Correlation between local clusters and structure of $Al_{71}Cu_{29}$ melt [①]

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Abstract: The structures of $Al_{1-4}Cu_{1-2}$ clusters were optimized by B3LYP method and the six geometries ground states were obtained. $Al_{71}Cu_{29}$ alloy melt has been investigated using X-ray diffractometry at 700 ℃. The experimental data were compared with calculated results to find the relation between the structures of Al-Cu clusters and melt structure. It is shown that there exists a strong interaction between Al and Cu atoms. The bond length in some geometries is very close to the experimental atomic distance. Such optimized geometries have close correlation with the liquid structure of Al-Cu alloy.

Key words: cluster; ground states; Al-Cu alloy; X-ray diffractometry

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1　INTRODUCTION

Much attention has been devoted to the research on the liquid structure of metals in recent years. The atoms in melt are neither regularly arranged in long-range, nor completely disordered. How to describe the distribution of atoms in liquid is still a problem unsolved. Many methods have been used to study the structure of clusters in liquid. The molecular dynamics is widely used in computer simulation of melt and many researches have discussed the microstructure of liquid alloys[1, 2]. However, the exact structure of the short-range order in liquid is difficult to describe. The ground state of cluster can be confirmed by ab initio calculation. Intensive studies are now focused on clusters of metal atoms, among which many deal with aluminum clusters such as Upton[3, 4] and Jones[5, 6]. Exploring the cluster structure has great importance to understand the melt process. However, the authors have not found many reports about the combination of cluster structure with melt structure, and even less work had carried out about the ab initio research of the small cluster structure in the AlCu alloy.

2　EXPERIMENTAL

The structures of $Al_{1-4}Cu_{1-2}$ micro clusters were chosen to be calculated using DFT ab initio method according to the short-range order in Al-Cu melt and the existence of Al_2Cu compound in the Al-Cu alloy. The abinitio calculation was carried out using Gaus-sian98 program[7]. The geometries were optimized at B3LYP level, using the LANL2DZ basis set, which is a double-zeta basis set containing effective core potential (ECP)[8, 9]. Harmonic frequencies were calculated at the same level to examine the stability of the optimized structures.

The alloy specimen was prepared from high purity Al (99. 999%) and Cu (99. 98%) in a crucible made of Al_2O_3 in size of 8 mm × 25 mm × 30 mm. The X-ray diffraction intensity from the molten alloy was measured using a θ − θ diffractometer, allowing the sample to be held in a stationary horizontal position and the X-ray tube and detector moved in opposite directions. All the diffraction measurements were performed in a high-purity helium atmosphere of 1. 3 × 10^5 Pa before the chamber was cleaned in a vacuum of 2 × 10^{-6} Pa. The intensity profiles were obtained at 700 ℃ by Mo K_α radiation (λ= 0. 071 nm) coupled with a graphite monochromator in the diffraction beam, in the diffraction angle 2θ from 5° to 90°, which covers the values of wave vector $Q = 4\pi \sin\theta / \lambda$ between 5 − 120 nm^{-1}.
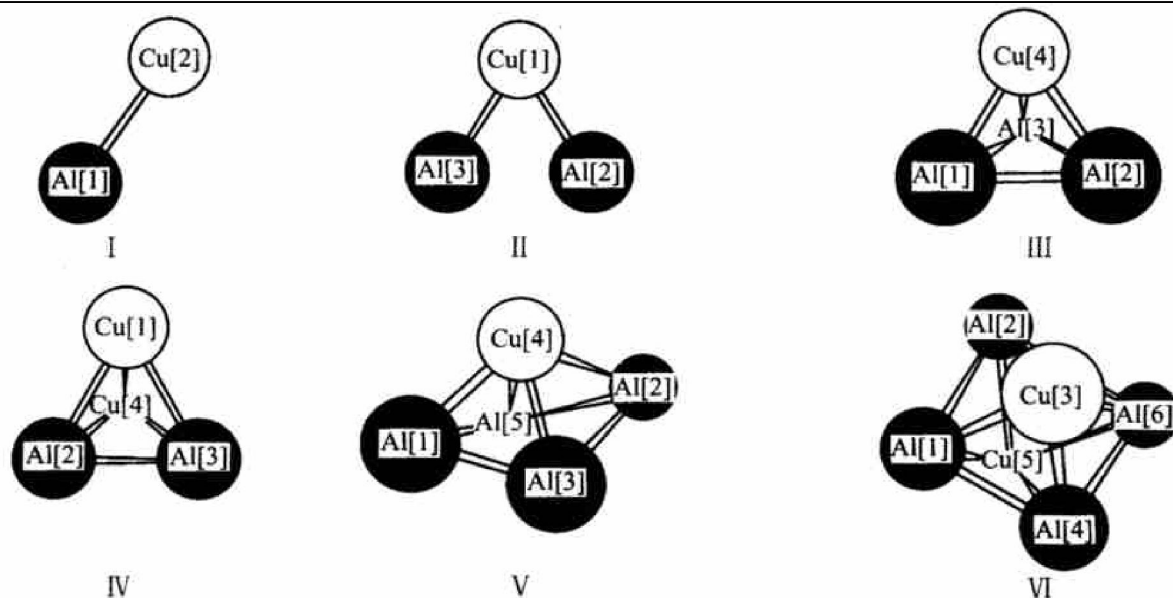
3　RESULTS AND DISCUSSION

