First-principles study of mechanical and thermodynamic properties of Ti-Ga intermetallic compounds

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Abstract: A systematically investigation of Ti-Ga intermetallic compounds was performed to explore their mechanical and thermodynamic properties using density functional theory (DFT). Based on the experimental and theoretical reported data, a series of Ti-Ga alloys are chosen to study in this work. By assessing the elastic property of Ti-Ga alloys including bulk modulus, shear modulus, Young's modulus and Poisson's ratio, the results indicate that these Ti-Ga alloys are mechanically stable. The Pugh's ratio B/G is calculated to reveal that these Ti-Ga alloys display ductile character, except for Ga_3Ti and Ga_3Ti_2 . Meanwhile, the anisotropy factor A and Vickers hardness H_v are studied, and the hardness is found in the order: $Ga_3Ti > Ga_3Ti_2 > Ga_3Ti_5 > GaTi_2 > GaTi > GaTi_3$. Furthermore, the thermodynamic property is predicted by means of different empirical formulae, the results reveal that the alloys exhibit more high melting point and thermal conductivity. By the evaluation of the heat capacity with temperature 0~80 K, indicating that the electron excitations plays a main role below 17 K, while the phonon excitations mainly contribute to the heat capacity in the range of 31~80 K.

Keywords: Ti-Ga alloys, Elastic constants, Mechanical property, Thermodynamic property, Vickers hardness, Melting point

1. Introduction

Over recent years, Titanium-based alloys have caught a substantial attention of solid state and material scientists. That's precisely because of the excellent physical properties of Ti-based intermetallic compounds (ICs) which resulted in wide prospects in the aeronautical materials [1] and metallic biomaterials fields [2-7], such as load-bearing orthopedics, dental implants, denture frameworks etc [8-12].

As a new type of biomedical materials [13, 14], the phase diagram about Ti-Ga ICs have been drawn by Kaufman and Nesor [15] with thermodynamic calculation since the end of 20th century. Subsequently, Murray, Antonova and Li, et al. [16-18] conducted a supplement about phase diagram of the Ti-Ga system by experiments and thermodynamic assessment. Especially in recently years, the formation enthalpy of GaTi_3 was measured by Meschel and Kleppa [19] with the experimental method. Then, Qiu, et al. [20] investigated the microstructure, mechanical properties, electrochemical behaviors and cytotoxicity of three Ti-Ga alloys (Ti-2Ga, Ti-5Ga, Ti-10Ga) by optical microscopy and X-ray diffraction technique. These experimental results suggested that Ti-2Ga alloy displayed the optimal comprehensive performance and had potential for dental applications. Nevertheless, as a new biomedical material, there is no systematic study about the mechanical properties of Ti-Ga alloys system so far [21-23].

In order to get insight into the mechanical properties of Ti-Ga ICs, the first principles calculation have been performed on GaTi_3 , GaTi_2 , Ga_3Ti_5 , GaTi , Ga_3Ti_2 and Ga_2Ti intermetallic compounds by using the projector augmented wave (PAW) method. A set of physical parameters of Ti-Ga ICs, such as lattice constants, the density of states and mechanical properties (e.g. elastic constants, bulk and shear modulus, Young's modulus, anisotropy factor A and Pugh's ratio etc.), are evaluated and analyzed. Additionally, Debye temperature, melting point and heat capacity of those ICs are also predicted and discussed.

2. Calculation methods

All the relevant calculations are performed by using the Vienna ab initio Simulation Package (VASP) code [24, 25] based on density functional theory. The projector augmented wave (PAW) [26] pseudo-potential is used to deal with the electron-ion interactions. And the exchange and correlation function is treated by the Generalized Gradient Approximation Perdew-Burke-Ernzerhof parameterization [27]. The electron configurations are $3d^24s^2$ and $4s^24p^1$ for Ti and Ga atoms, respectively. A plane wave energy cutoff of 500 eV is employed. The Monkhorst-Pack parameters with the specified separation $0.02 \text{ \AA}^{-1}$ between neighboring grid points is adopted in Brillouin zone [28]. The atomic geometry of the system is fully relaxed until the Hellmann-Feynman forces exerting on all atoms are less than $0.01\text{eV/\AA}$ by the conjugate gradient algorithm. The elastic constants can be derived from the strain-stress relationship [29]. After obtaining the single-crystal elastic constants C_{ij} , polycrystalline properties such as bulk modulus, shear modulus, ductile/brittle and melting point are calculated by using the Voigt-Reuss-Hill approximation [30].

