



Structural, electronic, elastic and magnetic properties of heavier REIr₃ (RE = Gd, Tb and Ho) intermetallic compounds

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Abstract. We present results on the bonding nature, structural, electronic, magnetic and elastic properties of REIr₃ (RE = Gd, Tb and Ho) intermetallic compounds adopting simple cubic AuCu₃-type structure obtained using the full-potential linearised augmented plane wave (FP-LAPW) method based on density functional theory. The local spin density approximation (LSDA) with Hubbard parameter (LSDA + *U*) has been used for exchange and correlation effects to get accurate results because of the presence of highly localised 4*f* electrons of rare-earth (RE) (RE = Gd, Tb and Ho) atoms. The calculated lattice parameter is found to be consistent with the experimental results. The calculated magnetic moments predict ferromagnetic behaviour of these compounds. The electronic and bonding properties have been solved in terms of band structure, density of states (DOS) and charge density plots. These results confirm the metallic nature of these compounds. The bonding appearances of these compounds have also been interpreted from charge density plots. The elastic constants, shear modulus and Cauchy's pressure are computed and they reveal that GdIr₃ and TbIr₃ compounds are ductile while HoIr₃ shows brittle character.

Keywords. Rare-earth transition metal compounds; spin polarisation; Hubbard parameter; structural, electronic and elastic properties.

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1. Introduction

The rare-earth (RE) intermetallic compounds are heavily correlated electron systems, where REIr₃ (RE = rare earth) are the most astonishing for their impressive physics. These types of compounds have attracted both experimental and theoretical attentions because of their diverse bulk properties [1]. The binary compounds REIr₃ (RE = Gd, Tb and Ho) are found in two different phases: C15 and AuCu₃. The binary AB₃ compounds are found in a wide diversity of crystal (C15, AuCu₃, CeNi₃, PuNi₃-type) structures depending on the rare-earth and transition metals in the systems [2–8]. These compounds are of great significance due to their physical and mechanical properties as well as high magnetic memory effect, ferromagnetic ordering and heat capacity, which are crucial for technological applications such as storage materials and in power generators. We can note here that the different member of binary RPt₃ compounds (R = rare-earth) are known to build two different crystal structures: C15b-type for R = La–Tb and AuCu₃-type for R = Dy–Lu

[2–5]. Additionally, it was found that C15b-type structure of TbPt₃ appears to be metastable in nature as it changes to AuCu₃-type on annealing [2]. Another binary series RERh₃ is also reported to form different crystal structures (CeNi₃-, PuNi₃-, AuCu₃-types) for different rare analogues. Only LaRh₃ has been found in two different structures [6–8]. In such scheme, one can anticipate multiple crystal structures in RIr₃ series too, because Ir has outer electron configuration similar to Rh, and has only one electron less than Pt.

Gornicka *et al* [9] have found superconductivity in CeIr₃ by X-ray photoelectron spectroscopy and he also inspected the electronic structure calculation using full-potential linearised augmented plane-wave method with local orbitals (LAPW + LO), as implemented in the WIEN2k package. As RE elements oxidise without difficulty, the amount of REs should be a little greater than its nominal calculated amount. The dispersion spectra of DyIr₃, GdIr₃ and NdIr₃ are calculated by Yuan-Tao *et al* [10]. The examination on critical behaviour of (Gd, Tb and Ho)Ir₃ compounds by the dc-magnetisation

and heat capacity measurement around the transition temperature for both C15b- and AuCu₃-type phases have been done by Mondal *et al* [11]. They also described various magnetic properties of a few compounds (R = Gd, Tb and Ho) of REIr₃ series of intermetallic compounds.

The REs along transition metals positioned with intermetallic compounds have been attractive for the basic consideration of electronic structure, heavy ferromagnetic behaviour, the high Curie temperature. The physical properties and their technological applicability have also been investigated theoretically and experimentally [12]. These compounds can crystallise in cubic AuCu₃-type structure (space group Fm-3m, No. 221) with ferromagnetic order. Theoretical investigations were not done on structural, electronic, elastic and magnetic properties of the GdIr₃, TbIr₃ and HoIr₃ intermetallic compounds in literature, though the experimental work is available for these compounds. Such materials have immense academic importance in understanding the role of RE-*f* electrons in their electronic properties.

