FIRST PRINCIPLE STUDIES ON GdCu

A.H. ERGUN[1], Y.O. CIFTCI[1], K. COLAKOGLU[1], H. OZISIK[2]

[1]*Department of Physics, Gazi University, 06500 Ankara, Turkey*
[2]*Physics Department, Aksaray University, 68100 Aksaray, Turkey*

Ab initio calculations have been carried out to find the structural, electronic, elastic and thermodynamic properties of GdCu, using density functional theory within generalized-gradient (GGA) apraximation. For the total-energy calculation we have used the projected augmented plane-wave (PAW) implementation of the Vienna Ab initio Simulation Package (VASP). Our results are compared to other theoretical and experimental works, and excellent agreement is obtained. We have used to examine structure parameter in different structures such as in NaCl(B1), CsCl(B2) and ZB(B3). We have performed the thermodynamics properties for GdCu by using quasi-harmonic Debye model. We have, also, predicted the temperature and pressure variation of the volume, bulk modulus, thermal expansion coefficient, heat capacities and Debye temperatures in a wide pressure (0 – 50 GPa) and temperature ranges (0- 1000 K).

I. INTRODUCTION

Binary qui-atomic intermetallic compounds of rare earth elements and group Ib and IIb metals exhibit a variety of interesting magnetic phases [1]. When Ni is substituted by a group Ib element (Cu or Ag) the structure changes to the cubic CsCI-type structure with an antiferromagnetic ordered ground state [2]

In this study, as A.V Postnikov et al.[2] and others studies, elastic and thermodynamic properties of GdCu compounds, whose magnetic and electronic properties was mainly examined in previous studies, are investigated. In that studies, where magnetic properties are concentrated on [2], elastic and thermodynamic properties are not mentioned. Therefore, in this study, these properties, which were not examined for B1, B2 and B3 phases of GdCu compound, have reported in detail.

The aim of the present paper is to reveal bulk, structural properties in NaCl(B1), CsCl(B2), ZB(B3) phase and thermodynamical and elastic properties of GdCu in B2 phase, using VASP method with plane-wave pseudopotential.

At section 3, calculations are made with this method and lastly the results of the calculations are summarized in conclusions

II. METHOD OF CALCULATION

In the present work, all the calculations have been carried out using the Vienna ab initio simulation package (VASP) [3-4] based on the density functional theory (DFT). The electron-ion interaction was considered in the form of the projector-augmented-wave (PAW) method with plane wave up to energy of 600 eV [5-6]. This cut-off was found to be adequate for the structural, elastic properties as well as for the electronic structure. We do not find any significant changes in the key parameters when the energy cut-off is increased from 600 eV to 650 eV. For the exchange and correlation terms in the electron-electron interaction, Perdew and Zunger-type functional [7-8] was used within the generalized gradient approximation (GGA) [10]. The 12x12x12 Monkhorst and Pack [9] grid of k-points have been used for integration in the irreducible Brillouin zone. Thus, this mesh ensures a convergence of total energy to less than 10^{-5} ev/atom.

We used the quasi-harmonic Debye model to obtain the thermodynamic properties of GdCu [10-11], in which the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the form of

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

In Eq.(1), $E(V)$ is the total energy for per unit cell of GdCu, PV corresponds to the constant hydrostatic pressure condition , $\theta(V)$ the Debye temperature and A_{Vib} is the vibration term, which can be written using the Debye model of the phonon density of states as

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

where n is the number of atoms per formula unit, $D\left(\frac{\theta}{T}\right)$ the Debye integral, and for an isotropic solid, θ is expressed as [12]

$$\theta_D = \frac{\hbar}{k}\left[6\pi^2 V^{1/2}n\right]^{1/3} f(\sigma)\sqrt{\frac{B_s}{M}} \qquad (3)$$

where M is the molecular mass per unit cell and B_S the adiabatic bulk modulus, which is approximated given by the static compressibility [13]:

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

$f(\sigma)$ is given by Refs. [12-14] and the Poisson ratio are used as 0.28242 for GdCu. For GdCu, $n=4$ $M=$ 220.796 a.u, respectively. Therefore, the non-equilibrium Gibbs function $G^*(V; P, T)$ as a function of $(V; P, T)$ can be minimized with respect to volume V.

