

Theoretical investigation of the Structural, electronic, and thermodynamics properties of $MM'Ge$ ($M=Ta$, $M'=Rh$) Intermetallic Compounds

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Abstract

An organized theoretical study implementing ab initio density functional theory (DFT) based on the full potential linearized plane wave (FP-LAPW) method to accomplish the investigation of structural, electronic, and thermodynamic properties of AB-Non-magnetic intermetallic compounds of $MM'Ge$ i.e., equiatomic transition germanide type structure with ($M= Ta$), ($M'= Rh$) intermetallic compounds. Structural properties are depicted in terms of energy versus volume histograms, lattice parameters, bulk modulus, and its first-order pressure derivative. Electronic properties were measured in terms of band structure and density of states. Thermodynamic properties of $MM'Ge$ were calculated using the quasiharmonic Debye model in the broad temperature range $0 < T < 300$ K. Electronic properties show that “s” and “d” orbital electrons of Ge and Rh have the dominant character in the valence region respectively. whereas Ta-d states are prominent in the conduction region. In thermodynamic properties, bulk modulus for TaRhGe shows a special character in different temperature ranges which have been discussed.

Keywords:

Intermetallics, Structural properties, Electronic properties, Thermodynamic properties.

Introduction

The existence of Equiatomic Ternary phase transition metal germanide compounds of the structure type $MM'Ge$ contain two d - transition metals i.e., M is a larger and electropositive metal and M' is a small transition metal from the iron group has been a topic of research.[1][2] These compounds have been studied in detail due to their crystal properties, electronic properties, thermodynamic and thermoelectric properties.[3] Previous studies include compounds that are formed by the combination of ($M = Ti, Mn, Zr, Nb, Ta$, and $M' = Ru, Rh, Pd, Fe$).[3][4] These combinations have led to the formation of various compounds such as TiRhSi, TiPdSi, MnRhSi, ZrFeGe, ZrRhGe, ZrPdGe, and NbRhGe), FeZrP (ZrRuSi), and TiFeSi (TiRuSi).[1][5][6] These structures as we observe are ternary

silicide or germanide with anti-PbCl₂ order.[7]The equiatomic transition metal silicide and germanide have been reported previously but only silicide has been discussed in detail regarding the crystal structure, electronic properties, and thermodynamic properties whereas germanide of transition metals though reported but has not been explored. TaRhGe compound was reported as a by-product in sealed tantalum tubes for compounds lithium-rhodium-germanide and europium-rhodium-germanide.[8] Though inert, this tantalum reacted with the rhodium-containing samples and lead to the synthesis of TaRhGe in bulk amounts.

Computational approach

Full-potential linearize augmented plane wave plus local orbitals (FP-LAPW + lo) method based on density functional theory (DFT) [9][10][11] using generalized gradient approximation (GGA) [12] for the purpose of exchange-correlation energy functional has been used to calculate structural and electronic properties of MM'Ge (M = Ta, M' = Rh) in orthorhombic phase. Quasi-harmonic Debye model [13][14] has been used to calculate temperature-dependent thermodynamical calculations. The k and E convergences were checked by increasing the number of k points and the energy convergence criteria. In the fundamental part of the Brillouin zone, 14 x 14 x 14 k points were used to calculate the total and partial density of states.

The quasi-harmonic Debye model was implemented using the Gibbs2 package [13][14], the non-equilibrium Gibbs function $G^*(V; P, T)$ is

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

Total energy per unit cell $E(V)$ of MM'Ge (M = Ta, M' = Rh), PV denotes the constant hydrostatic pressure, Debye temperature $\theta(V)$, and the vibration term (A_{vib}) which can be expressed using Debye model of the phonon density of states [15]

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

Here, n is the number of atoms per unit formula unit, $D(\theta/T)$ is the Debye integral. Thus, for an isotropic solid, θ is expressed as

$$\theta_D = \frac{\hbar}{k} \left[6\pi V^{\frac{1}{3}} n \right]^{\frac{1}{3}} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (3)$$

