Ab Initio Study of CeIn₃ Intermetallic Compound Under Pressure by Electronic Structure Calculations

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Abstract

Electronic structure and hyperfine electric interaction of CeIn₃ compound under pressures up to 22 GPa are found. The calculations are done utilizing the density functional simulation through the full-potential (linear) augmented plane-waves method, FP-(L)APW, within the generalized-gradient approximation. The electronic density of states and electric field gradients (EFG’s), at In sites are calculated under pressure. Our result shows that by increasing the pressure, the density of states at Fermi level are decreased and this causes an increase in EFG. At ambient pressure, there is a good agreement between EFG’s and bulk modulus with experimental measurements. Also, the spin magnetic moment of Ce, which is strongly pressure dependent, is computed under pressure. By increasing the pressure, Cerium f states move away from the Fermi level into the conduction band and this suppresses the spin magnetic moment in the vicinity of some quantum critical point, i.e. 14 GPa.

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Keywords: Density functional calculations, Electronic density of states, Electric field gradient, Magnetic moment

1. Introduction

The intermetallic compound CeIn₃ is a concentrated Kondo system with a heavy fermion behavior at low temperatures [1]. It also exhibits an antiferromagnetic order below T_N= 10 K [2] with saturated ordered moment of 0.65±0.1 µB per Ce atom at ambient pressure. The magnetic moments usually preserved in the crystalline environment being screened from the outer conduction electrons [3]. There is a competition between Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction [4] and the Kondo effect in this compound. At low temperature the RKKY interaction, which couples the Ce-4f magnetic moments to each other, predominates and the compound orders antiferromagnetically. The moments are aligned in opposite directions in consecutive (111) planes of the cubic CeIn₃ structure with a lattice parameter of 4.689 Å, where Ce atoms are located at the corners and In atoms are located at the face-centered positions of a cubic unit cell. CeIn₃ has AuCu₃ prototype, which is stable under pressures up to 10 GPa [5]. Magnetic moment of this compound is strongly pressure dependent and might be suppressed at a critical pressure P_C ~ 2.5 GPa [6]. Under increasing the hydrostatic pressure, the Kondo state is stabilized and the antiferromagnetic state becomes unstable so that T_N decreases to 0 K [7]. It is believed that by increasing the pressure or temperature, CeIn₃ goes through the sequence: magnetically ordered trivalence, non-magnetic trivalence (Kondo effect), intermediate valence (IV) and tetravalence, as 4f level is gradually raised from well below E_F to well above E_F [8].

CeIn₃ shows superconductivity in a narrow region of pressure and temperature, below 0.2 K around P_C ~ 2.5-2.7 GPa, in the vicinity of a Quantum Critical Point [2]. Superconductivity appears near the magnetic ordering and it indicates that the magnetic interaction, which is maximum near P_C, influences superconductivity.

CeIn₃ crystallizes in the space group of Pm̅3m. The point group of Ce and In atoms are the cubic m̅3m and non-cubic 4/mmm, respectively. The In atoms are surrounded by Ce atoms and, due to non-cubic symmetry; there is an electric field gradient (EFG) at the In sites. Using the Time Differential Perturbed Angular Correlation (TDPAC) technique to measure

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Table 1. Bulk modulus, B₀, and linear coefficient of specific heat, γ, of CeIn₃.

<table>
<thead>
<tr>
<th></th>
<th>Experiment</th>
<th>GGA</th>
<th>GGA+U</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₀</td>
<td>67 [5]</td>
<td>58 *</td>
<td>56.65*</td>
<td>GPa</td>
</tr>
<tr>
<td></td>
<td>33.3 *</td>
<td>30.34*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Present work
the electric field gradient at In site of CeIn$_3$ at temperature range of 4.2-10 K showed a $V_{zz} = 4.07 \times 10^{21}$ V/m$^2$ [7]. The electric field gradient at In site is also measured using $^{115}$In Nuclear Quadrupole Resonance (NQR) at 4.2 K and showed $V_{zz} = 11 \times 10^{21}$ V/m$^2$ [9].

Hyperfine interactions have a very important role in obtaining the crystalline ground state and carry the major part of information about the electric charge and spin distribution close to the nucleus. Despite of many available experimental data about the physical properties of CeIn$_3$ [3, 5, 7, 10-13], to our knowledge the magnetic moment and electric field gradient under pressure and its critical pressure have not been yet calculated.

