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First Principles Calculations on Elastic, Thermodynamic and Electronic Properties of Co_2Zr and Co_2Ti at High Temperature and Pressure

Mi-An Xue ¹, Xiaoli Yuan ^{2,*}, Cheng Zhong ³ and Peng Wan ²

¹ Key Laboratory of Coastal Disaster and Defence (Hohai University), Ministry of Education, Nanjing 210024, China; coexue@hhu.edu.cn

² College of Science, Hohai University, Nanjing 210024, China; sunsetglow3@hhu.edu.cn

³ Department of Physics, School of Physical Sciences, University of Science and Technology of China, Hefei 230026, China; zhongche@mail.ustc.edu.cn

* Correspondence: xlyuan@hhu.edu.cn

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Abstract: Co_2Zr and Co_2Ti are both cubic crystals with a Cu_2Mg -type structure. The elastic, thermodynamic and electronic properties of the intermetallic compounds Co_2Zr and Co_2Ti are investigated by using ab initio plane-wave pseudopotential density functional theory (PWPdFT) and generalized gradient approximation (GGA) under high temperature and pressure. The partially calculated results are consistent with the available experimental data. The elastic properties of Co_2Zr and Co_2Ti under high pressure were first studied by first principles calculations. The results indicate that the elastic constants, elastic modulus and Poisson's ratio are functions of pressure, indicating that the effect of pressure on the ductility and anisotropy is significant. The thermodynamic properties are also calculated by the quasi-harmonic Debye model. In the range of 0–100 GPa pressure and 0–1500 K temperature, the Debye temperature Θ , the heat capacity C_V and the thermal expansion α vary with pressure and temperature. Co_2Ti has a higher Debye temperature than Co_2Zr under the same pressure. Decreasing temperature and increasing pressure have the same effects on C_V and α . The electron density difference and density of states of Co_2Zr and Co_2Ti are finally investigated. The results show that both Co_2Zr and Co_2Ti are typically metal crystals but Co_2Zr has greater covalence than Co_2Ti .

Keywords: elastic properties; thermodynamic properties; electronic properties; Co_2Zr and Co_2Ti ; high pressure

1. Introduction

Intermetallic compounds are widely exploited and utilized due to their distinguished properties among the common metal in mechanical, electrical, magnetic and chemical properties [1–3]. For instance, they show high tensile strength, good ductility, high corrosion resistance and thermal stability, which are attributed to the divergences in the chemical bonding of metal atoms [4–10]. In addition, intermetallic compounds can fill the existing gap between metal and non-metal materials due to their specific properties [11].

In order to make better use of intermetallic compounds as well as exerting their value, it is of importance for us to study their properties. The first principles calculations with ab initio plane-wave pseudopotential density functional theory (PWPdFT) and generalized gradient approximation (GGA) is, in general, considered to be the most effective and convenient method to study the properties of metal materials, since it does not require any experimental parameters but needs some basic physical constants to obtain the basic properties of the ground state of the system. The stability of the crystal structure is the most important properties of intermetallic compounds. First principles calculation with

density functional theory (DFT) has been successfully used to evaluate the stability of intermetallic compounds and predict their relevant properties [12–14]. Moreover, first principles calculations are also a very useful tool to calculate the equation of state (EOS) and thermodynamic properties in materials studies [15–17].

