

## RESEARCH ARTICLE

# Chemical stability and thermodynamics of new Zr<sub>2</sub>-based heusler alloys

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**Abstract:** We present the spin polarized calculations on the new Zr<sub>2</sub>NiX (X = Al, Ga) alloys. Band structure analysis present them as half-metallic compounds with integral spin magnetic moment of 3 B following the general Slater-Pauling rule. Thermal effects on some macroscopic properties using quasi-harmonic Debye model which considers the phononic effects, the effects of pressure and temperature are taken into account. The variations of the thermal expansion coefficient, Debye temperature, Gruneisen parameter  $\gamma$  and heat capacity for the compounds have been investigated for the first time. These thermodynamic properties may prove as a reference for their synthesis.

**Keywords:** density functional theory, transition-metal compounds, thermodynamics

## 1 Introduction

The history of the Heusler alloys began in 1903. Friedrich Heusler discovered Cu<sub>2</sub>MnAl to be ferromagnetic, although its elements are all non-ferromagnetic.<sup>[1]</sup> The search initiated for other Heusler alloys with similar unit cells, only after when in 1929, scientists understood the microstructure completely. The theoretical prediction of 100% spin polarization of some Heusler alloys<sup>[2]</sup> especially Co<sub>2</sub>MnSi<sup>[3]</sup> makes them interesting for spin-electronic applications as an alternative for conventional 3d Ferro-magnets, such as Fe, Co or Ni and their alloys, exhibiting only 51% spin polarization at low temperatures.<sup>[4]</sup> The two Co sub-lattices are positioned at (0, 0, 0) and (1/2, 1/2, 1/2), where the Mn sub-lattice is at (1/4, 1/4, 1/4) and the Sb sub-lattice at (3/4, 3/4, 3/4) in the unit cell. Thus, eight cobalt atoms surround silicon and manganese atoms. Each cobalt atom has four silicon and four manganese atoms as next neighbors.

In present scenario efforts are focussed on the search of the new materials mainly focussed to use for spin technology to fulfil the basic demands of present technological era such as the powerful new generation of computing devices, shape memory devices etc.<sup>[5–7]</sup> Spintronics and magneto electronics which are the backbone in these

fields desire for the search of novel material which possibly will revolutionise these fields.<sup>[8,9]</sup> The advancement in spintronic devices have proven from the efficient and desirable 100% spin-polarized currents obtained at the Fermi level. These properties are proven by the eminent materials like half metallic materials that have electrons of unique spin polarization, around the Fermi level.<sup>[10–14]</sup> They are proving to be the promising candidate for use as spin injectors.<sup>[15]</sup>

The Zirconium based Heusler alloys have rarely been studied so far and hence, the present study is aimed to investigate the electronic structure, magnetism and transport properties of Zr<sub>2</sub>NiX Heusler compounds. The less toxic nature of zirconium has attracted the search of novel spintronic materials with unusual properties at the room temperature.

## 2 Computational methods

The calculations were carried out using the First-principles full-potential linearized augmented plane wave method (FP-LAPW).<sup>[16]</sup> The generalised gradient approximation (GGA)<sup>[17]</sup> is taken for the exchange-correlation potential. Inside the non-overlapping spheres of muffin-tin radius ( $R_{MT}$ ), the linear combination of radial solution of the Schrödinger equation times the spherical harmonics is used, whereas the plane basis set is chosen in the interstitial region. The muffin tin radii for Zr, Ni were set to 2.3 a.u. and 2.35 a.u., respectively while as 1.8 a.u and 1.9 a.u for Al and Ga, respectively.  $R_{MT}$  is chosen in such a way that there is no charge leakage from the core and the total energy convergence is ensured. Further, for the energy Eigen-value convergence, the wave function in the interstitial region is ex-

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panded in terms of plane waves with a cut-off parameter  $K_{MAX}R_{MT} = 9.00$ . The maximum value of the angular momentum  $l_{MAX} = 10$  is taken for the wave function expansion inside the atomic spheres. In the interstitial region the charge density and the potential were expanded as a Fourier series with the wave vector up to  $G_{MAX} = 12 \text{ a.u}^{-1}$ . The  $k$ -integration mesh was set to a size of  $(17 \times 17 \times 17)$  during the self-consistent cycles and a doubled  $k$ -mesh for calculation of the density of states. The self-consistent calculations are considered to converge only when the calculated total energy of the crystal converges to less than  $10^{-4}$  Ry.

