

AB-INITIO MOLECULAR DYNAMICS STUDIES OF A Ga_{13} CLUSTERX.G. Gong^a, Q.Q. Zheng^a and R.S. Han^b^a: Institute of Solid State Physics, Academia Sinica, 230031-Hefei, China.^b: Department of Physics, Beijing University, 100080-Beijing, China

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We report the results on the structural and electronic properties of a Ga_{13} cluster carried out by the *ab-initio* molecular dynamics method. We found an icosahedron with some Jahn–Teller distortion to be the lowest energy structure for the Ga_{13} cluster. The charge density in the cluster is much lower than that in the bulk α -Ga, which implies that the bonding is still metallic.

Keywords: A. disordered systems, A. metals.

The electronic structures and physical properties of the atomic clusters are one of the important current research fields for the physics, chemists and material scientists. The 13-atom clusters are usually considered as a special interesting in the study of physics of clusters. Geometrically, thirteen atoms can fill the first shell of the icosahedral, cubo-octahedral (fcc-like) and anti-cubo-octahedral (hcp-like) structures. The icosahedron is the most compact structure for the thirteen atom cluster, with a sphere-like shape. In experiments, the 13-atom cluster of the rare gases is found to be a magic cluster[1], which can be theoretically explained by the Lennard-Jones interaction in the rare-gases[2]. But for the metal and semiconductor elements, generally the 13-atom cluster is not magic cluster. For instance in alkali-metal elements, the magic numbers in experimental mass spectrum[3] are at $N=8, 20$, et al., which can be well predicted by the jellium model[4], the equilibrium structure of Na_{13} cluster is found to be largely deviated from an icosahedron[5]. In the divalent elements, although there is no enough available experimental data, the *ab-initio* molecular-dynamics studies show that all the 13-atom clusters are not icosahedral-like, the equilibrium structures are very complicated[6]. For the trivalent element clusters, only the Al clusters have been extensively studied. In experimental mass spectrum, the enhanced stability seems

occurring at $N=13$ or $N=14$ dependent on the charge state of the clusters[7]. Many theoretical studies show that the structure of neutral Al_{13} cluster is nearly an icosahedron[8]. Because the highest occupied molecular orbital (HOMO) in Al_{13} cluster is three-fold degenerate and is not completely occupied, a small Jahn-Teller distortion would lower the energy. In fact there are 39 valence electrons in the Al_{13} cluster, this number is very close to 40 which can close a electronic shell predicted by the jellium model[4], Gong and Kumar have discussed a way to enhance the stability of Al_{13} cluster through a proper doping or charging[9]. Actually the doping or charging just adds one more electron to the cluster leading to a closed shell with a enhancement of stability. In the clusters of semiconductor elements like Si, although the experiments found Si_{13} cluster to be inert in the reaction with several molecules [10], the results of *ab initio* molecular dynamics studies and the quantum mechanical calculations[11] suggest that the icosahedral-like Si_{13} cluster is not stable. In the solid phases, the local icosahedral units of Al_n clusters have been observed in many systems. The most typical case is the Al-based icosahedral quasicrystal with icosahedral units which have stimulated very much research interesting in the past a few years[12]. Although the formation and stability of these icosahedral quasicrystals have not been well understood yet, it can be believed that

the local icosahedral units have played a very important role[13]. Another relevant and in fact remarkable structure which has local icosahedral order is the crystalline Al_{12}W phase, in which the icosahedral Al_{12}W unit with W atom at the center is the building blocks of the bcc structure[14]. The Ga atom has two s and one p valence electrons which is similar to the Al atom. The similarity has been observed in simulated annealing studies on the small gallium and aluminum clusters (up to ten atoms). Also many kinds of gallium based alloys with icosahedral unit have been observed [16], it seems that Ga has also a tendency to form the icosahedral structure. But solid gallium is a unusually metal and is quite different from solid aluminum in many aspects[15]. In this paper we present the results of the Ga_{13} cluster obtained by *ab-initio* molecular dynamics method.

The *ab-initio* molecular dynamics method has been successfully applied to many non-crystalline systems, such as liquids, amorphous and atomic clusters. With this method, Gong and Tosatti have studied the Ga_n (n up to 8) clusters by simulated annealing[17]. R.O. Jones has also performed more extensively calculations on both the Al_n and Ga_n clusters (n up to 10)[18], and significant differences in bond angles and bond lengths have been observed between the results for aluminum and gallium clusters, although some similarities exist. In the present study, the calculations are performed using the similar method described in detail elsewhere[17]. We have used a simple cubic cell with lattice constant of 25a.u. in which the cluster is put, the cell is big enough for the cluster to have zero charge density around the edge of the cell. The interaction between the cluster and its image is negligible. We have also made a calculation at a lattice constant of 30a.u., no significant changes on the structures are found. We have used a first-principle nonlocal norm-conserving pseudopotential constructed from the tables of Stump et al.[19], and KB[20] scheme to factorize the form of the nonlocal pseudopotential which can reduce significantly the cost in calculating the nonlocal pseudopotential matrix elements. The electron wave functions are expanded by the plane waves up to an energy cutoff of 10Ry. The Perdew and

Zunger form[21] of the exchange-correlation interaction has been used. To study the equilibrium structures of the clusters, first we calculated the total energies for the high symmetrical structures and relaxed the structures to obtain an equilibrium atomic distances. Starting with these structures, we release the constrain of symmetry and heat the clusters up to 100K ~ 200K for a few hundred steps, then we performed the steepest decent for the ions to bring ions to its local equilibrium position. The integration time step is 20.0a.u. and the fictitious electron mass is about 5000a.u.

