PAPER • OPEN ACCESS

Ab initio density-functional studies of 13-atom Cu and Ag clusters

To cite this article: Dil K. Limbu et al 2019 J. Phys.: Conf. Ser. 1252 012009

View the article online for updates and enhancements.



IOP ebooks[™]

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Ab initio density-functional studies of 13-atom Cu and Ag clusters

Dil K. Limbu¹, Michael U. Madueke², Raymond Atta-Fynn², David A. Drabold³ and Parthapratim Biswas¹

¹ Department of Physics and Astronomy, The University of Southern Mississippi, Hattiesburg, Mississippi 39406, USA

² Department of Physics, University of Texas, Arlington, Texas 76019, USA

³ Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701, USA

E-mail: partha.biswas@usm.edu

Abstract. The putative ground-state structures of 13-atom Cu and Ag clusters have been studied using ab initio molecular-dynamics (AIMD) based on density-functional theory (DFT). An ensemble of lowenergy configurations, collected along the AIMD trajectory and optimized to nearest local minimum-energy configurations, were studied. An analysis of the results suggests the existence of low-symmetric bilayer structures as strong candidates for the putative ground-state structure of Cu_{13} and Ag_{13} clusters. These bilayer structures are markedly different from a buckled bi-planar (BBP) configuration and energetically favorable, by about 0.4–0.5 eV, than the latter proposed earlier by others. Our study reveals that the structure of the resulting putative global-minimum configuration is essentially independent of the nature of basis functions (i.e., plane waves vs. pseudoatomic orbitals) employed in the calculations, for a given exchangecorrelation functional. The structural configurations obtained from plane-wave-based DFT calculations show a noticeably tighter or dense first-shell of Cu and Ag atoms. A comparison of our results with recent full-potential DFT simulations is presented.

1. Introduction

Transition-metal (TM) clusters have been studied extensively from computational and experimental points of view [1-5] due to their potential applications in catalysis [6], photonics [7] and carbon nanotubes [8]. Owing to the difficulties associated with experimental determination of the structures of small clusters [1], Monte Carlo and molecular-dynamics simulations play important roles in the structural characterization of small clusters. While computational studies based on classical interatomic potentials indicate that the icosahedral structure is the preferred ground state of 13-atom Cu and Ag clusters [2,9], ab initio studies based on density-functional theory (DFT) [10] indicate the presence of a few competing structures as possible ground-state structures [11-19], depending upon the types of the basis functions and exchange-correlation (XC) functionals employed in the DFT calculations. Furthermore, given the computational complexity of *ab initio* calculations, the results can depend considerably on the total simulation time and the method used to sample candidate structures from the potential-energy surface (PES) during simulations. Of particular interest among ab initio studies on 13-atom Ag and Cu clusters are the work by Oviedo and Palmer [11] and that by Chang and Chou [12], using the first-principles density-functional code VASP [20]. The former indicated the presence of a few 'amorphous-like' lowenergy isomers with bilayer structures, whereas the latter concluded the existence of a buckled biplanar (BBP) structure as a putative ground state of 13-atom Ag and Cu clusters. A similar conclusion was

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

reached by Longo and Gallego [13], who employed pseudoatomic orbitals as basis functions in their calculations, using the local-basis DFT code SIESTA [21]. Recently, Chaves *et al.* have reported bilayer structures of 13-atom Cu and Ag clusters using full-potential density-functional calculations. However, a number of Gaussian-orbital-based and plane-wave-based DFT studies [22–25] reported different structures for Cu_{13} and Ag_{13} clusters. To this end, the aim of the current study is to present results from *ab initio* molecular-dynamics simulations, lasting for a few hundreds of picoseconds and sampling structural configurations from *ab initio* potential-energy surfaces (PES), using both plane-wave and local-basis DFT calculations.

2. Computational Method

Spin-polarized DFT [10] calculations were performed within the Perdew-Burke-Ernzerhof (PBE) formulation [26] of the generalized gradient approximation (GGA) using the DFT code SIESTA [21]. Pseudoatomic-orbital double-zeta basis with polarization (DZP) functions and norm-conserving Troullier-Martins pseudopotentials [27] were employed. All calculations were performed using a cubic simulation cell of size 30 Å. The large simulation cell permitted us to sample the Brillouin zone using the Γ -point only. A large number of low-energy configurations of Ag₁₃ and Cu₁₃ clusters were generated from *ab initio* molecular-dynamics simulations in the canonical ensemble followed by geometry optimizations. The details are as follows. A randomly generated 13-atom cluster placed in the box. The system was initially equilibrated at 1500 K for 20 ps. The temperature was then reduced gradually from 1500 K to 300 K for 240 ps. A total of 40 low-energy structures were collected in the temperature range of 300 K to 500 K during the AIMD simulations; the geometries of the collected structures were then optimized by minimizing their respective total energies. The optimizations were based on the conjugate-gradient (CG) algorithm; a structure is considered to be fully optimized if the force on each atom is less than 0.005 eV/Å. The stability of each structure was further examined by minimizing the total energy using the more accurate plane-wave-based DFT method as implemented in the DFT code VASP [20].