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

By solving Eq. (5), one can obtain the thermal equation-of-equation (EOS) $V(P, T)$. The heat capacity at

constant volume C_V, the heat capacity at constant pressure C_p, and the thermal expansion coefficient α are given [15] as follows:

$$C_v = 3nk \left[4D\left(\frac{\theta}{T}\right) - \frac{3\theta/T}{e^{\theta/T}-1} \right] \qquad (6)$$

$$S = nk \left[4D\left(\frac{\theta}{T}\right) - 3\ln(1 - e^{-\theta/T}) \right] \qquad (7)$$

$$\alpha = \frac{\gamma C_v}{B_T V} \qquad (8)$$

$$C_p = C_v(1 + \alpha\gamma T) \qquad (9)$$

Here γ represent the Grüneisen parameter and it is expressed as

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

III. RESULTS AND DISCUSSION
3.1. Structural and Electronic Properties

Firstly, the equilibrium lattice parameter has been computed by minimizing the crystal total energy calculated for different values of lattice constant by means of Murnaghan's equation of state (eos) [16] as in Figure.1. The bulk modulus, and its pressure derivative have also been calculated based on the same Murnaghan's equation of state, and the results are given in Table 1 along with the experimental and other theoretical values. The calculated value of lattice parameters are 5.807 A^0 in B1 (NaCl) phase, 3.509A^0 in B2 (CsCl) phase, 6.265 A^0 in B3 (ZB) phase for GdCu, respectively. The present values for lattice constants are also listed in Table 1, and the obtained results are quite accord with the other experimental values [17].
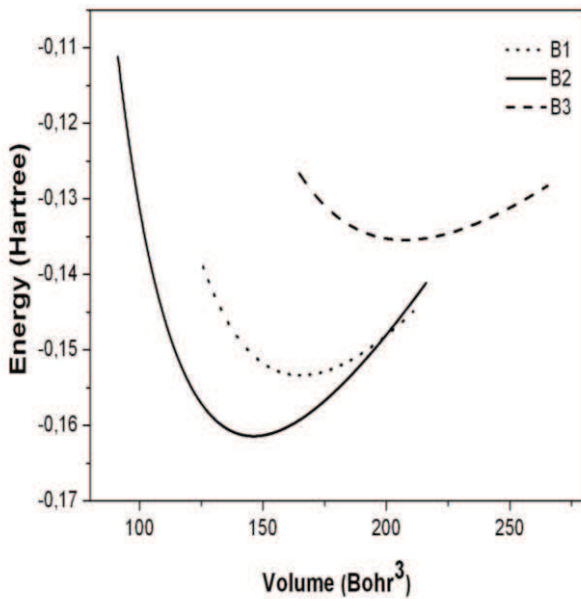

Fig.1. Total energy versus volume curve of GdCu in B1(NaCl), B2(CsCl), B3(ZB) phases.

Table1. Calculated equilibrium lattice constants (a_0), bulk modulus (*B*), pressure erivatives of bulk modulus (*B'*), formation enthalpy (ΔH) and other theoretical works for GdCu in B1, B2, B3 structures

Material	Structure	Ref.	a	B(GPa)	B'	ΔH
GdCu	B1	Present	5.807	57.233	3.728	4.54
	B2	Present	3.509	64.199	3.749	4.10
		Exp[17]	3.503			
	B3	Present	6.265	39.112	4.102	5.52

We have plotted the phase diagrams (equation of state) for B2 phase in Figure 2. We have also plotted the normalized volume pressure diagram of GdCu in B2 phase at the temperatures of 200K, 600K and 1000K in Figure 3.
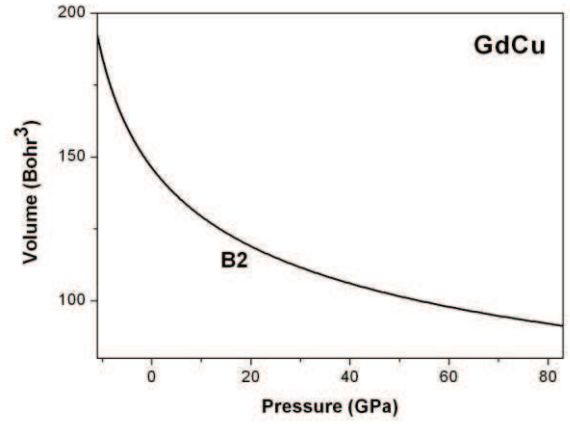

