Formation and Stability of Low-Dimensional Structures for Group VIIIIB and IB Transition Metals: The Role of $s^d^4$ Hybridization

Jianhui Yang, Qiuju Zhang, Liang Chen,* Gang Wang,* and Xiaolong Chen*

Since the discovery of beautiful low-dimensional carbon nanostructures, such as fullerene,[1] carbon nanotubes and graphene,[2,3] tremendous efforts have been devoted to exploring similar nanostuctures for transition metals (TMs) and exploiting their potential applications in electronic devices and selective catalysis.[4–10] To date, various carbon-like low-dimensional TM, particularly in Group VIIIIB and IB, nanostructures have been successfully realized. For example, Huang et al. proved the existence of Au nanocages with similar structures as fullerenes as shown by photoelectron absorption experiments and first principles calculations.[11] For the 1D case, Ugarte et al. observed the formation of the smallest Ag nanotube with a square cross-section during the elongation of Ag nanocontacts.[12,13] Kondo et al. prepared helical Pt and Au nanowires and nanotubes with an electron beam thinning technique.[14,15] These 1D TM small size nanostructures preferentially adopt hollow or multiwalled structures, which are exactly the analogue of carbon nanotubes. For the 2D case, Li et al. successfully fabricated organic ligand-supported Rh nanosheets by a facile solvothermal method.[4] Another example is the template-synthesized folding Pd$_{11}$ nanosheet through the treatment of a ladder polysilane.[5] In both examples, the planar single-layer structures were stabilized by the TM–ligand interactions.

Among the TMs, Au has received particularly intensive attention. A variety of stable Au nanocages, nanowires, and nanotubes have been successfully fabricated.[6,14,16–18] Correspondingly, many mechanistic studies have been conducted and unraveled the structural evolution of small Au nanoclusters with size. Essentially, these studies attempted to ascertain the difference of Au from other TMs (i.e., the uniqueness of Au usually associated with the scalar-relativistic effect) and explained why Au can form these carbon-like structures.[19–22] However, as mentioned above, many other TMs can also form the carbon-like structures, but with lower stability. We believe that there should exist some generic mechanism for the formation and stability of TM low-dimensional nanostructures, which is still far unclear.

Indeed, the fundamental mechanism is critical for understanding the properties and exploring the applications of TM nanostructures. In particular, the surface electron state, which directly determines the physical and chemical properties of TM nanostructures, would be easily unraveled on the basis of the formation mechanism. In the present study, we revealed the dimensionality-driven hybridization of $s$ and $d$ electron orbitals in the face-centered cubic (FCC) TMs including six group VIIIIB (Co, Ni, Rh, Pd, Ir, and Pt) and three group IB (Cu, Ag, and Au) elements. Note that Co can exist in both FCC and hexagonal close-packed (HCP) phases, and the energy difference between them is smaller than 0.03 eV atom$^{-1}$.[23] Various 0D, 1D, and 2D Au nanostructures were considered and compared in this study (see Figure S1, Supporting Information). A new quasi-$s^d^4$ hybridization state involving s-orbital and four d orbitals in a low dimension was identified, in contrast to the $s^5$ hybridization state involving all s and d orbitals in bulk. We proposed a control parameter to evaluate the stability of the quasi-$s^d^4$ hybridization state for all FCC metals, and the stability of their low-dimensional nanostructures. Au low-dimensional nanostructures are found to possess the highest stability due to the number of valence electrons and scalar-relativistic effect. Using the 1D Au nanostructures as an example, we demonstrated how the hybridization states determine the structure—particularly the low-dimensional nanostructures and physicochemical properties.

