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Thermodynamic properties of Zr_2Al under high pressure from first-principles calculations

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Abstract. The equations of state (EOS) and other thermodynamic properties of hcp structure Zr_2Al are studied using first-principles calculations based on the plane wave pseudopotential density functional theory method within the generalized gradient approximation (GGA) for exchange and correlation. It is demonstrated that the ratio c/a of about 1.208 is the most stable structure for the hcp Zr_2Al, which is consistent with the experimental data. Through the quasi-harmonic Debye model, in which the phononic effects are considered, the dependences of relative volume V/V_0 on pressure P, cell volume V on temperature T are successfully obtained. The variations of the Debye temperature Θ, the thermal expansion a , the Grüneisen parameter γ and the heat capacity C_v with pressure P and temperature T are investigated systematically in the ranges of 0–100 GPa and 0–1500 K.

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Key words: equations of state, thermodynamic properties, generalized gradient approximation,Zr_2Al

1 Introduction

The equation of state (EOS) and other thermodynamic properties for crystalline materials are fundamentally important in studying the high pressure physics of solids and applied sciences, which provide insight into the nature of solid state theories. Intermetallic compounds and ordered alloys recently attracted much attention as practical materials, zirconium-aluminum

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alloys have potential application in aircraft turbine engines, medical, and the nuclear energy fields used as fuel-element-cladding materials due to their high strength, light weight, corrosion resistance and low neutron capture cross sections [1]. There are also numerous applications of zirconium-aluminum alloys as hydrogen getters in vacuum systems and microwave lasers. The zirconium-aluminum system is characterized by a number of intermetallic compounds which have been studied crystallographically by several investigators [2–10]. Especially, considerable work has been done to investigate the phase diagram and thermodynamic properities [11–16]. For example, Schneider *et al.* reported the free energies of formation of three compounds: $ZrAL_2$, Zr_2A1_3, Zr_4Al_3, measured by solution calorimetry at one temperature [17]; Kematick *et al.* studied the heats of formation of the zirconium-aluminum intermetallic compounds $ZrAl_3$, $ZrAl_2$, Zr_2Al_3, ZrAl, Zr_5Al_4, Zr_3Al_2, Zr_5Al_3 [15]. However, to date few thermodynamic data have been reported for Zr_2Al system.

In this paper, the equations of state (EOS) and other thermodynamic properties of hcp structure Zr_2Al are investigated by applying the first-principles plane-wave method within the generalized gradient approximation correction (GGA) in the frame of density functional theory [18] based on the Cambridge Serial Total Energy Package (CASTEP) program [19,20] and the quasi-harmonic Debye model [22], which allows us to obtain all thermodynamics quantities from the calculated energy-volume points.

2 Method of calculation

2.1 Total energy electronic structure calculations

In the present electronic structure calculation, we apply the GGA for the exchange-correlation functional in the scheme of Perdew-Burke-Ernzerhof (PBE) [22] to describe the exchange and correlation potential. A plane-wave basis set with energy cut-off 360 eV is applied. Pseudo atomic calculations are performed for $Zr(4d^2 5s^2)$ and $Al(3s^2 3p^1)$. For the Brillouin-zone sampling, we use the $9\times9\times8$ Monkhorst-Pack mesh, where the self-consistent convergence of the total energy is at 1.0×10^{-6} eV/Atom. All the total energy electronic structure calculations are implemented through the CASTEP code [19,20].

2.2 Thermodynamic properties

To investigate the thermodynamic properties of the hcp structure Zr_2Al, the quasi-harmonic Debye model is adopted. Our calculations are implemented through the Gibbs code by Blanco *et al.* [21], which is used to obtain as much thermodynamic information as possible from a minimum set of (E,V) data. In the following, a brief description for this model is presented.

In the quasi-harmonic Debye model, the non-equilibrium Gibbs function $G^*(V;P,T)$ is written as following

$$G^*(V;P,T)=E(V)+PV+A_{vib}(V;T), \tag{1}$$

where $E(V)$ is the total energy per unit cell for Zr_2Al, PV corresponds to the constant hydrostatic pressure condition, A_{vib} is the vibrational Helmholtz. Considering the quasi-harmonic