In the present paper, for the first time we are describing the structural, electronic, elastic and magnetic properties of REIr₃ intermetallic compounds, which offer an improved fundamental knowledge of bonding character, electronic structure and physical properties using density functional theory (DFT). In addition to have a proper understanding of the electronic structure of REIr₃ intermetallic compounds which involve RE element (localised 4*f* electron) and transition metal (5*d* local electrons), we have used the local spin density approximation with Hubbard parameter (LSDA + *U*) approximation to determine the band structure (BS), density of states (DOS) and charge density plots.

This paper is planned as follows: §2 gives a brief explanation of the method used in the calculations, §3 presents the analysis of the calculated results and lastly the conclusion is given in §4.

2. Computational method

The computation has been carried out by using the full potential-linearised augmented plane wave (FP-LAPW) method within DFT [13,14]. The exchange correlation effects are determined using the LSDA + *U* approach [15,16]. The atomic location of REIr₃ [11], where the RE atoms sit in the cubic corner location 1a (0, 0, 0) while Ir atoms reside at the face centre location 3c (0, 0.5, 0.5). To achieve energy convergence, the basis functions expanded up to $R_{\text{MT}}^* K_{\text{MAX}} = 7$, where R_{MT} is the smallest atomic radius in the unit cell and K_{MAX} refers to the magnitude of the largest *k* vector

in the plane-wave expansion. The maximum value for partial waves inside the atomic sphere is $l_{\text{max}} = 10$, while the charge density is Fourier expanded up to $G_{\text{max}} = 12$ (a.u.)⁻¹. The self-consistent calculations are converged when total energy of the system is stable within 10⁻⁴ Ry. Energy to separate the core and the valence states is -6.0 Ry. A dense mesh of 1000 *k* points and the tetrahedral method [17] have been engaged for the Brillouin zone integration. In LSDA + *U* method, the effective parameter $U_{\text{eff}} = U - J$, where *U* is the Coulomb interaction (Hubbard) parameter and *J* is the exchange parameter; different values are taken for contrasting atoms of REIr₃. The confined (4*f*-electrons) behaviour develops from electron correlation effects induced by the Coulomb interaction [18]. We adopt values of Coulomb interaction parameter *U* = 4.6 eV for Gd, 5.0 eV for Tb and 4.9 eV for Ho and the exchange parameter *J* = 0.7 eV for all RE atoms [19]. A good explanation of the electronic properties of REIr₃ compounds is expected with LSDA + *U* approximation due to the presence of 4*f* electrons in RE atoms and 5*d* electrons in Ir atoms.

3. Result and discussions

3.1 Structural properties

In the current study, the ground-state structural properties of REIr₃ intermetallic compounds are acquired by the minimisation of total energy as the objective of unit cell volume using LSDA + *U* approximation for exchange correlation (XC) potential. The estimated total energies fit well with Birch–Murnaghan’s equation of state [20] to resolve the ground-state properties such as equilibrium lattice constants (*a*₀), bulk modulus (*B*) and pressure derivative of the bulk modulus (*B*′). Our aim of minimising the total energy with respect to volume using LSDA + *U* is shown in figures 1a–1c. The determined ground-state properties and other theoretical information are given in table 1 showing that lattice parameters are consistently larger compared to the earlier described experimental values [2], because Hubbard parameter plays a role of electron–electron interaction in terms of Columbic repulsion and rifts the 4*f*-state into two manifolds 4*f*_{7/2} and 4*f*_{5/2} [21,22] for GdIr₃, TbIr₃ and HoIr₃. From table 1 it can be seen that, the computed magnetic moments of these compounds are in decreasing order from GdIr₃ to HoIr₃ with lower number of irregular electron. An observation of the compressibility and hardness of these compounds discloses that HoIr₃ has the largest bulk modulus, pointing out that this compound is the hardest and least compressible compared to GdIr₃ and TbIr₃.