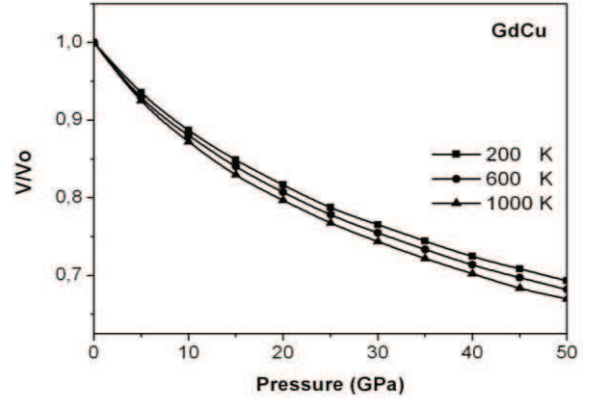*Fig. 2.* Pressure versus volume curve of GdCu

Fig. 3. The normalized volume-pressure diagram of the B2 for GdCu at different temperatures

The present first – principles code (VASP) have also been used to calculate the band structures for GdCu. The obtained results for high symmetry directions are shown in Figure 4 for B2 structures of GdCu. It can be seen from the Figure 4 that no band gap exists for studied compound, and they exhibit nearly metallic charecter. The total electronic density of states (DOS) corresponding to the present band structures are, also, depicted in Figure 4, and the disappearing of the energy gap in DOS conforms the metallic nature of GdCu. The similar stuation is observed for LaN in our recent work [18].
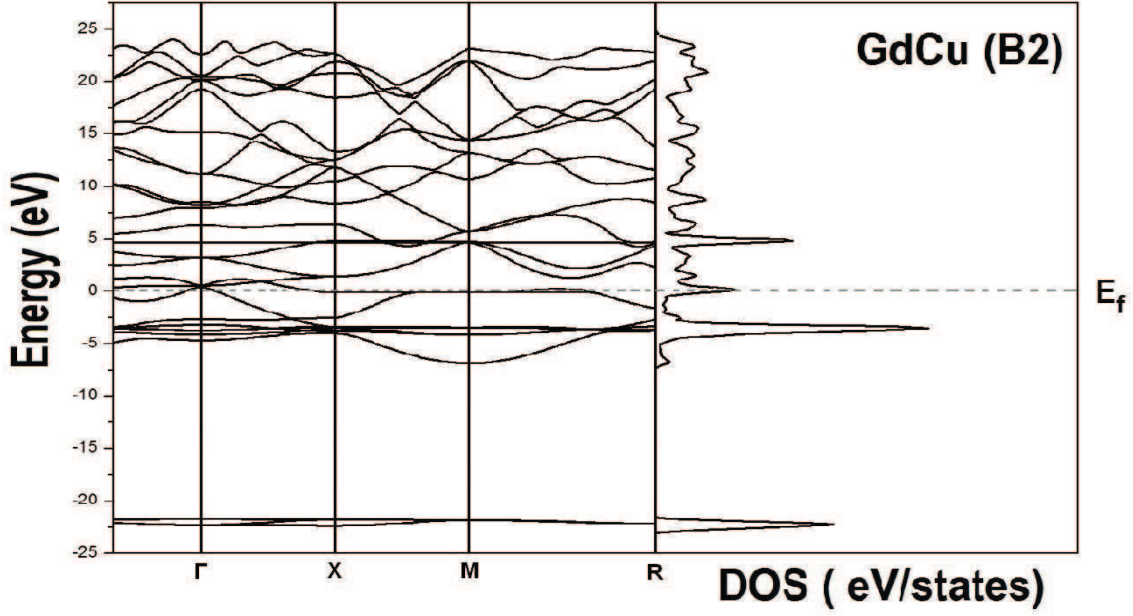
Fig. 4. Calculated band structure of GdCu in phase B2

