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Theoretical investigation of the electronic structure and structural phase stability of $CeGa_2$ under pressure

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Abstract

Recently, Chandra Shekar et al. (Phys. Stat. Sol. B 241(2004)2893), studied the structural stability of $CeGa_2$ under high pressure up to ~32 GPa and reported a structural transition from hexagonal AlB_2-type to omega trigonal-type starting at ~16 GPa with a volume collapse of ~6%. The high-pressure omega triginal phase is found to coexist with the parent phase up to 32 GPa. In this paper, we report the results of our band structure calculations on this system as a function of reduced volume by the tight-binding linear muffin–tin orbital (TB-LMTO) method, in order to look into this structural transition and to understand it in terms of changes in its electronic structure. Our calculations indicate a structural transition at ~30.6 GPa with a volume collapse of 3.5%, in good agreement with the experimental results. The possible mechanism of the phase transition may be due to f→d electron transfer under pressure. The theoretically calculated ground-state properties, namely the lattice parameters and the bulk modulus are also in good agreement with the experimental values.

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Keywords: Rare-earth intermetallic; High pressure; Phase transition; Electronic band structure

1. Introduction

The rare-earth intermetallic compound cerium di-gallide crystallizes in the AlB_2-type structure at ambient conditions with space group symmetry P6/mmm. Chandra Shekar et al. [1–3] have investigated several systems exhibiting the AlB_2-type structure and shown that these systems have a tendency to follow a specific structural sequence under pressure, namely, AlB_2 (P6/mmm) to $ZrSi_2$ (Cmcm) to $ThSi_2$ (I4_1/amd) to Cu_2Sb (P4/nmm) type. Very recently, they have prepared $CeGa_2$ by a standard arc-melting technique and characterized the sample by X-ray diffraction. $CeGa_2$ was

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found to be of AlB_2-type structure with lattice constants $a=4.298\pm0.001$ Å and $c=4.334\pm0.001$ Å [4]. They have also carried out high-pressure X-ray diffraction studies up to 32 GPa and reported a structural transition to an omega triginal structure at ~16 GPa. Also, the high-pressure phase coexisted up to 32 GPa. The motivation of the present work was to investigate the nature of this transition by performing electronic structure calculations by means of a first-principle tight-binding linear muffin–tin orbital method (TB-LMTO) within the density functional formalism.

2. Methodology

In $CeGa_2$ with AlB_2-type structure (Space group: P6/mmm) at STP, the Ce and Ga atoms occupy the positions $(0,0,0)$ and $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$. The reported high-pressure phase of $CeGa_2$ with space group symmetry P-3m1 has the atomic co-ordinates Ce $(0,0,0)$ and Ga $(\frac{1}{3},\frac{1}{3},\frac{1}{2})$ with c/a ratio of 0.7825. Within the framework of the density functional theory, the electronic structure calculations are performed using the TB-LMTO approach [5,6]. The exchange-correlation potential within the local density approximation is calculated using the parameterization scheme of von Barth and Hedin [7]. We have used the scalar relativistic approach that includes the mass velocity and Darwin corrections, but omits the spin–orbit couplings. All K-space integrations are performed with the tetrahedron method [8] and the self-consistency in the charge density is obtained with 624 irreducible K-points. The basis set consists of 6s, 5d and 4f orbitals for Ce and 4s, 4p and 3d orbitals for Ga. The 6p orbtials of Ce are treated by the down folding technique. The Ga 3d orbitals are treated as valence states. The combined correction terms are also included which account for the non-spherical shape of the atomic polyhedron. Also, the truncation of the higher partial waves inside the spheres were included so as to minimize the errors in the LMTO method. The Wigner–Seitz sphere radii are chosen in such a way that the sphere boundary potential is minimum and the charge flow is in accordance with the electronegativity criteria. The total energy of $CeGa_2$ is calculated as a function of volume in a manner similar to our earlier works [9,10]. Here the c/a ratio is fixed at the experimental value. By fitting this total energy to the Birch equation of state [11], the pressure is calculated using the expression $P=-\mathrm{d}E/\mathrm{d}V$. The P–V and the bulk modulus are also calculated. The theoretically calculated value of the bulk modulus is 96.74 GPa to be compared to the experimental value 71 GPa. It is also very close to the values reported for other digallides like $HoGa_2$ and $TmGa_2$ [12,13]. The theoretically calculated value of the lattice parameter differs from the experimental value by 3.5%. Usually LDA will underestimate the lattice parameter value up to 2%. The calculation was carried out first without Ga d states and then the error is around 1.5%. Then, after observing the energy of free atoms, the Ga d states have to be brought in as valence states. After this is done, the error comes around 3.5%.