3. Results and Discussions

As mentioned earlier, an ensemble of low-energy structural configurations, collected during the course of *ab initio* molecular-dynamics simulations, constitutes a set of candidate structures for determining the putative ground-state configuration of 13-atom Ag and Cu clusters. Further relaxation of these structures, using the plane-wave density-functional code VASP, provides the final structure for Ag₁₃ and Cu₁₃ clusters. The potential energy of the putative global minimum for Ag and Cu clusters is listed in Table 1, with respect to the potential energy of the corresponding icosahedral structure. The bilayer nature of these structures is evident from Fig. 1, where a three-dimensional ball-and-stick model of the structures are presented. The results are consistent with the recent study by Chaves *et al.* [18], where similar bilayer structures of 13-atom Cu and Ag clusters were reported using DFT calculations.

In order to characterize the three-dimensional distribution of the atoms in Ag₁₃ and Cu₁₃ clusters, we have computed the radial and bond-angle distributions, and the average bond length (\bar{d}_i) and the effective coordination number (C_i) of an atom at site *i*. The average bond length of an atom at site *i* is given by,

$$\bar{d}_i = \sum_j d_{ij} p_{ij}, \quad p_{ij} = \frac{e^{f(d_{ij})}}{\sum_j e^{f(d_{ij})}}, \quad f(d_{ij}) = \left[1 - \left(\frac{d_{ij}}{\bar{d}_i}\right)^6\right],$$
 (1)

where d_{ij} is the radial distance between two atoms at sites *i* and *j*. The site-average bond length (d_{av}) and the average coordination number (C_{av}) are given by,

$$d_{av} = \frac{1}{N} \sum_{i=1}^{N} \bar{d}_i, \quad C_{av} = \frac{1}{N} \sum_{i=1}^{N} C_i, \quad C_i = \sum_{j=1}^{N} e^{f(d_{ij})}$$
(2)

Symmetry -	$Cu_{13}: \Delta E (eV)$		$Ag_{13}: \Delta E (eV)$	
	Siesta	VASP	Siesta	VASP
ICO	0.0	0.0	0.0	0.0
BBP	-0.460	-0.462	-0.514	-0.785
Bilayer	-0.926	-0.972	-0.934	-1.231
Bilayer*	-1.014		-1.300	

Table 1. Total-energy differences (in eV) for 13-atom Cu and Ag clusters from their icosahedral counterpart, using SIESTA and VASP.

*From Ref. [18]



Figure 1. The structure of putative global minimum of Cu_{13} (left) and Ag_{13} (right) obtained from *ab initio* simulations, using SIESTA and VASP. The maximum nearest-neighbor distance in each case corresponds to the value obtained from the respective pair-correlation function.

Fable 2. Average bond len	gth (d_{av}) and coor	dination number (C_{av})	for Cu and Ag clusters
----------------------------------	-------------------------	----------------------------	------------------------

System	Cu_{13}		Ag_{13}	
Symmetry	d _{av} (Å)	C_{av}	d _{av} (Å)	C_{av}
	Siesta(Vasp)	Siesta(Vasp)	Siesta(Vasp)	Siesta(Vasp)
ICO	2.612 (2.500)	6.395 (6.396)	3.037 (2.894)	6.396 (6.396)
BBP	2.563 (2.454)	5.469 (5.463)	2.982 (2.838)	5.468 (5.460)
Bilayer	2.570 (2.460)	5.702 (5.701)	2.994 (2.845)	5.709 (5.647)
Bilayer [§]	2.459	5.699	2.835	5.654

[§]From Ref. [18]

Equations (1) and (2) permit us to calculate the average coordination number and bond length of a cluster self-consistently without introducing any arbitrary cutoff distance [16, 18, 28]. Starting with an approximate value of \bar{d}_i , one can use Eq. (1) to improve the estimate of \bar{d}_i iteratively. Table 2 lists the average bond lengths and coordination numbers for icosahedral, BBP and bilayer structures of 13-atoms Cu and Ag clusters obtained from SIESTA and VASP. The corresponding values computed



Figure 2. The pair-correlation function of a) Cu_{13} and b) Ag_{13} clusters. For comparison, the radial distances are normalized by the corresponding average bond length, d_{av} , from VASP reported in Table 2.



Figure 3. The bond-angle distributions for a) Cu_{13} and b) Ag_{13} clusters.



