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First-principles investigation on the mechanical, vibrational and thermodynamics properties of $AuCu_3$-type X_3Sc (X = Al, Ga, In) intermetallic compounds

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ABSTRACT

First-principles calculation is performed to systematically study the structural stabilities, mechanical properties, vibrational and thermodynamic properties for $AuCu_3$-type Al_3Sc, Ga_3Sc and In_3Sc compounds. The calculated formation enthalpy and cohesive energy indicate that these compounds all have the high thermodynamics stability. The elastic constants are satisfied with mechanical stability criteria. The mechanical parameters predict that Al_3Sc has higher hardness than other two compounds. In the meantime, Al_3Sc possess brittle nature, but Ga_3Sc and In_3Sc are ductile. The mechanical anisotropy is predicted by anisotropic constants A^G, A^U, A^Z and 3D curved surface of Young's moduli. These results show that Al_3Sc is isotropic, but Ga_3Sc and In_3Sc are elastically anisotropic. The sound velocities in different directions and Debye temperature for Al_3Sc, Ga_3Sc and In_3Sc are also predicted. The calculated vibrational properties indicate that three compounds would keep the dynamical stability in $AuCu_3$ structure. Finally, we also calculate the thermodynamics properties and give out the relationships between thermal parameters and temperature.

1. Introduction

The $AuCu_3$-type Al_3Sc precipitates can form a stable and fine-grain structure and block the mobile dislocations. The outstanding features make Al based alloys with Sc elements have excellent mechanical properties at ambient and elevated temperatures. Al_3Sc precipitates are stable against coarsening up to temperatures of 350 °C, much higher than the capabilities of other commercial alloys containing Cu, Si and Mg. In general, the Al_3Sc have been deemed as an effective strengthening phase in the development of novel Al based alloys [1–7]. The physical properties of Al_3Sc have extensively investigated over the past twenty years. The elastic constants and mechanical properties of Al_3Sc have been investigated [8–16], indicating Al_3Sc is a brittle phase at ambient temperature. The investigations on the electronic properties indicate that Al_3Sc have the valence-bonding hybridization and more character of covalent bonds [16–19]. The thermodynamics and optical properties of Al_3Sc have also reported [16,17,20–23]. Li et al. [20] investigated the thermal properties of Al_3Sc over a wide range of pressure and temperature by means of using density functional theory and density function perturbation theory. They gave out the thermal parameters under different pressures, such as thermal expansion coefficients, heat capacity and entropy. Lee et al. [22] measured and calculated the optical conductivity by spectroscopic ellipsometry and FP-LAPW method. They found the curve for conductivity showed two peaks in the range of 1.5–5.5 eV. Chen et al. [23] also found the same results by using first-principle calculations.

Ga, In and Al are the same group elements, namely the 3A group elements. Ga/In and Sc also can form the $AuCu_3$-type intermetallic compounds, such as Ga_3Sc and In_3Sc [24–27]. Although many interesting experimental and theoretical works on physical properties of Al_3Sc have been reported in the past twenty years, only a few ones reported the physics properties of Ga_3Sc and In_3Sc. Markiv et al. [26] have studied the geometry of the Fermi surface of the Ga_3Sc by using the de Hassvan Alphen (dHvA) effect. Dwight et al. [27] have studied the structural, electronic, optical and thermodynamics properties of Ga_3Sc compounds with the FP-L(APW+lo) method. They demonstrated that Ga_3Sc had metallic character and ductile nature. However, to the best of our knowledge, many physical properties of Ga_3Sc and In_3Sc are still not well established or not yet investigated, such as phonon properties, mechanical behavior, thermodynamics properties and so on. We

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employ first-principles to systematically investigate physical properties of Ga_3Sc and In_3Sc. The main objective of the present work is to clarify the relative stabilities, mechanical, vibrational and thermodynamics properties of X_3Sc (X = Al, Ga, In) and perform a systematic and comparative investigation on physical properties for the three compounds. We hope that our work could provide a helpful guidance for future experimental and theoretical works.

2. Computational methods

We performed the first-principles calculations by means of using the VASP code [28] with the generalized gradient approximation (GGA) [29] and local density approximation (LDA) [30] exchange-correlation functional in the framework of density functional theory. We used all electron projector augmented wave (PAW) functions [31]. The cutoff energy of the plane-wave basis set was 500 eV. The Monkhorst-Pack special *k*-point scheme was $12 \times 12 \times 12$ grid meshes [32] in the Brillouin zone. During the geometrical optimization, all forces on atoms were converged to less than 1.0×10^{-4} eV Å^{-1}. In order to obtain the vibrational properties, we employed supercells approach to carry out the phonon calculation. We use the $3 \times 3 \times 3$ supercells for X_3Sc (X = Al, Ga and In). Real-space force constants are calculated by the density functional perturbation theory implemented in the VASP code. Phonon frequencies are calculated by using the PHONOPY code [33].