Here, M is the molecular weight per unit cell and B_s is the adiabatic bulk modulus, which is nearly equal to static and the compressibility is

$$B_s = B(V) = V \frac{d^2 E(V)}{d^2 V} \quad (4)$$

And $f(\sigma)$ is given by

$$f(\sigma) = \left[3 \left\{ 2 \left(\frac{2(1+\sigma)}{3(1-2\sigma)} \right)^{\frac{3}{2}} + \left(\frac{1+\sigma}{3(1-\sigma)} \right)^{\frac{3}{2}} \right\}^{-1} \right]^{\frac{1}{3}} \quad (5)$$

The non-equilibrium Gibbs functions as a function of ($V; P, T$) is minimized with

respect to volume V :

$$\left[\frac{\partial G^*(V;P,T)}{\partial V} \right]_{P,T} = 0 \quad (6)$$

By solving the above equation, we thus obtain the thermal equation of state (EOS) $V(P, T)$. The specific heat at constant volume and pressure (C_V, C_p) and thermal expansion coefficient α by using the expressions:

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

$$S = nk \left[4D \left(\frac{\theta}{T} \right) - 3 \ln \left(e^{\frac{\theta}{T}} - 1 \right) \right] \quad (8)$$

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

$$C_p = C_v(1 + \alpha \gamma T) \quad (10)$$

Here γ is the Grüneisen parameter, shown by

$$\gamma = \frac{d \ln \theta(V)}{d \ln V} \quad (11)$$

Result and Discussion:

Structural properties:

MM'Ge (M = Ta, M' = Rh) compound is stable in the orthorhombic phase with lattice parameters ($a = 6.38 \text{ \AA}$, $b = 3.80 \text{ \AA}$, $c = 7.40 \text{ \AA}$ for TaRhGe. Unit cell structures of MM'Ge (M = Ta, M' = Rh) generated by the "Xcrysden package[16] are shown in figure 1 (a-d). Structural characteristics in equilibrium state i.e., Energy versus volume histograms, lattice parameters (a_0, b_0, c_0), Bulk modulus (B_0) and its first order pressure derivative (B'_0) are calculated by fitting the total energy according to the birch-murnaghan's equation of state.[17][18]

$$E_{Total} = E_0(V) + \frac{B_0 V_0}{B'_0(B'_0 - 1)} \left[B'_0 \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{B'_0} - 1 \right] \quad (12)$$

Where, $E_0(V)$ and V_0 are energy and volume at equilibrium. B_0 and B'_0 are the equilibrium bulk modulus and its first order pressure derivative. The energy versus volume curves for MM'Ge (M = Ta, M' = Rh) have been shown in Figures 2 (a).

Measured lattice parameters (a_0, b_0, c_0), bulk modulus (B_0) and first order pressure derivative (B'_0) are shown in Table 1

Table 1. Equilibrium volume V_0 (a. u.)³, Lattice constant a_0 (Å), Bulk modulus B_0 (GPa), Pressure derivative of bulk modulus B'_0 (GPa) in equilibrium condition for TaRhGe using GGA.

S.No.	a .	b .	c .	V .	E .	B .	B' .
1	6.38	3.80	7.40	1239.13	-180084.19	219.07	4.50
2	6.40	3.83	7.41				

