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Nonmetal–metal transition in Ba_n clusters

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Abstract

Understanding the development of metallic behavior with increasing cluster size has been one of the important questions in cluster science. Based on Kubo's criterion and optimized structures with ab initio calculations, the nonmetal to metal transition in Ba clusters is studied. It has been found that the critical size for this transition is around 32, in agreement with the mass spectra experiment. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

The study of nonmetal to metal transitions has a very long history extending for several decades [1]. In recent years, a lot of new attention has also been devoted to this field due to the rapid development of surface science and cluster science. Rich behaviors have been found for the nonmetal–metal transition, which can be induced by pressure (as in bulk), by thickness (as in thin film), and by size (as in cluster). In this sense, divalent metal (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg) are specially interesting systems. Because of the closed shell ns^2 electronic configuration of their atoms, their dimers are weakly bonded. As the parameters (pressure, thickness, or size) change, the ns states hybridize with the unoccupied states which leads to the metallization, exhibiting nonmetal–metal transition. Therefore, many studies have been devoted to the divalent system. For example, the nonmetal to metal transitions in Be cluster [2,3] and Mg cluster [3–5] and Hg cluster [6–9]; the nonmetal to metal transitions in alkaline earth monolayers (Be, Mg, Ca, Sr, Ba) [10], in bulk Ba [11] and bulk Hg [5].

Atomic clusters constitute an intermediate phase between atom and bulk phases, which can be used to understand how physical properties and structures evolve from atom to molecule to cluster to ultrafine particle, and in the end to the bulk phase. In a metal cluster, there will be a transition from nonmetallic to metallic behavior with increasing cluster size. What we are interested in this paper is the nonmetal to metal transition in Ba cluster, which is motivated by two points: first, the nonmetal to metal transitions in bulk Ba [11] and monolayer Ba [10] have been studied recently. How about the nonmetal to metal transition in Ba cluster? Second, it has been found that the magic numbers in Ba clusters are 13, 19, 23, 26, 29, and 32 [12]; which magic cluster is in the metallic state in the room temperature?

2. Method

Small cluster has a discrete distribution of electronic state, it can be considered nonmetallic, and a critical size N_c is needed before this distribution turns into a quasi-continuous one in the region around the Fermi level. According to Kubo's criterion [13] a cluster that has metallic character when the average level spacing becomes smaller than the thermal energy k_BT and the discrete energy levels begins to form a quasi-continuous band, or formulated in terms of the density of states (DOS) $D(E)$, when $D(E)$ at the Fermi level(E_F) exceeds $1/k_BT$

$$D(E_F) \geq 1/k_BT \tag{1}$$

Although the Kubo's criterion is in principle simple to apply, there are many materials for which the critical cluster size is still unknown, mainly duo to the absence of calculations of $D(E_F)$ and the lack of a precise knowledge of the

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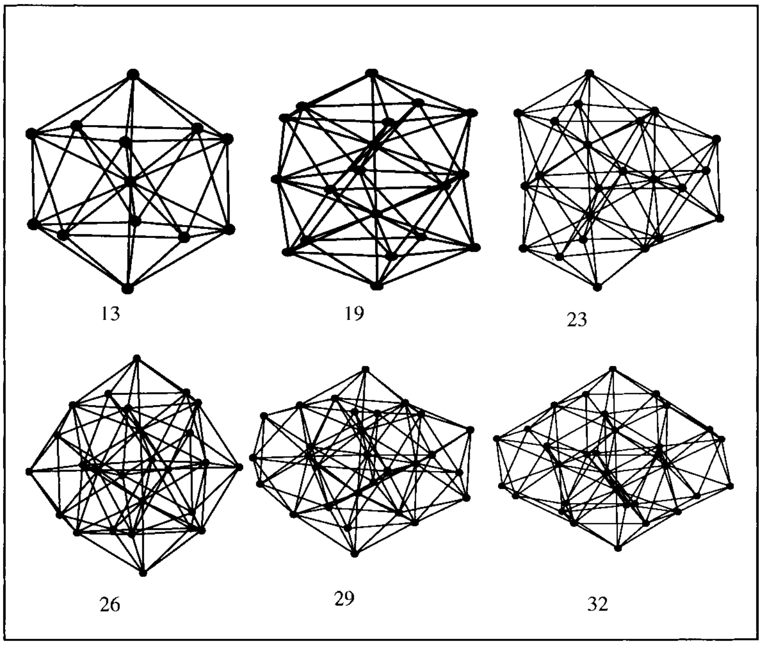