3. Results and discussion

3.1. Equilibrium structural properties

The crystal structures of Ti-Ga ICs (GaTi_3 , GaTi_2 , Ga_3Ti_5 , GaTi , Ga_3Ti_2 and Ga_3Ti) are studied in this work, as shown in Fig. 1. The optimized lattice parameters are summarized in Table 1 along with the corresponding experimental and others theoretical results. The formation enthalpy E_f and cohesive energy E_c of Ti-Ga ICs are calculated by the following definitions:

$$E_f(\text{Ti}_x\text{Ga}_y) = \frac{1}{x+y} [E(\text{Ti}_x\text{Ga}_y) - xE_b(\text{Ti}) - yE_b(\text{Ga})]$$

$$E_c(\text{Ti}_x\text{Ga}_y) = -\frac{1}{x+y} [E(\text{Ti}_x\text{Ga}_y) - xE_a(\text{Ti}) - yE_a(\text{Ga})]$$

where $E(\text{Ti}_x\text{Ga}_y)$ refers to the total energy of the binary Ti_xGa_y alloys, x , y , $E_a(\text{Ti})$, $E_a(\text{Ga})$ are the number and energy of an isolated Ti or Ga atom, respectively. $E_b(\text{Ti})$ and $E_b(\text{Ga})$ are the energy of bulk Ti and Ga. The structural

parameters and formation enthalpy of the different stoichiometric of the binary Ti_xGa_y alloys are given in Table 1. It is noteworthy for bulk material, the ground state of Ti is selected as α -Ti, whereas for Ga this is selected as Ga ($I4/mmm$) which has a much similar structure with Ga-rich Ti-Ga ICs.

Table 1

Calculated lattice constants (a, c), cohesive energy E_c (eV/atom) and formation enthalpy E_f (eV/atom) of equilibrium structures of Ti-Ga ICs.

Phase	Pearson symbol	Space group	E_c	E_f	A		c	
					This work;	Ref	This work;	Ref
Ga	tI2	I4/mmm	---	---	2.860	---	4.637	---
Ga_3Ti	tI8	I4/mmm	-4.249	-0.380	3.802	3.789^a	8.814	8.73
Ga_3Ti_2	tP10	P4/m	-4.905	-0.458	6.297	6.282^b	3.995	3.99
GaTi	tP4	P4/mmm	-5.299	-0.465	3.976	3.967^a	3.974	3.97
Ga_3Ti_5	hP16	P63/mcm	-5.707	-0.391	7.615	7.609^a	5.271	5.31
$GaTi_2$	hP6	P63/mmc	-5.872	-0.395	4.526	4.526^a	5.442	5.52
$GaTi_3$	hP8	P63/mmc	-6.120	-0.322	5.685	5.75^{a,d}	4.640	4.64
Ti	hP2	P63/M	---	---	2.923	2.951^c	4.631	4.67

^a[31]

^b[17]

^c[18]

^d[43]

Clearly, the computed lattice parameters of Ti-Ga ICs have the satisfactory agreement with the previous experiments and the reported theoretical data [17, 18, 31, 43]. The maximum deviation is 1.5% for $GaTi_3$. As shown in Table 1, the negative cohesive energies and formation enthalpy [32] suggest that these Ti-Ga ICs are thermodynamic stable, and both them tend to decrease with increasing of Ti content in Ti-Ga systems. According to the changing of formation energy, we conclude that the thermodynamic stability sequence is: $GaTi > Ga_3Ti_2 > GaTi_2 > Ga_3Ti_5 > Ga_3Ti > GaTi_3$.

Fig. 1. Crystal structures of Ti-Ga ICs: (a) Ga; (b) Ga_3Ti ; (c) Ga_3Ti_2 ; (d) GaTi ; (e) Ga_3Ti_5 ; (f) GaTi_2 ; (g) GaTi_3 ; (h) Ti; the blue and green sphere are Ti and Ga atoms, respectively.

