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Electronic structure of GdN, and the influence of exact exchange

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Abstract
GdN bulk is studied with the local density approximation, on the Hartree–Fock level, and on the level of the hybrid functional B3LYP. A local basis set formalism is used, as implemented in the present CRYSTAL06 release. It is demonstrated that the code is technically capable of treating this system with its 4f electrons explicitly, i.e. out of the core. The band structure at the level of the local density approximation is in good agreement with earlier calculations and is found to be half-metallic. The Hartree–Fock band structure is insulating with a large gap. Interestingly, three solutions were found at the B3LYP level. The lowest of them is insulating for majority spin, and the Fermi surface for minority spin consists only of points, resulting in a very low density of states around the Fermi level.

1. Introduction

GdN crystallizes in a rock salt structure and is by now established as a ferromagnet with a Curie temperature of ~69 K [1–4]. The question whether it is an insulator or not is still under discussion. In the transmittance spectrum, a gap of 1 eV was observed [5]. From optical reflection and derivation of the plasma resonance and from the Hall effect [6] it was argued that GdN was a semimetal. Thin GdN layers were found to be insulating in resistivity measurements [7]. In x-ray photoelectron spectroscopy (XPS) experiments, the occupied 4f bands were found at a binding energy of 7.8 eV for GdN [8]. For the related systems GdX (X = P, As, Sb, Bi), the occupied Gd 4f states were found at ~9 eV, and the unoccupied states at ~5 eV in XPS and x-ray bremsstrahlung isochromat spectroscopy (X-BIS) measurements [9].

The first theoretical study of GdN was an augmented plane wave calculation using the Slater exchange potential [10], which resulted in an insulator with a very small gap [11]. The f electrons were treated as core states in this calculation. A further calculation with the f electrons in core [12] using the local density approximation (LDA) gave a similar band structure, but without gap. The spin-polarized solution was found to be metallic for majority, and insulating for minority spin. Recently, several calculations with explicitly treating the f electrons were performed. When the pure LDA was used, a metal was obtained [13, 14], with the occupied f states at ~−4 to −3 eV below the Fermi level. To take into account the strongly correlated nature of the f electrons, a Hubbard U_f term was applied to these states [15, 13, 14]. This still resulted in a metallic solution, and only when also a U_d term was applied to the Gd *d* states, an insulator was obtained [13]. Similarly, in [15], LDA + U calculations gave a metallic ground state, and by applying further rigid shifts to the 5d and 4f states, an insulating state was found. When the lattice was expanded, also a transition to an insulator was predicted, at the LDA+U level [16]. A slightly different approach to take into account the strongly correlated nature of this system is to apply a self-interaction correction. This led again to a half-metallic ground state for GdN, with a gap in the minority channel [17].

Therefore, there are many reasons to study GdN. Besides these aforementioned reasons, from the theory point of view, a further point is that it would be interesting to test the performance of hybrid functionals, as a further method to treat strongly correlated systems. It has been shown that they give surprisingly good values for the band gaps for such systems, where the local density approximation and other standard functionals often fail [18–20]. Recently, the B3LYP hybrid functional was applied to UO_2, with explicitly treated f electrons, and also a good value for the gap was obtained [21]. Also, plutonium oxides were found to be well described by hybrid functionals [22]. Cerium oxides were studied using screened hybrid density functionals with a local basis set [23], and with a plane wave basis set and hybrid functionals [24].

The CRYSTAL code used in the present work is based on a local Gaussian basis set. The first version released in 1988 was a pure Hartree–Fock code. Hybrid functionals, which use an admixture of exact (Fock) exchange, were

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available from the 1998 release onwards. It turned out that, in the CRYSTAL implementation, the CPU times for calculations with hybrid functionals are comparable to the CPU times for calculations with standard functionals such as the LDA or gradient corrected functionals, and also the memory requirements are similar in both cases.