Fig. 1. Optimized structures for magic Ba_n clusters with $n = 13, 19, 23, 26, 29$, and 32.

cluster geometry. Recently, Kubo's criterion has been successfully applied to study the of nonmetal–metal transition for Ni [14], Co [15], Rh and Ru [16] clusters by using a self-consistent tight-binding method and a Hubbard tight-binding Hamiltonian to calculate the density of states.

For magic Ba_n clusters with $n = 13, 19, 23, 26, 29$, and 32 atoms, the equilibrium structures are found to be icosahedral or polyicosahedral structures in our previous study [17]. The center(s) of the icosahedral form(s) monomer, dimer, equilateral triangle, a tetrahedron, a trigonal bipyramid and so on, as shown in Fig. 1. Based on these optimized structures, the energy eigenvalues of Kohn–Sham equation are calculated by using ab initio ultrasoft pseudopotential scheme with plane-wave basis (Vienna Ab initio Simulation Program (VASP)) [18–20], in which the finite-temperature local-density functional theory developed by Mermin [21] is used, and variational quantity is the electronic free energy. Finite-temperature leads to the broadening of the one-electron levels that is very helpful to improve the convergence of Brillouin-zone integrations. The electron–ion interaction is described by a fully nonlocal optimized ultrasoft pseudopotential [22]. The minimization of the free energy over the degrees of freedom of electron densities and atomic positions is performed using the conjugate-gradient iterative minimization technique [23]. The edge length chosen for the super cubic cell is 33 Å. In such a big supercell only the Γ point can be used to represent the Brillouin zone. The exchange-correlation energy of valence electrons adopts the form of Ceperly and Alder [24] as parameterized by Perdew and Zunger [25]. To get the electronic density of states from the Kohn–Sham energy eigenvalues, Gaussian expansion scheme is used with the width of 0.05 eV.

3. Results and discussions

In Fig. 2, the density of states $D(E)$ were constructed for magic Ba_n clusters corresponding to the geometries in Fig. 1. The Fermi level is shifted to 0 and denoted by the doted lines. According to Kubo's criterion, the cluster with $D(E_f)$ larger than $1/k_BT$ is metallic. The nonmetal to metal transition depends on three factors: geometric structure, cluster size, and temperature. For magic Ba_n clusters with icosahedral or polyicosahedral geometry, clearly, the metallic behavior is controlled by cluster size and temperature. Fig. 3 presents the main result of this paper, which is the phase diagram for the nonmetal–metal transition, where the circles are the results obtained from the Kubo's criterion, and the continuous line corresponds to the least square fitting for aiding the eye, which describes an average behavior from nonmetallic to metallic regime in the direction of increasing cluster size. We can see from the changes of transition temperature with cluster size, that at vicinity of the room temperature, Ba_{32} is already in the transition region from nonmetal to metal, which corresponds the high DOS at the Fermi level as shown in Fig. 2. This is the possible reason why the magic number terminates around 32 in the mass spectra of Ba_n clusters [12], beyond this size the bonding nature will be changed. At low temperature none of the

