



Electronic structure of GdX_2 ($X = Fe, Co$ and Ni) intermetallic compounds studied by the GGA + U method



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ABSTRACT

The electronic and magnetic properties of the ferromagnetic laves-phase GdX_2 ($X = Fe, Co$ and Ni) intermetallic compounds were calculated by using an all-electron full-potential linear muffin-tin orbital method (FP-LMTO) within GGA and GGA + U. The so-called GGA + U method is applied to properly treat the Gd-4f electron in the electronic structure calculation. The GGA improves the agreement between experiments and calculations for the lattice constants; however the GGA + U overestimates them, but gives a better representation of the band structure, density of states and magnetic moments compared to GGA alone. The reduction of the Co and Ni magnetic moments in the $GdCo_2$ and $GdNi_2$ compared to that in pure metals is due to the different localization strength of the transition metal and the same reason in the enormous reduction of the Curie temperatures.

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1. Introduction

Rare-earth transition-metal (RE-TM) intermetallic compounds have presented an interesting subject since 1960 in condensed matter physics, they are of considerable technological and scientific interest due to their extraordinary unique magnetic properties and wide industrial applications as permanent magnets and magneto-optical storage media. Among various intermetallic compounds of rare-earths (RE) with transition-metals (TM), the RX_2 laves phase alloys with ferromagnetic (FM) X ($=Fe, Co$ or Ni) have been attractive for the basic understanding of the electronic structure, the high Curie temperature, investigating the physical properties and technological applicability of (RE-TM) compounds.

The $GdFe_2$, $GdCo_2$ and $GdNi_2$ belong to the (RE-TM) compounds, they crystallize in the cubic laves ($MgCu_2$) phase (C15) type of structure [1] with the rare-earth atoms arranged in the diamond structures consisting of two FCC lattices displaced from each other by one-fourth of the body diagonal. The transition-metal atoms are located at sites of rhombohedral symmetry ($3m$) in a tetrahedral arrangement with four rare-earth atoms as next-nearest neigh-

bours. $GdFe_2$, $GdCo_2$ and $GdNi_2$ are ferrimagnetic, i.e. the magnetic moments of Fe/Co/Ni atoms align anti-parallel to those of Gd atoms but their Curie temperatures are different, 790 K for $GdFe_2$ [2], 404 K for $GdCo_2$ [3,4] and 79.3 K for $GdNi_2$ [1] this different Curie temperatures are expected nearly to come from different interaction strength between the rare earth and the transition metal sublattice which couples the opposite 4f and 3d spin.

In this work we present a study of some of the electronic and magnetic properties of intermetallic compounds $GdFe_2$, $GdCo_2$ and $GdNi_2$, our calculations based on the GGA + U method within density functional theory. The GGA + U method explicitly includes the on-site Coulomb interaction term in the conventional Hamiltonian. It is well known to describe strongly correlated systems which contain transition metal (3d local electrons) or rare earth elements RE (localized 4f electrons) with partially filled d (or f) shells. The previous theoretical studies showed the influence of the potential U on the magnetic moments [5] and the behaviour of Gd-4f states [6]. To see these influences we have increased the value of U and J to see the limits of these influences of the potential of Hubbard U .

The organization of the paper is as follows: we explain the computational method in Section 2. The results are presented and discussed in Section 3 for structural, electronic and magnetic properties and a brief conclusion is drawn in the last section.

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2. Method of calculations

The present calculations were carried out using the full potential linear muffin–tin orbital (FP-LMTO) method based on the density functional theory (DFT [7,8] as implemented in the recent version of lmtart computer package. The space in (FP-LMTO) method is divided into non-overlapping muffin–tin (MT) spheres centered at the atomic sites separated by an interstitial region (IR). In the IR region, the basis functions are represented by Fourier series. Inside the MT spheres, the basis functions are expanded in combinations of spherical harmonics functions. The exchange–correlation (XC) potential is treated by the generalized-gradient approximation (GGA) of Perdew–Wang [9].