The present CRYSTAL release [25] was announced of being able to use f-functions as polarization functions. In this paper, it will be shown that it is also technically possible to perform calculations on systems with f electrons, with GdN as an example. There are various reasons why GdN was chosen as a test case: firstly, the f-occupancy if f^7, and the half-filled f-shell is probably one of the easiest examples to start with calculations on f-electron systems. Also, the crystal structure is fairly simple (NaCl type). In addition, as mentioned earlier, the system has already been theoretically described with other codes. This gives the opportunity to compare the present calculations, where possible, with the results obtained earlier.

2. Method and calculational details

The calculations were performed with the CRYSTAL06 code [25] which uses a local basis set. GdN was considered in the face centered cubic lattice. A ferromagnetic order was assumed, as this is the experimentally observed state.

The local density approximation, the Hartree–Fock approach (HF), and the B3LYP hybrid functional were employed. The local basis sets were chosen as follows: for Gd, a small core pseudopotential [26] was used, which includes scalar-relativistic effects (mass–velocity, Darwin and averaged spin–orbit operator [27]). Together with the pseudopotential, the corresponding basis set was used [28], with the following modification: the inner [8s7p4d4f] were kept as in the original basis set, and in addition one diffuse s, p and d function with exponent 0.12 were added, so that a [9s8p5d4f] basis set was obtained. The [3s2p1d] nitrogen basis set from reference [29] was used (6-21G as in [30] and a d-function with exponent 0.8). The present release of CRYSTAL06 can not compute the atomic solution of atoms with occupied f-orbitals. This solution would normally be used as an initial guess for the subsequent calculations on the periodic system. To overcome this problem, the atomic occupancy of Gd was chosen as $4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^8 6s^2$ which is obviously unusual, but sufficient to overcome the problem of having f-orbitals occupied ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ electrons are described by the pseudopotential). For nitrogen, the $1s^2 2s^2 2p^3$ state was occupied. No convergence is achieved for the Gd atom which is not too surprising due to the unusual occupancy, but this does not cause severe problems either. To converge GdN bulk, one convergence strategy is then e.g. to use the Anderson mixing scheme [31] with 80% mixing, and in addition to keep the spin locked to a value of $7/2$ in the first few (e.g. 10) cycles. In some cases, slight variations of this approach were necessary, but in the end convergence could be achieved in all cases. The cases of LDA and HF are more straightforward, whereas B3LYP has the additional difficulty that three different solutions were found. To compute the corresponding potential curves and determine the minimum, one certain solution was used as the initial guess for the other geometries. This way, the potential curves on the B3LYP level could be computed for all three solutions found.

Table 1. The computed equilibrium lattice constant and bulk modulus of GdN, at various levels of theory.

	a (Å)	B (GPa)
HF	5.10	167
LDA	4.91	174
LDA [12], 4f in core	4.999	188
LDA [13], 4f explicit	4.98	
B3LYP (solution with lowest energy)	5.10	137
Exp.	4.99 [33]	192 ± 35 [34]

A sampling with $16 \times 16 \times 16$ $\vec{k}$-points in the reciprocal lattice was used. In the case of B3LYP, calculations without smearing and with a smearing of 0.01 E_{h} (E_{h} are Hartree units, $1 E_{\mathrm{h}} = 27.2114$ eV) were performed, to explore possible changes due to the different decay properties of the density matrix in metallic systems [32]. However, no severe differences between the calculations with and without smearing temperature were observed.

The remaining parameters such as grids for the numerical density functional integration were chosen as the default. The only parameter which needed to be varied were the various thresholds for integral selection[1].

3. Results

3.1. LDA calculations

The computed LDA equilibrium lattice constant of 4.91 Å and the bulk modulus of 174 GPa (table 1) agree reasonably well with the literature. The LDA band structure is displayed in figure 1. It is half-metallic, because the bands for majority spin cross the Fermi energy, whereas the minority bands have a gap. The f-bands are positioned at ~ -3.1 eV below and ~ 2.6 eV above the Fermi energy. The remaining bands are as follows: the lowest band displayed is N s, followed by three N p bands which hybridize with the Gd d bands which are next higher in energy. The band structure is in good agreement with the recent linearized muffin tin orbital approach [13, 14].