3.2. Elastic Properties

The elastic constants of solids provide a link between the mechanical and dynamical behaviour of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials. Their ab-initio calculation requires precise methods, since the forces and the elastic constants are functions of the first and second-order derivatives of the potentials. Their calculation will provide a further check on the accuracy of the calculation of forces in solids. The effect of pressure on the elastic constants is essential, especially, for understanding interatomic interactions, mechanical stability, and phase transition mechanisms. It also provides valuable data for developing interatomic potentials

There are two common methods [19-20] for obtaining the elastic data through the ab-initio modelling of materials from their known crystal structures: an approach based on analysis of the total energy of properly strained states of the material (volume conserving technique) and an approach based on the analysis of changes in calculated stress values resulting from changes in the strain (stress-strain) method. Here we have used the "stress-strain" technique for obtaining the second-oreder elastic constants (C_{ij}). The listed values for C_{ij} in Table 2 are in reasonable order.

Table 2. The calculated elastic constants (in GPa unit) in different structures for GdCu

Material	Structure	C_{11}	C_{12}	C_{44}
GdCu	B1	92.784	40.321	5.627
	B2	108.699	48.170	34.392
	B3	31.684	44.128	22.188

The calculated elastic constants values of B2 structure for GdCu at 10, 20, 30, 40, 50, 60 GPa pressure values, respectively and they are also listed in Table 3.

Table 3. The elastic constants values (in GPa unit) of the B2 structure for GdCu at different pressures.

Material	Structure	Pressure (GPa)	C_{11}	C_{12}	C_{14}
GdCu	B2	10	133,27	79,16	48,65
		20	150,71	109,10	59,69
		30	167,72	135,76	69,02
		40	182,71	158,20	77,30
		50	196,79	180,26	84,45
		60	209,81	202,90	90,97

The Zener anisotropy factor A, Poisson ratio v, and Young's modulus Y, which are the most interesting elastic properties for applications, are also calculated in terms of the computed data using the following relations [21] :

$$A = \frac{2C_{44}}{C_{11} - C_{12}}, \tag{1}$$

$$v = \frac{1}{2}\left[\frac{(B - \frac{2}{3}G)}{(B + \frac{1}{3}G)}\right], \tag{2}$$

and

$$Y = \frac{9GB}{G + 3B} \tag{3}$$

where G = (G_V + G_R) /2 is the isotropic shear modulus, G_V is Voigt's shear modulus corresponding to the upper bound of G values, and G_R is Reuss's shear modulus corresponding to the lower bound of G values, and can be

written as $G_V = (C_{11} - C_{12} + 3C_{44})/5$, and $5/G_R = 4/(C_{11} - C_{12}) + 3/C_{44}$. The calculated Zener anisotropy factor (A), Poisson ratio (v), Young's modulus (Y), and Shear modulus ($C' = (C_{11} - C_{12} + 2C_{44})/4$) for GdCu are given in Table 4 and they are close to those obtained for the similar structural symmetry.

Table 4. The calculated Zener anisotropy factor (A), Poisson ratio (v), Young's modulus (Y), Shear modulus (C') for GdCu in B2 structure

Material	A	v	Y(GPa)	C' (GPa)
GdCu	1.136	0.282	83.811	32.328

3.3. Thermodynamics Properties

The Debye temperature (θ_D) is known as an important fundamental parameter closely related to many physical propertied such as specific heat and melting temperature. At low temperatures the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperatures the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. We have calculated the Debye temperature, θ_D, from the elastic constants data using the average sound velocity, v_m, by the following common relation given [22]

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

where $\hbar$ is Planck's constants, k is Boltzmann's constants, N_A Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per

formula unit, $\rho(= M/V)$ is the density, and v_m is obtained from

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{1/3} \quad (5)$$

where v_l and v_t, are the longitudinal and transverse elastic wave velocities, respectively, which are obtained from Navier's equations [23]:

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}} \quad (6)$$

And

$$v_t = \sqrt{\frac{G}{\rho}}. \quad (7)$$

The calculated average longitudinal and transverse elastic wave velocities, Debye temperature and melting temperature for GdCu are given in Table 5. No other theoretical or experimental data are exist for comparison with the present values.