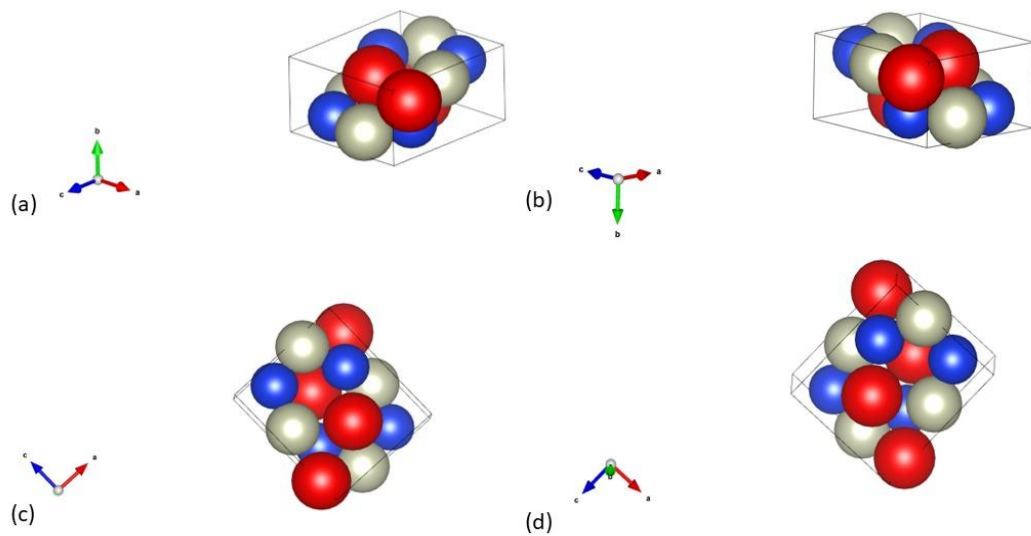


Figure 1: The unit cell structure of TaRhGe.

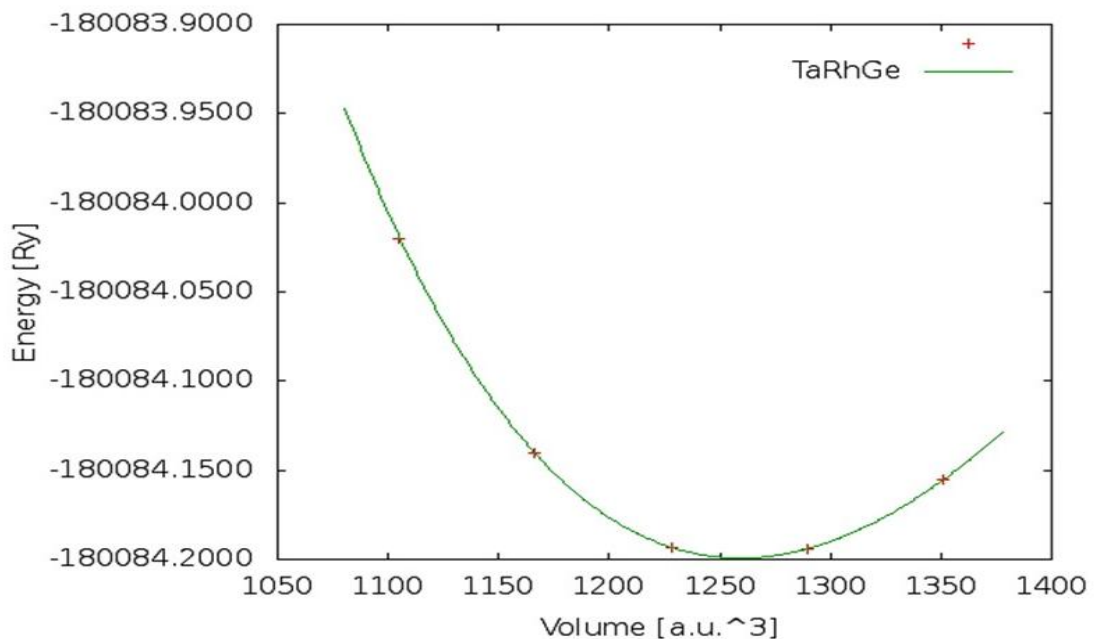


Figure 2: Total energy as a function of volume for TaRhGe.

Electronic properties:

Here, electronic properties are discussed by means of total and partial density of states. Total density of states (TDOS) plots for TaRhGe and projected density of states (PDOS) plots for Ta, Rh and Ge have been shown in figures 3 (a-e) respectively. In figure 3(a-e) the dotted lines at the origin indicate the Fermi level (E_F). The energy range is approximately between -10 eV to 10 eV for TaRhGe and Ta, Rh and Ge. In figure 3 (a) the

compound TaRhGe has a prominent share in the valence band region as compared to conduction band region. It is also visible in figure 3 (b) we acknowledge that Rh-d and Ge-s contribute more to the valence band from -10eV to Fermi level as compared to Ta-d which is broader in the valence band region. Also, Ta-d is responsible for the contribution to the conduction band around 1-2 eV. It is noticed in figure 3 (c-e) the PDOS of s, p and d states for Ta, Rh and Ge shows that the Ta-d state has a major contribution in the conduction band region. Whereas Rh-d and Ge-s states contribute to the valence band region. Bonding is observed as major in the valence part of the Rh 4d states i.e., from -6 up to -1 eV. Also tantalum shows positive bonding with contribution by larger Ta-Rh than Ta-Ge. Thus making it vital that strong hybridization exists between Ta, Rh and Ge.