Co, Zr and Ti are transition metals and the three most basic elements making up alloy materials which under high temperature and high pressure used in business and industry. In the past ten years, more and more attention has been paid to Co-Zr and Co-Ti alloys. In the Co-Zr system, the presence of six compounds (i.e., $\text{Co}_{11}\text{Zr}_2$, $\text{Co}_{23}\text{Zr}_6$, Co_2Zr , CoZr , CoZr_2 , CoZr_3) was confirmed and their phase diagrams and thermodynamic evaluation were reported [18,19]. Likewise, there are five kinds of compound (TiCo_3 , h-TiCo_2 , c-TiCo_2 , TiCo and Ti_2Co) in Co-Ti system. Tetsuji Saito [20] studied the microstructure and magnetic properties of alloys in the Co-Zr system with an experimental technique. Liu et al. [21] used CALPHAD (calculation of phase diagrams) to evaluate the thermodynamics of the Co-Zr system. Wollmershauser et al. [22] computed the extension properties of CoZr and CoTi with the elastic plastic self-consistent (EPSC) polycrystal model. Nong et al. [23] made simple analysis about the elastic properties of Co_2Ti with first principles calculation. Xu et al. [24] studied the structural, elastic and thermodynamic properties of Co_3Ti by first principle. Meanwhile, the structural, electronic, elastic and thermal properties of CoZr and CoTi were calculated and compared by Acharya et al. [25]. Acharya et al. [26] studied the structure, elastic and thermal properties of CoX ($\text{X}=\text{Zr}$, Ti , Hf) by the methods of ab initio full potential linear augmented plane wave (FP-LAPW) and generalized gradient approximation (GGA). Shahab et al. [27] explored the kinetic energy and solute vacancy binding properties of Co_3Ti and Co_2Zr via first principles calculations. Ram et al. [28] investigated the synthesis, characterization and hydrogen storage properties of ternary alloy, Co-Zr-Ti, by the methods of XRD, SEM and EDS.

Alloy materials work at high temperatures, and some can even perform under high pressures in the aerospace and nuclear industries. The elastic properties and structural anisotropy under high pressure are very important to these materials for further applications. The changes in elastic characteristics under high pressure directly affect the mechanical stability of materials, which is the crucial factor for applications. It is also necessary to produce high quality and light alloys. It is significant to compare the properties of Co-Zr and Co-Ti alloys since both Ti and Zr belong to the same family of metal elements in the periodic table of elements. However, the elastic and thermodynamic properties of Co_2Zr and Co_2Ti under high temperature and pressure have been seldom reported. It is valuable to investigate the structure and electronic, elastic and thermodynamic properties of Co_2Zr and Co_2Ti in a cubic structure under high temperature and high pressure based on the first principles calculations with ab initio plane-wave pseudopotential density functional theory (PWP-DFT) and the generalized gradient approximation (GGA), as well as by the quasi-harmonic Debye model.

2. Computational Principles and Methods

2.1. Calculation Parameters

In the study, the CASTEP code is employed to perform the first principles calculations of all total energy electronic structures. Calculations were performed using norm-conserving pseudopotentials [29] with $3d^7 4s^2$ electrons used as valence for Co, $4d^2 5s^2$ electrons used as valence for Zr and $3s^2 3p^6 3d^2 4s^2$ electrons used as valence for Ti. The exchange-correlation energy of electrons is calculated through GGA-PBE function that is the combination of the Perdew-Burke-Ernzerhof (PBE) system and generalized gradient function (GGA) [30]. It can measure precisely the relaxed lattice constants, ensuring high accuracy of calculation. In our computations, the cutoff energy of plane waves expanding the electronic wave functions that is set for Co_2Zr and Co_2Ti is 540 eV, 500 eV for Co_3Ti [24]. Referring to the conclusion of Monkhorst-Pack [31], the k-points of Co_2Zr and Co_2Ti are set as $6 \times 6 \times 6$ and $7 \times 7 \times 7$, and $15 \times 15 \times 15$ for Co_3Ti [24], respectively, for Brillouin zone integration. Based on these parameters, the total energy of Co_2Zr and Co_2Ti is self-consistent converging to 3.4×10^{-7} eV/atom

and 2.0×10^{-7} eV/atom. These parameters are sufficient to calculate well converged total energy, geometrical configurations and elastic stiffness coefficients.

2.2. Elastic Properties

Elastic properties, indicating the bonding strength of the material atoms, anisotropy information and structural stability, are important parts of the study of metal materials. Elastic constants (C_{ij}) can help us to understand the mechanical and physical properties of metal alloys, such as ductility, hardness, melting point. Cubic crystal contains only three independent elastic constants (C_{11} , C_{12} and C_{44}). In addition, other physical quantity such as bulk modulus B , shear modulus G , Young's modulus E and Poisson's ratio σ can be also used to describe elastic properties. In cubic crystals, the following formulas are often used [32–34]:

$$B = B_S = (C_{11} + 2C_{12})/3, G = (G_V + G_R)/2 \quad (1)$$

where

$$C = (C_{11} - C_{12})/2, G_V = (2C + 3C_{44})/5, G_R = 15(6/C + 9/C_{44})^{-1} \quad (2)$$

$$E = \frac{9B_S G}{3B_S + G}, \sigma = \frac{3B_S - 2G}{2(3B_S + G)} \quad (3)$$

where G_V is the Voigt shear modulus and G_R is the Reuss shear modulus, B_S is the adiabatic bulk modulus. For cubic crystals, the mechanical stability is judged by Born stability criteria [35,36]:

$$C_{11} + 2C_{12} + P > 0, C_{44} - P > 0, C_{11} - C_{12} - 2P > 0 \quad (4)$$

where P is pressure.