In order to achieve energy eigenvalues convergence, the charge density and potential inside the muffin–tin spheres are represented by spherical harmonics up to $l_{\max} = 6$. The k -integration over the Brillouin zone is performed up to (10, 10, 10) grid in the irreducible Brillouin zone (IBZ), using the tetrahedron method [10].

In our case we used the GGA + U method proposed by Anisimov et al. [11], in which the orbital dependent one-electron potential is written as

$$V_{m_1, m_2}^{\sigma} = \sum_{m_3, m_4}^{\sigma} (\langle m_1, m_3 | V^{ee} | m_2, m_4 \rangle - \langle m_1, m_3 | V^{ee} | m_2, m_4 \rangle \delta_{\sigma, \sigma'}) n_{m_3, m_4}^{-\sigma} - \delta_{m_1, m_2} U \left(n - \frac{1}{2} \right) + \delta_{m_1, m_2} J \left(n^{\sigma} - \frac{1}{2} \right) \quad (1)$$

where V^{ee} are the screened Coulomb interactions among the nl -electrons (n denotes the main quantum number, and l denotes the orbital quantum number) and U, J are screened Coulomb and exchange parameters, respectively. The matrix elements can be expressed.

In terms of complex spherical harmonics and effective Slater integrals F^k [12] as

$$\langle m_1, m_3 | V^{ee} | m_2, m_4 \rangle = \sum_k a_k(m_1, m_2, m_3, m_4) F^k \quad (2)$$

where $0 \leq k \leq 2l$ and

$$a_k(m_1, m_2, m_3, m_4) = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle l m_1 | Y_{kq} | l m_2 \rangle \langle l m_3 | Y_{kq}^* | l m_4 \rangle \quad (3)$$

For N electron, the relations between the parameters used are $U = F^0$; $J = (286F^2 + 195F^4 + 250F^6)/6435$; $F^4 = 0.625F^2$; and $F^6 = 0.5F^2$ [13]. Thus if the averaged parameters U and J are known, F^0, F^2, F^6 and also the matrices can be obtained through the above relations. The average Coulomb U parameter for Gd ions was taken to be 8.0 eV and the exchange parameter J was fixed at 1.2 eV.

3. Results and discussions

3.1. Structural properties

Practically, our basic procedure in this work is to calculate the total energy as a function of unit-cell volume around the equilibrium cell volume V_0 . The calculated total energies versus volume are fitted with the Birch's equation of state (EOS) [14] to determine the ground-state properties such as the equilibrium lattice constant a_0 , the bulk modulus B_0 and the pressure derivative of the bulk modulus B' . The exchange–correlation (XC) potential is treated by two approximations GGA and GGA + U.

Deduced results are presented in Table 1, which also contains earlier experimental and theoretical data for comparison. From Table 1, the calculated equilibrium lattice constants for GdFe₂, GdCo₂ and GdNi₂ with GGA method are 14.06, 13.636 and 13.64

Table 1

Calculated total energy (eV), lattice parameter a (in a.u.), bulk modulus B_0 (in GPa) and its pressure derivatives B' for GdFe₂, GdCo₂ and GdNi₂ compounds, compared to the experimental data and previous theoretical calculations.

| | E_{\min} (eV/f u) | a_0 (a.u.) | B_0 (GPa) | B'_0 |
|-------------------------|---------------------|---------------------|-------------|--------|
| GdFe₂ | | | | |
| FP-LMTO: GGA | –27,656, 17,995 | 14.06 | 189.6 | 3.17 |
| GGA + U | –27,656, 91,932 | 14.11 | 140.67 | 3.19 |
| Experiment: | | 13.96 ^a | | |
| Other works: | | 13.85 ^b | | |
| | | 13.73 ^c | | |
| | | 13.993 ^d | | |
| | | 13.938 ^e | | |
| | | 14.23 ^f | | |
| GdCo₂ | | | | |
| FP-LMTO: GGA | –28,139, 104,395 | 13.636 | 132.6 | 3.859 |
| GGA + U | –28,139, 851,985 | 13.77 | 215,502 | 3.451 |
| Experiment: | | 13.69 ^a | | |
| Other works: | | 13.65 ^b | | |
| | | 13.56 ^c | | |
| | | 13.74 ^d | | |
| | | 13.723 ^f | | |
| | | 13.817 ^g | | |
| GdNi₂ | | | | |
| FP-LMTO: GGA | –28,648,704,090 | 13.64 | 148.47 | 3.28 |
| GGA + U | –28,649,3,062,400 | 13.75 | 124.80 | 3.94 |
| Experiment: | | 13.62 ^a | | |
| Other works: | | 13.553 ^c | | |
| | | 13.593 ^h | | |
| | | 13.617 ⁱ | | |

^a Ref. [15,16].