In order to study thermal effects, quasi-harmonic Debye model. The model is sufficiently flexible in giving all thermo-dynamical quantities by incorporating the obtained results of energy and volume. In this model, non-equilibrium Gibbs function  $G^*(V; P, T)$  is defined as follows

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

where  $E(V)$  represents the total energy/formula unit,  $PV$  is the constant hydrostatic pressure condition,  $\theta(V)$ , is the Debye temperature and  $A_{vib}$  is the lattice vibration expressed as

$$A_{vib}(\theta, T) = nk_B T \left[ \frac{9\theta}{8T} + 3 \ln(1 - e^{-\frac{\theta}{T}}) - D(\theta/T) \right] \quad (2)$$

where  $n$  represents the number of atoms/formula unit,  $D(\theta/T)$  represents the Debye integral, where for the anisotropic solid,  $\theta$  is expressed by the following expression:

$$\theta = \frac{h}{k} \left[ 6\pi^2 V^{1/2} n \right]^{1/3} f(\nu) \sqrt{\frac{B_s}{M}} \quad (3)$$

here  $M$  is the molecular mass, and  $B_s$  the adiabatic bulk modulus, and  $f(\nu)$  is defined as

$$f(\nu) = \left\{ 3 \left[ 2 \left( \frac{21 + \sigma}{31 - 2\sigma} \right)^{3/2} + \left( \frac{11 + \sigma}{31 - \sigma} \right)^{3/2} \right]^{-1} \right\}^{1/3} \quad (4)$$

And  $\sigma$  is the Poisson ratio in the above relation. In order to get minimized value of the non-equilibrium Gibbs function with respect to volume at constant pressure and temperature mathematically is obtained as

$$\left( \frac{\partial G^*(V; P, T)}{\partial V} \right)_{P, T} = 0 \quad (5)$$

After solving above equation, one can obtain a relation for  $V(P, T)$ , i.e., thermal equation of state (EOS). Using Eq. (5) for different thermal properties, i.e., isothermal bulk modulus ( $B_T$ ), specific heat capacity values at con-

stant volume ( $C_V$ ) and at constant pressure ( $C_P$ ) and thermal expansion coefficient can be evaluated using the following formulas:

$$B_T(P, T) = V \left( \frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right) \quad (6)$$

$$C_V = 3nk_B \left[ 4D(\theta/T) - \frac{3\theta/T}{e^{\theta/T} - 1} \right] \quad (7)$$

$$C_P = C_V(1 + \alpha\gamma T) \quad (8)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (9)$$

Where  $\gamma$  is the Gruneisen parameter and is calculated from the following expression:

$$\gamma = - \frac{d \ln \theta(V)}{d \ln V} \quad (10)$$

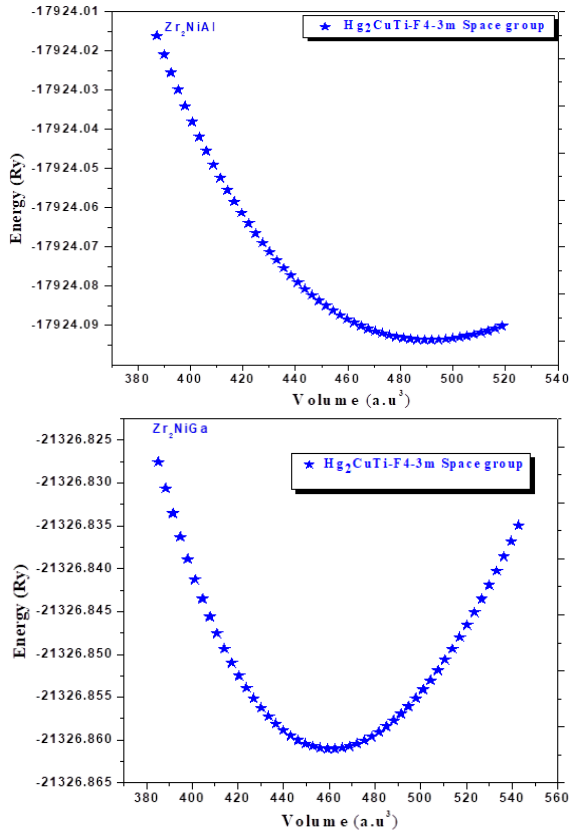
### 3 Results and discussion

#### 3.1 Structural properties and chemical stability

Highly magnetic materials mainly having either the  $L2_1$  and or  $C1_b$ <sup>[18]</sup> crystallographic phases have been of interest for both theorists and experimentalists since their discovery. The interest is mainly focused due to their strong ferromagnetic character, subsequently their usage as the testing grounds for the development of new magnetic systems. These novel class families share simultaneously the property of an energy gap between valence and conduction bands for electrons of one spin polarization and the property of continuous band for other spin polarization. This asymmetric character reflects the character of  $L2_1$  structure itself. In general, experimental preparation and interpretation of true half-metallic compounds are still scarce, therefore from the beginning, structural optimization is needed to estimate the magnetically and structurally stable phase by means of the total energy minimization. In the present series of new  $Zr_2NiX$  ( $Z=Al, Ga$ ) alloys we have investigated the stable ground state phase among the structures possible. Mostly the zirconium based Heusler alloys crystallize in the cubic ordered Full-Heusler ( $L2_1$ ) structure of  $Hg_2CuTi$ -type, with space group  $F-43m$  at ambient conditions. For the present compounds,  $Hg_2CuTi$  (space group 216) is found to be the stable ground state as shown in Figure 1.

Firstly, in order to assure their chemical stability and existence, we have calculated the formation energy of these alloys defined by the following equation:

$$E_f = E_{Zr_2NiZ} - 2E_{Zr} - E_{Ni} - E_Z \quad (11)$$



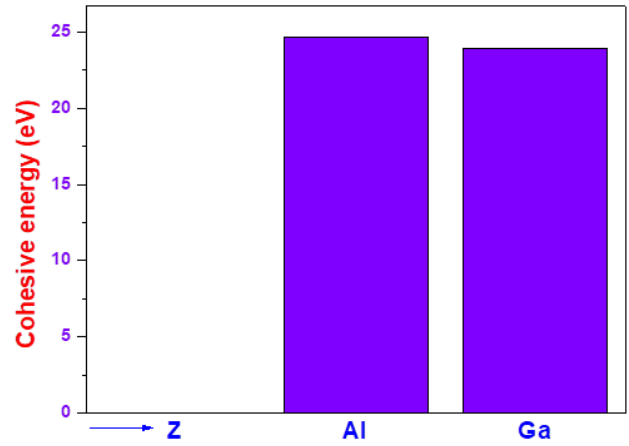
**Figure 1.** Calculated total energy as a function of unit cell volume of Zr<sub>2</sub>NiAl and Zr<sub>2</sub>NiGa in Hg<sub>2</sub>CuTi-type structures with F4-3m space group

where  $E_{Zr_2NiZ}$  are the calculated equilibrium total energies of alloys per formula unit,  $E_{Zr}$ ,  $E_{Ni}$  and  $E_Z$  are the chemical potential of these atoms in their stable bulk phases. Results showed that the  $E_{formation}$  of the Zr<sub>2</sub>NiZ (Z= Al, Ga) alloys are  $-2.33$  eV,  $-2.63$  eV, respectively. The calculated formation energy turns out to be negative and comparable for the same kind of compounds.<sup>[19]</sup> Negative formation energy indicates that the alloys are thermodynamically stable. In addition, we also calculate the cohesive energy to evaluate the strength of bonding of studied alloys. The cohesive energy is obtained from the following relation:<sup>[20]</sup>

$$E_{coh} = 2E_{atom}^{Zr} + E_{atom}^{Ni} + E_{atom}^Z + E_{total}^{Zr_2NiZ} \quad (12)$$

where  $E_{total}^{Zr_2NiZ}$  is the total energies of alloys at equilibrium per formula unit, and  $E_{atom}^{Zr}$ ,  $E_{atom}^{Ni}$ ,  $E_{atom}^Z$  are the total energies of the pure atomic components. It is evident that the cohesive energy is the energy required to break the crystal into isolated atoms, which is not only an indicator of the bonds strength but also an indicator of the mobility of atoms in crystal. In Figure 2, we show the cohesive energy of alloys, it is observed that Zr<sub>2</sub>NiAl

has the strongest bonding in comparison to the Zr<sub>2</sub>NiGa due to its larger cohesive energy, implying that it is difficult to deform in comparison to the latter.



