Magnetic anisotropy in Gd, GdN, and $GdFe_2$ tuned by the energy of gadolinium 4*f* states

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(Received 7 August 2008; revised manuscript received 10 December 2008; published 5 February 2009)

The tiny magnetocrystalline anisotropy energies (MAEs) of bulk Gd, GdN, and $GdFe_2$ have been calculated by means of the force theorem in conjunction with the full-potential linear augmented plane-wave (FLAPW) method. The generalized gradient correction including the Hubbard interaction U (GGA+U) produced the best possible agreement with the experimental MAE strength compared to either the generalized gradient approximation (GGA), where the 4*f* electrons are treated as valence states, or the GGA core, where they are treated as core electrons. Indeed, the magnetic anisotropy is three times that of the GGA+U if the 4*f* orbitals are *prevented* to hybridize correctly with the other orbitals like in the GGA-core calculation and 1 order of magnitude if they hybridize too much, like in the GGA calculation. The GGA+U results can be explained in terms of orbital moment anisotropy using Bruno's model showing that the MAE is due to the orbital magnetic-moment anisotropy. In addition, because the 4*f* states of Gd are half filled their orbital moment and spin-orbit coupling are zero; the Gd MAE is tuned by the spin-orbit coupling of 5*d* states rather than by that of the 4*f* states like in other rare-earth systems, such as Tb or Dy. Nevertheless, the strength of MAE is found to depend on the energy position of the 4*f* states. The MAE of Gd is therefore much similar to that of a transition metal rather than that of a typical rare-earth metal such as Tb or Dy. It is not surprising that Gd shows a calculated easy axis along the (0001) direction like hcp cobalt. All converged calculations within the GGA, the GGA core, or the GGA+U methods show that the magnetization is along the c axis, in disagreement with an experiment and a recent calculation which show that the easy axis makes an angle of 20° with the hcp c direction. Based on the present calculations, the disagreement with experiment might be due to possible presence of symmetry-breaking imperfections, such as defect states or impurities, and cannot be explained using bulk MAE calculations. As for the MAE of GdN and $GdFe_2$ compounds, crystallizing in, respectively, cubic rocksalt and Laves phase structures, despite the qualitative agreement with Bruno's model, their interpretation is much more complex. Indeed, their predicted magnetization easy axis is along one of the symmetry equivalent (100), (010), and (001) directions rather than the (111) direction of fcc nickel, and their MAEs are much smaller than that of Gd. The removal of N from the GdN structure without changing the lattice parameter re-established the easy axis along the (111) direction as expected, showing that the easy axis of GdN is a consequence of Gd 5*d* and N 2*p* hybridizations.

DOI: 10.1103/PhysRevB.79.054406 PACS number(s): 75.30.Gw, 71.15.Mb, 71.15.Nc

I. INTRODUCTION

The magnetocrystalline anisotropy energy (MAE) is the energy required to rotate the magnetization from its ground-state direction called the easy direction to the hardest direction. This rotation influences the magnetic properties of films, low-dimensional magnetic nanostructures, or atomic chains. Its application field is growing fast, e.g., permanent magnetic materials anisotropy,[1–4] perpendicular magnetic anisotropy of ultrathin films and surfaces,[5–8] or parallel interfacial magnetic anisotropy of ferromagnetic (FM) and antiferromagnetic (AFN) bilayers[9–11] known to be at the origin of the exchange-bias phenomena are promising for high-density magneto-optical storage media or for spin valve devices and low-dimensional nanostructures.[12] Atomic chain or nanowire[13] magnetic anisotropy is a challenging candidate for high-density magnetic storage materials because of the peculiar physical properties of the nanoscale materials. The growing interest of the scientific community working on magnetic anisotropy is therefore not surprising.