2.3. Thermodynamic Properties

In order to study the thermodynamic properties of Co_2Ti and Co_2Zr , Blanco et al. [37] proposed the quasi-harmonic Debye model (QHDM), in which Debye temperature Θ , heat capacity C_V and thermal expansion coefficient α are often adopted [38]:

$$\Theta = \frac{h}{k_B} \left(\frac{3nN_A \rho}{4\pi M} \right)^{1/3} V_m \quad (5)$$

$$C_V = 3nk_B \left[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T} - 1} \right] \quad (6)$$

$$\alpha = \frac{\gamma C_V}{BTV} \quad (7)$$

In Equation (5), h is Planck's constant, k_B is Boltzmann constant, n represents the number of atoms in a chemical formula, N_A is Avogadro's number, ρ stands for crystal density, M means molecular weight, V_m is the average sound velocity and is given in the following formula [38]:

$$V_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (8)$$

$$v_s = \sqrt{\frac{G}{\rho}}, v_l = \sqrt{\frac{B_s + \frac{4}{3}G}{\rho}} \quad (9)$$

where v_s and v_l , respectively, stand for transverse and longitudinal elastic wave velocity, as obtained in Equation (9), namely the Navier equation.

In Equation (6), $D(\Theta/T)$ represents Debye integral; in Equation (7), γ stands for the Grüneisen parameters, B_T is the isothermal bulk modulus, and C_V is the heat capacity, while V is the volume [38].

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

$$B_T(P, T) = V \left(\frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right)_{P, T} \quad (11)$$

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

$$G^*(V; P, T) = E(V) + PV + A_{\text{vib}}(\Theta(V); T) \quad (12)$$

where $E(V)$ means total energy, and $A_{\text{vib}}(\Theta(V); T)$ is contribution of crystal vibration that can be written as:

$$A_{\text{vib}} = nk_B \left[\frac{9\Theta}{8T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right] \quad (13)$$

These formulas are used to calculate the thermodynamic properties of Co_2Zr and Co_2Ti .

3. Results and Discussion

3.1. Elastic Properties

The structural parameters of metal compounds, such as lattice constant a , cell volume V , structure and space group, should be figured out before analyzing their elastic properties. In Table 1, detailed structural information and reference data (Ref. [18]) of Co_2Zr and Co_2Ti at zero pressure are given. We can find that the optimized lattice constant, crystal volume and so on are in accordance with the given experimental and other theoretical results. The errors of lattice parameters are 0.47% and 0.25% for Co_2Zr and Co_2Ti , respectively. In addition, the values of B_0 , B_0' and B_0'' under 0 GPa pressure are provided, where B_0 is the bulk elastic modulus, B_0' is the pressure derivative of the bulk modulus, and B_0'' is the second pressure derivative of the bulk modulus. It can be seen from the table that the values of B_0 , B_0' and B_0'' of Co_2Zr crystal derived from the quasi-harmonic Debye model were 192 GPa, 4.370 and -0.031 , respectively, while those that are 192 GPa, 4.426 and -0.034 derived from the natural strain equation of state (EOS). For Co_2Ti , we can get $B_0 = 213$ GPa, $B_0' = 4.533$, and $B_0'' = -0.033$ through the Debye model along with $B_0 = 199$ GPa, $B_0' = 5.247$ and $B_0'' = -0.045$ through natural strain equation of state. Although Co_2Zr and Co_2Ti have the same cubic structure, lattice constant a of Co_2Zr is larger than that of Co_2Ti while values of B_0 and B_0' are smaller than the counterparts under the same condition. There are three independent elastic constants, C_{11} , C_{12} and C_{44} , in cubic crystal, and their values at 0 GPa, 0 K are given in Table 2. We can calculate adiabatic bulk modulus B_s , shear modulus G and Debye temperature Θ through Formulas (1), (2), and (5) with their results recorded in the Table 2. It was seen that the calculated values of Co_2Ti basically coincide with the reference values from Ref. [23]. Meanwhile, the data of other structures, such as CoTi [26] and Co_3Ti [24], are adopted to make comparison with these values. Unfortunately, there are no data available to compare with our results of Co_2Zr , thus we only exhibit the data of CoZr [26].