**Figure 2.** The calculated cohesive energy is presented for Zr<sub>2</sub>NiZ alloys with respect to atomic no. (Z)

### 3.2 Magnetic Properties

Magnetic materials are now-a-days regarded as the potential candidates for spintronics. Mostly in case of Heusler alloys, the Y sites contributes greater to the total magnetic moment in comparison to the atoms at X site. In case of Heusler alloys the total magnetic moment is characterized by their total valence electron count defined through the Slater-Pauling rule. Here in our group of compounds the total valence electron count is 21. They satisfy the  $Z_T-18$  rule,<sup>[21,22]</sup> according to which they present a magnetic moment of  $3\mu_B$  per unit cell. The total magnetic moment with contributions from various components is given in Table 1. The magnetic alignment is ferromagnetic with maximum contribution from Z<sub>r</sub> atoms per unit cell in both compounds. Further it is the different occupation of the *d*-bands for the majority and minority spins that leads to the magnetization in these compounds.

**Table 1.** The total and atomic magnetic moments of Zr<sub>2</sub>NiAl and Zr<sub>2</sub>NiGa Compounds where  $M_{Int}$  ( $\mu_B$ ): magnetic moment in the interstitial region and  $M_{tot}$  ( $\mu_B$ ) is total magnetic moment.

| Compound             | $M_{Zr(a)}$ | $M_{Zr(b)}$ | $M_{Ni}$ | $M_{(Z=Al,Ga)}$ | $M_{int.}$ | $M_{tot}$ |
|----------------------|-------------|-------------|----------|-----------------|------------|-----------|
| Zr <sub>2</sub> NiAl | 1.02        | 0.98        | 0.61     | 0.15            | 0.11       | 2.87      |
| Zr <sub>2</sub> NiGa | 1.06        | 0.81        | 0.58     | 0.21            | 0.20       | 2.86      |

### 3.3 Thermodynamic properties

In order to calculate the pressure and temperature dependence of the thermodynamic properties, we

used quasi-harmonic (QH) approximation.<sup>[23,24]</sup> Specialty is that the values of thermodynamic parameters are computed at the level of the quasi-harmonic Debye model<sup>[25,26]</sup> approach for full-Heusler  $Zr_2NiAl$  and  $Zr_2NiGa$  alloys. Several properties are calculated which include the specific heats at constant volume ( $C_V$ ) and constant pressure ( $C_P$ ), Debye temperature ( $\theta_D$ ), thermal expansion coefficient ( $\alpha$ ), and Gruneisen parameter ( $\gamma$ ) in temperature range of 0 K to 800 K in steps of 100 K and at pressure ranging from 0 GPa to 70 GPa ( $Zr_2NiAl$ ) and 0 GPa to 30 GPa ( $Zr_2NiGa$ ) in steps of 5 GPa.

The graphical variations of various properties are shown in Figure 3, 4 (a, b), our calculated results for  $C_V$  and  $C_P$  each as a function of temperature are illustrated for  $Zr_2NiAl$  and  $Zr_2NiGa$  respectively. The important thermodynamic property viz, specific heat capacity is strictly related to the temperature dependence of ultimate thermodynamic functions, and it is utmost central constraint for associating thermodynamics with dynamics and microscopic structure. From the graphical variation, we can see that when the temperature is below 650 K,  $C_V$  and  $C_P$  variations are very close together demonstrating strong dependence on temperature owing to the anharmonic approximation used in this scheme of calculations. Further, we can also argue that at high temperatures,  $C_V$  approaches to a constant value of ( $97 \text{ Jmol}^{-1}\text{K}^{-1}$ ), obeying Dulong and Petit's rule, which is followed by all solids at high temperatures, owing to the suppression of the anharmonic effect.<sup>[27]</sup> The concluding statement which is quite interesting is that the specific heat capacity at constant pressure  $C_P$  increases monotonically with the increase of temperature.