3. Results and discussion

3.1. Structural properties

The binary intermetallics X_3Sc (X = Al, Ga and In) have the cubic $AuCu_3$ ($L1_2$) crystal structure with the spatial group of Pm-3m (No. 221). The X and Sc atoms occupy the Wyckoff positions 3c (1/2,1/2,1/2) and 1a (0,0,0), respectively. Using both GGA and LDA methods, the equilibrium lattice constants are determined by minimizing the total energy with respect to variation of the cell volume. We fit the total energy vs. volume data to the Vinet equation of state (EOS) [34] and obtain the equilibrium lattice constant a_0. The structural parameters at zero pressure for X_3Sc compounds are shown in Table 1. In Table 1, we can see that the calculated lattice parameters are all in agreement with the available experimental and theoretical values. We can note that the results obtained by the GGA method are closer to the experimental values than that obtained by the LDA method. Therefore, we believe that the GGA method is a more reasonable method and will focus on the results from GGA calculations in the following discussions.

In order to determine the relative stability and alloying ability of X_3Sc (X = Al, Ga and In) intermetallics, the cohesive energy and formation enthalpy of each intermetallics are estimated by following formulas [35]:

$$\Delta H = \frac{1}{x+y}\left[E_{tot} - xE^{A}_{solid} - yE^{B}_{solid}\right] \quad (1)$$

$$E_{coh} = \frac{1}{x+y}\left[E_{tot} - xE^{A}_{atom} - yE^{B}_{atom}\right] \quad (2)$$

In Eqs. (1) and (2), E_{tot} is the total energy, x/y is the number of Al and X atoms, respectively. $E^{A}_{atom}/E^{B}_{atom}$ are the energies of Al and X atoms in the freedom states, respectively. $E^{A}_{solid}/E^{B}_{solid}$ are the energies of Al and X atom in the solids, respectively. The calculated results of E_{coh} and ΔH have also been listed in Table 1. Our values of E_{coh} and ΔH for Al_3Sc are in good agreement with the available experimental and theoretical data. It indicates that the calculated values of Ga_3Sc and In_3Sc are also reasonable, although these values of Ga_3Sc and In_3Sc are not reported by experimental and theoretical works so far. The calculated values of cohesive energies are −4.633 eV/atom, −5.271 eV/atom and −5.679 eV/atom for Al_3Sc, Ga_3Sc and In_3Sc, respectively. The values of E_{coh} are all negative, indicating their energetic stabilization. The values of formation energies are −1.84 eV/atom, −1.63 eV/atom and −1.48 eV/atom for Al_3Sc, Ga_3Sc and In_3Sc, respectively. The value of formation enthalpy is lower, the alloying ability is stronger [36,37]. Therefore, we can note that alloying ability of three compounds follows the order: $Al_3Sc > Ga_3Sc > In_3Sc$.

Table 2
Calculated elastic constants C_{ij} for Al_3Sc, Ga_3Sc and In_3Sc, including the reported experimental and theoretical data.

Compounds	C_{11}	C_{12}	C_{44}	References
Al_3Sc	183.2	39.96	71.32	This work
	183	46	68	Expt. [13]
	189	43	66	FLAPW [8]
	181.5	37.8	71.0	GGA-PW91 [9]
	191	43	82	VASP-UP [11]
	187.84	35.14	73.32	DFT-LDA [15]
	184.41	46	68	PBEsol [16]
	179.52	39.19	67.62	GGA-UP [23]
Ga_3Sc	138.76	42.17	36.37	This work
In_3Sc	92.36	39.99	18.62	This work

Table 1
The calculated lattice constant a_0 (Å), formation enthalpy ΔH (eV/atom) and cohesive energy E_{coh} (eV/atom) of X_3Sc together with available experimental and theoretical results.

Compounds	a_0	E_{coh}	ΔH	
Al_3Sc	4.103	GGA (This work)	−4.633 GGA (This work)	−1.84 GGA (This work)
	4.020	LDA (This work)	−4.644 PBEsol [16]	−1.80 Expt. [42]
	4.101	Expt. [38]	−4.64 LDA-CASTP [17]	−1.81 GGA [10]
	4.04	FLAPW [8]	−4.19 PW91-GGA [41]	−1.99 LDA [10]
	4.098	PBEsol [16]		−1.96 LDA [43]
	4.103	GGA-VASP [10]		−1.99 LDA [44]
	4.038	LDA-DPT [39]		
	4.055	ASA-LMTO [12]		
Ga_3Sc	4.121	GGA (This work)	−5.271 GGA (This work)	−1.63 GGA (This work)
	4.023	LDA (This work)		
	4.097	Expt. [25]		
	4.12	FPLAPW [29]		
In_3Sc	4.538	GGA (This work)	−5.679 GGA (This work)	−1.48 GGA (This work)
	4.216	LDA (This work)		
	4.477	Expt. [24]		