^b Ref. [16].

^c Ref. [6].

^d Ref. [18].

^e Ref. [19].

^f Ref. [20].

^g Ref. [21].

^h Ref. [22].

ⁱ Ref. [23].

a.u. respectively. These values agree very well with their experimental counterpart [15,16]: 13.96, 13.69 and 13.62 a.u., however the application of the GGA + U method slightly overestimates them. This overestimation of the theoretical lattice constants for GdFe₂, GdCo₂ and GdNi₂ are about 1%, 0.6% and 0.9%, respectively. The bulk modulus decreases from GdFe₂ to GdNi₂ suggesting that the compressibility increase from GdFe₂ to GdNi₂.

3.2. Electronic structure and magnetic properties

For a system where the f-electrons are well localized, and where the spin orbital interactions cannot be neglected, the GGA method is insufficient to describe such systems in particular the electronic properties. However, the GGA + U approach was initially suggested to describe correctly these later systems. Then the Hubbard term (U) which describes the d – d or f – f interaction is added to the GGA energy. This method has proven its effectiveness for strongly correlated systems. The calculated energy band structure of both GdBi, and GdSb compounds along the higher symmetry direction in the Brillouin zone is shown in Figs. 1–3. We notice that the band structures of spin-up states are similar to those for spin-down states except that the spin-up Gd-f bands are occupied and lie well below the E_F and the spin-down Gd-f bands are unoccupied and lie well above E_F . The spin-down Gd-f bands hybridize with the Gd-p, -d and Fe/Co/Ni p spin-down states while the spin-up f bands remains unhybridized. Also we can see the majority Gd-f bands are centred around ~ -12 eV for the three compounds far below E_F , and the minority Gd-f bands are centred around ~ 5.5 eV, so the GGA + U enhances the exchange splitting of the Gd-f bands to ~ 19 eV (from ~ 5 eV with GGA) by pushing the 4f spin-up states

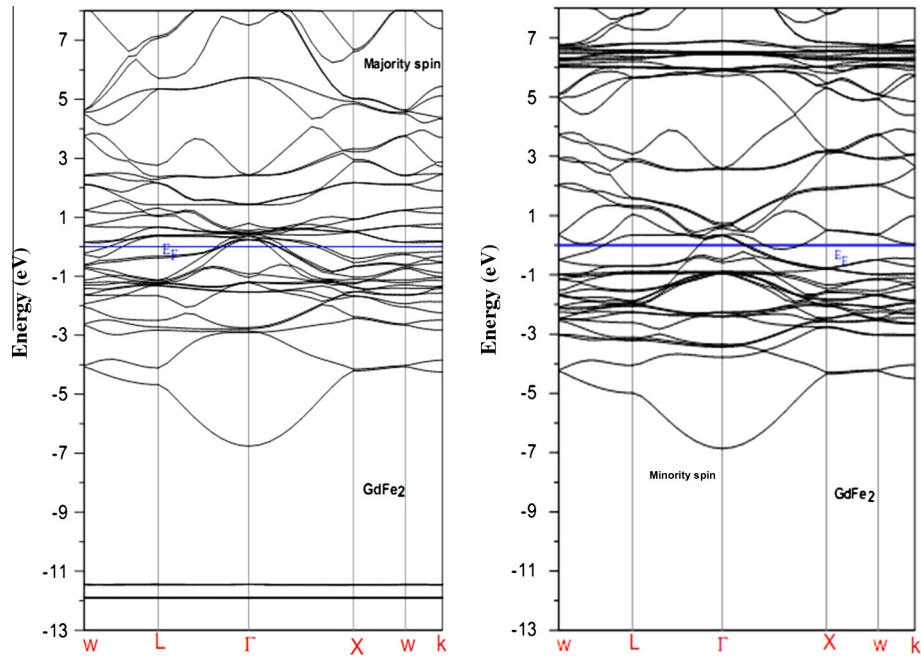


Fig. 1. The band structure of GdFe₂ obtained within GGA + U for majority spin and minority spin.