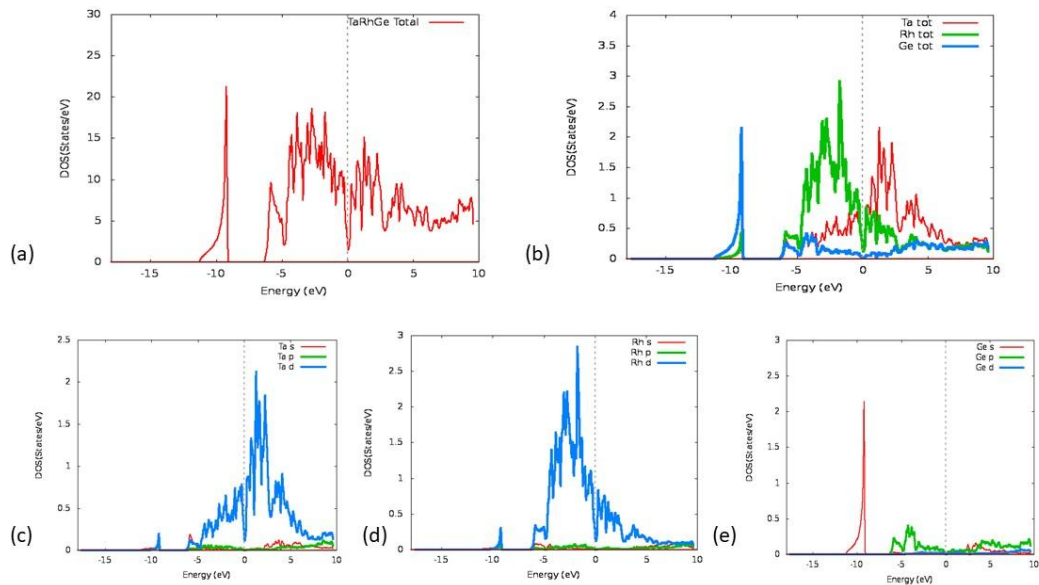


Figure 3. Calculated (i) Total density of states for (a) TaRhGe (b) Ta, Rh, Ge (ii) Projected density of states for (c) Ta- “s”, “p”, ”d” (d) Rh-“s”, “p”, “d” (e) Ge- “s”, “p”, “d” orbital. **Thermodynamic properties**

Thermodynamic characteristics of $MM'Ge$ ($M = Ta, M' = Rh$) were calculated using Quasi-harmonic Debye model effectively. Temperature variation of V , B , θ_D , γ , C_V and α for TaRhGe have been shown in Figures 4 (a-f). It is noted from figures 4(a) that unit cell volume (V) remains constants up to 200 K and it grows with temperature for the TaRhGe compound. The unit cell volume boosts with temperature due to the growth of its dimensions with temperature. Bulk modulus being property of material confirms the degree of resistance of a material for compression. Greater degree of resistance is offered because of the larger bulk modulus. Figure 4 (b) shows that bulk modulus behaves interestingly with respect to temperature for TaRhGe. Thus, we observe that bulk modulus of TaRhGe compound decreases because with increasing temperature in the whole temperature range 0-1400K i.e., it becomes flexible in this range.