3.2. Elastic properties and mechanical stability

Quite generally, a study of the elastic properties for biomedical materials is very important for practical applications. Elastic properties of substances are directly related to initial fundamental mechanical and thermal properties, likely, the ductile/brittle nature, compressibility, chemical bonds, specific heat, melting point, Debye temperature and thermal expansion coefficient et al. To get more knowledge about mechanical and thermal properties of Ti-Ga ICs by elastic constants, the PBE and PBE-sol approaches [33] are used to calculate the elastic constants of Ti-Ga ICs (Table 2), both methods give the broadly consistent elastic constants. In comparison with the PBE-sol method, the PBE method is in better agreement with the experimental values [34]. Thus the subsequent computations will be done by the PBE method.

The mechanical stability of Ti-Ga ICs is verified by the following standards for different crystals. For tetragonal crystal, the mechanical stability criteria have been list [35]: $C_{ii} > 0$, $i=1\sim6$; $C_{11}-C_{12} > 0$; $C_{11}+C_{22}-2C_{12} > 0$; $C_{11}+C_{33}-2C_{13} > 0$; $C_{22}+C_{33}-2C_{23} > 0$; $C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23}) > 0$; and the stability of hexagonal structure has to meet the following conditions [36]: $C_{11} > 0$; $C_{44} > 0$; $C_{12} > 0$; $C_{11}-C_{12} > 0$; $(C_{11}+C_{12})C_{33}-2C_{13}^2 > 0$.

From Table 2, it is found that the elastic constants of the binary Ti-Ga ICs are

higher than the pure Ga and Ti. It denotes that the different stoichiometric Ti-Ga ICs have a function of controlling to the mechanical properties of pure Ti or Ga. In general, the stiffness (elastic) constants of C_{11} or C_{33} are showing a character how easily the principle crystallographic a- or c-direction resistance to the linear response. In this work, the elastic constants C_{11} are obviously lower than C_{33} for those study structures except for Ga_3Ti_2 and Ga_3Ti_5 . The results suggest that those structures are more easy to compress along the a- axis than c- axis.

For the deduced Cauchy pressure $C_{12}-C_{44}$ [37], it is often used to describe the angular and brittle/ductile characters of a compound. As shown in Table 2, the calculated Cauchy pressure for most of Ti-Ga ICs are positive number, which reveals their ionic character and ductile behavior, whereas it is a negative value for Ga_3Ti_2 and GaTi meaning that they are classed as weak covalent and exhibit brittle character. Furthermore, according to the discussion of stable criteria, the elastic constants of all Ti-Ga structures satisfy these stability conditions, indicating that those structures are mechanically stable under normal pressure and temperature surroundings.

Table 2

The elastic constants (in GPa), Cauchy pressure $C_{12}-C_{44}$ (in GPa) of Ti-Ga ICs are calculated by using PBE and PBE-sol methods.

Phase	C_{11}		C_{33}		C_{44}		C_{66}		C_{12}		C_{13}		$C_{12}-C_{44}$	
	PBE	PBEsol	PBE	PBEsol	PBE	PBEsol	PBE	PBEsol	PBE	PBEsol	PBE	PBEsol	PBE	PBEsol
Ga	83.52	79.66	89.64	87.23	28.60	27.40	28.63	28.23	28.03	27.32	35.65	34.46	-0.57	-0.08
Ga_3Ti	182.99	180.04	190.05	185.65	70.97	69.95	110.04	107.08	85.83	81.70	49.11	47.01	14.86	11.75
Ga_3Ti_2	191.52	187.78	177.09	174.16	92.38	90.56	58.55	56.88	61.31	59.49	77.58	74.69	-31.07	-31.07
GaTi	178.41	174.41	180.33	177.06	103.22	101.12	63.61	61.24	86.76	83.97	90.38	87.48	-16.46	-17.15
Ga_3Ti_5	210.62	206.78	190.69	184.68	65.43	66.18	54.77	54.32	101.08	98.15	64.33	62.91	35.65	31.97
GaTi_2	208.74	203.70	219.68	211.48	64.91	64.52	49.31	48.14	110.13	107.40	63.21	62.45	45.22	42.88
GaTi_3	181.69	176.22	229.39	223.97	53.81	52.76	39.80	38.23	102.08	99.76	73.67	72.00	48.27	47.0
Ti	168.89	161.32	178.26	172.38	37.59	35.80	36.18	33.04	96.54	95.24	85.02	82.16	58.95	59.44