The optimized geometries are shown in Fig. 1, the geometry Ⅰ, Ⅱ, Ⅲ, Ⅳ, Ⅴ, Ⅵ are the ground state of AlCu, Al_2Cu, Al_3Cu, Al_2Cu_2, Al_4Cu and Al_4Cu_2, respectively. The symmetries, bond length and angles of these geometries are listed in Table 1. The bond length between Al and Cu is

Fig. 1 Ground state geometries of Al-Cu clusters

Table 1 Symmetry, bond length R, bond angles A and dihedral angels D of optimized geometries

Structure	Symmetry	B3LYP/ LAZL2DZ
AlCu (I)	Cv	$R(1, 2) = 2.459$
Al$_2$Cu (II)	Cs	$R(1, 2) = 2.5175$ $R(2, 3) = 2.5175$
Al$_2$Cu$_2$ (III)	C$_1$	$R(1, 2) = 2.5324$ $R(1, 3) = 2.5324$ $R(1, 4) = 2.6231$ $R(2, 3) = 2.6589$ $R(2, 4) = 2.5332$ $R(3, 4) = 2.5332$ $A(1, 2, 3) = 63.3338$ $A(1, 2, 4) = 62.374$ $A(1, 3, 4) = 62.374$ $A(2, 4, 3) = 63.3126$
Al$_3$Cu (IV)	C$_1$	$R(1, 2) = 2.7642$ $R(1, 3) = 2.7637$ $R(1, 4) = 2.5917$ $R(2, 3) = 2.7637$ $R(2, 4) = 2.5917$ $R(3, 4) = 2.5925$
Al$_4$Cu (V)	C$_1$	$R(1, 3) = 2.7617$ $R(1, 4) = 2.7136$ $R(1, 5) = 2.7577$ $R(2, 3) = 2.754$ $R(2, 4) = 2.713$ $R(2, 5) = 2.7544$ $R(3, 4) = 2.7133$ $R(4, 5) = 2.7135$ $A(3, 1, 5) = 90.2919$ $A(3, 2, 5) = 90.52$ $A(1, 3, 2) = 89.5541$ $A(1, 4, 2) = 91.4357$ $A(3, 4, 5) = 92.272$ $A(1, 5, 2) = 89.628$ $D(5, 1, 3, 2) = -0.5875$ $D(3, 1, 5, 2) = 0.5874$ $D(5, 2, 3, 1) = 0.5882$ $D(3, 2, 5, 1) = -0.5891$
Al$_4$Cu$_2$ (VI)	C$_1$	$R(1, 2) = 2.954$ $R(1, 3) = 2.6669$ $R(1, 4) = 2.9502$ $R(1, 5) = 2.6631$ $R(2, 3) = 2.6541$ $R(2, 5) = 2.6731$ $R(2, 6) = 2.9504$ $R(3, 4) = 2.6731$ $R(3, 6) = 2.663$ $R(4, 5) = 2.6542$ $R(4, 6) = 2.954$ $R(5, 6) = 2.6669$ $A(2, 1, 4) = 89.9538$ $A(3, 1, 5) = 76.8125$ $A(1, 2, 6) = 90.0458$ $A(3, 2, 5) = 76.86$ $A(1, 3, 6) = 103.1866$ $A(2, 3, 4) = 103.1414$ $A(1, 4, 6) = 90.0485$ $A(3, 4, 5) = 76.8587$ $A(1, 5, 6) = 103.1859$ $A(2, 5, 4) = 103.1399$ $A(2, 6, 4) = 89.9518$ $A(3, 6, 5) = 76.815$ $D(4, 1, 2, 6) = 0.0004$ $D(5, 1, 3, 6) = -0.0032$ $D(2, 1, 4, 6) = -0.0004$ $D(3, 1, 5, 6) = 0.0032$ $D(5, 2, 3, 4) = -0.0038$ $D(3, 2, 5, 4) = 0.0038$ $D(1, 2, 6, 4) = -0.0004$ $D(2, 3, 4, 5) = 0.0038$ $D(1, 3, 6, 5) = 0.0032$ $D(3, 4, 5, 2) = -0.0038$ $D(1, 4, 6, 2) = 0.0004$ $D(1, 5, 6, 3) = -0.0032$

