

Size-dependent metal-nonmetal change of groups IB and IIB metal clusters

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Abstract. The electronic structure calculations of clusters Cu_n , Ag_n and Au_n ($n = 2-20$) of the group-IB and Zn_n , Cd_n and Hg_n ($n = 2-20$) of the group-IIB have been performed by the relativistic density functional theory (RDFT) approach. Our analysis of the calculated results has deduced that the size-dependent metal-nonmetal change of the clusters consisting of both the IB and IIB elements is of metal-Fermiglass character.

PACS. 71.30.+h Metal-insulator transition and other electronic transitions – 73.63.-b Electrical transport in nanoscale materials and structures

1 Introduction

As fundamentals of metal physics, the electronic structure and related properties of metal clusters have been widely studied [1–5]. The size-dependent metal-nonmetal change becomes of particular interests for minimizing the size of semiconductor devices in the microelectronic technique. For example, the special characters and applications of the metal-nonmetal transition in Cu_n , Ag_n and Au_n of group-IB and Zn_n , Cd_n , Hg_n of group-IIB clusters have been intensively studied both experimentally and theoretically [1, 2, 4–6]. The measurements [1], have shown that the size-induced metal-nonmetal change of these metal clusters occurs within the size range less than about 1 nm. This has been interpreted by the confinement effect and the appearance of an energy gap of the successive quantum levels about the Fermi energy E_F , for an example, by the occurrence of the Kubo gap $d = 4E_F/3n$ [6, 7]. The size-dependent metal-nonmetal change properties have also been discussed based on the conducting spherical droplet (CSD) model [5]. Nevertheless, these interpretations have not considered the role of surface-induced-localized states (SILS) [8], while the effect of these states obviously cannot be negligible due to the large specific surface area (SSA), which is defined as the surface area divided by the mass of the relevant interior phase, of the small metal clusters. Therefore, the relationship between the metal-nonmetal transition and the change of electronic-structure features of a series of different-size clusters has not been well explained yet [4]. To probe this problem we have carried out

the electronic structure calculations for the series of clusters Cu_n , Ag_n and Au_n ($n = 2-20$) of the group IB and Zn_n , Cd_n , Hg_n ($n = 2-20$) of the group-IIB by the relativistic density functional approach. Our analysis of the calculated results with the consideration of SILS has led to a new interpretation of the size-dependent metal-nonmetal change. We thus argue that for both the discussed groups of metals, the metal-nonmetal transition is of the metal-Fermiglass [9a] character, namely, the disappearance of the electric conductivity in the cluster originates from the localization of states near E_F but not from an energy gap.

2 Computational models and details

The relativistic density functional calculations have been performed using the Amsterdam Density Functional (ADF2004) program [10]. The $3d$, $4s$ of Cu and Zn, $4d$, $5s$ of Ag and Cd, and $5d$, $6s$ of Au and Hg are considered as valence shells. The STO-3 ζ basis for the valence and STO-2 ζ for the core plus polarization functions are employed and the VWN plus Becke88 and Perdew86 [11–13] are used as the exchange-correction functional. The optimal geometry structures of cluster Au_n ($n = 2-20$) reported in reference [3] are adopted as the initial geometry structures of the clusters.

3 Results and discussion

To understand the mechanism of size-dependent metal-nonmetal change of metal clusters, we have calculated the

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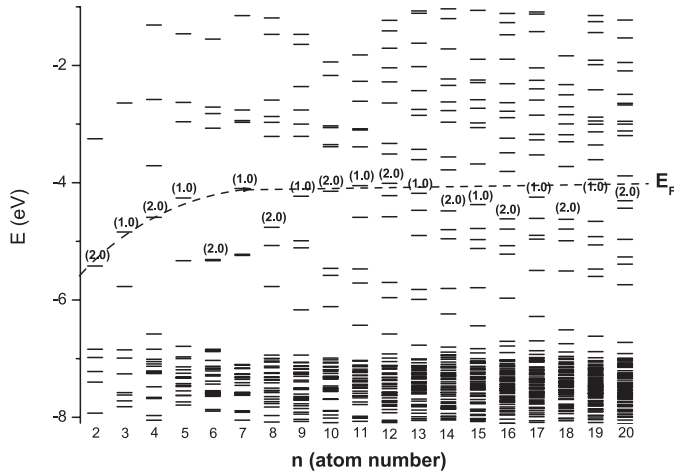


Fig. 1. Electronic structures of the clusters Ag_n ($n = 2-20$). The numbers in parenthesis are the Mulliken populations on the HOMO. E_F is the Fermi level.