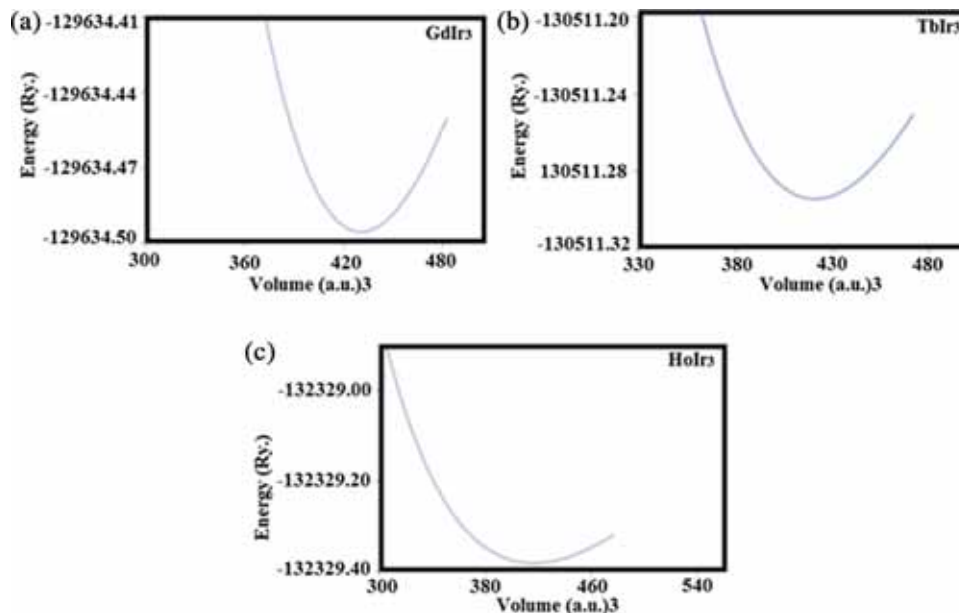


Figure 1. Energy vs. volume curve for GdIr₃ (a), TbIr₃ (b) and HoIr₃ (c) using LSDA + U approximation.

3.2 Electronic properties and magnetic properties

To understand the electronic properties of REIr₃ intermetallic compounds, in which the f -electrons are well localised, we have estimated spin-polarised band structure, total and partial density of states and charge density plots by using LSDA + U procedures. This process contains powerful electronic correlation of the $4f$ -state of RE atoms, and this development demonstrates a major role in resolving the electronic properties of REIr₃ compounds. The electronic properties are computed with distinct values of Hubbard parameter varying from 1 to 9 eV [11]. In the existing calculations, we have used the effective parameter $U_{\text{eff}} = U - J$, where U is the Hubbard parameter and J is the exchange parameter. We have set $U = 4.6$ eV (Gd), 5.0 eV (Tb), 4.9 eV (Ho) and $J = 0.70$ eV. The determined spin channels in the first Brillouin zone are shown in figures 2a–2f. The metallic behaviour of all REIr₃ compounds is confirmed from the values of non-zero DOS at Fermi-level $N(E_F)$ in both spin channels which are shown in table 1. As can be seen in figures 2a–2f, the electronic band structure profile of all REIr₃ compounds are perfectly identical in both spin channels, excluding, that the spin-up RE- f bands located well below the Fermi level (E_F) and the spin-down RE- $4f$ bands are situated well at E_F . The calculated DOSs (total and partial) with LSDA + U for both spin configurations are shown in figures 3a–3f. From the analysis of electronic band structure with DOSs (figures 2 and 3) it can be indicated that, in the spin-up profile, the bands below the Fermi level are due to the d

states of Ir atoms, which are between -6.5 and -1.0 eV. The $5d$ state of Ir atom is responsible for the interaction with RE- $5d$ state in the valence and conduction area. It is also perceived that, the intermix d and itinerant f -states of RE atoms generate the bundle of band at the Fermi level which is accountable for the resolute metallic behaviour. It is recognised in distinct energy order for all these compounds and marginally relocated towards the Fermi level from GdIr₃ to HoIr₃ in spin-down channel. The bands above the Fermi level are developed due to the hybridisation of d states of RE and Ir atom. In the spin-down profile, the bands around the Fermi level (-6.5 eV to -1.0 eV) are mainly due to the d -states of Ir atom. The unhybridised f -state of RE atom induces the bundle of bands above the Fermi level.

We have computed the total and partial DOS for the abovementioned compounds using LSDA + U approximation as shown in figure 3. It can be seen that the acute peak of spin-up (DOS) is primarily due to RE- $4f$ states and it move towards the Fermi level in spin-down channel. The interplay between RE- $4f$ states and Ir- $5d$ states can also be observed in the valence band region for both the spin channels, which rises with increasing number of f -electrons in the RE- $4f$ states. The d -states of Ir atom primarily govern the energy range (-6 eV to 6 eV) which is hybridised with f -states of RE atoms at the Fermi level in the spin-up description and d -state of RE atoms in the spin-down description.