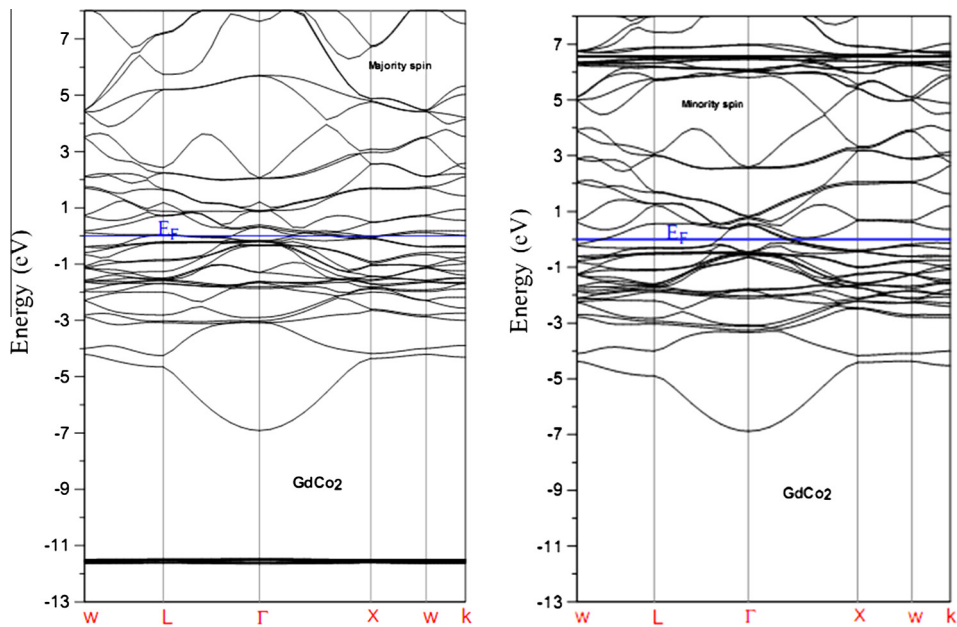


Fig. 2. The band structure of GdCo₂ obtained within GGA + U for majority spin and minority spin.

much below E_F and 4f spin-down states well below E_F as it shown in Fig. 1(a and b) above (just the case of band structure of GdFe₂ with GGA is taken here), the same cases for the two other compounds (note plotted here). Besides the Gd-f states, there is a group of bands in the energy range from -4 to -2.5 eV mainly due to (Fe, Co, Ni)-s, d and Gd-d states, the bands from -2.5 to 5 eV are due to the hybridization of (Fe, Co, Ni) p, d and Gd-d states. Above 5 eV only Gd-p and d states constitute the bands structures.

In order to understand clearly the electronic structure and the differences in the magnetic properties between GdFe₂, GdCo₂ and GdNi₂, the total density of states of the compounds were calculated (for all the atoms in unit cell) along with partial d DOS (per atom) using GGA + U approximation and their curves are plotted in

Figs. 4–6. All the compounds show a typical metallic behaviour in both minority and majority components. The sharp peaks at about -12.0 eV below E_F in the up-spin DOS and about 6.0 eV above E_F in the down-spin DOS are due to Gd-4f states; the 3d states of Fe/Co/Ni are mainly dominated in the energy range -4.0 – 2.0 eV. On the other hand, Gd-5d states are situated between -4.0 and 8.0 eV, which are strongly hybridized with and 3d states of Fe/Co/Ni. We noticed the same behaviour of states with the values of U and J used by Liu et al. [6], there is only a difference in the energy range where are localized the states f/d .