In the present work, an electronic structure calculation of CeIn$_3$ is performed by first principles using the WIEN2k code [14]. The electric field gradient around the In nucleus and Ce magnetic moment are calculated. In addition, we have investigated the effect of pressure on the electric field gradient close to In nuclei. We have also studied the structural and electronic properties of CeIn$_3$, specially the behavior of Ce-4f electrons under pressure and obtained the critical pressure. Furthermore, we have investigated the effect of variation of the density of states at Fermi level under pressure on EFG values.

### 2. Calculation Method

The calculated results in this paper were obtained using the highly accurate full-potential (linearized) augmented plane-waves plus local orbital method (L) APW$^{+}$lo, as embodied in the WIEN2k code. We have taken the generalized gradient approximation (GGA96) [15] into account for the exchange-correlation functional. The muffin-tin radii ($R_{MT}$), non-overlapping spheres centered at each nuclear position, were chosen to be 2.3 Bohr ($1\text{Bohr}=0.529177$ Å) for both In and Ce atoms. The following atomic states of Ce (5s$^2$, 5p$^6$, 4f$^1$, 5d$^1$, 6s$^2$) and In (4p$^6$, 4d$^{10}$, 5s$^2$, 5p$^1$) were considered as valence states. In the process of solving the Dirac’s equation these states are treated within the scalar-relativistic approach while the core states are relaxed in a fully relativistic manner. The maximum quantum number $\ell$ for atomic wave functions inside the sphere was confined to $\ell_{\text{max}} = 10$. The wave vector cut-off for the plane wave expansion of the wave function in the interstitial region was chosen $K_{\text{max}}R_{\text{MT}} = 7.00$, where $R_{\text{MT}}$ is the smallest muffin-tin radius in the unit cell and $K_{\text{max}}$ is the maximum of reciprocal lattice vector. The charge density was Fourier expanded up to $G_{\text{max}} = 10$. We used a mixing parameter of 0.1 in the Broyden’s scheme. A mesh of 72 k-point was generated in the irreducible wedge of the Brillouin zone, which corresponds to the grids of $12 \times 12 \times 12$ in the scheme of Monkhorst-Pack. A 2×2×2 antiferromagnetic supercell is obtained. Fig. 1. shows the spin ordering of (↑↓) imposed to the Ce moments along (111) axis in constructed conventional supercell.

![Fig. 1. The spin ordering of Ce in constructed conventional supercell of CeIn$_3$.](image)

![Fig. 2. Comparison between V/V$_0$ as a function of computed pressures with experimental Oomi results [5] for CeIn$_3$.](image)

![Fig. 3. The Fermi energy of CeIn$_3$ under pressure.](image)
3. Results and Discussion

3.1. Static Equation of State and Bulk Modulus

The total energy was computed for 16 different volumes from 1113.16 to 1530.6 bohr$^3$. For each volume, the forces on atoms were computed. Results show these forces are equal to zero. This can be the result of the type of space group (fcc). The EOSFIT program was used for fitting energies calculated using FP-LAPW GGA method, to the Birch-Murnaghan equation of state (EOS) [16]:

$$E(V) = E_0 + \frac{B_0V}{B'_0} \left( \frac{V_0}{V} \right)^{\frac{B'_0}{B'_0 - 1}} - \frac{B_0V_0}{B'_0 - 1}$$  \hspace{1cm} (1)

where the subscript 0 throughout represents the standard state $P=0$ and $B$ is bulk modulus and $B'=\partial B/\partial P$.

The equation of state here is for a static situation ($T=0$ K). Pressures were obtained analytically from the relation:

$$P(V) = \frac{B_0}{B'_0} \left( \frac{V}{V_0} \right)^{\frac{B'_0}{B'_0 - 1}}$$  \hspace{1cm} (2)

Oomi et al. [5] measured $V/V_0$ as a function of the pressure up to 10 GPa. In Fig. 2 the calculated equation of state, from -3.5 GPa to +22 GPa, is compared with their experimental data. As it can be seen in this figure the discrepancies between theory and experiment are larger at high pressures. These deviations are related to different high- and low-pressure behavior of CeIn$_3$. It is known that the systematic deviations from the simple equation of state can be used to find the phase transition [17]. As we will discuss in the next section, the band structure and density of states show a major reconfiguration of the Fermi surface. This electronic topological transition is the reason of this different behavior.