3. Results and discussions

(a) Electronic properties: The self-consistent scalar relativistic band structure is obtained at equilibrium volume within the LDA along the high-symmetry directions, and is shown in Fig. 1. The bands lying around −1.2 Ry are due to Ga 3d like states, and the bands above this value are due to Ce ‘s’ like, followed by Ga ‘s’ like bands. The bands that are very close to the Fermi level are due to Ce ‘d’ like and Ga ‘p’ like states. Ce ‘f’ like states are very close to the Fermi level and there is a very strong hybridization of Ce ‘f’ like and ‘d’like states just below the Fermi level. The density of states is plotted in Fig. 2. From this plot, one can see that the ‘f’ like states are very close to the Fermi level and the pseudo-gap firmly sits on the Fermi level. This clearly indicates that $CeGa_2$ is very stable in this phase at ambient conditions.

(b) Structural phase transition: In order to understand the reported structural transition, the electronic structure and the total energies are calculated for the high-pressure phase, also in a similar manner as reported earlier. The total energies as a function of volume are given in Fig. 3

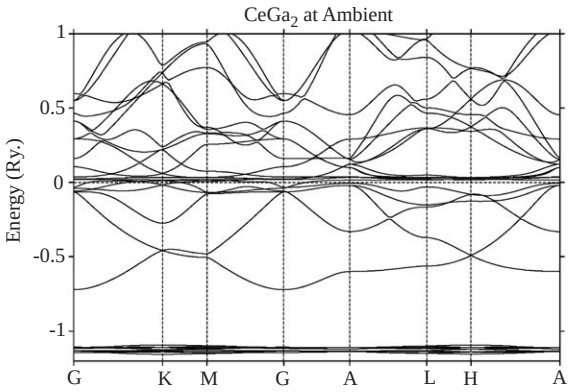

Fig. 1. Self-consistent scalar relativistic band structure obtained at equilibrium volume within the LDA along the high-symmetry directions for the parent P6/mmm structure at ambient conditions.

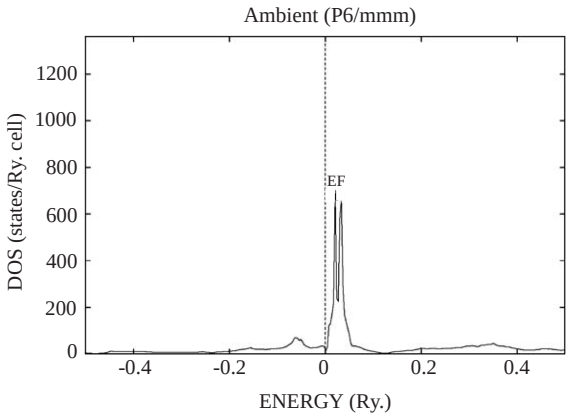

Fig. 2. Density of states plot for the P6/mmm phase at ambient conditions.

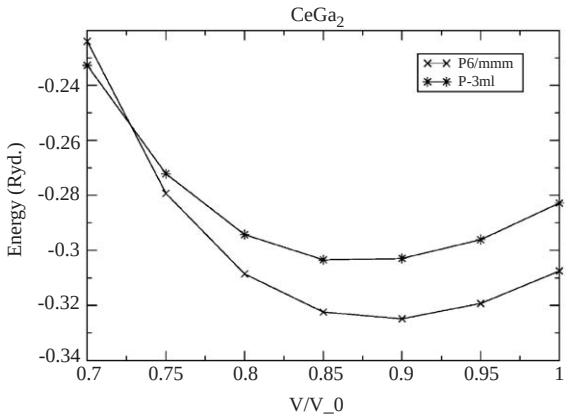

Fig. 3. Total energies as a function of volume for both the parent and the high-pressure structures.