The empirical relation [24], $T_m = 553$ K+ (591/Mbar)C_{11} ± 300, is used to estimate the melting temperature for GdCu, and found to be 1195 ± 300K. This value is lower than those obtained for Gd (1585 K). We hope that the present results are a reliable estimation for these compounds as it contains only C_{11} which has a reasonable value.

Table 5. The longitudinal, transverse, average elastic wave velocities, and Debye temperature for GdCu in B2 structure.

Material	$v_l(m/s)$	$v_t(m/s)$	$v_m(m/s)$	$\theta_D(K)$	$T_m(K)$
GdCu	1781.53	981.00	1093.35	116.89	1195± 300

The thermal properties are determined in the temperature range from 0 to 1000 K for GdCu, where the quasi-harmonic model remains fully valid. The pressure effect is studied in the 0-50 GPa range. The relationship between normalized volume and pressure at different temperature is shown in Figure 3 for GdCu. It can be seen that when the pressure increases from 0 GPa to 50 GPa, the volume decreases. The reason of this changing can be attributed to the atoms in the interlayer become closer, and their interactions become stronger. For GdCu compound the normalized volume decreases with increasing temperature. Temperature effects on bulk modules (B) are given in Fig. 4. and can be seen that B decreases as temperature increases. Because cell volume changes rapidly as temperature increases. The relationship between bulk modulus (B) and pressure (P) at different temperatures (200, 600, and 1000K) is shown

in Fig. 5. for GdCu. It can be seen that bulk modulus decreases with the temperature at a given pressure and increases with pressure at a given temperature. It shows that the effect of increasing pressure on GdCu is the same as decreasing its temperature.

The variations of the thermal expansion coefficient (α) with temperature and pressure are shown in Fig.6 and Fig.7 for GdCu, respectively. It is shown that, the thermal expansion coefficient α also increases with T at lower temperatures and gradually approaches linear increases at higher temperatures, while the thermal expansion coefficient α decreases with pressure. At different temperature, α decreases nonlinearly at lower pressure and decreases almost linearly at higher pressure. Also, It can be seen from Fig. 6 that the temperature

dependence of α is very small at high temperature and higher pressure.
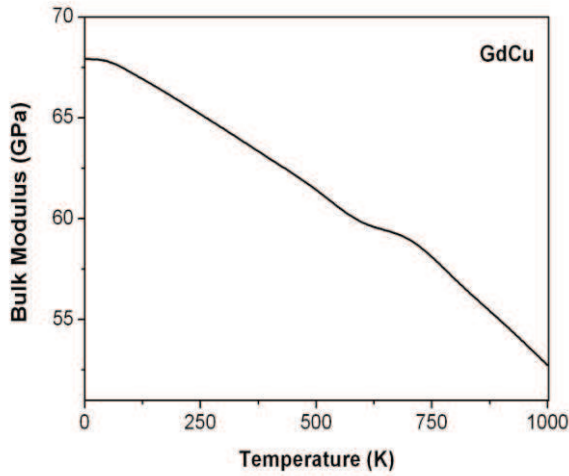

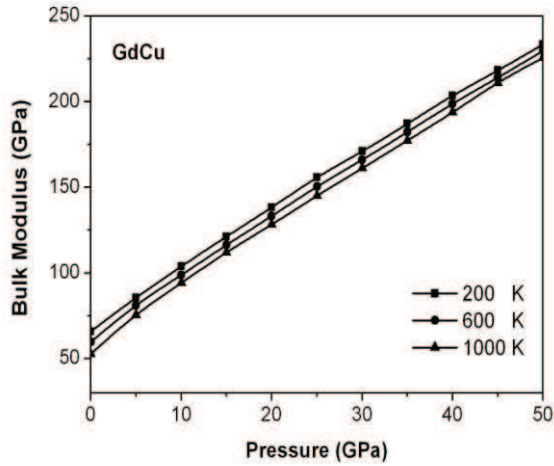*Fig.4.* The bulk modulus (B) for GdCu as a function temperature T at P=0.