It was also observed from Figures 4 (c), Debye temperature θ_D first it remains constant till 200k and then decreases with growing temperature. It is evidently visible that the

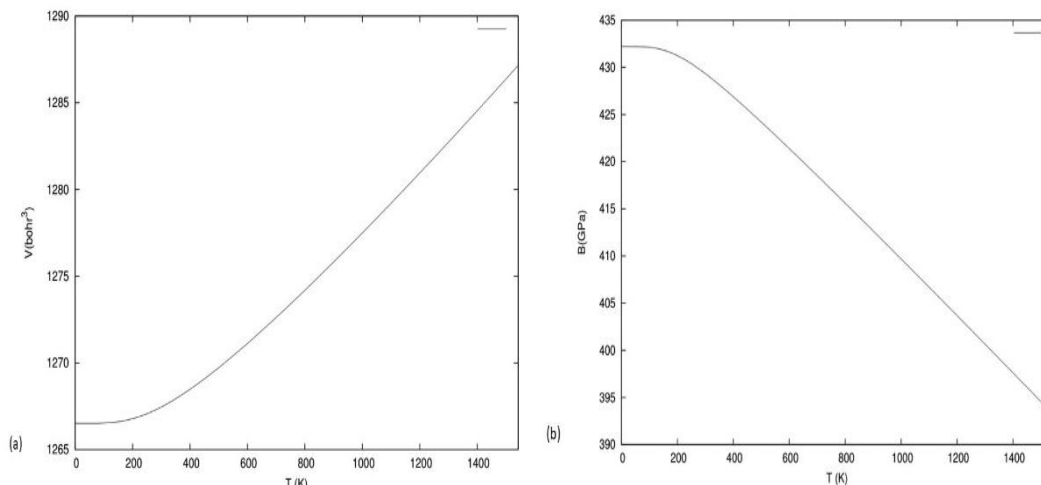
larger deviation in θ_D with temperature, demonstrates larger effect of temperature on θ_D . We observe that the fluctuation of Debye temperature θ_D with temperature signifies the reality that thermal vibration frequency of the atoms changes mostly with temperature.

In figures 4 (d) the variation in temperature for Grüneisen parameter. It is observed from the figure and the Grüneisen parameter first remains constant till 200 K and then increases with temperature. Increase in Grüneisen parameter which is almost monotonic with temperature showing that temperature has no significant role on Grüneisen parameter.

The heat capacity at constant volume C_V behaviour is displayed in Figures 4 (e). We observe from these figures that C_V grows with the temperature till $T \approx 600$ K (follows Debye T^3 law) and at temperature $T > 600$, approaches a constant value i.e., (Dulong-Petit limit) which is indicative of more impact of temperature on the heat capacity C_V . Figures 4 (f) show the variation of thermal expansion coefficient, α as a function of temperature.

Rapid increase in thermal expansion coefficient especially in temperature range $0 < T < 500$ K, while it gradually increases in higher temperature range $500 < T < 1400$ K.

An intriguing characteristic of temperature dependent thermodynamic properties figures 4 (a-f) is the minimal effect of temperature on V , B , θ_D , γ and α in temperature range 0-200 K because in this range no variation is found in V , B , θ_D , γ and α because of temperature.