The mechanical properties, such as shear modulus (G), Young's modulus (E) and

Poisson's ratio (σ) of Ti-Ga ICs, are obtained from elastic constants employing Voigt-Reuss-Hill approximation [30] given in Eq. (1–9). For the tetragonal symmetry, the Voigt bounds of bulk modulus B and shear modulus G are [34, 38]:

$$G_V = \frac{12(C_{44}+C_{66})+C_{11}+C_{12}+2C_{33}-4C_{13}}{30} \quad (1)$$

$$B_V = \frac{2(C_{11}+C_{12})+4C_{13}+C_{33}}{9} \quad (2)$$

$$G_R = \frac{5(C_{11}-C_{12})C_{44}}{4C_{44}+3(C_{11}-C_{12})} \quad (3)$$

$$B_R = \frac{C_{33}(C_{11}+C_{12})-2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}} \quad (4)$$

For hexagonal, bulk modulus B and shear modulus G are given by Reuss and Voigt as follows equations [35, 39]:

$$G_V = \frac{2C_{11}+C_{33}-C_{12}-2C_{13}}{15} + \frac{2C_{44}+C_{66}}{5} \quad (5)$$

$$B_V = \frac{2(C_{11}+C_{12}+2C_{13}+0.5C_{33})}{9} \quad (6)$$

$$B_R = \frac{1}{2(S_{11}+S_{33})+2(S_{12}+2S_{13})} \quad (7)$$

$$G_R = \frac{15}{4(2S_{11}+S_{33})-4(S_{12}+2S_{13})+3(2S_{44}+S_{66})} \quad (8)$$

where the S_{ij} are the elastic compliance constants.

The elastic moduli of Ti-Ga ICs are calculated by Hill's average, $B_H = \frac{1}{2}(B_V + B_R)$ for bulk modulus and $G_H = \frac{1}{2}(G_V + G_R)$ for shear modulus. Beyond that, Young's modulus E and Poisson's ratio σ are also calculated by the following equations, respectively:

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

Table 3

Calculated bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Pugh's ratio B/G, Poisson's ratio σ of Ti-Ga ICs.

Structure	B			G			E		B/G	σ
	B _V	B _R	B _H	G _V	G _R	G _H	E (this work)	E (Ref)		
Ga	50.6	50.3	50.5	27.7	27.5	27.6	70.0	---	1.83	0.27
Ga₃Ti	102.7	102.2	102.5	75.2	70.3	72.7	176.4	---	1.41	0.21
Ga₃Ti₂	110.3	110.3	110.3	71.6	67.3	69.4	172.2	---	1.59	0.24
GaTi	119.1	119.1	119.1	72.0	62.8	67.4	170.1	---	1.77	0.26
Ga₃Ti₅	119.1	117.0	118.2	62.2	61.3	61.8	157.8	---	1.91	0.28
GaTi₂	123.4	122.8	123.1	62.5	60.0	61.3	157.7	---	2.01	0.29
GaTi₃	121.3	121.1	121.2	52.4	49.6	51.0	134.1	---	2.38	0.32
Ti	116.6	116.6	116.6	38.9	38.5	38.7	104.6	104.5^a	3.01	0.35

^a[20]

The obtained results of B, G, E, σ and the Pugh's ratio B/G have been presented in Table 3. According to Pugh's criteria [40], when the B/G is larger than 1.75, the material displays a ductile manner, or else indicates brittle nature. Here, we can clearly see that the value of B/G for most of Ti-Ga ICs, except the Ga₃Ti and Ga₃Ti₂, is greater than 1.75 in Table 3, which verifies the ductile character of Ga₃Ti and Ga₃Ti₂. Frantsevich et al. gave a new rule [41] on the base of Poison's ratio σ that the crystal is considered as a ductile material when σ is more than 0.26. This result further proves the same conclusions with the Pugh's ratio.