We have also calculated the total and partial magnetic moments along the optimised lattice constants using LSDA + U approximation and the calculated values are listed in table 1. From table 1, we can see that the

Table 1. Calculated ground-state properties of REIr₃ intermetallic compounds.

| Solid netic | Appr. | a_0 (Å) | B_0 (GPa) | B'_0 | $N(E_F)$ (States/eV) | | Mag. moment per Er atom (μ_B) | Mag. moment per X atom (μ_B) | Total mag. moment of ErX ₃ |
|-------------------|---------------------|--------------------|-------------|--------|----------------------|-------|-------------------------------------|------------------------------------|---------------------------------------|
| | | | | | ↑ | ↓ | | | |
| GdIr ₃ | (Pre.) | 3.791 | 255.0 | 3.82 | 2.49 | 1.87 | 6.750 | -0.037 | 6.773 |
| | LSDA + U (Expt.) | 3.994 ^a | 4 | | | | | | |
| TbIr ₃ | (Pre.) | 3.776 | 263.0 | 4.70 | 1.79 | 2.67 | 6.272 | -0.922 | 9.780 |
| | LSDA + U (Expt.) | 3.966 ^a | 7 | | | | | | |
| HoIr ₃ | (Pre.) | 3.793 | 272.9 | 4.37 | 1.81 | 14.11 | 4.311 | -0.708 | 7.789 |
| | LSDA + U (Expt.) | 3.951 ^a | 4 | | | | | | |

Pre. = Present, Expt. = Experiment, ^aref. [11].

magnetic moment is essentially located at RE atoms and the positive and negative signs of the RE and Ir atoms indicate that, they line up opposite to one another.

In addition, to interpret the bonding description and charge transmission amid the fundamental element of REIr₃ compounds, we have drawn charge density plots for both spins along (100) plane which are shown in figures 4a–4f. From figure 4, it can be observed that the plots for both spins are largely similar. If the charge density plots are spherical and set apart from each other, then the bonding character is ionic. In our examined outcomes the ionic bonding exists among RE and Ir atoms. If the charge densities are combined or overlay, the covalent bonding is expected to be present between the cation and the anion. In our calculated results, partial covalent bonding is present between RE–RE (RE = Gd, Tb and In) atoms. It can also be recognised from figure 4 that the charge transmission from RE atoms towards Ir atom is due to the higher electronegativity of Ir atoms. This evidence indicates the existence of ionic bonding between them. The bonding within Gd–Gd, Tb–Tb and Ho–Ho is metallic. One can also detect the screening effect amidst RE–RE atoms due to the presence of *f*-electrons.

3.3 Elastic properties

The elastic characteristics are very crucial to decide the capacity of any material to go through deformation and then improve and come back to its original frame after stress ceases. The elastic constants for REIr₃ intermetallic compounds are determined at ambient pressure by using the approach developed by Charpin [23] and this method is combined in the WIEN2k package [13] with LDA approximation. For cubic crystals, there are only three independent elastic parameters C_{11} , C_{12} and C_{44} . We have computed three elastic constants at ambient pressure. It can be observed that the estimated values of elastic constants, given in table 2, satisfy the required mechanical stability measurement for cubic crystal leading to the following constraints: $C_{11} - C_{12} > 0$, $C_{11} + 2C_{12} > 0$, $C_{11} > B > C_{12}$ [24,25], which precisely reveal that these compounds are balanced in cubic AuCu₃-type structure. Ductility of these materials have been analysed by the ratio between the bulk modulus and shear modulus (B_0/G_H), which was suggested by Pugh [26]. From Pugh's criteria a material acts in ductile manner, if $(B_0/G_H) > 1.75$. Otherwise it is brittle. The Cauchy's pressure ($C_{12} - C_{44}$), is a different parameter to explain the elastic character of these compounds. If the Cauchy's pressure is positive, the material is anticipated to be ductile and if the pressure is negative then the material shows brittle disposition [28]. From