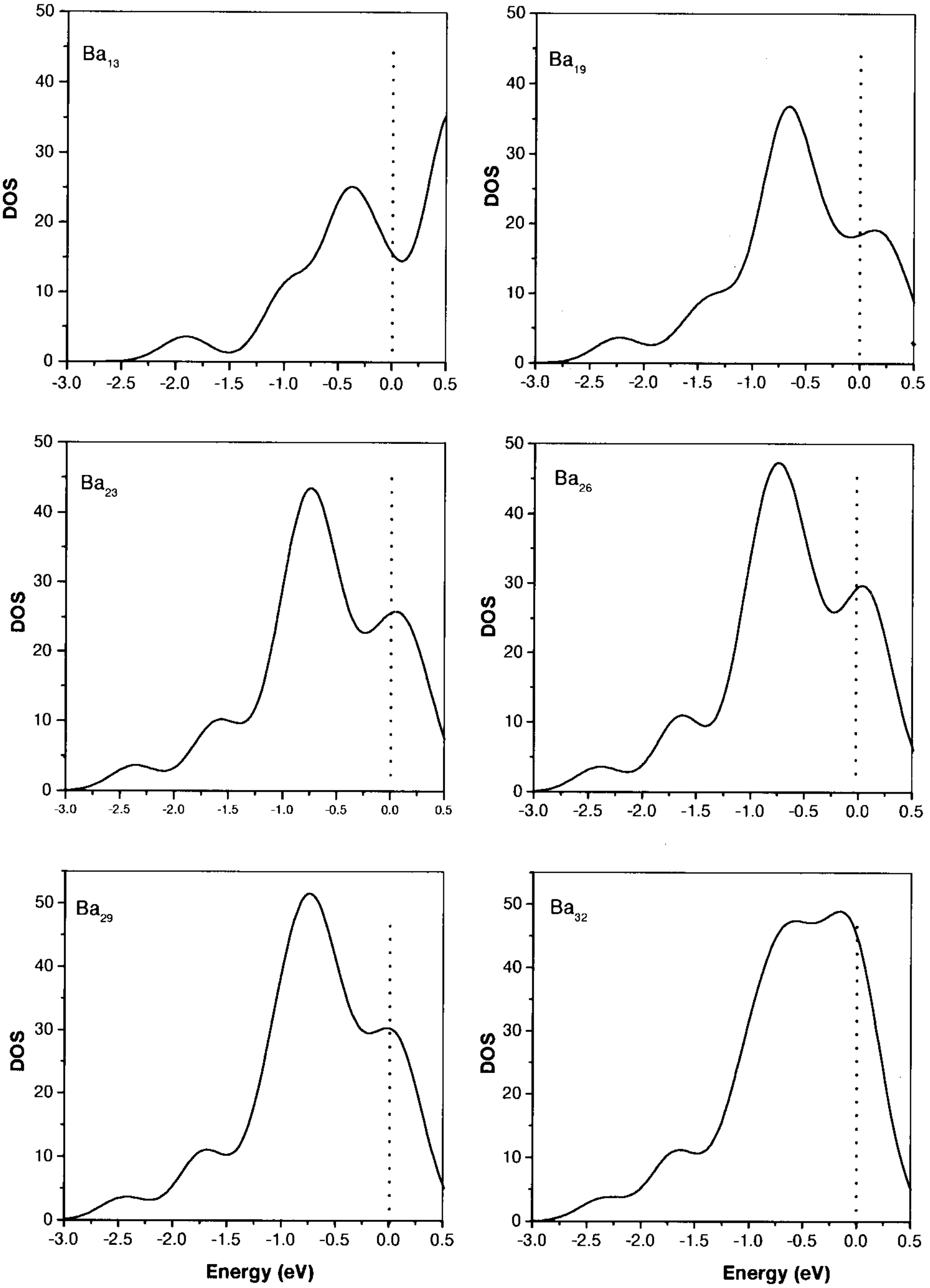

Fig. 2. Density of states (DOS) for magic Ba_n clusters with $n = 13$, 19, 23, 26, 29, and 32.

magic Ba_n clusters is in the metallic state. In this sense, we can see that among the experimental conditions, temperature is one of the key factors in observing the magic number.