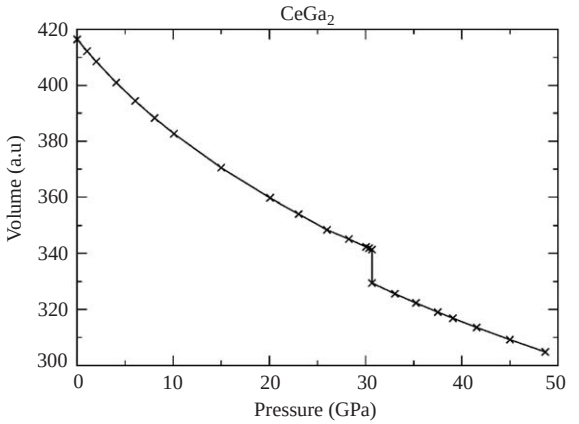

Fig. 4. P–V curve for $CeGa_2$. The calculation predicts the transition from P6/mmm to P-3m1 at about 30.6 GPa with a 3.5% volume collapse.

for both the structures. From this figure one observes that $CeGa_2$ is stable with space group symmetry P6/mmm up to $V/V_0 \sim 0.71$, and it has undergone a structural phase transition below this value. In order to calculate the transition pressure the Gibb's free energy is calculated for the two phases using the expression

$$G = E_{\text{tot}} + PV - TS.$$

Since the theoretical calculations are perfomed at 0 K, the Gibb's free energy will become equal to the enthalpy (H)

$$H = E_{\text{tot}} + PV.$$

At a given pressure, a stable structure is one in which the enthalpy has its lowest value. The transition pressures are calculated at which the enthalpies of the two phases are equal. The transition pressure is estimated to be around 30.6 GPa with a volume collapse of 3.5% compared to the experimental value of 6%. The P–V graph is also given in Fig. 4 for the two phases. In order to investigate the possible reason for this phase transition, the band structure and the density of states are plotted just before and after the structural phase transition. They are given in Figs. 5a–d. From the band structure plot, one can easily observe that a hybridized Ce 'df' like band