The Mulliken population analysis gives a charge transfer of -0.7 to the nitrogen atoms. The Gd f population is 7.1, the 5d population is 1.3, and the 6s and 6p populations are 0.4 each. The spin population is 7.1 on Gd (6.9 due to the f electrons and 0.2 due to the d electrons) and -0.1 on N (due to the p states), which agrees well with earlier LDA calculation where the f states were treated in core [12].

The corresponding density of states is displayed in figure 2. In the selected energy range, the mainly occupied states are N (s and p), Gd d and Gd f. The density of states, projected on these states is also shown.

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[1] In the HF case, the values for the selection of the Coulomb integrals (parameter one and two) and exchange integrals (parameter three, four and five, as defined in the manual [25]) were chosen as 10^{-9}, 10^{-9}, 10^{-9}, 10^{-9}, 10^{-18}, in order to avoid linear dependence problems. In the case of LDA and B3LYP, the default values (10^{-6}, 10^{-6}, 10^{-6}, 10^{-6}, 10^{-12}) led to numerically stable solutions.

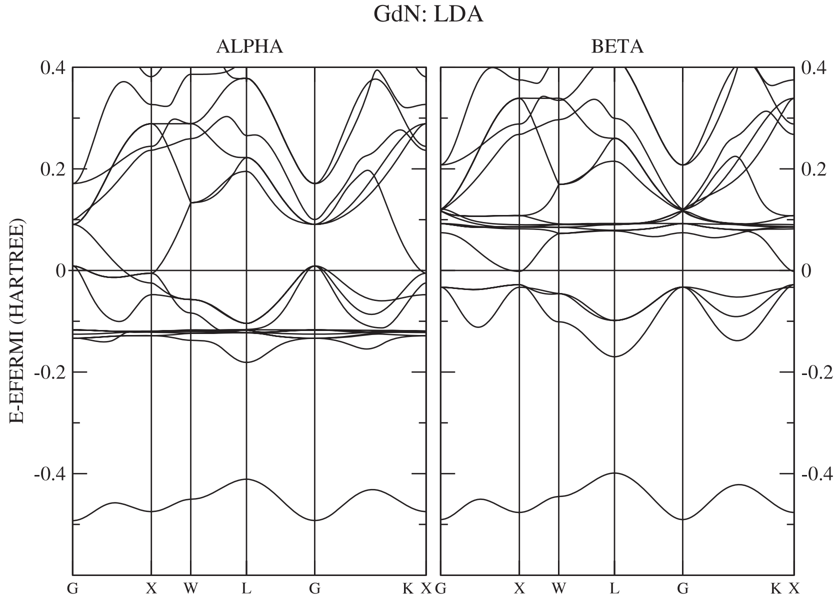

Figure 1. LDA band structure of GdN at the computed equilibrium lattice constant of 4.91 Å. The Fermi energy is positioned at 0.