We have studied Ga_{13} cluster with icosahedral, fcc-like, hcp-like, capped hexagonal, capped anti-hexagonal and other high symmetrical structures obtained for Si_{13} cluster by theoretical studies[11]. It is found that the icosahedral, fcc-like and hcp-like structures have lower energies. For the other structures, the total energies are very high, apparently it will be very unfavorable for Ga_{13} cluster with these structures. So in the following, we only concentrate on the first three close pack structures. The equilibrium atomic distances and the total energies for the undistorted icosahedral, fcc-like and hcp-like structures are presented in Tab.1. In the minimization of the total energy for the hcp-like structure, we found that a little bit larger axis ratio c/a (1.66) than the ideal value (1.62) is energetically more favorable, which consequently reduced the number of the nearest neighbors for the center atom. We find that the icosahedral structure has the lowest total energy, which indicates that the Ga_{13} cluster should be icosahedral like, and the fcc-like structure has the highest energy. We obtained

Tab.1 The relative total energies (eV) and the average nearest neighbour distances(a.u.) of distorted and undistorted Ga_{13} cluster.

Cluster	Undistorted		Distorted	
	E_t	R_0	E_t	R_0
Ih	0.0	4.78	-29.12063	4.73
hcp	0.309	4.67	0.523	4.66
fcc	0.827	4.68	0.867	4.65

the same sequence of total energies for the calculated three high symmetrical clusters as what obtained in Al_{13} cluster[8]. The average bond lengths in hcp-like and fcc-like structure are very close, but all of them are longer than the equilibrium distance of Ga_2 molecule and Ga-Ga bond length in bulk α -Ga[15].

After we obtained the equilibrium structure of undistorted high symmetrical clusters, we let the ions in the clusters moving and heated the clusters up to 100K ~ 200K which is equilibrated by Nose dynamics[22], and then we performed a combined steepest decent for ions and electrons simultaneously. At this low temperature we did not find any structural transformation from one symmetry to another except for some distortions from the starting symmetry. Upon the distortion, the total energies of the clusters decrease. The energy gain by distortion is the largest for the icosahedral structure, and the smallest for hcp-like structure. This might be because of the former having the highest symmetry and the hcp structure having the lowest symmetry. From Tab.1, we can see that the distortion has a tendency to decrease the average bond length but it is still much larger than the equilibrium distances of our pseudopotential results on free Ga_2 molecule (4.3a.u.) and Ga-Ga bond length (4.48a.u.) in bulk α -Ga, interestingly this bond length is quite close to the distances between the second neighbors in the bulk α -Ga. From ref. [11], we know that the bonding between the second neighbors is metallic. In Fig.1, we have plotted the structures of Ga_{13} cluster with the icosahedral-like and cubo-octahedral-like symmetry. The thick lines show the undistorted structure, the thin lines connect the atoms (circle) in the distorted structure. The black dots represent the atoms in the undistorted structure. Since the distortion in hcp structure is very small, we did not include this structure in the figure. From Fig.1, we can see, the distortion decreased the number of the nearest neighbors. Especially in the icosahedral structure, each atoms at the vertex reduce its six nearest neighbors to the four neighbors. Clearly icosahedral symmetry exists no more, there is a tendency for one C_5 axis to become C_3 axis, but far away from a real C_3 axis formed

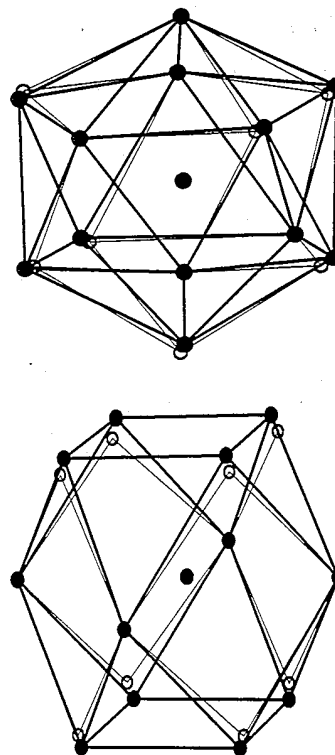


Fig.1 The icosahedral-like and fcc-like structures of Ga_{13} cluster.

like what found in icosahedral-like Al_{13} cluster obtained by ref.[11]. In the fcc-like structure, the distortion is tetragonal, which changes the O_h symmetry to the D_{4h} symmetry, as shown clearly in the figure, we found a shrinkage of 5% along the C_4 axis, this is quite similar to fcc-like structure of Al_{13} cluster.