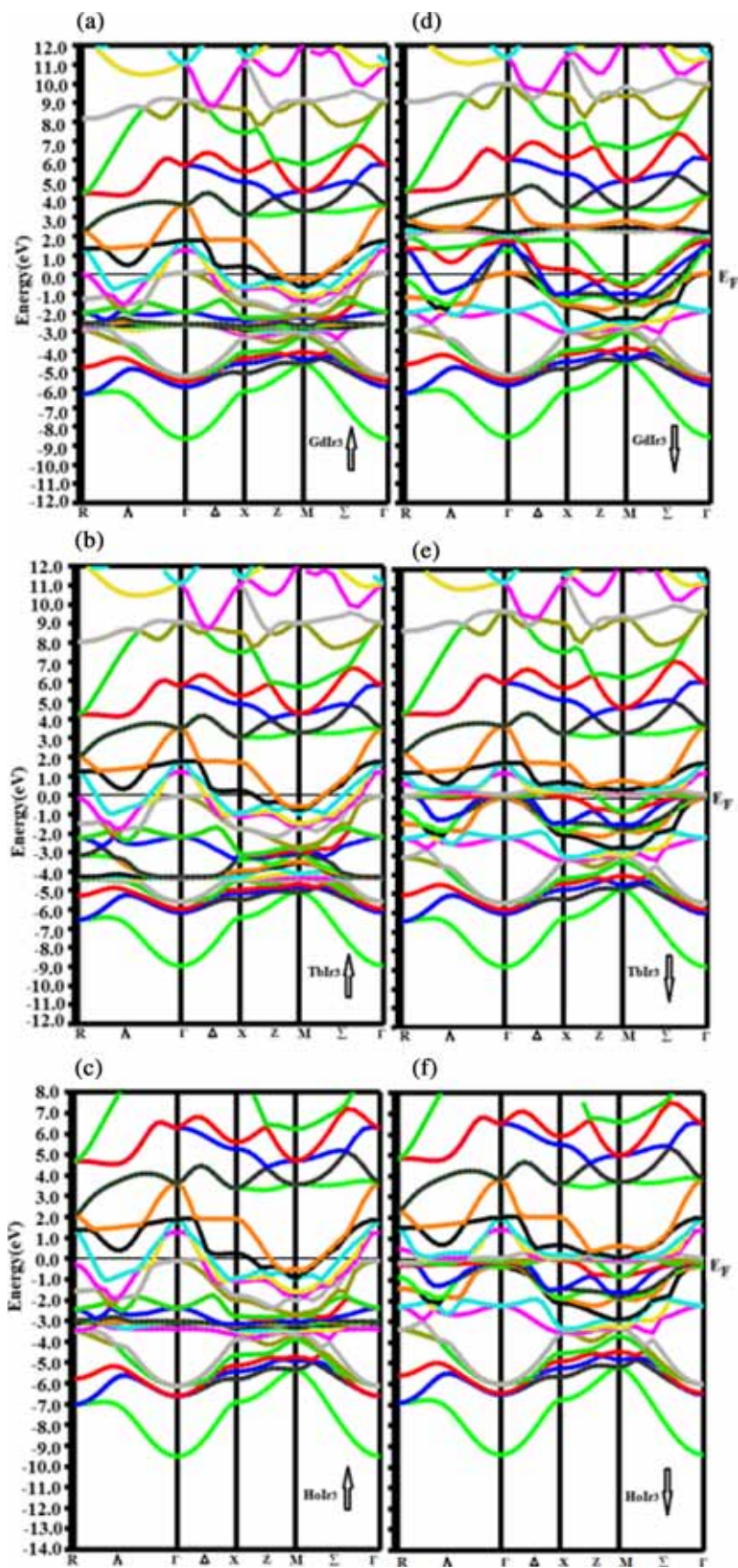


Figure 2. Electronic band structure for GdIr₃ (a, d), TbIr₃ (c, d) and HoIr₃ (e, f) using LSDA + *U* approximation in both spin channels.