Let us start from the analysis on Au, which is the most representative TM with carbon-like nanocages, nanowires, and nanotubes. We have investigated over 70 different low-dimensional Au nanostructures (see Figure S1, Supporting Information). Apparently, the similarity of Au and carbon nanostructures implies that the electronic structures of both elements share some similar features. For carbon, the major difference in electronic structures for 2D (graphene) and 3D (diamond) structures is whether the $2p_z$ orbitals are hybridized with $2s$, $2p_x$, and $2p_y$ orbitals (i.e., yielding the sp$^2$ and sp$^3$ hybridization states, respectively). In light of this distinction, we also compared the electronic structures of 2D layer and 3D FCC bulk for Au. It is known that the 5d and 6s orbitals are hybridized when Au–Au bonds are formed. As shown in Figure 1, all 5d and 6s
orbitals are resonant across a wide energy range (~7 to 0 eV) in the perfect FCC Au structure. In contrast, the d_{z^2} orbitals in the perfect 2D structure (i.e., a single Au(111) layer), termed as L_1 hereafter, are quite localized across a narrow energy range (~3.5 to ~1.7 eV) and have smaller energy resonant ranges with 6s and other 5d orbitals. Moreover, electrons assemble into the d_{z^2} orbital from the xy-plane, as shown in the right panel of Figure 1. Here, the d_{z^2} orbitals refer to the orbitals along the surface normal. This suggests that d_{z^2} orbitals have a rather small contribution to the Au–Au bond in L_1. Herein, we refer this type of hybridization state in L_1 to quasi-sd^4, and refer the hybridization state in perfect 3D FCC structure to sd^5. For the quasi-sd^4 hybridization, the d_{z^2} orbital is quite localized with narrow energy range and the d_{xy} and d_{xz} orbitals involving the z-direction components are also localized with slightly wider energy range. For the sd^5 hybridization, d_{z^2}, d_{xy}, and d_{xz} orbitals have similar energy resonance range and shape. Apparently, in an Au entity, only the under-coordinated surface atoms can adopt the quasi-sd^4 hybridization state, while the saturated inner atoms still prefer sd^5. Thus, L_1 and the derived structures (e.g., hollow cages and nanotubes) are extreme cases for the quasi-sd^4 hybridization state because all atoms are under-coordinated surface atoms.

Perfect quasi-sd^4 hybridization only exists in the case of L_1. Bending the sheet or introducing extra Au–Au bonds would force the d_{z^2} orbitals to participate in hybridization and destroy the perfect quasi-sd^4 hybridization.[24] To illustrate such variations of d_{z^2} orbitals, projected density of states (PDOS) of L_1 and Au nanotube T(7,3) with a curved surface is displayed in Figure 1. For L_1, the d_{z^2} orbitals are fully filled and located far away from the Fermi level. The d_{z^2} orbitals are weakly polarized as L_1 is rolled into T(7,3) with some higher energy antibonding states in the range of ~2 to ~1.5 eV. In the meantime, the energy of d_{xy} and d_{z^2} orbitals in the xy-plane shifts up, and the density of low energy states between ~7 and ~6 eV decreases. Overall, the quasi-sd^4 hybridization is weakened, and cohesive energy (E_c) is decreased. Therefore, E_c of L_1 (2.88 eV atom^{-1}) is the upper bound for these hollow 0D cages, 1D tubes, and 2D layer—all of which are derived from the planar L_1 sheet. As shown in Figure S2 of the Supporting Information, the E_c of cages are generally smaller than that of tubes with a similar radius because 0D cage structures are more distorted than 1D tube structures.

In fact, similar hybridization states also exist in other eight TMs (Figure S3, Supporting Information). To evaluate the stability of quasi-sd^4 hybridization states for different TMs, we defined a control parameter R_c that is the ratio of E_c for L_1 to FCC bulk. Clearly, higher R_c value indicates higher stability of the quasi-sd^4 hybridization state and thus higher stability of the associated low-dimensional structures. Figure 2 shows that this parameter correlates to the number of valence electrons (N_{ve}), which increases when N_{ve} increases from 9 to 11. In principle, the E_c of the bulk decreases as N_{ve} increases due to the fewer unfilled orbitals. In this study, we show that the E_c of L_1 also obeys this rule. As shown in Figure 1, the main difference between the PDOS of L_1 and FCC bulk is the localization of d_{z^2} states. The average energy of the d_{z^2} states is higher than that of s and other four d states. As a result, L_1 has lower E_c than the FCC bulk, which leads to R_c values below 1. As the N_{ve} increases, the nucleus holds electrons more firmly. The

![Figure 1.](image1.png) **Figure 1.** (Left panel): PDOS of L_1, bulk Au, and T(7,3). Fermi level was shifted to zero. (Right panel): Charge difference of FCC bulk Au and L_1. The green and red colors stand for gain and loss of electrons in the formation of Au–Au bonds, respectively.