Furthermore, we have calculated bulk modulus using Birch-Murnaghan equation of state, at pressures up to 22 GPa, and obtained the value of $B_0=58$ GPa, where zero subscript indicates $P=0$, at $T=0$ K. Oomi et al measured $B_0=67$ GPa at room temperature, at pressures up to 10 GPa. As is seen, there is an acceptable agreement between FP-LAPW result and experimental data, at different temperatures.

In addition, the calculated coefficient of electronic specific heat, $\gamma = C_v/T$, of CeIn$_3$ is compared with experimental and FP-LAPW results in Table 1. The
Large discrepancy between calculations and experiment shows that the formula of \( \frac{C_i}{T} = \frac{1}{3 \pi^2} K_j \langle D(E_i) \rangle \), which is used in WIEN2k code, is not so accurate to compute the \( \gamma \) for such a complicated CeIn\(_3\) compound. This disagreement is consistent with all the other ab initio calculations for other cases [20-23]. In order to take into account strong correlations of Ce-4f states, we have used the GGA+U method. We have adopted the values of 6.2 eV for Coulomb repulsion \( U \) parameter and 0.7 eV for exchange integral \( J \) such that \( U_{\text{eff}} = U - J = 5.5 \) eV for Ce in CeIn\(_3\) [18]. As is obvious from Table I using GGA+U does not amend the results.

### 3.2. Electronic Structure

We have computed the Fermi energy, magnetic moment of Ce and the critical pressure of spin polarized CeIn\(_3\) compound for pressures up to 22 GPa. We have also calculated the total and partial density of states. According to Fig. 3, the Fermi energy has the value of 0.57 Ry at ambient pressure and increases with pressure.

Total density of states in CeIn\(_3\) are shown at three different selected pressures, \( P=0.0, 8.0 \) and 14.0 GPa. All states which are considered as valence are present in this figure except the In-4p states, which lie deeper at the energy about -5 Ry, and Ce-5s states, which have a very small density of states at the energy of approximately -0.5 Ry. Ce-5p and In-4d states remain atomic-like, located at 1.29 Ry and 1.04 Ry below Fermi level, respectively. Other states, Ce (4f, 5d, 6s) and In (5s, 5p) are located around Fermi level. One can see in Fig. 4 that all states, which are considered as valence states, move into higher energies under pressure while Ce-5p and In-4d states keep their atomic-like nature. It is noticeable that during the displacement of Fermi level and valence states into higher energies under pressure, the Ce-5p states distance from Fermi level stays constant while the distance of In-4d states from it increase.

The band structure of CeIn\(_3\), as shown in Fig 5, does not show any drastic change with pressure.

#### Table 2. Magnetic moment, mm, and critical pressure, \( p_c \), of CeIn\(_3\).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Calculations</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM 0.65±0.1 T=5 K [3]</td>
<td>0.708 [20]</td>
<td>( \mu_B )</td>
</tr>
<tr>
<td>0.48±0.08 T=3 K [13]</td>
<td>0.657 *</td>
<td></td>
</tr>
</tbody>
</table>

\( p_c \) 2.5 [10] 14 * GPa


* Present work

#### Table 3. Main component of electric field gradient, \( \text{EFG} \), at In sites of CeIn\(_3\).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Calculations</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.944 *</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Present work

**Fig. 6.** The magnetic moment of Ce in CeIn\(_3\) under pressure

**Fig. 7.** Ce-4f density of states at three different pressures in CeIn\(_3\) is calculated using FP-LAPW method. The dotted lines indicate the Fermi levels.
general featureless behavior of this compound possibly indicates the stability of the structure under pressure. The compound does not show any structural transitions under pressures up to maximum pressure (i.e. 22 GPa), while the experiment shows that AuCu$_3$ structure of this compound is stable up to 10 GPa [5].