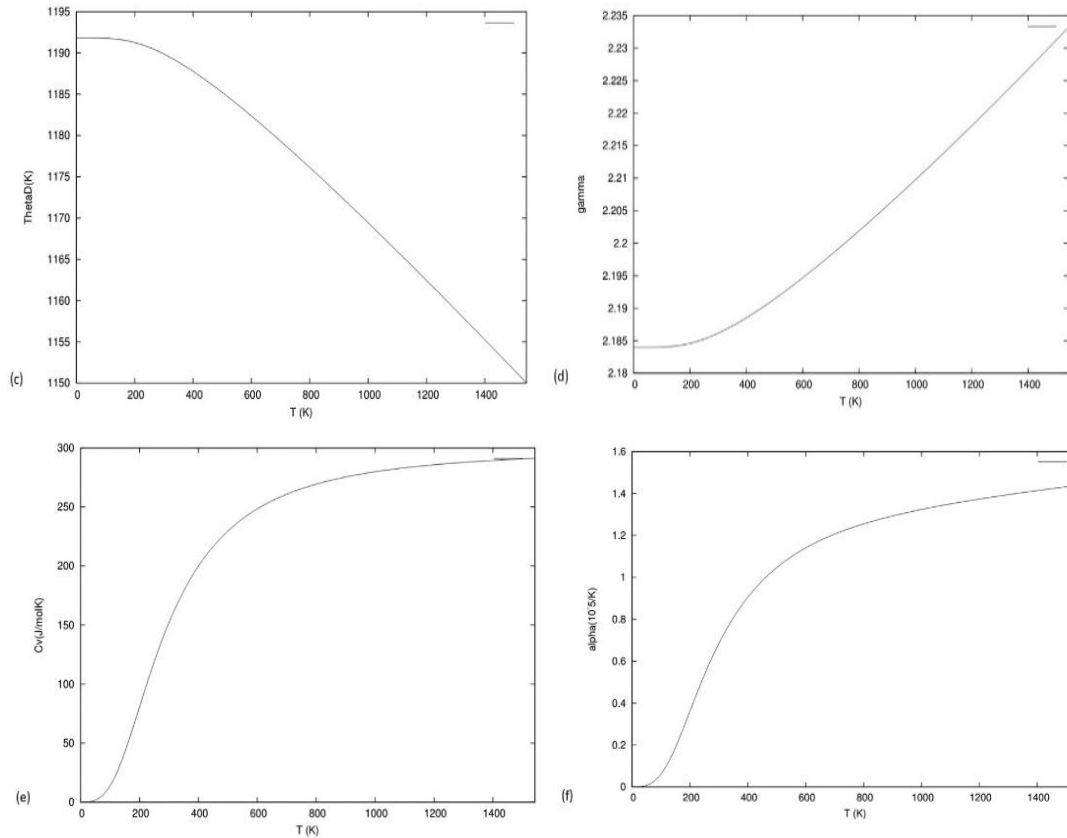


Figure 4: Temperature induced variation in (a) Volume(V) (b) Bulk Modulus (B) (c) Debye Temperature (θ_D) (d) Grüneisen parameter (γ) (e) specific heat(C_v) (f) Thermal expansion coefficient (α).

Table 2. Debye temperature $\theta_{D(K)}$, Gruneisen parameter γ , thermal expansion coefficient α ($10^{-5}/K$) at 300 K for TaRhGe using GGA.

	θ_D	γ	C_v	α
Calculated	1188	2.18	153	0.71×10^{-5}

Figure 5 (a) shows temperature dependence of thermopower S of TaRhGe. From literature, it is evident that thermoelectric power for Ta rich compounds the peak occurs before 100 K. Phonon scattering by holes is responsible for this low temperature peak of group V elements.[19] Here, the curve $S = f(T)$ shows a maximum at 100 K. This change in maxima can be attributed to the presence of group VII element Rh. We also observe a gradual decrease in thermopower till 150 K because of addition of tantalum to TaRhGe but later this drop till 800 K. It can be noticed that the absolute value of Seebeck coefficient decreases i.e. $11.8 \mu V/k$ noted at 300 K. Figure 5 (b) shows electrical conductivity per relaxation time. It can be seen there is a linear decrease, reasons can be attributed to decrease in the collision between the electrons and increase in the relaxation time between successive collision. It was measured to be $0.13 \times 10^3 \Omega^{-1} m^{-1} s^{-1}$ measured at 300 K. Figure 5 (c) linear increase in the graph after a short decrement is suggestive of the increase in overall conductivity of the compound. The

measured value is around $1.5 \times 10^{10} \text{ W/mk}^2\text{s}$. The reason can be attributed to the increase in phonon scattering by hole is thereby leading to such a behaviour and Figure (d) Shows Thermal conductivity K variation with temperature. The linear increase in conductivity with increase in temperature is a noticeable effect because at high temperature electron as well as lattice phonon are responsible for thermal conduction. It is measured to be around $10.6 \times 10^{164} \text{ W/m Ks}$.

Figure 5: Images showing Temperature dependence of (a) Thermopower, S ($\mu\text{V/K}$), (b) Electrical Conductivity per relaxation time, σ/τ ($1/\Omega \text{ m s}$), (d) Thermal conductivity k (W/m Ks) at 300 K near Fermi energy for TaRhGe using GGA.