The values of C_{11} , C_{12} and C_{44} of Co_2Zr and Co_2Ti at 0 K and 0~100 GPa are provided in Tables 3 and 4. It may be seen from this table that our values agree well with other theoretical and similar structural results, with the errors of C_{11} , C_{12} and C_{44} being, respectively, 10%, 14.9%, 3.9% for Co_2Ti compared with Ref. [23]. According to the well-known Born stability criteria [35,36,39,40], if the three independent elastic constants satisfy Formula (4), the crystals are stable. Therefore, we can find that Co_2Zr is always stable under the pressure from 0 to 100 GPa, whereas Co_2Ti can satisfy the Born stability criteria only under pressures smaller than 80 GPa, which indicates that Co_2Ti is unstable when the pressure is more than 80 GPa. What is more, it is possible that a transition phase exists under the pressure of 85 GPa.

Table 1. The structure parameters of Co₂Zr and Co₂Ti at 0 GPa and 0 K.

Compd.		Space Group	Structure Type	a (Å)	V (Å ³)	B ₀ (GPa)	B ₀ '	B ₀ ''
Co ₂ Zr	Present work	Fd $\bar{3}$ m	Cu ₂ Mg	6.918	331	192 ^a	4.370 ^a	−0.031 ^a
		—	—	—	—	192 ^b	4.426 ^b	−0.034 ^b
Co ₂ Ti	Ref. [18]	Fd $\bar{3}$ m	Cu ₂ Mg	6.951	336	—	—	—
	Present work	Fd $\bar{3}$ m	Cu ₂ Mg	6.675	297	213 ^a	4.533 ^a	−0.033 ^a
		—	—	—	—	199.29 ^b	5.247 ^b	−0.045 ^b
	Ref. [18]	Fd $\bar{3}$ m	Cu ₂ Mg	6.692	299.69	—	—	—

^a quasi-harmonic Debye model. ^b natural strain equation of state (EOS).**Table 2.** The C_{ij} (GPa), B_S (GPa), G (GPa) and Θ at 0 GPa and 0 K.

Compd.		C ₁₁	C ₁₂	C ₄₄	B _S	G	Θ
Co ₂ Ti	Present work	331	154	132	231	112	834
	Ref. [23]	300	134	127	—	107	—
	Ref. [26] CoTi	287	114	75	—	79	314
	Ref. [24] Co ₃ Ti	269	168	119	—	84	—
Co ₂ Zr	Present work	283	137	107	192	92	721
	Ref. [26] CoZr	201	113	45	—	45	207

Table 3. The C_{ij} (GPa), B (GPa), G (GPa), E (GPa), Θ, Poission ratio σ, anisotropy factor A and G/B of Co₂Zr at various pressure.

P (GPa)	C ₁₁	C ₁₂	C ₄₄	B	G _V	G _R	G	E	Θ	σ	A	G/B
0	283	137	107	186	93	90	92	193	721	0.326	0.238	0.493
10	262	92	125	149	109	105	107	214	790	0.260	0.302	0.718
20	421	231	141	295	122	118	120	256	850	0.355	0.219	0.407
30	349	141	158	211	137	131	134	268	906	0.288	0.310	0.635
40	501	275	171	351	148	142	145	306	952	0.355	0.232	0.413
50	551	309	184	390	159	152	155	329	997	0.359	0.226	0.399
60	600	342	196	428	169	162	166	352	1039	0.363	0.222	0.387
70	645	371	208	463	179	172	176	373	1080	0.366	0.219	0.379
80	691	403	219	499	189	181	185	394	1121	0.368	0.216	0.371
90	757	433	229	541	202	197	200	442	1151	0.364	0.178	0.369
100	774	402	240	566	206	197	202	429	1185	0.374	0.139	0.357

Table 4. The C_{ij} (GPa), B (GPa), G (GPa), E (GPa), Θ, Poission ratio σ, anisotropy factor A and G/B of Co₂Ti at various pressure.