For reaching more information about the nature of bonding, σ is also used to further analyze the bonding of Ti-Ga ICs. The value of σ ranges from 0.0 to 0.50 for different materials. Covalently bonded materials have a small value for σ i.e. ~0.1 [42], for ionic crystals the critical value is 0.25 whereas for metallic materials it is 0.33. In this paper, the σ values of most of Ti-Ga ICs are found to be more than the critical value 0.25 and smaller than 0.33, except for Ga₃Ti and Ga₃Ti₂, signifying a ionic nature. Due to the different ions/covalent characters, it leads to the different

ductile/brittle behavior for the various stoichiometric Ti_xGa_y ICs.

Fig. 2. The calculated Bulk, Shear, Young's modulus with the atomic Ti content.

As can be seen from Fig. 2, along with the increase of Ti content in Ti-Ga systems, bulk modulus is an increasing tendency, while the shear modulus and Young's modulus show a contrary trend. As for a material whose Young's modulus is very high can be approximated as rigid. It is noted that the Young's modulus of Ga_3Ti is more than that of the other compounds, revealing a strong stiffness of Ga_3Ti .

3.3. Anisotropy and Vickers hardness

The anisotropic factors A (Shear, Elastic anisotropy) on different crystallographic planes provide a research method to the extent of anisotropy in atomic bonding in different planes. Therefore, the shear anisotropic factors A_1 , A_2 , A_3 are calculated and discussed based on the following definitions:

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad \text{for (100) shear plane.} \quad (10)$$

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \quad \text{for (010) shear plane.} \quad (11)$$

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \quad \text{for (001) shear plane.} \quad (12)$$

Table 4

Shear anisotropy, Elastic anisotropy and Vickers hardness of Ti-Ga ICs.

Structure	Shear anisotropy	Elastic anisotropy	Vickers
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	A_1	A_2	A_3	$A_B (10^{-2})$	A_G	A^U	hardness
Ga_3Ti	1.03	1.03	2.27	0.24	0.03	0.35	13.44
Ga_3Ti_2	1.73	1.73	0.90	0.0	0.03	0.32	10.90
$GaTi$	2.32	2.32	1.40	0.01	0.07	0.73	6.04
Ga_3Ti_5	0.96	0.96	1.00	0.85	0.01	0.09	7.44
$GaTi_2$	0.86	0.86	1.00	0.23	0.02	0.21	6.82
$GaTi_3$	0.82	0.82	1.00	0.07	0.03	0.28	4.24

For an isotropic material, the factors A_1 , A_2 , A_3 must be equal to 1.0. Otherwise, it is an anisotropic crystal. The shear anisotropic factors A are shown in Table 4. Obviously, all considered Ti-Ga ICs are elastic anisotropic. As for $A_1=A_2$, demonstrating that shear anisotropy for (100) shear planes between $\langle 011 \rangle$ and $\langle 010 \rangle$ direction is equal to that (010) shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ direction. On the other sides, shear anisotropy demonstrates different character of bonding in different directions, which has some important initial properties for these calculated structures since it related with the possibility to induce micro-cracks in ICs materials. Therefore, the elastic anisotropy A_B (compression), A_G (shear) [44], A^U (the universal elastic anisotropy index) are calculated since the shear anisotropy does not take the contribution of shear and the bulk into accounts, which are proposed as follows:

$$A_B = \frac{B_V - B_R}{B_V + B_R}, \quad A_G = \frac{G_V - G_R}{G_V + G_R} \quad (13)$$

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \geq 0 \quad (14)$$

where B_V (G_V) and B_R (G_R) are the bulk modulus (shear modulus) in the Voigt and Reuss approximations, respectively. The values of A_B and A_G can range from zero (isotropic) to 1 (the maximum elastic anisotropy). The crystal with $A^U=0$ displays isotropic, the deviation of A^U from zero suggests the extent of the single crystal anisotropy, the results of elastic anisotropy are also listed in Table 4. It is found that the deviated degree of elastic anisotropy A_G and A^U from zero for each structure shows the similar trends. The order of the anisotropy degree in the universal elastic anisotropic index about Ti-Ga systems is: $GaTi > Ga_3Ti > Ga_3Ti_2 > GaTi_3 > GaTi_2 > Ga_3Ti_5$.