optimal electronic structures of group-IB Ag_n , Cu_n and Au_n ($n = 2-20$) clusters. Each atom in these clusters contributes one outer electron to form the metallic bond. Our results show that the electronic structure characters with size of Cu_n and Au_n ($n = 2-20$) clusters are similar to that of Ag_n ($n = 2-20$) and thus as an example of group IB that of Ag_n is presented in Figure 1. It is seen that for the clusters with size about $n > 9$, part of the occupied states and part of unoccupied states form a band and the Fermi level E_F (defined as the energy with single-electron-occupation) is of almost a steady value the same as that of metal bulk, and the electrons in this band satisfy Fermi-Dirac distribution. These features are in good agreement with the Jellium model of metals [14]. As a consequence, the principle of the metal-nonmetal change with the clusters size decreasing for group IB can be interpreted as follows based on the results above, the effect of size-dependent SSA and also the density of states (DOS) of Ag clusters shown in Figure 2a.

According to the Jellium model, for the large crystalline bulk metals of the group IB, the energy band, in which the E_F lies, originates from the metallic bond and the DOS can be given as Figure 2b(1). Because the SSA for bulk material is small and negligible, all the electron states in the band are extended. With the size decreasing and SSA increasing, the SILS of the metal cluster of group IB cannot be negligible and the states in band tails appear to be localized [9b], for example for Ag_{19} cluster, the DOS shown in Figure 2a ($n = 19$) show that the DOS near E_F is larger due to the overlap of occupied and unoccupied energy levels, the states near E_F are still remain extended and this case can be sketched as Figure 2b(2). Such cluster-material is still conductive. In case of the clusters with sufficiently large SSA (greater than some critical value), such as the DOS of Figure 2a for Ag_3 , the DOS near E_F is small and all the states in the band become localized, which can be sketched by Figure 2b(3). The cluster is a nonmetal with Fermiglass [9a] character. Therefore, the size-dependent metal-nonmetal change for

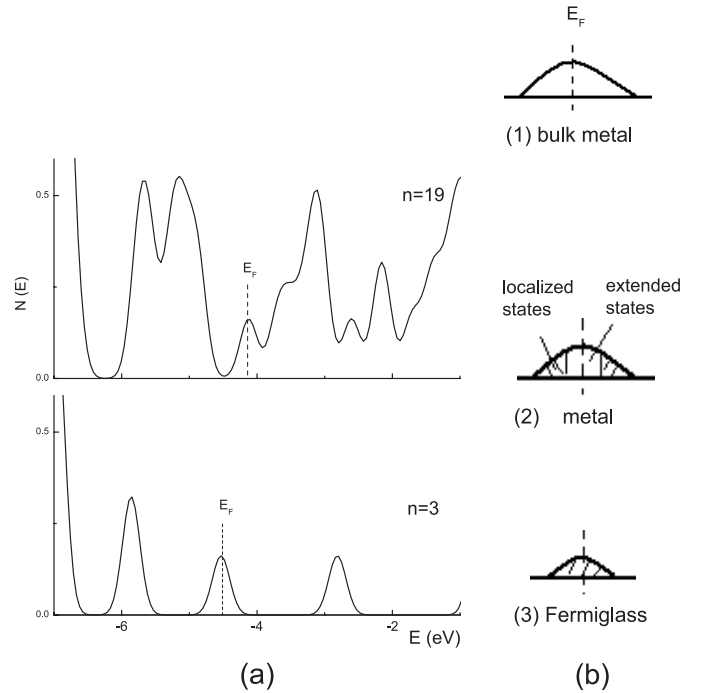


Fig. 2. (a) DOS of clusters Ag_n ($n = 19, 3$); (b) schematic illustration of metal-Fermiglass transition.

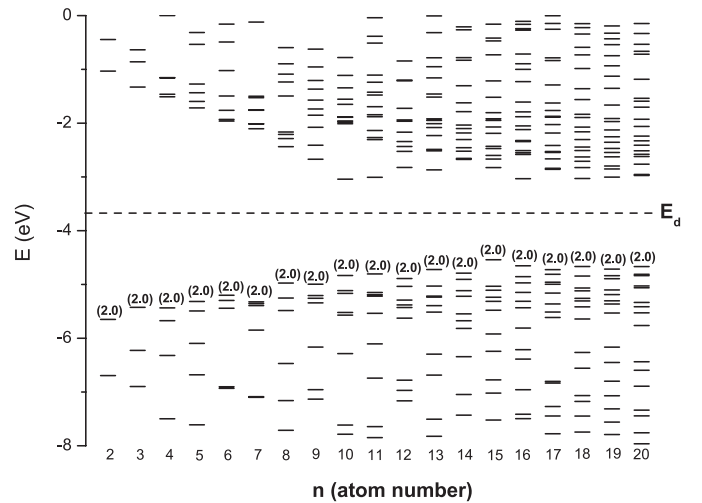


Fig. 3. Electronic structures of the clusters Zn_n ($n = 2-20$). The number in parenthesis are the Mulliken populations on the HOMO. E_d is about the center level between the HOMO and LUMO.