P (GPa)	C ₁₁	C ₁₂	C ₄₄	B	G _V	G _R	G	E	Θ	σ	A	G/B
0	331	154	132	213	114	110	112	233	834	0.317	0.253	0.528
10	390	190	149	257	130	125	127	266	920	0.327	0.253	0.496
20	327	154	129	211	112	108	110	228	929	0.320	0.259	0.519
30	317	144	129	202	112	108	110	227	1040	0.313	0.267	0.544
40	318	145	129	203	112	108	110	227	1098	0.313	0.267	0.542
50	313	140	129	198	112	108	110	227	1144	0.309	0.270	0.554
60	312	139	129	196	112	108	110	226	1191	0.308	0.271	0.559
70	312	139	129	197	112	108	110	226	1235	0.308	0.272	0.559
80	312	139	129	196	112	108	110	226	1276	0.308	0.271	0.558
90	318	145	129	203	112	108	110	227	1318	0.313	0.267	0.541
100	319	146	129	204	112	108	110	227	1359	0.314	0.266	0.539

The shear modulus G represents the plastic deformation resistance, while the bulk modulus B represents the fracture resistance. In 1954, the ratio between shear modulus G and bulk modulus B G/B was given by Pugh [41] to evaluate the ductility of given materials. A smaller G/B value indicates toughness while a larger G/B value shows brittleness, and $G/B = 0.57$ is the critical value between toughness and brittleness. The G/B values of Co_2Zr and Co_2Ti that change by pressure (0–100 GPa) at 0 K are given in Tables 3 and 4. For Co_2Zr crystal, the G/B values are abnormal at 10 and 30 GPa, which were 0.718 and 0.635, respectively, both over 0.57, which illustrates the Co_2Zr crystals are brittle at 10 and 30 GPa. Under other pressures, we can find that the G/B decreases continuously and is far less than 0.57 with the increase in pressure, indicating the toughness of Co_2Zr increases with the increment of pressure except at 10 and 30 GPa. For Co_2Ti , $G/B = 0.528$, Co_2Ti is apt to ductile at 0 K and 0 GPa. The G/B is in proportion to the pressure between 10 and 60 GPa, and the G/B is equal to 0.559 at the pressure of 60 and 70 GPa. When the pressure is greater than 70 GPa, the G/B is inversely proportional to the pressure, which manifests in the brittleness of Co_2Ti increasing with the increase in pressure when the pressure is less than uniaxial 60 GPa while the brittleness decreases with the pressure when the pressure is higher than 70 GPa. Comparing Tables 3 and 4, the G/B of Co_2Ti is always larger than that of Co_2Zr except when the pressure is 10 and 30 GPa, which illustrates that the toughness of Co_2Ti is weaker than that of Co_2Zr . Additionally, with its G/B value fluctuating around 0.55, the ductility of Co_2Ti varies little with pressure, being situated between toughness and brittleness.

Young's modulus presents the resistance of materials against tension. However, Poisson's ratio is defined as the ratio of transverse contraction strain versus longitudinal extension strain when materials are stretched. Poisson's ratio makes known the bonding properties within materials. Haines et al. [42] put forward that Poisson's ratio for pure covalent compounds is small (usually 0.1); for typical metals, the value is 0.33; for the ionic covalent crystal, it is between 0.2 and 0.3. The values of Co_2Ti are all over 0.3, which also confirms the metallic characteristic of Co_2Zr in the pressure range from approximately 0 to 100 GPa, whereas, the values of Co_2Zr are larger than 0.33, except for at 10 and 30 GPa, indicating the Co_2Zr is metallic but is an ionic covalent crystal at 10 and 30 GPa.