According to the elastic constants, we can deduce some other mechanic properties of materials such as hardness of materials. Here, the hardness (H_V) is relative to G (G_H) and B (B_H) through the empirical formula based on the Pugh ratio $k=G/B$ [45, 46]:

$$H_V = 2(K^2 G)^{0.585} - 3 \quad (15)$$

The Vickers hardness of Ti-Ga ICs are calculated by Eq. (15) and shown in Table 4. It is found that the H_V shows a decreasing trend with the increasing of the Ti content from 0.25 to 0.75% in Ti-Ga systems, and Ga_3Ti is the hardest in the Ti-Ga ICs. This provides useful information for the applying in the biomedical materials scientists.

3.4. Thermodynamic properties

3.4.1. Debye temperature, melting point and thermal conductivity

As an important physical property, the thermodynamic property is often looked as relating to Debye temperature and melting point, which is a close relative about application perspective of material. The Debye temperature is a demarcation point of the editing regulation about heat capacity of solid. The value of Debye temperature can be estimated using the semi-empirical formulae through elastic constants and the averaged sound velocity V_m , the longitudinal sound velocity V_l and transverse sound velocity V_t [47, 48]. The formulae are defined as follows:

$$\theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} V_m \quad (16)$$

$$V_m = \left[\frac{1}{3} \left(\frac{2}{V_t^3} + \frac{1}{V_l^3} \right) \right]^{-\frac{1}{3}}, V_l = \left(\frac{B+4G/3}{\rho} \right)^{\frac{1}{2}}, V_t = \left(\frac{G}{\rho} \right)^{\frac{1}{2}} \quad (17)$$

Here, h and k are Planck and Boltzmann's constant, N_A is Avogadro's number, ρ is the density, M is the molecular weight and n is the number of atoms in a formula unit.

Table 5

Calculated the density ρ (g/m^3), transverse, longitudinal, average sound velocity (V_t , V_l , V_m in Km/s), the Debye temperature θ_D (K), melting point T_m (K) and the minimum thermal conductivity K_{min} ($W/(m \cdot K)$), value of DOS at Fermi level D_f (states/eV), the lowing temperature parameters of electron γ ($J/(mol \cdot K^2)$), phonon β ($J/(mol \cdot K^4)$) heat capacity of Ti-Ga ICs.

Phase	$\rho(g/m^3)$	V_t	V_l	V_m	θ_D	T_m	K_{min}	D_f	$C_p = \gamma T + \beta T^3$
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						This work: ref			$\gamma(10^{-3})$ $\beta(10^{-5})$		
Ga	6.108	2.13	3.78	2.37	264.0	739,	---	0.629	---	---	---
Ga ₃ Ti	6.700	3.29	5.46	3.64	431.1	1188,	1293^a	1.0585	3.33	7.850	9.70
Ga ₃ Ti ₂	6.395	3.29	5.63	3.65	433.3	1194,	1250^a	1.0781	6.61	15.58	11.95
GaTi	6.217	3.29	5.80	3.66	435.3	1160,	1428^b	1.0985	2.90	6.84	4.72
Ga ₃ Ti ₅	5.630	3.31	5.97	3.69	431.0	1272,	1240^a	1.0794	21.69	51.13	19.42
GaTi ₂	5.694	3.28	5.99	3.66	431.6	1310,	1270^a	1.0961	12.76	30.08	7.25
GaTi ₃	5.457	3.06	5.89	3.42	402.4	1243,	1293^a	1.0415	3.85	9.076	11.93
Ti	4.642	2.89	6.02	3.25	375.2	1128,	1155^c	0.9877	---	---	---

^{a,c} [17,18,19]

^b [21]

Furthermore, the thermal conductivity $K_{\min}$ and melting temperature of Ti-Ga ICs have also been calculated by employing the empirical relations (Eq. (18-19)) [49].