![Figure 2.](image2.png) **Figure 2.** The calculated E_c (unit: eV) of L_1 (upper left), FCC bulk (upper right), and R_c (lower right) for different TMs.
tendency to fill electrons in the low-energy s and d states would be stronger in L$_1$. In turn, $R_C$ increases.

On the other hand, for the TMs of same group, 5d TMs generally have a higher $R_C$ than 3d and 4d TMs due to the scalar-relativistic effect. If the scalar-relativistic effect was excluded, the $R_C$ of the TMs of same group would be very close (Figure S4, Supporting Information). Particularly, Cu, Ag, and Au have virtually identical $R_C$ in the nonscalar-relativistic calculations. The contraction of s orbitals caused by the scalar-relativistic effect shortens the bond lengths in both the L$_1$ and FCC bulk (Figure S5, Supporting Information). This enhances $E_c$.[19] The bond lengths in L$_1$ are shortened more significantly than FCC bulk. However, the contraction of s orbitals also increases the shielding effect of d electrons and increases the energy level. As a result, the d orbital expanding reduces $E_c$. In L$_1$, the d$_{2}$2 orbitals are mainly distributed along the z-axis and far away from s orbitals (mainly in xy-plane). This reduces the shielding effect between the s and d orbitals. Therefore, the increased energy level (i.e., weakened $E_c$) caused by the scalar-relativistic effect is less significant for L$_1$ than bulk. Accordingly, a higher $R_C$ is seen for 5d TMs.

Overall, both factors ($N_{\text{v}}$ and scalar-relativistic effect) give rise to the highest $R_C$ for Au among the studied TMs. Indeed, Au prefers planar structures more than Pt and Ag, the critical number for 2D-to-3D transition (i.e., from planar belts to clusters) being 7,[19] 10,[25] and 14[26] for Ag, Pt, and Au, respectively. This is quite consistent with the order of $R_C$. Note that the planar belt is cut from L$_1$ along one specific direction and has dangling bonds on the edges. Moreover, for Au itself, anionic nanoclusters with extra valence electrons have more preferable 2D planar structures than cationic nanoclusters.[27]

Now let us look again at carbon. Carbon has a large $R_C$ (>1) because the sp$^2$ carbon structures are more stable than the sp$^3$ carbon structures in terms of thermodynamics. However, both of them can stably exist because of the high energy barrier for the sp$^2$–sp$^3$ hybridization transition. Unlike carbon, Au and other TMs have lower $R_C$ values (less than 1). There is no energy barrier for the quasi-sd$^4$ to sd$^3$ transition. As a result, the above quasi-sd$^4$ hybridized Au structures are not stable enough and thus they can only exist in small scales or low-dimensions in which the under-coordinated surface atoms are dominant. At some threshold size, they will spontaneously transform to the sd$^3$ hybridized structures. Indeed, the experimentally prepared TM nanosheets must be stabilized by protecting ligands to avoid converging to sd$^3$ hybridized structures.[3,4] This implies that some size-dependant structural evolution may occur.

We are aware that many theoretical and experimental studies have already been conducted for Au nanoclusters and concluded that Au nanoclusters undergo evolution with respect to size: the most stable structure of Au$_n$ clusters is planar for n < 14,[22] cage for 16 ≤ n ≤ 20,[11,16] and filled structures for n > 20.[21] In the present work, we placed our attention on the 1D Au nanostructures. We defined the atomic linear density ($\rho_1$), which is the number of Au atoms in a unit length to represent the “size” of 1D structures. Interestingly, we found that the evolution of 1D Au nanostructures with size have similar behavior to the nanoclusters. As shown in Figure 3, planar belts are the most stable structures for $\rho_1$ < 2.41 Å$^{-1}$ [corresponding to $\rho_1$ of T(6,1)], while hollow tubes become the most stable for 2.41 Å$^{-1}$ < $\rho_1$ < 4.43 Å$^{-1}$ [corresponding to $\rho_1$ of T(12,6)].