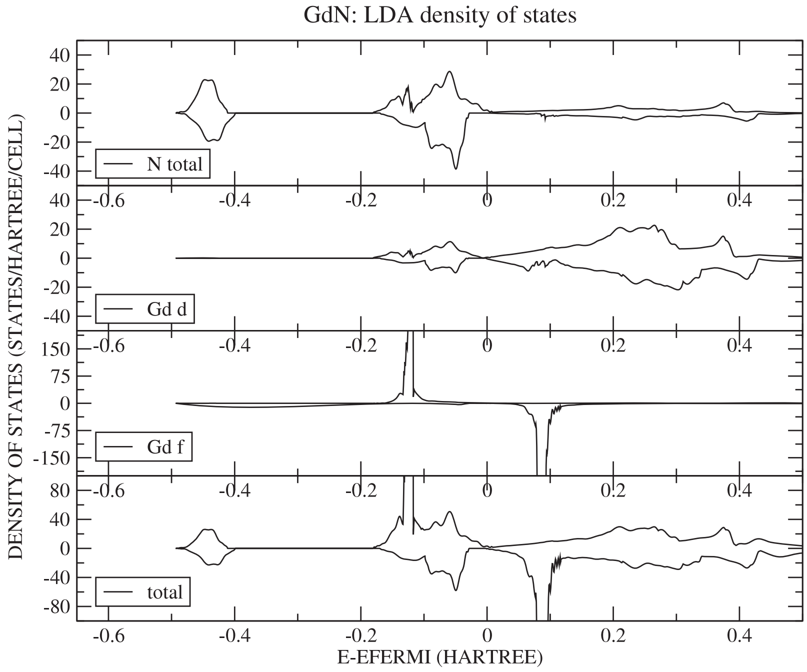

Figure 2. LDA density of states at the computed equilibrium lattice constant of 4.91 Å. Besides the total density of states, the projected density of states is shown for projections on N, Gd d, Gd f states. The Fermi energy is positioned at 0. The upper part of each panel is for majority spin, the lower part for minority spin.

3.2. HF calculations

The Hartree–Fock equilibrium lattice constant is 5.10 Å and thus slightly larger than the experimental value, which was also observed in an earlier Hartree–Fock calculation where the 4f electrons were treated as core electrons [35]. Similarly, the bulk modulus is slightly too small due to this overestimation of the lattice constant. The band structure at the Hartree–Fock level is displayed in figure 3. GdN is insulating on the HF level, with a gap of $\sim$5 eV. The occupied f bands are pushed downwards to ~ -15 eV below the top of the valence bands, and similarly the unoccupied f bands are pushed upwards to $\sim$22 eV. This is to be expected, since any screening, which is present on the LDA level, is missing at the HF level, and thus the localized f electrons feel the full, unscreened Coulomb repulsion. Another striking feature is that the N p bands and the Gd d bands are now well separated. This is also visible in the corresponding density of states in figure 4.

The total Mulliken population of N is $-1.1|e|$. The spin population is 7.2 on Gd (7.0 due to the Gd f electrons, and the

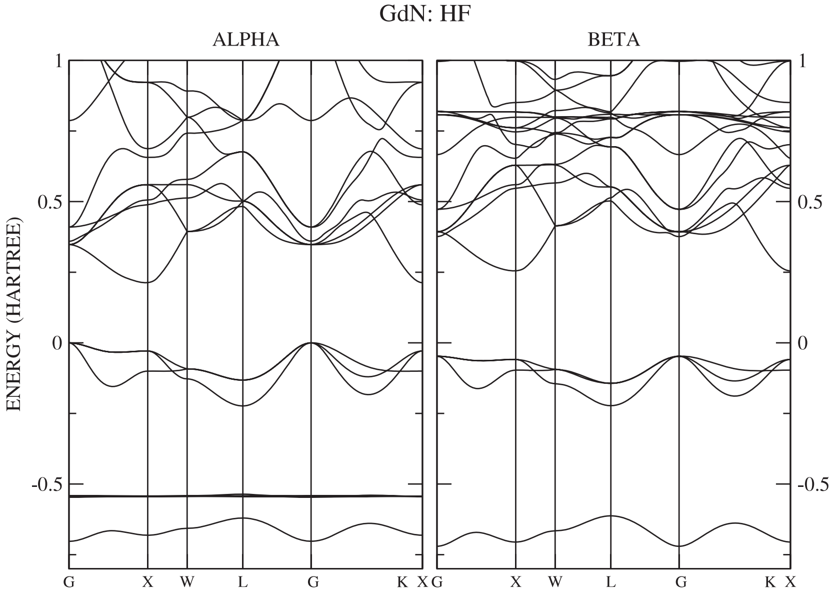

Figure 3. HF band structure of GdN at the computed equilibrium lattice constant of 5.10 Å. The top of the valence band is positioned at 0.