For bulk Ba, recent studies Refs. [10,11] found that the atomic coordination number and atomic distance are important factors in determining the nonmetal to metal transition. In Ba clusters, the average coordination number Z can be calculated from the formula [26]:

$$Z(n) = \frac{Z_\mathrm{b}(n-1)}{Z_\mathrm{b} + (n-1)} \tag{2}$$

where Z_b is the coordination number of bulk BCC Ba, and n is the cluster size. As shown in Fig. 4, the average coordination number increases with cluster size, which

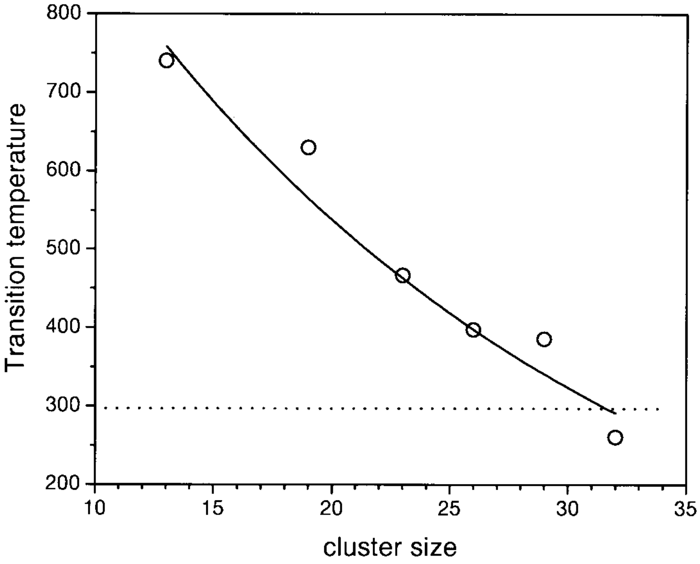

Fig. 3. The calculated nonmetal–metal phase diagram of magic Ba_n clusters. The continuous line corresponds to the least square fitting.

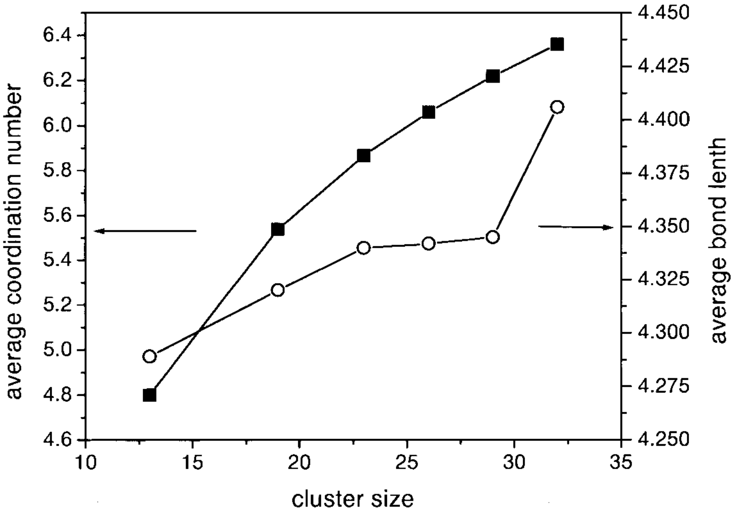

Fig. 4. Average coordination number (square) and average nearest neighbor bond length (circle) change with cluster size.

favors the metallization due to enhancing the hybridizations between the atomic orbitals. On the other hand, with the cluster increase, the average nearest neighbor atomic distance also increases (see Fig. 4), this is unfavorable for the metallization due to suppressing the hybridizations between the atomic orbitals. Therefore, increasing cluster size results in two competing factors, the compromise of these two factors in some critical size determines the nonmetal to metal transition in the given temperature.

In summary, we studied the size induced nonmetal to metal transition in Ba_n clusters, which will take place around $n = 32$ in the room temperature, in agreement with mass spectra experiment [12]. Combined with the studies on bulk and monolayer Ba [10,11], our results of Ba clusters are helpful for understanding the nonmetal to metal transitions of Ba related system in different environment.

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