**Table 2.** Calculated values of Debye temperature  $\theta$ (K) and Gruneisen parameter ( $\gamma$ ) of  $Zr_2NiAl$  and  $Zr_2NiGa$  at various pressures and temperatures

| Compound   | T (K) | Parameter | P (GPa) |        |        |        |
|------------|-------|-----------|---------|--------|--------|--------|
|            |       |           | 0       | 25     | 50     | 70     |
| $Zr_2NiAl$ | 300   | $\theta$  | 598.24  | 700.00 | 779.80 | 834.09 |
|            |       | $\gamma$  | 1.82    | 1.63   | 1.52   | 1.46   |
|            | 600   | $\theta$  | 592.84  | 696.38 | 776.83 | 831.51 |
|            |       | $\gamma$  | 1.83    | 1.63   | 1.52   | 1.46   |
|            | 800   | $\theta$  | 587.98  | 692.96 | 774.09 | 829.09 |
|            |       | $\gamma$  | 1.85    | 1.64   | 1.52   | 1.46   |
| $Zr_2NiGa$ | 250   | $\theta$  | 571.82  | 613.38 | 651.50 | 685.77 |
|            |       | $\gamma$  | 1.91    | 1.83   | 1.78   | 1.74   |
|            | 500   | $\theta$  | 567.48  | 610.13 | 648.15 | 684.69 |
|            |       | $\gamma$  | 1.92    | 1.84   | 1.78   | 1.74   |
|            | 700   | $\theta$  | 563.53  | 606.70 | 645.05 | 679.83 |
|            |       | $\gamma$  | 1.92    | 1.85   | 1.79   | 1.74   |

The thermodynamic properties with other physical properties of solids are closely related to the Debye tem-

perature ( $\theta_D$ ) and Gruneisen parameter ( $\gamma$ ). The variations of both the properties are respectively shown in Figure 3, 4 (c, d) with their numerical variation enlisted in Table 2. From the analysis of the properties, we can see that Debye temperature increases with increasing pressure whereas the Gruneisen parameter decreases when the temperature is kept constant. Here the concluding statement is that, at constant pressure, the Debye temperature decreases and the Gruneisen parameter increase as the temperature increases.

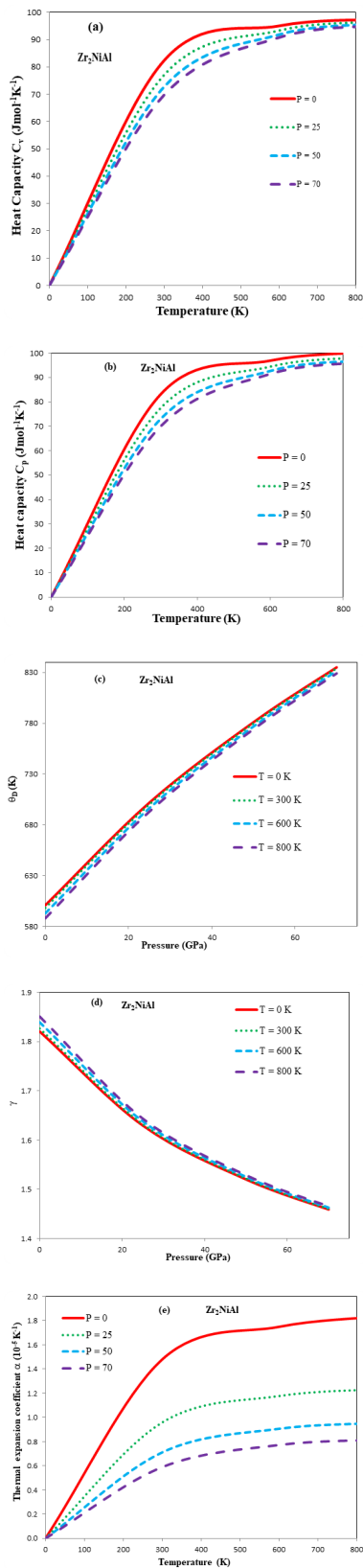
The mathematical formula reflecting the variation of volume thermal expansion coefficient ( $\alpha$ ) with volume at constant pressure is given as:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad (13)$$