Compared to L$_4$, the belts have lower $E_c$ because of dangling bonds on the edge. Rolling belts into tubes can eliminate the dangling bonds, while the curvature would incur energy penalty and decreases $E_c$. Thus, planar belt structures are preferred for small $\rho_1$. On the contrary, tube structures are preferred for large $\rho_1$ because the energy penalty from curvature is relatively small. Actually, the same trend is also applicable for the variation of 0D structures from a planar island to cages. When $\rho_1$ is larger than 4.43 Å$^{-1}$, the filled structures with inner Au atoms become the most stable because the inner atoms are usually saturated, and their valence electrons adopt the more stable sd$^3$ hybridization. Correspondingly, the $E_c$ of these filled structures exceed the upper bound for hollow tube structures.

For a TM structure, the inner atoms prefer the most stable and close-packed crystalline structures, while surface atoms adopt the second stable quasi-sd$^4$ hybridization and prefer the

---

**Figure 3.** The structural evolution of 1D Au nanostructures. The structures of each Au entities are shown in Figure S1 of the Supporting Information.
smooth and densest-packed arrangement. This has the lowest surface energy. The different and competitive tendencies of surface and inner atoms determine the final structures.\[18\] Apparently, if the number of surface atoms is dominant, the most stable inner close-packed structures would be sacrificed. As a result, spherical nanoclusters and cylindrical nanowires would be formed in the 0D and 1D cases, respectively. This is confirmed by geometric optimization of the nanowires truncated from bulk FCC TMs. We found that these truncated nanowires have smaller $\rho_n$ than belts and tubes in a small $\rho_C$. In particular, FCC110–4R, FCC110–6R, and FCC100–3R ($nR$ represents the number of atomic rows) are not stable and would transform to hollow tubes upon structural optimization as shown in Figure S6 of the Supporting Information. For example, the (100) face of FCC100–3R is reconstructed to the (111) facet accompanied with a disappearance of the inner Au–Au bonds. Correspondingly, the original FCC100–3R structure would eventually evolve to a hollow T(6,3) nanotube. In fact, these FCC100 Au nanowires are unstable due to their high surface activity, while FCC110 nanowires are much more stable.

On the contrary, the inner close-packed structures are preferred, and the smooth surface is destroyed if the number of surface atoms is sufficiently small. Experimentally, the HCP phase has been observed in Au nanoparticles.\[29\] As such, we designed a new three-shelled Au 1D nanostructure, which has a HCP interior core wrapped by a curved FCC-(111) shell. Note that the HCP arrangement can form a high-symmetry 1D structures and can be wrapped by a smooth surface—the FCC arrangement cannot. Hereafter, we will refer to this structure as shown in the inset of Figure 3 as IHCP-3s. Interestingly, we found that IHCP-3s is the most stable one among the structures with similar $\rho_L$ values (see Figure S7, Supporting Information), even including the experimentally synthesized nanowires.\[14\] Therefore, we expect that such structures can be experimentally prepared. Some recent experimental progresses are supportive and inspiring. For example, Kondo and Takayangi have prepared the helical Au nanowires by electron beam thinning technique.\[14\] Ugarte and co-workers obtained Ag nanotubes during the elongation of Ag nanocontacts.\[13\] Considering the higher energetics than that of these metastable structures, we propose that the IHCP-3s Au structure can be achieved by thinning Au wires down to a diameter of around 1.5 nm in vacuum or noble gas protection, followed by a thermal annealing. The vacuum or noble gas protection is necessary because the adsorption of other molecules may induce undesired surface reconstruction. Furthermore, it should be pointed out that the stability of the IHCP-3s Au structures is closely determined by the stability of quasi-s$d^4$ state and the resulting $R_C$ values. For example, Ag and Cu do not have stable IHCP-3s structures due to their smaller $R_C$.

In addition to the thermal stability, we next evaluated the surface stability of IHCP-3s versus FCC110–3s’, Au$_{38}$, and Au (111) surfaces using the adsorption of various chemicals as a probe. The calculations (see Figure 4) indicate that the order of surface activity is as follows: Au$_{38}$ > FCC110–3s’ > IHCP-3s = Au (111). The surface activity of IHCP-3s is quite low and comparable to that of Au(111). Particularly, O$_2$ and C$_2$H$_4$ can only be physisorbed on IHCP-3s, but can be chemisorbed on Au$_{38}$ and FCC110–3s’. Furthermore, the dissociation barrier of O$_2$ on IHCP-3s is calculated to be 1.09 eV, suggesting a low probability of dissociation at ambient conditions.