The magnetic moments with the optimized lattice constants are calculated and listed in Table 2. The negative sign of the Fe/Co/Ni moments implies that the Fe/Co/Ni aligned apposite to the Gd

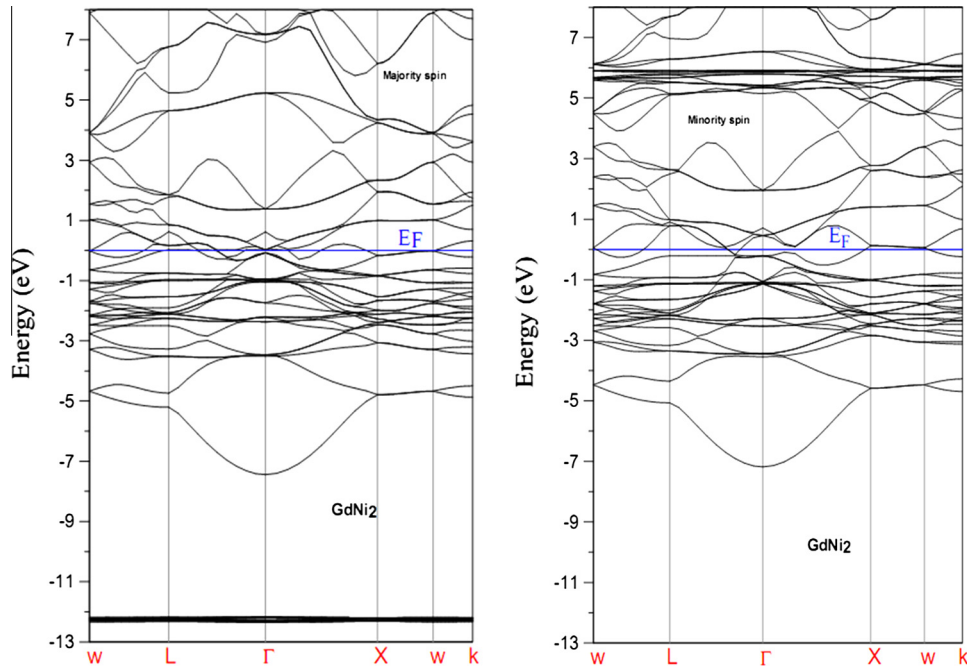


Fig. 3. The band structure of GdNi₂ obtained within GGA + U for majority spin and minority spin.

moment. As Table 2 shows, application of the GGA + U method also lead agreement between experiment and calculations than the GGA method. The calculated total magnetic moments of GdFe₂, GdCo₂ and GdNi₂ per formula unit are 3.475, 5.526 and 7.205 μ_B respectively, in adequate agreement with experiment [24,25]. We note that there is an increase in magnitude of the Gd and decrease

in magnitude of the Fe/Co/Ni moments. For the GGA + U the calculated Gd moments vary from about 7.26 μ_B to 7.618 μ_B (7.0 μ_B is said to come from the 4f orbital and the remaining from the spin polarization of the conduction electrons) [18,26], and for Fe/Co/Ni moments, it vary from about 2.395 to 0.168 μ_B . It is seen that for the case of GdFe₂ the values of the magnetic moments at the

Table 2

Calculated total and local magnetic moments (in μ_B) for GdFe₂, GdCo₂ and GdNi₂ compounds.