Anisotropy refers to a property that all or part of the physical or chemical properties of materials varies in direction, exhibiting the divergence in different directions. As an important property of crystal, anisotropy has significant value as it performs specifically in the elastic modulus, hardness, fracture resistance, yield strength, thermal expansion coefficient, thermal conductivity and so on. In the study of the anisotropy of crystals, we often use a dimensionless parameter A to represent it, that is, $A = [(C_{12} + 2C_{44})/C_{11}] - 1$ [38]. The anisotropic parameter A of Co_2Zr and Co_2Ti at 0 K and various pressures (0–100 GPa) has been given in the Tables 3 and 4. Table 3 shows that when the pressure is 20 GPa, there is a abnormal anisotropic parameter $A = 0.219$ in Co_2Zr . Except for 20 GPa, we can find that the anisotropy reaches its highest degree at the pressure of 30 GPa. When less than 30 GPa, the degree of anisotropy increases with the increasing of pressure while the trend is contrary when the pressure is more than 30 GPa. In addition, the degrees of anisotropy are equal at 20 and 70 GPa. The anisotropy of Co_2Ti varies regularly without any abnormal conditions. From 0 to 70 GPa, the degree of anisotropy increases with the increasing of pressure, whereas that is quite contrary above 70 GPa. We know that the anisotropy of Co_2Zr is larger than that of Co_2Ti only at 10 and 30 GPa by comparing Tables 3 and 4.

Finally, Figure 1a,b exhibit variation curves of elastic constants C_{ij} , elastic modulus E , shear modulus G and adiabatic bulk modulus B_S with pressure of these two crystals at 0 K. The elastic constant C_{11} stands for the elasticity in length and the longitudinal strain causes changes of it while C_{12} and C_{44} dominated by transverse strain, respectively, represent the elasticity in shape [31]. Figure 1a shows that in Co_2Zr , the changes in C_{11} and C_{12} with pressure are not monotonic, with the figures under 10 and 30 GPa lower than adjacent pressure. So, it is possible that the physical properties of Co_2Zr become abnormal, the reason for which is unknown under the present study. In addition, we can find that C_{44} increases monotonously with pressure. In all, however, as the pressure increases, C_{11} rises faster than C_{12} and C_{44} . Hence, C_{11} of Co_2Zr is more sensitive to pressure than C_{12} and C_{44} . However, the C_{11} , C_{12} , C_{44} of Co_2Ti are nearly insensitive to the pressure because the change curves of

these three elastic constants are approximately the same, and when the pressure is greater than 20 GPa, C_{11} , C_{12} , C_{44} tend to be stable, where C_{11} is much larger than C_{12} and C_{44} . So, the effect of pressure on the shape and length of Co_2Ti is very small.

Figure 1. The C_{ij} , E , G and B_s of (a) Co_2Zr and (b) Co_2Ti versus pressure at 0 K.

3.2. Thermodynamic Properties

The thermodynamic properties of Co_2Zr and Co_2Ti are analyzed with plane wave pseudo-potential density functional theory (DFT) based on quasi-harmonic Debye model (QHDM) [37] and generalized gradient approximation (GGA) method, concentrating on their Debye temperature Θ , Heat capacity C_V and thermal expansion coefficient α . The quasi-harmonic Debye model (QHDM) is used to study the physical properties of intermetallic compounds under high temperature [24,38]. Figure 2 shows that the V/V_0 of Co_2Zr and Co_2Ti are functions of pressure at 0, 500, 1000, and 1500 K. Under a certain temperature, pressure increases while the V/V_0 decreases monotonously. When the pressure is over 10 GPa, Co_2Zr decreases faster than Co_2Ti . When $P < 10$ GPa, the two crystals have the same V/V_0 , and will not be affected by temperature. When $P > 10$ GPa, V/V_0 decreases with increasing temperature at a certain pressure but the amount of variation is very small. What is more, the V/V_0 of Co_2Ti is always larger than that of Co_2Zr , which indicates the pressure has a greater impact on volume of Co_2Ti than that of Co_2Zr . Figure 3 illustrates the relationship between Bulk modulus B and pressure at a certain temperature (0 and 1500 K), as well as the relationship of bulk modulus B and temperature at 0 GPa. As shown in Figure 3, under the same temperature and pressure, the B of Co_2Ti is always larger than Co_2Zr . With the increasing of pressure, the B of these two crystals increases in the same trend under a certain temperature. At a certain pressure, the B value is inversely proportional to the temperature, and Co_2Ti falls more drastically than Co_2Zr does within the same temperature difference. Therefore, for both Co_2Zr and Co_2Ti , increasing the pressure and decreasing the temperature have the same effect on the B value.