The Ce-4f states carry the major part of the magnetic moment in CeIn$_3$. We have calculated spin magnetic moment at the Ce atom and In atom to be 0.657 $\mu_B$ and 0.0, respectively. Lalic et al. [24] have computed a value of 0.708 $\mu_B$, using FP-LAPW method. The calculated values and experimental data from neutron-diffraction measurements [3, 13] of Ce magnetic moment in CeIn$_3$ are compared in Table 2.

The behavior of Ce magnetic moment in CeIn$_3$ under pressure has been attractive for many experimental groups. The measurements by different methods show, by increasing the pressure, the magnetic moment of Ce is suppressed at a critical pressure, $P_C$. Settai et al. [10] investigated a change of the electronic state in CeIn$_3$ via de Haas-van Alphen (dHvA) experiments under pressures up to 2.7 GPa. They found a change in the shape of spherical Fermi surface with humps along (111) at $P_C = 2.5$ GPa and $T = 108$ mK. In another work, Settai et al. [11] found $P_C = 2.72$ GPa using the same method along (110). Grosche et al. [6] studied CeIn$_3$ in a series of resistivity measurements at high pressures up to 3.2 GPa and down to temperatures in the mK region. They found $P_C$ to be 2.55 GPa. We calculated the magnetic moment of Ce in different pressures. As it can be seen from Fig. 6, the spin magnetic moment of Ce is strongly pressure dependent and decreases by increasing the pressure. It can be estimated that this magnetic moment will be suppressed at approximately $P_C = 14$ GPa, which does not have good agreement with experimental data. It might be better if we add the Ce orbital magnetic moment to spin magnetic moment, although the orbital magnetic moment can not be computed accurately by LDA or GGA.

We investigated the density of states of Ce-4f under pressure. As Fig. 7 shows, the f-band broadens and simultaneously moves away from Fermi level into the conduction band. As f-electrons become more and more itinerant, the magnetic moment suppresses. But at the same time, the conduction band also moves away from Fermi level and their significance in controlling transport properties might decrease. The f-band width increases by pressure, which means that the effective mass of the electrons become relatively smaller. Oomi et al. [5] measured the resistivity of CeIn$_3$ at different pressures and their results indicate that resistivity increases under pressure at temperatures from room temperatures down to about 40 K but at lower temperatures the magnitude of resistivity is nearly constant.

3.3. Electric Field Gradient

Any nucleus with a nuclear spin quantum number $I \geq 1$ has a nonspherical nuclear charge distribution and an electric quadrupole moment $Q$. The nuclear quadrupole interaction can be used to probe the electronic charge distribution surrounding such a nuclear site. The EFG is the gradient of the electrostatic field at the nuclear position, dominantly produced by valence electrons inside the atomic sphere. The main component of the EFG, $V_{zz}$, and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ can be used to determine the independent components of EFG in the principal axes system.

In CeIn$_3$ compound only In nuclei due to the noncubic symmetry exhibit the electric quadrupole interaction. The asymmetry parameter $\eta$ is zero due to the presence of a three fold symmetry axis. We have obtained the value of $12.944 \times 10^{21}$ V/m$^2$ for In at ambient pressure. In Table 3, our results are compared with the experimental and other FP-LAPW results.
We have also investigated the effect of pressure on total density of states at Fermi level. As Fig. 8-a shows, the total density of states of CeIn₃ decreases by the pressure. On the other hand, we investigated the EFG behavior under pressure. The EFG at Ce site, having a cubic environment, is zero up to 22 GPa, while the EFG at In site increases with increasing the pressure, Fig. 8-b. It indicates that by imposing the pressure the symmetry around In site reduces. On the other hand EFG diagram as function of total density of states at Fermi level, Fig. 8-c, shows an almost two linear segments. The negative inclination increases from pressures more than nearly 2.5 GPa.

4. Conclusions

We have studied the variations of CeIn₃ electronic structure under pressures up to 22 GPa, using the first principal linear augmented plane-wave in antiferromagnetic phase. The f-band of Ce broadens and moves away from Fermi level by increasing the pressure. The Ce magnetic moments, which are ordered in opposite directions along the (111) axis, will be suppressed at the computational critical pressure of 14 GPa, which in comparison with the experiment is an overestimate. The electric field gradient, which dominantly belongs to In atoms, increases under pressure. Comparison of the behavior of EFG and DOS(E_F) under pressure, shows an approximately linear relation between EFG and density of states at Fermi level.

References

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