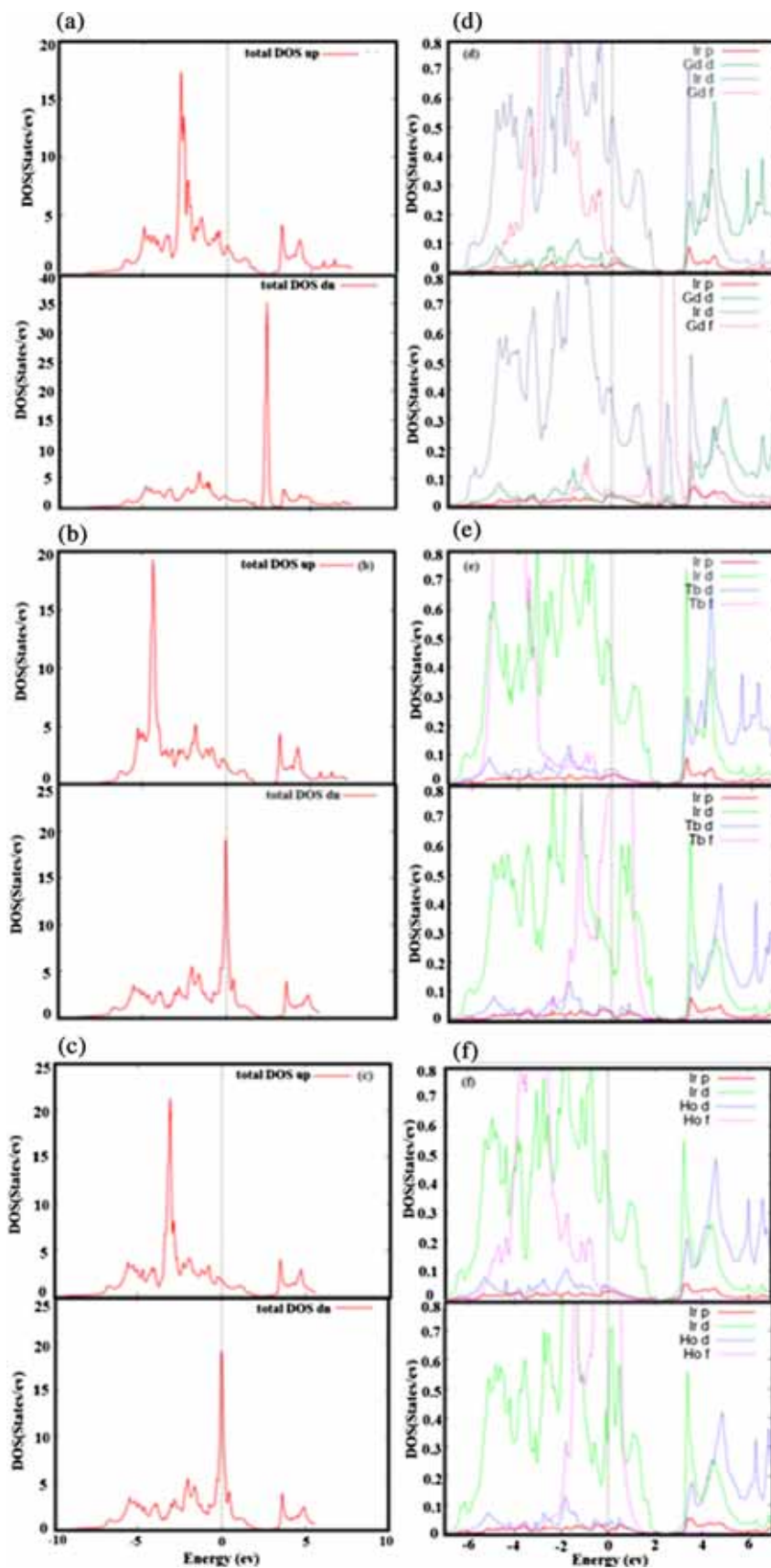


Figure 3. Total and partial density of states for GdIr₃ (a, d), TbIr₃ (b, e) and HoIr₃ (c, f) using LSDA + *U* approximation for both spin channels.