Figure 2. The V/V_0 of Co_2Zr and Co_2Ti versus pressure from 0 to 100 GPa at 0, 500, 1000 and 1500 K.

Figure 3. (a) The bulk modulus B versus pressure P at 0 and 1500 K, and (b) the bulk modulus B_0 versus temperature T from 0 up to 1500 K at $P = 0$ GPa.

In the Debye model, the vibration of the elastic wave of the crystal is the main factor contributing to the heat capacity that reflects the ability to absorb heat from the surrounding environment. Figure 4a–c, respectively, show how the C_V of Co_2Zr and Co_2Ti vary with temperature under certain pressures (0, 50, and 100 GPa). Due to the anharmonic approximations of the Debye model used, the C_V values of Co_2Zr and Co_2Ti rely on temperature and pressure when $T < 1300$ K and a small amount of temperature difference will cause a great change in heat capacity. At a high temperature, the curve tends to be horizontal, which means that the heat capacity is close to constant, and the effects of temperature and pressure can be ignored. The heat capacity increases with the increasing temperature, but decreases with the increasing pressure, which indicates that the decrease in temperature and the increase in pressure have the same effect on the heat capacity of C_V . In addition, under the same conditions, the heat capacity of Co_2Zr is always greater than Co_2Ti .

Figure 4. The heat capacity C_v of (a) Co_2Zr and (b) Co_2Ti versus temperature at 0, 50, and 100 GPa; (c) the heat capacity C_v of Co_2Zr and Co_2Ti versus temperature at 50 GPa.

In the Debye model, the Debye temperature Θ often reflects the vibrational frequency of crystal atoms [38]. Figure 5 illustrates the change curve of Debye temperature Θ that varies with pressure at the given temperature (0, 1500 K). As the pressure goes up, the Debye temperatures of two crystals increase monotonously in the similar trend. Yet the effect of temperature is much less from 0 to 1500 K as the amount of variation of Debye temperature is very small, and the amount of variation decreases continuously with increasing pressure. If the pressure is stable, no matter how temperature changes, the Debye temperature of Co_2Ti is always greater than that of Co_2Zr , as shown in Table 3.

Figure 5. The Debye temperature as a function of temperature and pressure.

As a vital physical property of the materials, the thermal expansion can be used to investigate the various issues of related solid state. The thermal expansion coefficient α indicates the ability of an object to expand and shrink due to temperature changes. Figure 6a,b show the thermal expansion α as

a function of temperature T at different pressures (10, 30, and 90 GPa) and as a function of pressure P at different temperatures (500, 1000, and 1500 K), respectively. From Figure 6a, the thermal expansion coefficient α of Co_2Zr increases fast with increasing temperature when $T < 700$ K and the variation of it with temperature T is like that of C_V . When $T > 700$ K, the thermal expansion coefficient α approaches a linear increase but the amount of increase is small, indicating that α is close to a constant. The thermal expansion coefficient α of Co_2Zr is larger than that of Co_2Ti at low temperatures while it is opposite at high temperatures under the same pressure. From Figure 6b, it is seen that the thermal expansion coefficient α of Co_2Zr and Co_2Ti decreases exponentially with increasing pressure and the variation of it with pressure P is similar with that of V/V_0 , which means that there is a large thermal expansion at low pressure. Moreover, the influence of pressure on thermal expansion coefficient is almost equal at high and low temperatures.

Figure 6. Thermal expansion α as a function of (a) temperature at 10, 30, and 90 GPa; and (b) pressure at 500, 1000, and 1500 K for Co_2Zr and Co_2Ti .