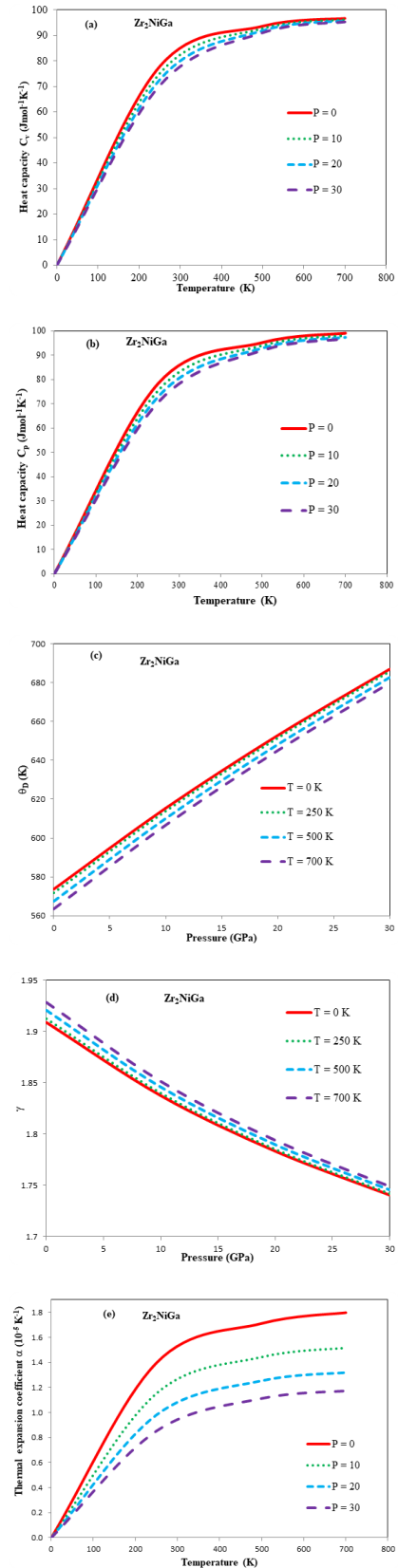
The variation of parameter is shown in Figure 3, 4 (e) with temperature at different pressures for the two compounds. The variation shows that the thermal expansion increases sharply with temperature up to 300 K after then slowly for temperature higher than 300 K, and gradually turns into a linear increase. Furthermore, we can also see that, at a fixed temperature, higher the pressure, smaller the thermal expansion coefficient, indicating that high pressure suppresses thermal expansion. At zero pressure and 300 K, the values of the thermal expansion for  $Zr_2NiAl$  and  $Zr_2NiGa$  are  $1.48 \times 10^{-5} \text{ K}^{-1}$  and  $1.43 \times 10^{-5} \text{ K}^{-1}$ , respectively.

## 4 Conclusion

First principle spin-polarised calculations for new inverse Heusler alloys within the GGA approach show the F4-3m as the ground state of  $Zr_2NiZ$  alloys with  $L2_1$  ordered structure. Magnetic moment of  $3\mu_B$  is characterised with the help of generalised Slater-Pauling rule of  $Z_T-18$  rule. Formation energy analysis show that these alloys are chemically stable and can be synthesised experimentally. Finally, the thermodynamic properties including volume variation, heat capacity, Debye temperature, and thermal expansion coefficients of the full-Heusler  $Zr_2NiAl$  and  $Zr_2NiGa$  compounds are investigated. The observed variations are well according with the results of the Debye theory, which is regularly applied to several materials.



**Figure 3.** Calculated thermodynamic properties of  $Zr_2NiAl$ : (a), (b)—Heat capacity, (c) Debye temperature, (d) Gruneisen parameter, (e) Thermal expansion coefficient.



**Figure 4.** Calculated thermodynamic properties of  $Zr_2NiGa$ : (a), (b)—Heat capacity, (c) Debye temperature, (d) Gruneisen parameter, (e) Thermal expansion coefficient.

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