$$K_{\min} = \frac{K_B}{2.48} n^{0.67} (2V_t + V_l) \quad (18)$$

$$T_m = 354 + 4.5 \frac{2C_{11} + C_{33}}{3} \quad (19)$$

The calculated values of θ_D , T_m , $K_{\min}$ of Ti-Ga ICs are listed in Table 5. As seen in Table 5, the predicted θ_D , T_m , $K_{\min}$ of the Ti-Ga ICs are higher than the pure Ti or Ga. The deduced melting points are also approximately in agreement with the theory value [18]. The Debye temperature of pure Ti crystal is consistency with others' study (374K) [49]. But for the Debye temperature and $K_{\min}$ of Ti-Ga ICs, it is difficult to estimate error between the calculated and experimental data which has never been found.

3.4.2. Low temperature heat capacity

The heat capacity (C_p) at low-temperature are estimated by using electronic structures and Debye temperature of Ti-Ga ICs, defined as follows [50]:

$$\gamma = \frac{\pi^2 K_B^2 D_f}{3}, \quad \beta = \frac{12\pi^4 R n}{5\theta_D^3}, \quad C_p = \gamma T + \beta T^3 \quad (20)$$

For above formulae, γ , β represent the electronic and phonon contributions to the low-temperature specific heat, respectively. k_B , R are the Boltzmann, molar gas constant, D_f is the value of density of states (DOS) at the Fermi level and n is the total

number of atoms per formula unit. As shown in the formula (20), the low temperature heat capacity has been divided into two parts: electron and phonon excitations.

Fig. 3. Low temperature heat capacity of Ti-Ga ICs plot in range of 0~80K.

As shown in Table 5, GaTi has the smallest γ ($\gamma = 6.84 \times 10^{-3} \text{ J}/(\text{mol} \cdot \text{K}^2)$), which is attributed to its smallest value of DOS at the Fermi surface, revealing that the GaTi has the weakest metallic feature in the considered Ti-Ga compounds. The relationships between low temperature heat capacity and temperature of Ti-Ga ICs is analyzed and plotted in Fig. 3. It is obviously seen that the C_p of all Ti-Ga ICs increases with the increasing of temperature. Interestingly, the value of C_p follows the order of $\text{Ga}_3\text{Ti}_5 < \text{GaTi}_2 < \text{Ga}_3\text{Ti}_2 < \text{GaTi}_3 < \text{Ga}_3\text{Ti} < \text{GaTi}$ in the range 0~17.5 K. This sequence is agreed well with the sequence of γ , which indicates that electrons are playing a leading role in C_p in the range of 0 to 17.5 K. In the range of 31~80 K, the order of C_p ($\text{Ga}_3\text{Ti}_5 < \text{Ga}_3\text{Ti}_2 < \text{GaTi}_3 < \text{Ga}_3\text{Ti} < \text{GaTi}_2 < \text{GaTi}$) is the same as the sequence of β , manifesting that the phonon excitations has dominant contributions to the heat capacities within this temperature range. Therefore, we gain a conclude that electron excitations contributed to the low temperature heat capacity C_p foremost at very low temperatures near ~ 17 K. Otherwise, phonon excitations dominate when T rises .

4. Conclusions

In present work, the structural, elastic, mechanical and thermodynamic properties of Ti-Ga ICs are systematically studied by DFT within the generalized gradient

approximation (GGA):

- (1) The all Ti-Ga ICs are checked to be stable in mechanically and thermodynamic, and the dynamic stabilization of GaTi is the best in the Ti-Ga systems.
- (2) The Cauchy pressure and Pugh's ratio B/G are calculated. According to those results, both of them reveal that the Ti-Ga ICs display ductile character, except for Ga_3Ti and Ga_3Ti_2 .
- (3) Analysis of the anisotropy factor and Hardness prove that the Ti-Ga ICs display different degree anisotropy and Ga_3Ti is the hardest structure among Ti-Ga ICs.
- (4) Thermodynamic properties including the Debye temperature, melting point, thermal conductivity and heat capacity are predicted and discussion.
- (5) By the evaluation of the low temperature heat capacity with temperature at 0~80 K, revealing that the electron excitations plays a main role below 17 K, while the phonon excitations mainly contribute to the low temperature heat capacity in the range of 31~80K.

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