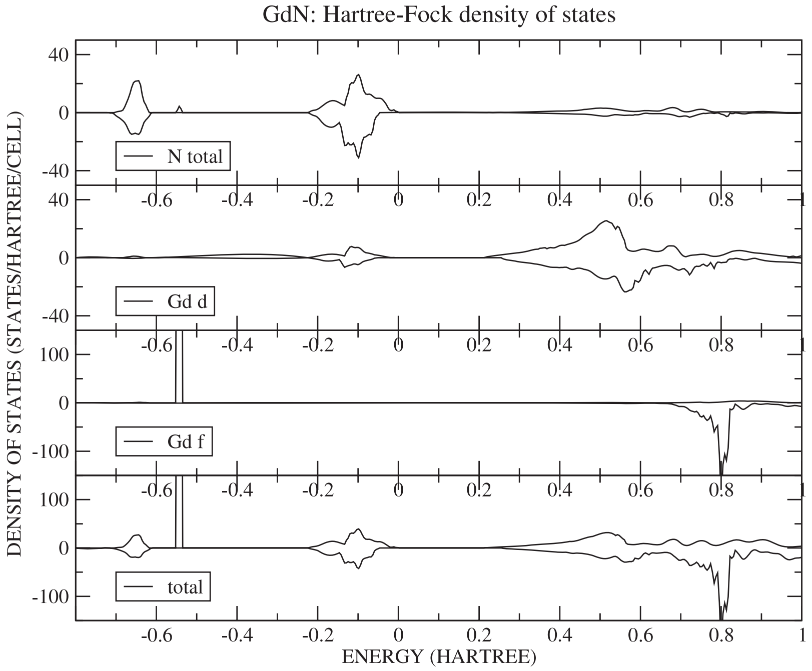

Figure 4. HF density of states at the computed equilibrium lattice constant of 5.10 Å. Besides the total density of states, the projected density of states is shown for projections on N, Gd d, Gd f states. The top of the valence band is positioned at 0.

remaining 0.2 mainly due to the Gd d states), and −0.2 for N (practically completely due to the N p states).

4. B3LYP calculations

The B3LYP calculations provided the somewhat surprising result that two states were found, which are close in energy. The state with the lowest energy will be discussed first. The computed lattice constant of this state is 5.10 Å. Its band structure is displayed in figure 5, and the corresponding density of states in figure 6. The f bands are positioned at ~ -5 eV below and ~ 7 eV above the Fermi energy, which agrees better with the experiment, compared to LDA and HF. In this case, the majority bands have a gap, in contrast to the LDA. The minority valence and conduction bands only touch in various places, so that the density of states at the top of the valence band practically vanishes.

The N population is $-0.8|e|$. The Gd spin population is 6.8 (7.0 due to the f electrons, 0.1 due to the d electrons and −0.3 due to the Gd s basis functions), and the N spin population is 0.2.

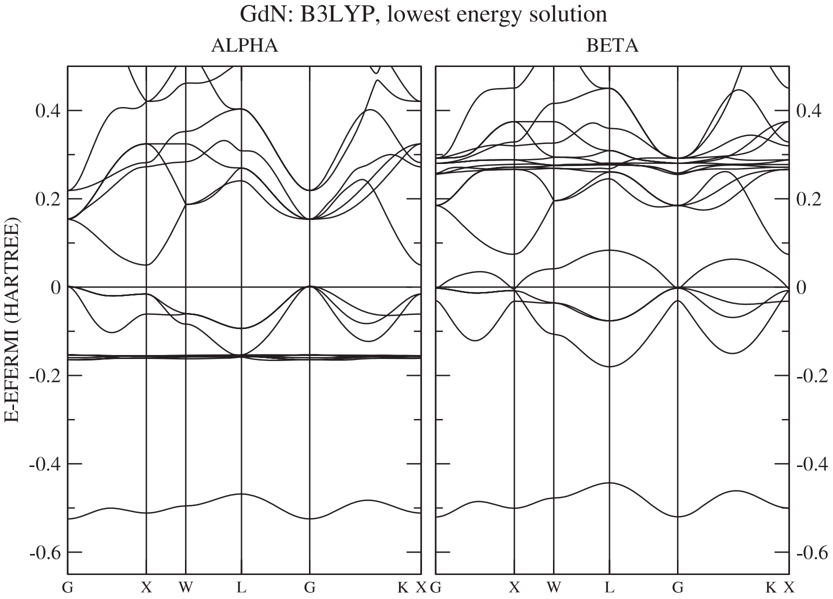

Figure 5. B3LYP band structure of GdN at the computed equilibrium lattice constant of 5.10 Å, for the energetically most favorable solution. The Fermi energy is positioned at 0.