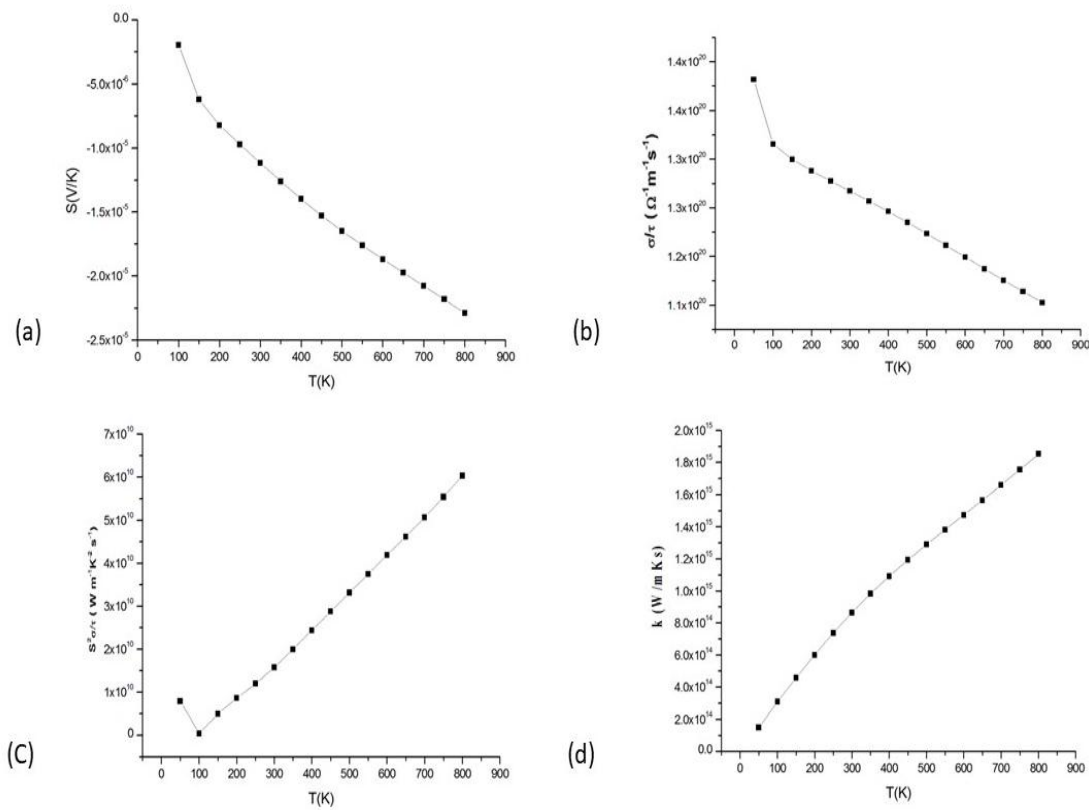


Table 2. Thermopower S ($\mu\text{V/K}$), Electrical Conductivity per relaxation time σ/τ ($1/\Omega \text{ m s}$), Thermal conductivity K (W/m Ks) at 300 k near Fermi energy for TaRhGe using GGA.

	S	$\frac{\sigma}{\tau}$	$S^2 \frac{\sigma}{\tau}$	K
Calculated	11.8	0.13×10^3	1.5×10^{10}	10.6×10^{164}

Conclusion:

We observed the structural, electronic and thermodynamics properties of $MM'Ge$ ($M=Ta$, $M'=Rh$) intermetallic compound. The crystal structure parameters like lattice constant, bulk modulus and its pressure derivative are explained. The obtained theoretical value for lattice constant, gives their agreement with the experimental results. Electronic properties suggest that $MM'Ge$ ($M=Ta$, $M'=Rh$) has a metallic nature. The thermodynamic parameters like that Debye temperature, α , thermal expansion coefficient, and Grüneisen parameter are also investigated which confirms that the conductivity increases with increasing temperature.

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Conflict of interest:

The authors declare no competing financial interests.

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