IB group clusters is of the metal-Fermiglass character instead of the metal-insulator with appearance of an energy gap.

To investigate the origin of size-dependent metal-nonmetal change of the metal clusters of group IIB elements, we have carried on the electronic structure calculations of the clusters Zn_n , Cd_n and Hg_n ($n = 2-20$). For discussion the DOS of cluster Zn_{47} is calculated too. The results indicate that their electronic structures are very similar, and thus we present only the result of Zn_n as an example of group IIB clusters in Figure 3. Obviously, two

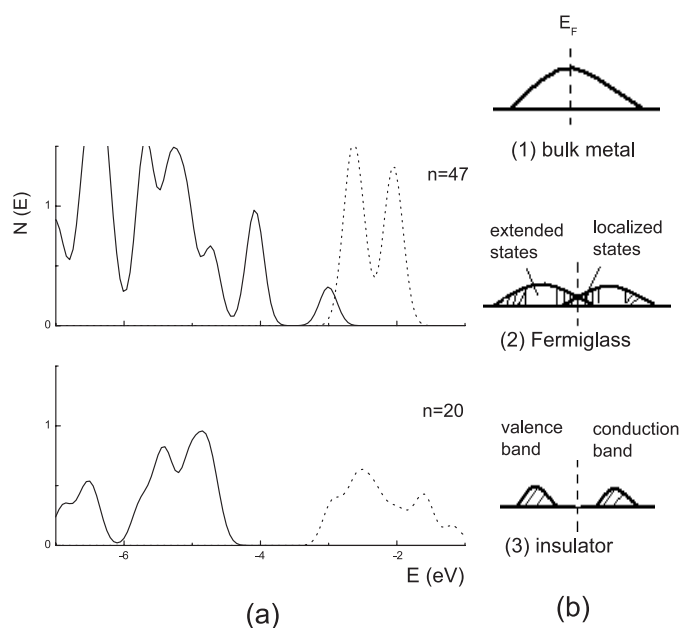


Fig. 4. (a) DOS of clusters Zn_n ($n = 47, 20$), the solid and the dot lines represent the occupied states and unoccupied states density, respectively; (b) schematic illustration of metal-Fermi-glass-insulator transition.

bands form, the fully occupied lower band and the vacant upper band, which is different from that of group IB due to the different electron configuration. This is consistent with Pauling's chemical-bond theory of metals, as the consequence of forming chemical bonds, two bands appear with the lower band as the valence band of full-occupied bonding states and the upper band as the conduction band of unoccupied antibonding states. The Fermi level E_F lies in about the middle between the highest occupied orbitals (HOMO) and the lowest unoccupied orbitals (LUMO).

The above results may lead to the following interpretation of the metal-nonmetal change with cluster size decreasing for group IIB. The ideal infinite metal cluster is a good conducting material because the valence and conduction band cross and all states are extended as sketched in Figure 4b(1). For the finite metal cluster, the band tail-states become localized due to the presence of efficient SSA related surface states and/or some disorders [9b]. With the size decreasing, the valence and conduction band become dividable and the number of localized part of states increases with the SSA increasing. For a sufficiently small cluster, such as Zn_{47} , the DOS presented in Figure 4a ($n = 47$) show that there are still band cross, but the band-crossing states near E_F are localized due to the sufficiently large SSA and disorders. Such cluster is

non-metal with the Fermi-glass character and can be sketched as Figure 4b(2). As the size further decreases, the localized states divided into two bands, such as the DOS of Zn_{20} shown in Figure 4a ($n = 20$), and the nonmetal cluster is of insulating character, which can be sketched as Figure 4b(3).

4 Concluding remarks

Physical origins of size-dependent metal-nonmetal change of group IB and IIB metal clusters are investigated using RDFT approach. Based on the analysis of the electronic structures and the DOS of the group IB clusters and the IIB clusters, we proposed two kinds of models for the two group metal clusters respectively and conclude that the size-dependent metal-nonmetal change for both IB and IIB groups of metals is of metal-Fermi-glass character.

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