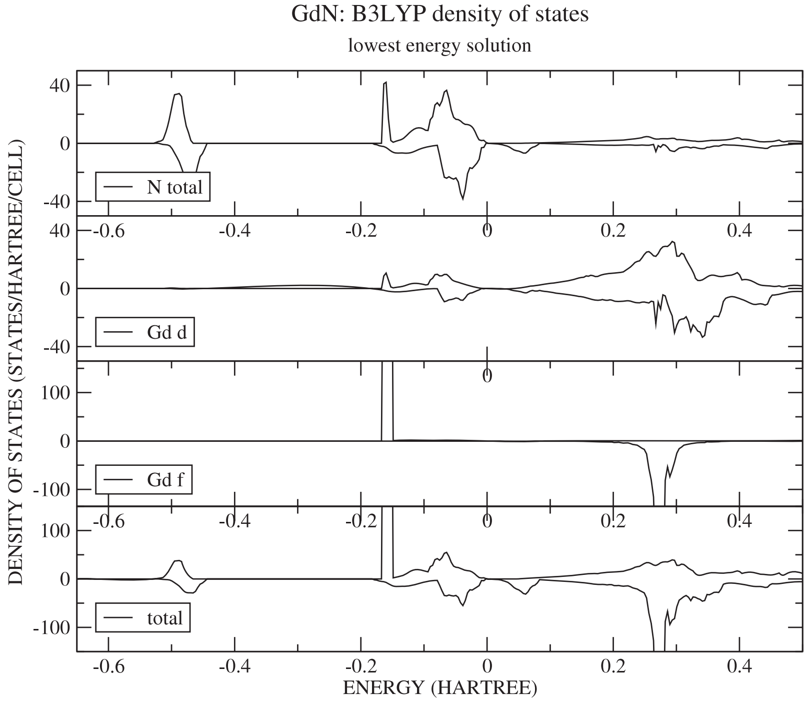

Figure 6. B3LYP density of states at the computed equilibrium lattice constant of 5.10 Å, for the energetically most favorable solution. Besides the total density of states, the projected density of states is shown for projections on N, Gd d, Gd f states. The Fermi energy is positioned at 0.

The second state is 0.004 E_h (0.1 eV) higher in energy, with a minimum at 5.11 Å, and a bulk modulus of 133 GPa. Its band structure is displayed in figure 7, and the corresponding density of states in figure 8. The f bands are similarly to those of the first state (the one lowest in energy) positioned at ~ -5 eV below and $\sim$7 eV above the Fermi level. This state is half-metallic, in the same way as the LDA solution: the majority bands do not have a gap, whereas the minority bands have a gap.

The N population is also $-0.8|e|$. The Gd spin population is 7.4 (7.0 due to the f electrons, 0.1 due to the d electron and 0.3 due to the Gd s basis functions). The N spin is -0.4 and thus antiparallel to the total Gd spin, as in the LDA.

The fact that there are two solutions close is energy is apparently due to the large overlap of the f bands with the mainly nitrogen bands, especially at the L point where the nitrogen band minimum coincides with the Gd f bands. This overlap also explains why the spin populations are a bit