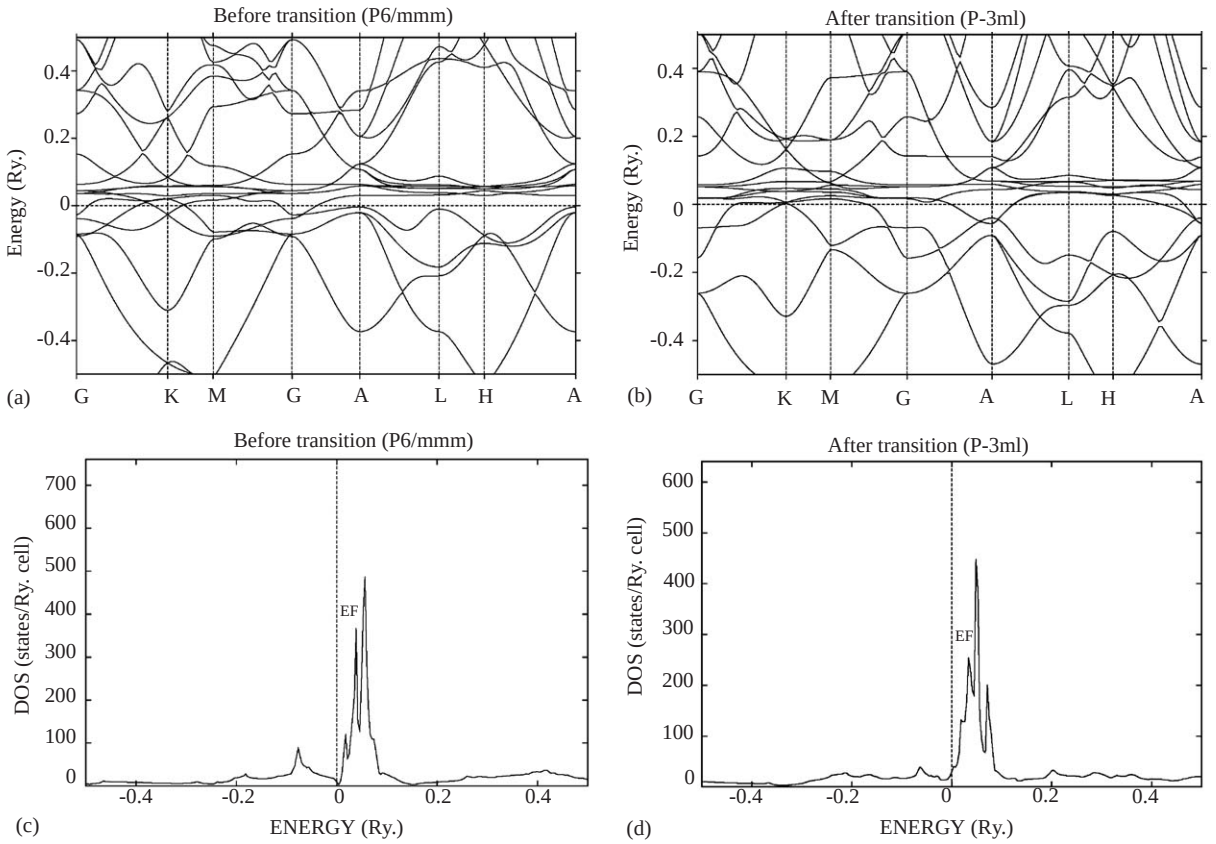

Fig. 5. (a (top)–d (bottom)) In order to investigate the possible reason for the phase transition in $CeGa_2$, band structure (a and b) and density of states (c and d) are plotted for the parent (P6/mmm) and the high-pressure (P-3m1) phases, just before and after the structural phase transition.

lies on the Fermi level at ambient conditions along the symmetry direction *K–M*. When the compound is compressed, the Ce 'f' like states get delocalized and there is a transfer of electrons from 'f' like to 'd' like bands. The hybridized 'df' like band of Ce starts moving upwards under pressure, and this causes the structural phase transition. This is confirmed by calculating the number of electrons at the two different sites, namely Ce and Ga, under compression. These numbers are given in Table 1. From the table, it is very clear that there is a continuous f→d electron transfer under pressure, which must be responsible for this phase transition. This is also seen from the density of states plot, in which the pseudo-gap, which sits firmly on the Fermi level at ambient pressure, now moves away. This indicates that the system is unstable under pressure and it is likely to go to some other structure in which it will be more stable. After the transition, the pseudo-gap once more lies on the Fermi level (Fig. 5d). Also, since the total energies of the two phases are very close, the coexistence of the two phases as observed experimentally seems logical. It is also consistent with the result that the transformation was found to be akin to the well-known omega transformation observed in the transition metals and their alloys [4]. The ω-transformation is generally sluggish and time-dependent and it is also reported that two wide phase regimes under pressure are seen in several transition metal alloys [14].

Table 1
Number of electrons at the two different sites, namely Ce and Ga, under compression. These numbers clearly indicate that there is a continuous f→d electron transfer under pressure which is responsible for the observed structural phase transition

V/V_0	Cerium				Gallium			DOS
	s	p	d	f	s	p	d	
0.90	0.523	0.819	2.369	1.260	1.080	1.440	9.990	16.476
0.85	0.519	0.836	2.442	1.233	1.058	1.441	9.984	12.481
0.80	0.515	0.857	2.519	1.206	1.035	1.437	9.976	10.665
0.75	0.511	0.883	2.599	1.181	1.012	1.432	9.967	9.442
0.70	0.512	0.926	2.699	1.164	0.984	1.410	9.953	7.099

4. Conclusion

In summary, we have performed the total energy calculations using the first-principle density functional formalism in two different structures, with space group symmetry P6/mmm and P-3m1, as a function of cell volume. From the study, we conclude that $CeGa_2$ undergoes a structural phase transition around a pressure of 30.6 GPa with a volume collapse of 3.5% in agreement with the experimentally observed values. The phase transition may be due to f→d electron transfer under pressure. The theoretically calculated ground-state properties, namely the lattice parameter and the bulk modulus are also in good agreement with the experimental values.

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