The intrinsic origin of the low surface activity of IHCP-3s can be explained by the PDOS of inner (Au$^i$) and surface atoms (Au$^s$). As shown in Figure S9 of the Supporting Information, the $d_{2}$ orbitals of Au$^s$ is similar to that of L$_1$, which is mainly localized in the energy range from $-4$ to $-1$ eV and far away from the Fermi level. It indicates that the $d_{2}$ orbitals of Au$^s$ are nearly filled. According to Hammer and Norskov’s theory, Au is the most inert TM partly because of its high filling degree of $d$ bands.\[10\] In the case of 1D Au nanostructures, the $d_{2}$ orbital is the major component of $d$ bands to participate in the reaction and interaction with upcoming chemical molecules. Thus, the nearly filled feature of $d_{2}$ orbitals leads to the low surface activity of IHCP-3s. On the other hand, Au$^i$ and Au atoms in bulk share a similar feature in PDOS. Clearly, the low surface adsorption activity implies that IHCP-3s may be chemically stable after being exposed to air. This is very advantageous because applications of nanostructures are usually hindered by their high surface activity particularly when subjected to oxidation in air.

It is known that nanostructures usually have an extreme curvature on their edges, which leads to low work function due to the point effect. In contrast, IHCP-3s has a high work function (5.33 eV), which stems from the smooth surface that constitutes the quasi-s$d^4$ hybridized atoms. This value is similar to that of Au(111) (5.31 eV).\[30\] The high work function of IHCP-3s makes electrons hard to escape from the surface, which may ensure the stability of current in electronic devices. Finally, we calculated the conductance of IHCP-3s to investigate the electron transport properties. As shown in the inset of Figure 4, IHCP-3s shows notable quantum conductance around the Fermi level.
Fermi level. The conductance of IHCP-3s is 14 G_0 below the Fermi level (= −0.01 to −0.1 eV). It decreases to 6 G_0 in the range of 0.02–0.11 eV. This means that the conductance can be tuned more than twofold by changing the gate bias. For comparison, the FCC110—3s’ with similar radius—which is the most stable truncated nanowires in the FCC arrangement—has weaker quantum conductance variations (15 to 18 G_0) around the Fermi level. Combined with the high chemical and thermal stability, we anticipate that IHCP-3s may be a promising material for nanoelectronics. Indeed, we also found that a four-shelled IHCP-4s structure is energetically favorable and exhibits similar features with IHCP-3s. However, this feature would disappear when the IHCP wire becomes thicker. This is consistent with the aforementioned structural evolution.

In summary, we identified a relatively stable quasi-sd^4 hybridization state in addition to the sd^3 hybridization state for FCC TMs. The stability of quasi-sd^4 hybridization state is determined by the number of valence electrons and scalar-relativistic effect. Both factors enable Au to adopt the stable nanostructures with quasi-sd^4 hybridized states. For Au nanostructures, the surface atoms prefer smooth FCC(111)-like surface in quasi-sd^4 hybridization, while inner atoms prefer close-packed arrangements in sd^3 hybridization. Competition of these two tendencies determines the final structural arrangements of Au nanostructures. We designed a stable three-shelled IHCP structure, which could be a promising material for electronic devices owing to the high stability and large quantum conductance variations around the Fermi level.

Spin-polarized density functional theory (DFT) computations were performed using the Vienna ab initio simulation package (VASP).[^32] The PW91 exchange-correlation functional[^33] was employed with the electron–ion interactions described by the projector augmented wave (PAW) potentials[^34]. We have also comparatively applied PBE functional and found essentially consistent results. The scalar-relativistic effect and spin–orbit coupling were included for 5d TMs. Full structural optimizations were performed until the force on each atom was less than 0.02 eV Å\(^{-1}\). The density of K-points in real space was less than 0.034 × 0.034 × 0.034 Å\(^{-3}\) for all calculations, based on the Monkhorst–Pack method.[^35] The transition states for reactions were identified by using the climbing nudged elastic band method (cNEB)[^36] and further confirmed by the frequency calculations. \(E_\text{c}\) used to describe the stability of these systems was calculated as following: \(E_\text{c} = E_\text{M} - E_i/N_i\), where \(E_\text{M}\) is the energy of single atom, \(E_i\) is the total energy of systems, and \(N_i\) is the total number of atoms.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

### Acknowledgements

The authors acknowledge the helpful discussion of Prof. Hanssong Cheng, Prof. De-en Jiang, and Prof. Wei Huang. This work was financially supported by National Key Basic Research Program of China (2013CB934800), NSFC (51472255 and 51322211), NSF of Zhejiang Province (LR14E020004), and the program for Ningbo Municipal Science and Technology Innovation Research Team (2015B11002).