Bond length R in Å, bond angle A and dihedral angle D in degree.

about 2. 459 Å in I , 2. 517 5 Å in II, 2. 532 4 Å in III, 2. 591 7 Å in IV, and 2. 713 3 Å in V, and 2. 66 Å in VI respectively. The optimized structures of the five clusters have no imaginary frequency, indicating that all the geometries are the minimum points on the potential energy surface.

It can be seen from Table 1 that the bond length of Al-Cu atoms in the II, III, IV, VI is shorter than those of Al-Al and Cu-Cu. It is generally considered that the shorter the bond length, the stronger the bond. So the interaction between atom Al and Cu is strong and steady chemical bond can form between Al and Cu in these clusters.

The distributions of Mulliken Charges of the optimized geometries are shown in Table 2. The calculated results show that negative charge centralizes on Cu and positive charge on Al in all the clusters and electrons shift from Al to Cu. The dipole moments of these clusters are also shown in Table 2. Dipole moments of II and IV are much larger than others.

The pair distribution function $g(r)$ curve of the $Al_{71}Cu_{29}$ alloy was obtained at 700 ℃ by X-ray diffraction experiment. The pair distribution function $g(r)$ may be defined as follows: $g(r)$ is proportional to the probability of finding another atom, at the same instance, at a distance r from the reference atom located at $r = 0$[10]. The first main peak is obvious in the $g(r)$ curve, as shown in Fig. 2. The value of r corresponding to the first maximum can be regarded as the nearest neighboring distance among atoms. It can be seen from Fig. 2 that the nearest neighboring distance between atoms in the $Al_{71}Cu_{29}$ alloy is about 2. 55 Å, which is close to the Al-Cu bond length in most of the optimized geometries. It reveals that the Al and Cu are easily to bond and there are large quantities of Al-Cu bonds in the melt. This agrees well with the fact that different atoms are easily to bond in melt[11]. Thus the nearest neighboring distance is mostly Al-Cu bonds in the melt.

It is seen that the Al-Cu bond in the optimized geometries becomes longer with the increasing number of atoms. The bonds become weak and departure from the experimental data. The Al-Al bond is close to the Al-Cu bonds in V, which is inconsistent with the fact that different atoms are easily to bond in melt. The Al-Cu bond in V (2. 75 Å) is far from the nearest neighboring distance in Fig. 2. So the geometry V might not exist in the $Al_{71}Cu_{29}$ melt. However, the bond lengths in the geometry II, III, IV are very close to the experimental data. The atomic ratio of Al and Cu in II, III, VI clusters is close to that in the alloy (2. 45: 1).