| | M_{Tot} (μ_B) | M_{Gd} (μ_B) | M_{Fe} (μ_B) | M_{Co} (μ_B) | M_{Ni} (μ_B) | M_{int} (μ_B) |
|-------------------|-----------------------|----------------------|----------------------|----------------------|----------------------|-----------------------|
| GdFe ₂ | | | | | | |
| Present work: GGA | 4.36 | 7.247 | -1.555 | | | 0.218 |
| GGA + U | 3.475 | 7.618 | -2.395 | | | 0.64 |
| Experiment: | 3.46 ^a | | | | | |
| Other works: | 3.85 ^b | 7.58 ^b | -1.96 ^b | | | |
| | 3.9 ^c | 7.83 ^c | -1.96 ^c | | | |
| | 3.385 ^e | 7.552 ^e | -2.263 ^e | | | 0.359 ^e |
| | 3.714 ^f | 7.536 ^f | -2.05 ^f | | | 0.298 ^f |
| | 3.39 ^k | 7.51 ^k | -2.13 ^k | | | |
| GdCo ₂ | | | | | | |
| Present work: GGA | 6.77 | 6.878 | | -0.045 | | 0.086 |
| GGA + U | 5.526 | 7.433 | | -1.175 | | 0.443 |
| Experiment: | 5.34 ^a | | | | | |
| Other works: | 4.99 ^b | 7.46 ^b | | -1.24 ^b | | |
| | 5.2 ^c | 7.58 ^c | | -1.19 ^c | | |
| | 5.234 ^f | 7.349 ^f | | -1.18 ^f | | 0.255 ^f |
| | 5.14 ^k | 7.31 ^k | | -1.15 ^k | | |
| GdNi ₂ | | | | | | |
| Present work: GGA | 8.01 | 6.829 | | | 0.548 | 0.085 |
| GGA + U | 7.205 | 7.264 | | | -0.168 | 0.277 |
| Experiment: | 7.208 ^a | | | | -0.20 ^f | |
| Other works: | 7.0 ^c | 7.31 ^c | | | -0.11 ^c | |
| | 6.94 ^k | 7.03 ^k | | | -0.03 ^k | |

^a Refs. [15,16].

^b Ref. [17].

^c Ref. [6].

^e Ref. [19].

^f Ref. [20].

ⁱ Ref. [23].

^j Ref. [29].

^k Ref. [27].

Gd site ($7.618 \mu_B$) is much closer to that in pure Gd ($7.63 \mu_B$) and at the Fe site ($2.395 \mu_B$) is quite close to that in pure Fe ($2.21 \mu_B$). On the other hand in $GdCo_2$ and $GdNi_2$, the magnetic moments at the Gd site is 7.43 and $7.264 \mu_B$ showing a $\sim 3\%$ and $\sim 5\%$ drop and that of Co and Ni show even stronger impact dropping by 27% and 73% respectively in comparison with that in elements Co ($1.66 \mu_B$) [27], and Ni ($0.62 \mu_B$) [28], this suggests that the interatomic interactions in $GdCo_2$ are stronger and in $GdNi_2$ are much stronger, and affect the Co and Ni atoms more, than in $GdFe_2$. We note also that the magnetic moments in the interstitial regions increase within GGA + U approximation, this explains that the term added in GGA + U takes better account of electron correlations and localization of strongly correlated electrons. This phenomenon can be explained by the d DOS states of the transition metal as expected in Figs. 4–6, it seen that the corresponding energy splitting between the majority and minority 3d DOS reduced because of the shift of the minority (up-spin) 3d DOS to lower energy (this is due to the filling of the minority-spin d bands of Co and Ni by the conduction electrons from Gd atoms), this explained the reduction of the Co

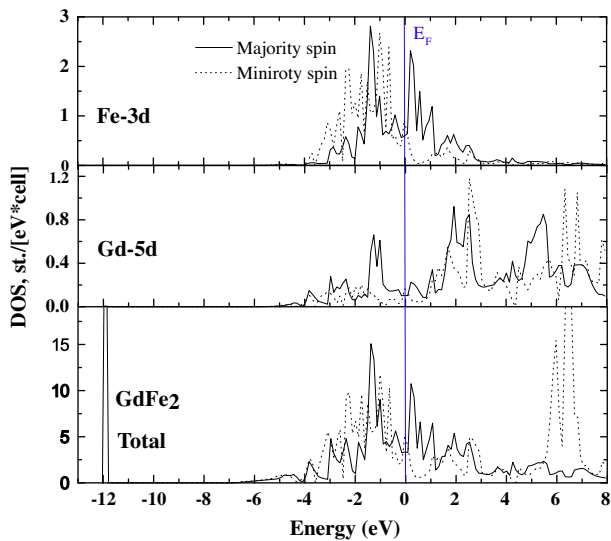


Fig. 4. The total DOS of $GdFe_2$ (majority spin (solid line) and minority spin (dashed line)) obtained with GGA + U calculations.

