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Effects of spin orbital coupling on atomic and electronic structures in Al_2Cu and Al_2Au crystal and liquid phases via *ab initio* molecular dynamics simulations

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ABSTRACT

The origin of different melting points between Al_2Cu and Al_2Au has been studied using *ab initio* molecular dynamics simulations. Cohesive energy, electronic structures and structure information of both crystal and liquid phases have been analyzed. It is found that spin orbital coupling (SOC) plays an important role on the cohesive energy of crystal phase, consistent with the different melting points of these two alloys. Whereas, it seems that SOC has no effect on the formation energy and structure of liquid phase. Possible mechanism of reduced SOC effect at liquid phase is proposed. Our results are helpful to understand the glass formation ability difference between Al_2Cu and Al_2Au.

1. Introduction

Melting point is considered to be an important parameter for alloys [1,2]. The Al_2Cu alloy is composed of Al and Cu elements and very similar to Al_2Au alloy [3–5], as Cu and Au elements belong to the same main group with similar chemical reactivity [6–8]. Several studies on their atomic structure evolution in metallic liquids have been recently carried out [9–11], however, the melting point of 1333 K for Al_2Au is largely different from 890 K for Al_2Cu. Although the atomic structure of Al_2Au crystal phase (CaF_2-type face-centered cubic structure with space group of Fm-3m) is much more regular than that of Al_2Cu (mcm space group), the origin of the melting point difference for both alloys is still unsolved. In this paper we investigated both crystal and liquid phases of Al_2Cu and Al_2Au alloys. In case of crystal phases, it is revealed almost no difference in cohesive energy, electronic states and charge transfer between them without taking spin orbital coupling (SOC) into consideration. Whereas, all properties of Al_2Au vary largely when SOC was taken into account, which is largely different from Al_2Cu. The SOC is an interaction of a particle's spin with its motion (mainly between the electron's spin and the magnetic field generated by the electron's orbit around the nucleus). It has an important influence on heavy metal element atoms [12–14]. Distinct local atomic configurations in liquid phase between these two alloys may also play an important role in the origin of melting point difference [15–17]. In case of liquid phases, however, no significant changes of geometrical structure was found when SOC was considered for both Al_2Cu and Al_2Au melts through the analysis of pair-correlation functions, bond angle distributions, Honeycutt–Anderson (HA) index and Voronoi tessellation methods. The SOC effect on crystal phase is totally different from that on liquid phase and we confirmed the origin of this could be the random atomic positions of liquid phase, which reduces the SOC effect on structural and electronic properties of disordered system.

The paper is organized as following: Section 2, we present the theoretical background and the details of simulations; Section 3 contains calculation results together with their discussions. A brief summary and the main conclusion are given in Section 4.

2. First-principles methods

The first-principles calculations were performed using density functional theory from Vienna *ab initio* simulation package [18] with a plane wave basis and we employed Perdew–Burke–Ernzerhof (PBE) for the exchange and correlation functional [19]. The core electrons were represented by the projector-augmented-wave (PAW) potential. A plane wave basis with a

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cutoff of 400 eV was used to converge the structure. For geometric optimization, a cell containing 8 Al and 4 Au (Cu) atoms with periodic boundary conditions was built, the Brillouin zone integration was performed with 8 × 8 × 8 *k*-point sampling in Al_2Au (8 × 8 × 10 *k*-point sampling in Al_2Cu). For the calculation of electronic properties, Monkhors–Park 12 × 12 × 12 *k*-point sampling was used in the case of Al_2Au (12 × 12 × 15 in Al_2Cu).

Ab initio molecular dynamics (AIMD) simulations was performed for liquid structure with NVT ensemble (fixed number, volume and temperature) [20,21]. The potential was treated the same as crystal phases calculations. And only the Γ point was used to sample the Brillouim zone of supercell with an acceptable accuracy. An cell containing 96 Al and 48 Au (Cu) atoms was melted at about 300 K above the melting point (Al_2Au in 1600 K and Al_2Cu in 1200 K). After that an equilibration with 8000 MD steps (time step 3 fs) is performed to acquire the final stable configuration. It is noted that VASP only supports constant volume MD simulations and we adjusted the cell volume to make the external pressure of the cell to be nearly zero.

3. Results and discussion

Al_2Au crystal phase has a CaF_2-type structure with Fm-3m space group (No. 225). It looks like a simple cubic cell consisting of Au atoms occupied face centered cubic (FCC) sites and Al atoms occupied simple cubic (SC) sites. Its unit cell contains 4 formula units as shown in Fig. 1(a). The lattice constants we obtained is 6.054 Å with SOC (and 6.065 Å without SOC), in agreement with those of previous simulations based on plane wave basis [22]. Each Au atom has eight Al neighbors with the Au–Al distance of 2.621 Å, whereas each Al atom has four Au neighbors. On the other hand, Al_2Cu has a relatively complicated structure with space group I4/mcm (No. 140), shown in Fig. 1(b). The lattice constants are $a = 6.043$ Å and $c = 4.898$ Å with SOC ($a = 6.060$ Å and $c = 4.879$ Å without SOC). Each Cu atom has eight neighboring Al atoms with the Cu–Al distance of 2.584 Å and Cu–Cu distance of 2.449 Å. As the Cu–Cu bond length is shorter than Cu–Al bond length, Cu atoms seem to form the structure of Cu–Cu linear chain, which will be discussed later.