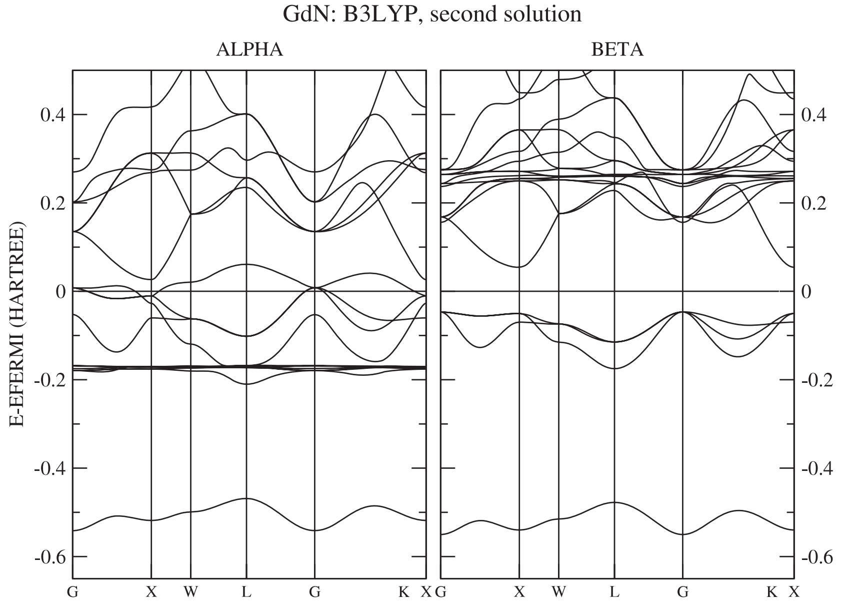

Figure 7. B3LYP band structure of GdN at the computed equilibrium lattice constant of 5.10 Å. This solution is slightly higher (0.1 eV) in energy than the solution in figure 5. The Fermi energy is positioned at 0.

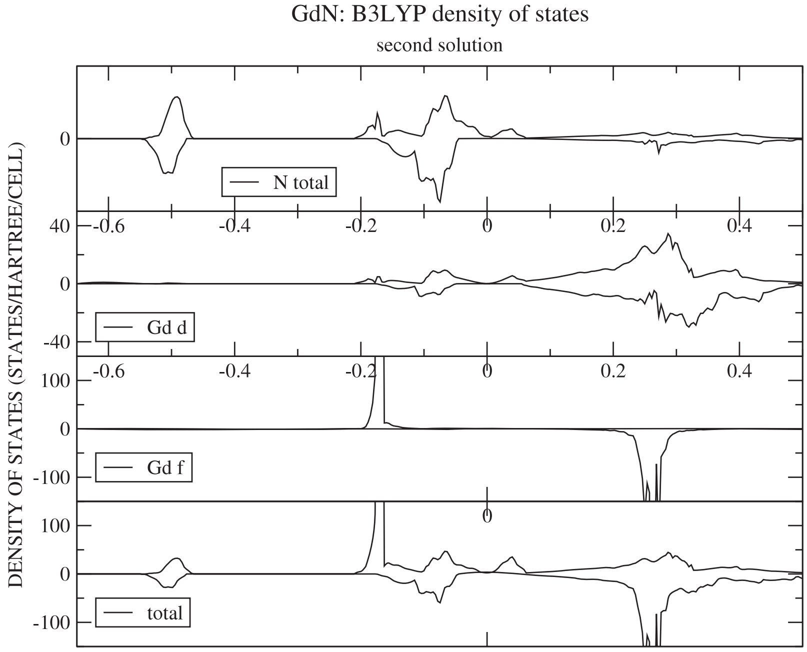

Figure 8. B3LYP density of states at the computed equilibrium lattice constant of 5.10 Å. This solution is slightly (0.1 eV) higher in energy than the lowest one in figure 6. Besides the total density of states, the projected density of states is shown for projections on N, Gd d, Gd f states. The Fermi energy is positioned at 0.

different from the LDA and HF values. Having the nitrogen spin parallel or antiparallel does apparently not make a huge energy difference at the B3LYP level, and these states are close in energy.