Al and Cu atoms do not distribute randomly in melt and some structural information in solid state may affect the liquid structure. It can be seen from the phase diagram[12] of Al-Cu alloy that Al_2Cu compound exists in the solid $Al_{71}Cu_{29}$ alloy. The crystal lattice of Al_2Cu is C16 and lattice parameters are $a = 6. 066$ Å, $c = 4. 874$ Å respectively[13]. The nearest neighboring distance of Al-Cu in the crystal lattice is 2. 567 Å, which is very close to the experimental data above. So there exists some correlation between the liquid and the solid. Al_2Cu might still exist in $Al_{71}Cu_{29}$ melt near the melting point. With the increase of atomic dispersion , the

Table 2　Distribution of Mulliken Charges in optimized geometry

| Geometry	Mulliken charges				Dipole moment
AlCu (I)	1-Al	0. 253 041	2-Cu	− 0. 253 041	0. 272 5
Al_2Cu (II)	1-Cu	− 0. 250 915	2-Al	0. 125 457	0. 689 6
	3-Al	0. 125 458			
Al_3Cu (III)	1-Al	0. 157 674	2-Al	0. 157 674	0. 300 2
	3-Al	0. 157 468	4-Cu	− 0. 472 817	
Al_2Cu_2(VI)	1-Cu	− 0. 347 748	2-Al	0. 347 385	0. 689 6
	3-Al	0. 347 385	4-Cu	− 0. 347 022	
Al_4Cu (V)	1-Al	0. 102 764	2-Al	0. 101 804	0. 542 7
	3-Al	0. 104 440	4-Cu	− 0. 413 081	
	5-Al	0. 104 073			
Al_4Cu_2(VI)	1-Al	0. 285 095	2-Al	0. 285 642	0
	3-Cu	− 0. 570 757	4-Al	0. 285 606	
	5-Cu	− 0. 570 731	6-Al	0. 285 145	

Dipole moment in Debye.
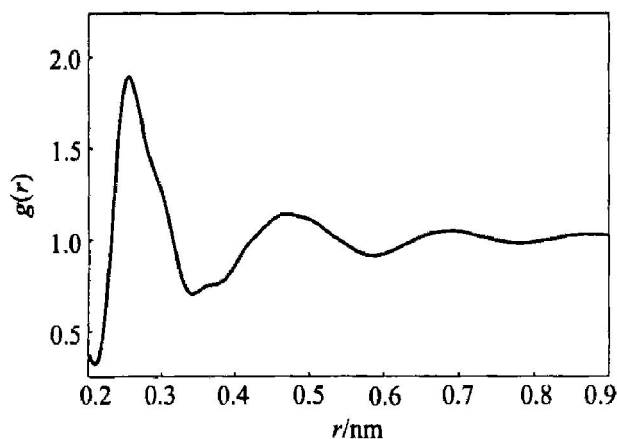
Fig. 2 Pair distribution function of liquid $Al_{71}Cu_{29}$ at 700 ℃

bonding might break up and more configurations will appear in the melt. The atomic group clusters in liquids may be formed by the combination of some molecules (or small clusters), such as the geometries in the Fig. 1, which has strong interactions among the internal atoms. The atom ratio between Al and Cu in the alloy is about 2. 45: 1. which is close to that in II, III and VI. So the optimized geometries (II, III, IV, VI) have a close correlation with the liquid structure of Al-Cu alloy.

4 CONCLUSIONS

Six geometries ground state of $Al_{1-4}Cu_{1-2}$ clusters were obtained by the abinitio. The average nearest atomic distance in the $Al_{71}Cu_{29}$ melt is about 2. 55 Å according to the X-ray diffraction experiment, which is close to the Al-Cu bond length in the calculated results. There are many Al-Cu bonds existing in the melt and the interactions between them are strong. The optimized geometries II, III, IV, VI have a close correlation with the liquid structure of Al-Cu alloy.

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