Cohesive energy is generally associated with the structural stability of crystal phase and a crystal phase with relatively lower cohesive energy is more stable than the one with higher cohesive energy [10]. Cohesive energy averaged on each atom are calculated according to equation

$$E_c = \frac{1}{x+y}(E[\mathrm{Al}_x\mathrm{M}_y] - x\mu_{\mathrm{Al}} - y\mu_{\mathrm{M}}) \qquad (1)$$

where x and y represent the number of Al and M (M = Au or Cu) atom in the cell, and $E[\mathrm{Al}_x\mathrm{M}_y]$ is the total energy of the cell of Al_2Au or Al_2Cu, μ is the chemical potential of single atom (Al/Au/Cu), which is calculated in a box of lattice constant more 20 Å with periodic condition. The calculated results of E_c are listed in Table 1: all the values are negative indicating their thermally stability [23,24]. It is found that the cohesive energy of Al_2Cu with and without SOC is almost same. While, the cohesive energy of Al_2Au with SOC is about 130 meV/atom lower (3.5%) than that without SOC. Although the cohesive energy difference between them is very small without SOC, the cohesive energy of Al_2Au is about 170 meV/atom lower in energy than Al_2Cu, indicating that Al_2Au crystal phase including SOC exhibits a higher structural stability relative to Al_2Cu. This means that SOC effect plays an important role for crystal stability and it might be helpful to understand the remarkable difference of the melting points between them.

SOC effect has an obvious influence on cohesive energy of crystal phases, which relates to the melting points. Does SOC also have an effect on the local structure of liquid phases, which is important for melting points. To investigate atomic structures of liquid Al_2Cu and Al_2Au with and without SOC, their structural evolutions were calculated by using *ab initio* molecular dynamics simulations. The atomic configurations have been analyzed by several statistics methods such as pair correlation function $g(r)$, bond angle distributions, Honeycutt–Anderson (HA) index and Voronoi tessellation index. It is found that the liquid local atomic structure of Al_2Au is distinct from Al_2Cu. However, no significant change is found when SOC was considered for both systems. The origin of this phenomena might be the random atomic positions of liquid phase, which reduce the SOC effect on amorphous system.

3.1. Liquid structures analysis

The pair correlation function (PCF) $g(r)$ is a very significant parameter for structural characterization of liquid or amorphous materials [22]. PCF is the statistic average of two body correlation over the system. It interprets the short range structure and chemical order. It is well known that the atomic structure of amorphous is similar to liquid structure. The total and partial PCFs for both systems are shown in Fig. 2. Comparing with Al_2Au system, the first peak of PCF becomes narrower and has a higher value in Al_2Cu system. It illustrates that there are more neighboring atoms for each atom in Al_2Cu within first atomic shell. The r value of first peak of Al_2Au is lower than that of Al_2Cu, indicating the averaged local atomic distances of Al_2Au are shorter than that of Al_2Cu. Especially, in partial PCFs for Cu–Cu and Au–Au, the shapes of the main peaks are obviously different and the first peak of Cu–Cu has a

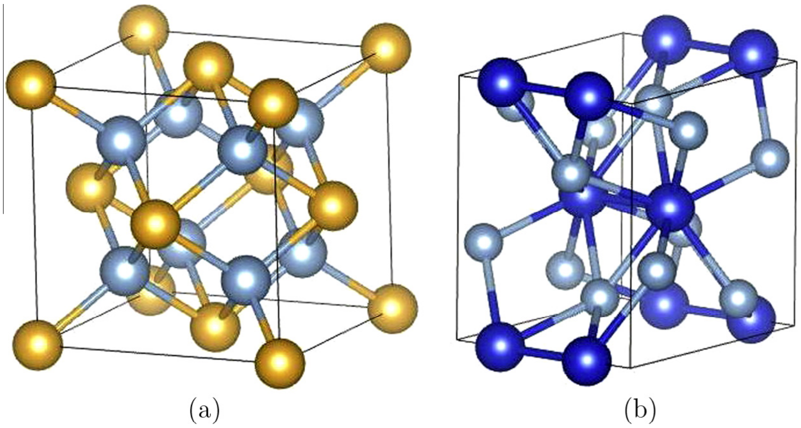
(a) (b)

Fig. 1. Atomic crystal structures of Al_2Au (a) and Al_2Cu (b). The small steel grey balls represent the Al atoms, the big brown (blue) balls represent the Au atoms (Cu atoms). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)