[^1]: H. W. Kroto, Nature 1987, 329, 529.
[^2]: S. Iijima, Nature 1991, 354, 56.
[^3]: K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 2004, 306, 666.
[^4]: H. Duan, N. Yan, R. Yu, C. R. Chang, G. Zhou, H. S. Hu, H. Rong, Z. Niu, J. Mao, H. Asakura, T. Tanaka, P. J. Dyson, J. Li, Y. Li, Nat. Commun. 2014, 5, 3093.
[^5]: Y. Sunada, R. Haige, K. Otsuka, S. Kyushin, H. Nagashima, Nat. Commun. 2013, 4, 2014.
[^6]: Y. Kurui, Y. Oshima, M. Okamoto, K. Takayanagi, Phys. Rev. B 2008, 77, 161403.
[^7]: A. S. K. Hashmi, G. J. Hutchings, Angew. Chem. Int. Ed. 2006, 45, 7896.
[^8]: J. John, E. Gravel, A. Hagege, H. Li, T. Gacoin, E. Doris, Angew. Chem. Int. Ed. 2011, 50, 7531.
[^9]: C. H. Christensen, J. K. Norskov, Science 2010, 327, 278.
[^10]: D. E. Jiang, M. Walter, Phys. Rev. B 2011, 84, 193402.
[^11]: W. Huang, S. Bulusu, X. C. Zeng, L. S. Wang, ACS Nano 2009, 3, 1225.
[^12]: P. A. S. Autredo, M. J. Lagos, F. Sato, J. Bettini, A. R. Rocha, V. Rodrigues, D. Ugarte, D. S. Galvao, Phys. Rev. Lett. 2011, 106, 4.
[^13]: M. J. Lagos, F. Sato, J. Bettini, V. Rodrigues, D. S. Galvao, D. Ugarte, Nat. Nanotechnol. 2009, 4, 149.
[^14]: Y. Kondo, K. Takayanagi, Science 2000, 289, 606.
[^15]: Y. Oshima, H. Koizumi, K. Mouri, H. Hirayama, K. Takayanagi, Y. Kondo, Phys. Rev. B 2002, 65, 121401.
[^16]: J. Li, L. Li, H. J. Zhai, L. S. Wang, Science 2003, 299, 864.
[^17]: S. Bulusu, X. Li, L. S. Wang, X. C. Zeng, Proc. Natl. Acad. Sci. USA 2006, 103, 8326.
[^18]: R. Ferrando, C. Barcaro, A. Fortunelli, Phys. Rev. Lett. 2009, 102, 216102.
[^19]: H. Hakkinen, M. Moseler, U. Landman, Phys. Rev. Lett. 2002, 89, 033401.
[^20]: L. Ferrighi, B. Hammer, G. K. H. Madsen, J. Am. Chem. Soc. 2012, 134, 11189.
[^21]: L. Ferrighi, B. Hammer, G. K. H. Madsen, J. Am. Chem. Soc. 2009, 131, 10605.
[^22]: S. B. Zhang, S. H. Wei, Phys. Rev. Lett. 2004, 92, 086102.
[^23]: A. F. Marshall, I. A. Goldthorpe, H. Ashkari, M. Koto, Y. C. Wang, L. L. Fu, E. Olsson, P. C. McIntyre, Nano Lett. 2010, 10, 3302.
[^24]: B. Hammer, J. K. Norskov, Nature 1995, 376, 238.
[^25]: H. L. Skriver, N. M. Rosengaard, Phys. Rev. B 1992, 46, 7175.
[^26]: G. Kresse, J. Furthmuller, Comput. Mater. Sci. 1996, 6, 15.
[^27]: J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, Phys. Rev. B 1992, 46, 6671.
[^28]: G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758.