Figure 4. The distribution of atomic-coordination numbers in a) Cu_{13} and b) Ag_{13} clusters. The distribution of the atoms in the first shell is identical as far as the bond angles are concerned.

by Chaves *et al.* [18] are also listed for a comparison. An examination of the results from Table 2 suggests that the total-energy values obtained from the pseudoatomic-orbital-based DFT code SIESTA slightly overestimates the value of total-energy than those obtained from the plane-wave-based VASP calculations in our work. This is also reflected in the average bond-length of Ag and Cu atoms. The bond lengths obtained from VASP relaxations are approximately 4% shorter than the ones calculated from using SIESTA. Figure 2 shows the pair-correlation functions (PCF) of Ag and Cu clusters. For comparison, the radial distances are normalized by the corresponding site-average bond length of Ag and Cu atoms, as listed in Table 2. The PCFs look essentially identical except for the height of the first peak, which is a reflection of the different average coordination number of Ag and Cu clusters. A further characterization of a three-dimensional distribution of atoms in the clusters is possible by examining the

Recent Developments in Computer Simulation Studies in Condensed Matter PhysicsIOP PublishingIOP Conf. Series: Journal of Physics: Conf. Series 1252 (2019) 012009doi:10.1088/1742-6596/1252/1/012009

bond-angle distribution, as shown in Fig. 3. Both the distributions exhibit a well-defined peaks near 60° and 110° . Likewise, the distributions of the effective coordination number of atomic sites, C_i , of the clusters are shown in Fig. 4.

4. Conclusion

In this paper, we have used *ab initio* molecular-dynamics simulations, coupled with geometry optimization, based on DFT-GGA to predict the putative ground state of 13-atom Cu and Ag clusters. An extensive search of competitive candidate structures from the *ab initio* potential-energy surface indicates that a low-symmetry bilayer structure is the most-likely candidate for the ground-state structure of Cu_{13} and Ag_{13} clusters. A comparison with a number of bilayer structures, optimized with pseudoatomic-orbital basis (SIESTA) and plane-wave basis (VASP), indicates that the resulting putative global-minimum configuration is essentially independent of the nature of basis function. The minimum-energy configurations obtained from VASP show a slightly shorter average bond length compared to the same obtained from SIESTA.

Acknowledgments

This work is partially supported by the U. S. National Science Foundation under Grants No. DMR 1507166, No. DMR 1507118, and No. DMR 1506836. We acknowledge the use of computing resources at the Texas Advanced Computing Center.

References

- [1] Baletto F and Ferrando R 2005 Rev. Mod. Phys. 77 371–423
- [2] Doye J P K and Wales D J 1998 New J. Chem. 22 733–744
- [3] Elliott J, Shibuta Y and Wales D 2009 Philos. Mag. 89 3311–3332
- [4] Parks E K, Zhu L, Ho J and Riley S J 1995 J. Chem. Phys. 102 7377–7389
- [5] Oyanagi H, Sun Z H, Jiang Y, Uehara M, Nakamura H, Yamashita K, Orimoto Y, Zhang L, Lee C, Fukano A and Maeda H 2012 J. Appl. Phys. 111 084315
- [6] Henry C R 1998 Surf. Sci. Rep. 31 231 325
- [7] Barnes W L, Dereux A and Ebbesen T W 2003 Nature 424 824830
- [8] Li Y L, Kinloch I A and Windle A H 2004 *Science* **304** 276–278
- [9] Limbu D K and Biswas P 2017 J. Phys.: Conf. Ser. 921 012010
- [10] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133–A1138
- [11] Oviedo J and Palmer R E 2002 J. Chem. Phys. **117** 9548–9551
- [12] Chang C M and Chou M Y 2004 Phys. Rev. Lett. 93 133401
- [13] Longo R C and Gallego L J 2006 Phys. Rev. B 74 193409
- [14] Sun Y, Zhang M and Fournier R 2008 Phys. Rev. B 77 075435
- [15] Piotrowski M J, Piquini P and Da Silva J L F 2010 Phys. Rev. B 81 155446
- [16] Chou J P, Hsing C R, Wei C M, Cheng C and Chang C M 2013 J Phys: Cond. Matt. 25 125305
- [17] McKee M L and Samokhvalov A 2017 J. Phys. Chem. A 121 5018–5028
- [18] Chaves A S, Piotrowski M J and Da Silva J L F 2017 Phys. Chem. Chem. Phys. 19 15484–15502
- [19] Limbu D K, Atta-Fynn R, Drabold D A, Elliott S R and Biswas P 2017 Phys. Rev. B 96 174208
- [20] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–11186
- [21] Soler J M, Artacho E, Gale J D, García A, Junquera J, Ordejón P and Sánchez-Portal D 2002 J. Phys.: Cond. Matt. 14 2745
- [22] Yang M, Jackson K A, Koehler C, Frauenheim T and Jellinek J 2006 J. Chem. Phys. 124 024308
- [23] Chaves A S, Rondina G G, Piotrowski M J, Tereshchuk P and Da Silva J L F 2014 J. Phys. Chem. A 118 10813–10821
- [24] Wang L L and Johnson D D 2007 Phys. Rev. B 75 235405
- [25] Chen M, Dyer J E, Li K and Dixon D A 2013 J. Chem. Phys. 117 8298–8313
- [26] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865–3868
- [27] Troullier N and Martins J L 1991 Phys. Rev. B 43 1993–2006
- [28] Hoppe R 1979 Z. Kristallogr. 150 23-52