In Fig.2, we have shown the contour plots of charge density on the plane including two vertex atoms and the center atom in the icosahedral structure. We have also calculated the average charge densities along the line from the center to the vertex atoms for the icosahedral-like, fcc-like and hcp-like structures for Ga_{13} cluster in Fig.3, we can see that, the lowest total energy icosahedral-like structure has the largest charge density piling up between the nearest neighbor, the highest total energy hcp-like structure has the lowest charge density. For the comparison, we also plotted the charge density along the line of the Ga-Ga bond in the bulk α -Ga[15]. We have noticed that the charge density in the cluster is much smaller than that of Ga_2 molecule and

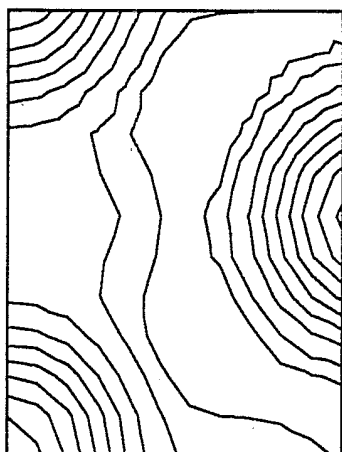


Fig.2 The contour plots of charge density for the icosahedral Ga_{13} cluster.

also smaller than that of Ga-Ga bond in α -Ga, this may be attributed to the too many neighbors in the clusters, the bond lengths are much longer, and the covalence bonding is very weak, hence it is very hard to define a bond charge like what have been done in the bulk phase.

In summary, our results on Ga_{13} cluster suggest that the optimistic structure of 13-atom gallium cluster is an icosahedron with small distortions, the other two high symmetrical structures constructed from the close pack bulk fcc and hcp phases have a little bit higher energies. All other high symmetrical structures and the structures obtained for Si_{13} cluster are found to be very high in energy for Ga_{13} cluster. The structural properties found for Ga_{13} cluster in the present study are very similar to the results of Al_{13} cluster. As discussed for Al_{13} cluster, because the HOMO of Ga_{13} cluster is not completely filled, the Jahn-Teller distortion can reduce the total energy. The atomic distances, which are larger than the equilibrium distances of Ga_2 molecule and Ga-Ga bond in bulk α -Ga as well as the lower charge density in the Ga_{13} cluster, suggest that the bonding in Ga_{13} cluster is more metallic than that in bulk phase of α -Ga. The finding of icosahedral-like structure of Ga_{13} cluster has provided an insight to understand the presence of icosahedral local units in many kinds of gallium

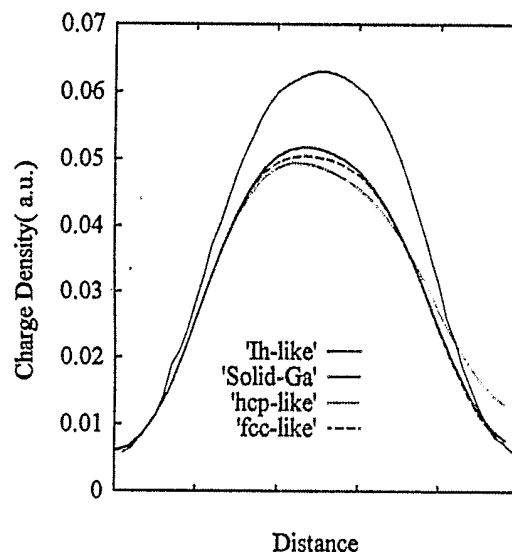


Fig.3 The average charge density between the nearest neighbours in the Ga_{13} cluster and in α -Ga.

based alloys[16]. The insertion of alkali-metal atom, which is found to enhance the stability of Ga-based alloys, can balance the deficiency of electrons in Ga_{13} cluster and fill the space among the large Ga_{13} clusters. In fact, the Ga_{13} cluster in many Ga-based alloys can be considered as a superatom, as discussed by Gong and Kumar[13] in Al-based alloys. In the studies of J.-Y. Yi et al., a transition for Al_n clusters from icosahedral like ($n=13$) to fcc-like, i.e. to the bulk structure of Al, is observed. As stated above, a close similarity has been obtained between small Al_n and Ga_n clusters up to $N=10$. From the present study we can see that even in 13-atom cluster, Al_{13} and Ga_{13} clusters are still similar in many aspects. It is interesting to further study the convergence of Ga_n clusters to the bulk structure of α -Ga which is quite different from fcc structure of bulk Al, and to study the changes of bond character from metallic-like in the small cluster to molecular-like in bulk α -Ga.

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