3.3. Electronic Properties

To find origins of band structures, the total density of states and partial density of states are calculated, as shown in Figure 7. From Figure 7a,c, the main bonding peak between -2.5 eV and -0.5 eV are dominated by Co-d and Zr-p, Zr-d for Co_2Zr (see Figure 7a), and between -3.5 eV and -0.5 eV are contributed by Co-d and Ti-p, Ti-d for Co_2Ti (see Figure 7d) at 0 GPa. It is illustrated that pressure has little effect on the density of states of Co_2Zr and Co_2Ti in Figure 7b,c,e,f. However, the energy dispersion spectrum crosses the Fermi level ($E_f = 0$ eV), indicating Co_2Zr and Co_2Ti compounds are both electrical conductors. In addition, there are two spikes on both sides of the Fermi level where the value of DOS (density of states) is not zero, and the width between two spikes represents the pseudo gap. The wider the pseudo gap is, the stronger covalence is. Therefore, Co_2Zr has greater covalence than Co_2Ti .

Electron density difference can be used to study transfer and accumulation of electrons when atoms form compounds. Positive values indicate an increase in electron density while negative ones show a loss of electron density. To see the electron transfer and bonding property of Co_2Zr and Co_2Ti , we calculated the electron density difference in the (110) plane of Co_2Zr and Co_2Ti , as shown in Figure 8 at 0, 10 and 30 GPa. It is seen that the atoms at the four vertices of the (110) plane of two crystals form metal ions with losing electrons while electrons accumulate at the center of the plane to form electron clouds. There are no electrons around the rest of the atoms, and they exist in crystalline atomic form. Therefore, there are both metal ions and metal atoms in the two crystals, indicating that both Co_2Zr and Co_2Ti are metal crystals. With the increase in pressure, the degree of electron accumulation deepens. Comparing the electron density difference of two substances at the same pressure, the gain and loss of electron capacity of Co_2Ti is stronger than that of Co_2Zr , which proves that the covalent property of Co_2Zr is stronger than that of Co_2Ti .

Figure 7. The total density of states and partial density of states of Co_2Zr at (a) 0, (b) 10, and (c) 30 GPa; and that of Co_2Ti at (d), (e) 10, and (f) 30 GPa.

Figure 8. (color online) The electron density difference in the (110) plane of Co₂Zr at (a) 0, (b) 10, and (c) 30 GPa; and that of Co₂Ti at (d) 0, (e) 10a, and (f) 30 GPa, isosurface value: 0.1 e/Å³.

4. Conclusions

In this work, the elastic, thermodynamic and electronic properties of intermetallic compounds Co₂Zr and Co₂Ti in cubic structure are investigated and compared by first principles calculations. Detailed structural information of Co₂Zr and Co₂Ti are presented, and the optimized lattice constant, crystal volume, is in accordance with the available experimental value. The elastic constants, bulk modulus B , shear modulus G , anisotropy, ductility, heat capacity C_V , Debye temperature, thermal expansion coefficient α are functions of pressure and temperature. Co₂Zr is always stable while Co₂Ti is unstable when the pressure is more than 80 GPa, and it is possible that a transition phase exists under the pressure of 85 GPa. Co₂Zr crystals are brittle at 10 and 30 GPa, whereas the toughness of Co₂Zr increases with the increment of pressure except at 10 and 30 GPa. The toughness of Co₂Ti is weaker than that of Co₂Zr and reaches the highest point at 60 and 70 GPa. It is also found that the anisotropy of Co₂Zr and Co₂Ti reaches its highest degree at 30 and 70 GPa. Moreover, the anisotropy of Co₂Zr is larger than that of Co₂Ti only at 10 and 30 GPa. The thermodynamic properties are also predicted successfully. Debye temperature is a function of pressure and increases monotonically with

increasing pressure. The Debye temperature of Co_2Zr is always larger than that of Co_2Ti at various temperatures under the same pressure. Both the heat capacity C_V and thermal expansion coefficient α of Co_2Zr and Co_2Ti increase non-linearly with increasing temperature and decrease monotonically with increasing pressure, showing that the effect of increasing temperature is just the same as that of decreasing pressure. In addition, Co_2Zr always has larger heat capacity C_V than Co_2Ti under same condition. The thermal expansion coefficient α of Co_2Zr is larger than that of Co_2Ti at low temperature, while it is the opposite at high temperature under same pressure. Finally, the electron density difference and density of states of Co_2Zr and Co_2Ti are investigated. What is more, the total density of states and partial density of states are calculated to find origins of band structures. Co_2Zr and Co_2Ti are all metal crystals, but Co_2Zr has greater covalence than Co_2Ti .

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