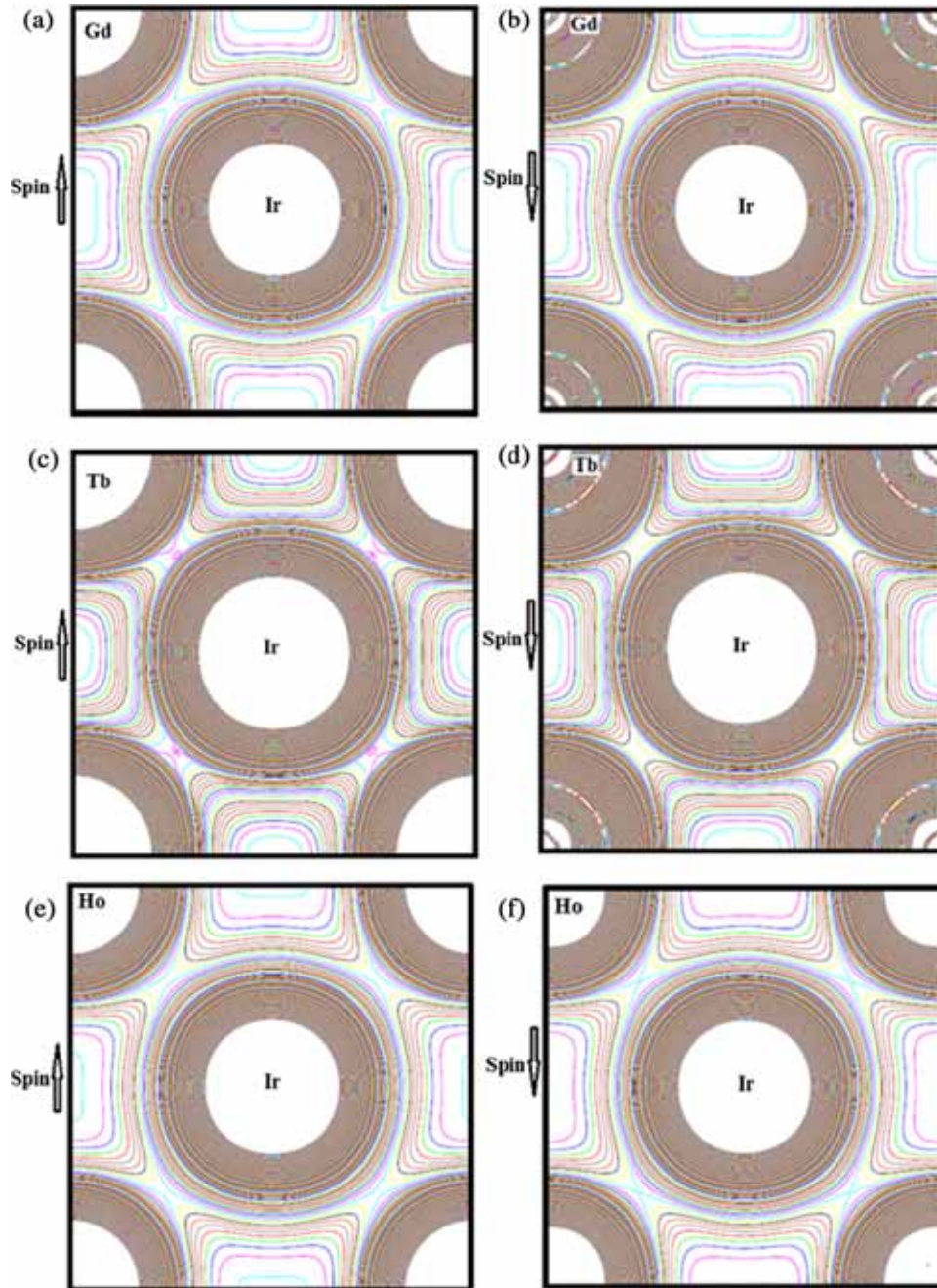


Figure 4. Charge density plots for GdIr_3 (a, b), TbIr_3 (c, d) and HoIr_3 (e, f) for both spins along 100 plane using LSDA + U approximation.

Table 2. Calculated elastic constants, B_0/G_H ratio and Cauchy's pressure ($C_{12} - C_{44}$) of REIr_3 intermetallic compounds with LDA approximation.

| Solids | C_{11} (GPa) | C_{12} (GPa) | C_{44} (GPa) | B_0/G_H | $C_{12} - C_{44}$ |
|-----------------|----------------|----------------|----------------|-----------|-------------------|
| GdIr_3 | 309.33 | 297.37 | 129.33 | 3.67 | 168.04 |
| TbIr_3 | 271.72 | 264.83 | 169.47 | 3.00 | 95.36 |
| HoIr_3 | 367.03 | 235.41 | 255.62 | 1.65 | -20.21 |

table 2, it can be seen that GdIr₃ and TbIr₃ are ductile while HoIr₃ is brittle at ambient pressure.

4. Conclusion

We have theoretically explored the structural, electronic, magnetic and elastic properties of REIr₃ intermetallic compounds. The estimated lattice constants are in good agreement with the available experimental values. But, other experimental or theoretical data are not available for comparison. The electronic band structures and DOS of REIr₃ certify their metallic character. *f* states of RE and *d* states of Ir play crucial roles in band structures and Fermi surfaces. We have also recognised from the charge density plots that REIr₃ demonstrated ionic–covalent bonding simultaneously (metallic bonding also is present). The elastic constants comply essential mechanical stability requirement for solids and it is established that all the investigated compounds are mechanically balanced.

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