. Rev. B 45 (1992) 8703.
- [26] G. Wertheim, D. Riffe, N. Smith, P. Citrin, Phys. Rev. B 46 (1992) 1955.
- [27] A.N. Alexandrova, A.I. Boldyrev, X. Li, H.W. Sarkas, J.H. Hendricks, S.T. Arnold, K.H. Bowen, J. Chem. Phys. 134 (2011) 044322.
- [28] P. Fuentealba, A. Savin, J. Phys. Chem. A 105 (2001) 11531.
- [29] C.Q. Sun, Relaxation of the Chemical Bond, Springer, 2014
- [30] M.A. Omar, Elementary solid state physics: principles and applications, Addison-Wesley, 1993.
- [31] L. Pauling, J. Am. Chem. Soc. 69 (1947) 542.

- [32] V.M. Goldschmidt, *Berichte Der Deutschen Chemischen Gesellschaft* 60 (1927) 1263.
- [33] J.P. Perdew, W. Yue, *Physical Review B* 33 (1986) 8800.
- [34] M. Bo, Y. Wang, Y. Huang, W. Zhou, C. Li, C.Q. Sun, *J. Mater. Chem. C* 2 (2014) 6090.
- [35] M. Schmidt, R. Kusche, W. Kronmüller, B. von Issendorff, H. Haberland, *Phys. Rev. Lett.* 79 (1997) 99.
- [36] V. Kumar, Y. Kawazoe, *Phys. Rev. B* 77 (2008) 205418.
- [37] H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser, B.R. Cuenya, *J. Am. Chem. Soc.* 136 (2014) 16473.
- [38] J.P.K. Doye, *Comp. Mater. Sci.* 35 (2006) 227.

*Graphical Abstract