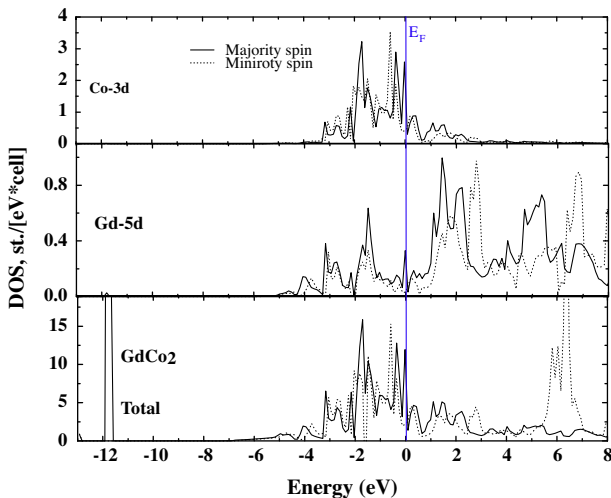


Fig. 5. The total DOS (States/eV) of $GdCo_2$ (majority spin (solid line) and minority spin (dashed line)) obtained with GGA + U calculations.

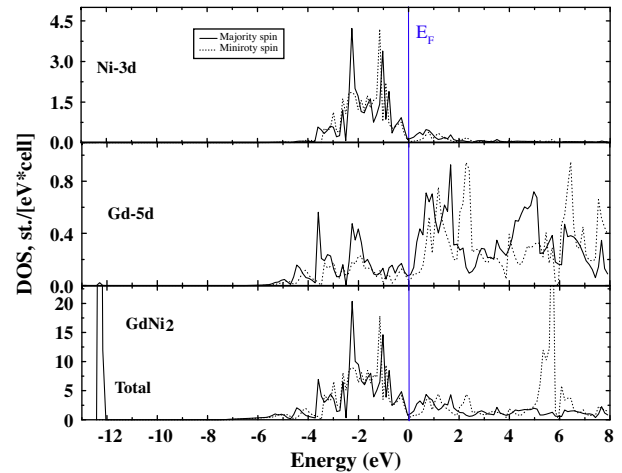


Fig. 6. The total DOS (States/eV) of $GdNi_2$ (majority spin (solid line) and minority spin (dashed line)) obtained with GGA + U calculations.

and Ni moments in $GdCo_2$ and $GdNi_2$ compared to the corresponding pure transition metals Co and Ni. Similarly, for the GGA, the calculated Gd and Fe/Co/Ni/ moments are lower than those calculated by GGA + U. These results indicate that the GGA + U approximation provides a more accurate structural and gives a better representation of the band structure, density of states and magnetic moments compared to GGA alone for GdX_2 compounds. Finally, the Comparison with previous studies [6] shows clearly that our values found by this potential of Hubbard tend to experimental values. Therefore we conclude that this model requires a strong interaction (high U) to obtain a qualitative agreement with experiments such as behaviour states d , f and the magnetic moments.

4. Conclusion

The electronic structures of the laves-phases $GdFe_2$, $GdCo_2$ and $GdNi_2$ compounds have been studied by employing first principles in the all-electrons FP-LMTO method. For the exchange and correlation potential, we used the generalized-gradient approximation (GGA) and GGA + U. We found a shifting majority as well as minority f bands away from Fermi level when GGA + U is used, leading to a better representation for the DOS at the Fermi level. Spin-polarized FP-LMTO band structure calculations revealed that the d bands of $GdNi_2$ near E_F have larger binding energies than the corresponding ones of $GdCo_2$ by about 0.7 eV and by about 1.0 eV than of $GdFe_2$, indicating that the hybridization interaction between Gd- d and Ni- d electrons is stronger than that between Gd- d and Co- d and much stronger than that between Gd- d and Fe- d electron. Also, calculating the 3d DOS of the transition metal in each compound revealed an electronic charge localization mainly in down spin 3d orbital resulting in reducing the total magnetic moments and broadening the 4f level leaves. Finally, this model (GGA + U) requires a strong interaction (high U) to obtain a qualitative agreement with experiments such as behaviour states d , f and the magnetic moments.

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