Even a third solution is found, with its band structure displayed in figure 9. This solution is however 0.089 E_h (~2.4 eV) higher in energy than the lowest solution (the equilibrium lattice constant would be slightly shorter, 5.05 Å, which does however not have a huge impact, and the properties of this state at 5.10 Å are similar). The computed bulk modulus of this solution is 159 GPa. Still, it is interesting to study this solution: the f bands are now separated from the nitrogen bands, and this solution is insulating, with a gap of ~0.7 eV. The charge transfer to nitrogen is ~−0.9, and the spin is now more similar to the LDA and HF solutions: 7.1 for Gd in total (7.0 due to the f electrons, 0.1 due to the d electrons),

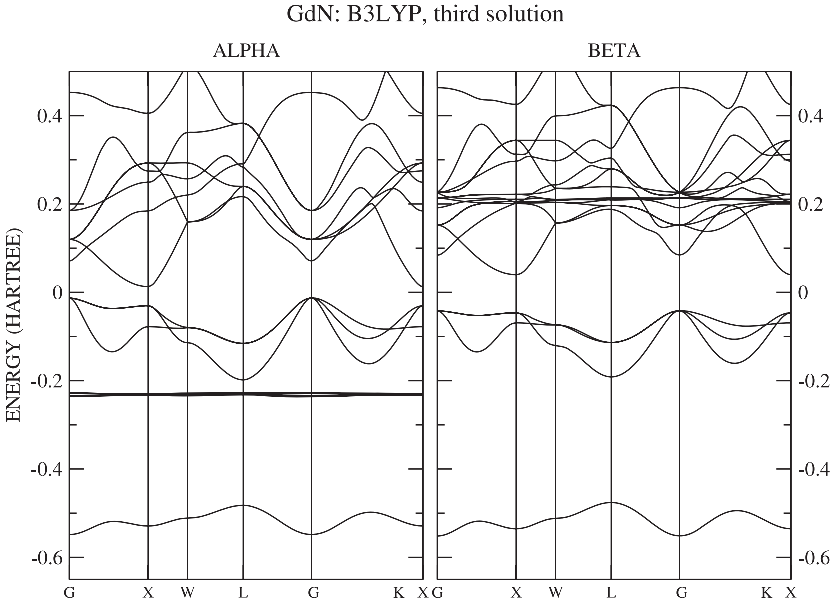

Figure 9. B3LYP band structure of GdN at the lattice constant of 5.10 Å, for the insulating solution. This solution is the highest found at the B3LYP level, about 2.4 eV higher than the energy of the lowest solution in figure 5. The middle of the gap is positioned at 0.

and −0.1 for N due to the p electrons. This confirms that the somewhat unusual population for the two lowest states on the B3LYP level are due to the hybridization at the L point. This third solution has also the property of ‘interpolating’ between LDA and HF (lattice constant, shape of the band structure), what is often observed for the B3LYP hybrid functional: due to the admixture of Fock exchange, the results for B3LYP calculations are usually expected to be in the range in between LDA and HF.

5. Conclusion

It was demonstrated that Gaussian type orbitals are technically capable for performing calculations on GdN bulk with f electrons explicitly treated. The LDA results are in very good agreement with previous calculations and give a half-metallic solution, with the majority bands being conducting and the minority bands insulating. The Hartree–Fock solution is insulating with a large gap of ∼5 eV, which is a typical overestimation of the gap at the Hartree–Fock level due to the lack of screening. On the B3LYP level, three solutions were found. The lowest one has a gap for majority spin; and for minority spin, the valence and conduction bands only touch at certain points of the Brillouin zone. The corresponding density of states is thus very small around the Fermi energy. The second solution is very close in energy (∼0.1 eV higher), and the majority bands cross the Fermi energy. A third solution was found to be insulating, but this third solution is about 2.4 eV higher in energy than the lowest solution. The fact that there are two nearly degenerate solutions makes the comparison with the experiment very difficult, and it is difficult to judge the performance of the hybrid functional B3LYP in this case. It is however also very interesting that two different solutions with very different Fermi surfaces are obtained in the calculations. As the experimental situation is not fully clear, experiments such as photoemission on this system might be very interesting to further elucidate the electronic structure of GdN (indeed, spin and angle resolved inverse photoemission spectroscopy was also suggested in another recent theoretical work [36]).

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