Fig.5. The reletionships of GdCu between bulk modulus (B) and pressure P at temperatures of 200 K, 600 K, 1000 K
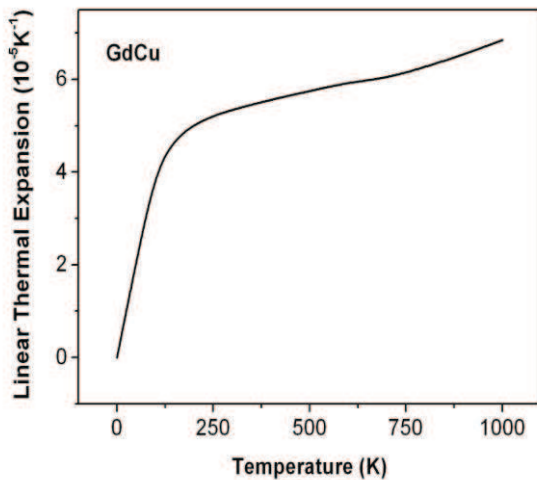

Fig. 6. The thermal expansion versues temperature for GdCu.

The relationship between heat capacity at constant pressure C_p and temperature, also the relationship

between capacity at constant volume C_v and temperature at different pressures P are shown in Fig.8 for ReB. It is realized from figures that when T<500 K, C_v increases very quickly with temperature; when T>500 K, C_v increases slowly with temperature and it almost approaches a constant called as Dulong-Petit limit ($C_v(T)\sim3R$ for mono atomic solids) at higher temperatures for GdCu.
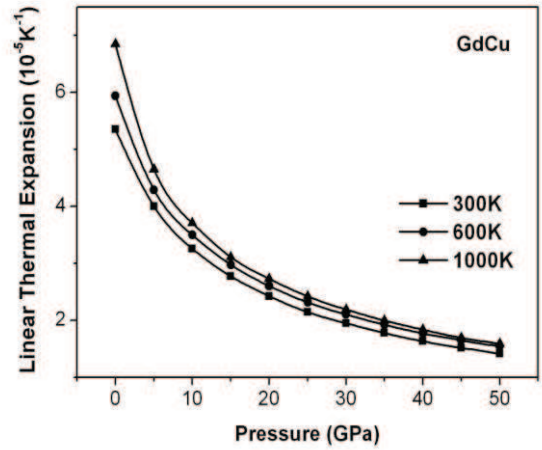

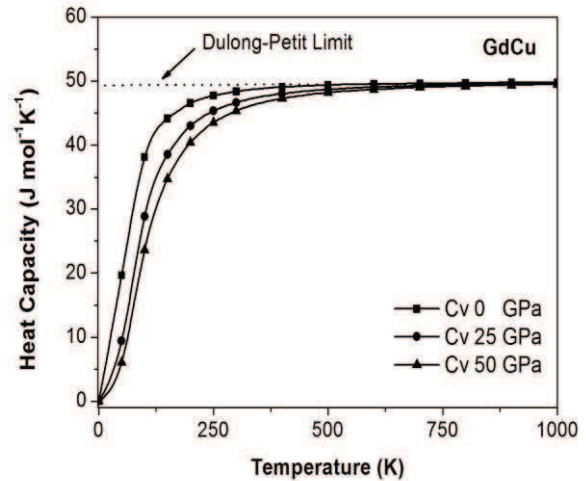*Fig. 7.* The thermal expansion versues pressure for GdCu.

Fig. 8. The heat capacity with temperature at different pressure for GdCu

IV. CONCLUSIONS

The fist–principles pseudopotential calculations have performed on the GdCu. Our present key results are on the elastic, electronic and structural properties for GdCu. The lattice parameters are excellent agreement with the other theoretical values. The computed band structures for GdCu shows metallic character. It is hoped that some our results, such as elastic constants, Debye temperatures, and melting temperatures estimated for the first time in this work, will be tested in future experimentally and theoretically.

We hope this study will help us to have a better understanding of elastic and thermodynamic properties of GdCu, whose magnetic properties are emphasized mostly.

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