The intrinsic coupling between the magnetization and the crystal lattice in ferromagnets is ensured by the strength of the spin-orbit coupling (SOC). For example, for the 3*d* ferromagnets the crystal lattice variation under pressure, doping, alloying, or compositional disorder gives rise to a significant change in the magnetic properties, such as the evolution of the MAE with respect to the pressure in bulk or thin-film cobalt,[7,14] which is known as the magnetostrictive effect and was investigated by means of element-specific x-ray magnetic circular dichroism (XMCD) spectroscopy. In particular, the cubic magnetic anisotropy of (Ga,Mn)As ferromagnetic semiconductor is observed to survive under doping,[15] while it changes due to the substrate- or layer-induced strain.[8,16] It has also been found that the compositional modulations of $Co_{0.5}Pt_{0.5}$ alloy have a significantly enhanced MAE compared to that of the intrinsic $L1_0$ structure (three times larger than that of the $L1_0$ structure) based on calculations within the spin-polarized relativistic Korringa-Kohn-Rostoker coherent-potential approximation (SPR-KKR-CPA).[1] The same approach applied, some years later, to bcc-iron (Fe)-based materials showed that the MAE of bcc-Fe bulk or bcc-$Fe_{1-c}V_c$ disordered bulk alloys is altered by volume or concentration variation.[2]

In the previously mentioned studies of 3*d*-based magnetic materials, the MAE ranges from a few tenths of μeV for bulk material, e.g., Co bulk,[14] to some meV for surfaces or alloys, e.g., $Co_{0.5}Pt_{0.5}$ thin film[17] or Fe on W(110).[8] Accord-

ing to the models of Bruno[5] and van der Laan,[18] this tiny MAE stems mainly from orbital moment anisotropy due to the small spin-orbit interaction in 3*d* magnetic materials. However, despite the very small SOC strength, the corresponding MAE is the result of a complex interplay of the crystal and the magnetic degrees of freedom. In this respect, the magnetostriction phenomena are still far from being fully understood. To put it in other words, the understanding of the complexity of magnetic-anisotropy phenomenon is a challenging task not only from the point of view of practical interests but also from that of fundamental physics.

Despite the applications of MAE for many industrial needs, it is surprising to notice that while it is intensively investigated for 3*d*-based magnetic materials, only little attention is paid to that of rare-earth materials, such as the gadolinium metal.[19–21] In this respect, our paper is mainly devoted to the investigation of the magnetic anisotropy of hcp Gd metal which is known to be the strongest magnetic material of the rare-earth elements, whereas those of terbium and dysprosium are only invoked for comparison. To get insight into the MAE of Gd compounds, the behavior of the Gd MAE in the presence of other elements GdN and $GdFe_2$ MAE is also calculated and discussed.

To the best of our knowledge, apart from the early MAE Gd investigations of Franse and Gersdorf[20] and that of the recent calculations of Colarieti-Tosti *et al.*,[21] the magnetic anisotropy of 4*f* rare-earth metals is lacking. Therefore studying the MAE of such materials or their compounds is enriching. Our MAE calculations for Gd are motivated by its interesting magnetic properties. Indeed, despite its 295 K Curie temperature, this metal is found to preserve a considerable spin magnetic moment up to an ultrahigh hydrostatic pressure of about ~110 GPa.[22,23] This magnetic moment, of about $7\mu_B$, is much higher than that of a 3*d* transition metal because it stems mostly from the half-filled 4*f* shell.

In the present work, we made use of the force theorem[24] to study the magnetic anisotropy of Gd, GdN, and $GdFe_2$ by means of the first-principles full-potential linear augmented plane-wave (FLAPW) method. We have first shown that, like for the electronic and structural properties of Gd (Ref. 25) and GdN,[26] the results of MAE obtained within the GGA $+U$ method are in better agreement with experiment than those obtained within the generalized gradient approximation (GGA) or GGA-core methods. This shows that the MAE strength is related to the energy position of the 4*f* states with respect to the Fermi level.

This paper is organized as follows. In Sec. II we provide some details of the computational method and discuss the parameters used in the calculations, such as the values of Hubbard U and exchange J used for calculations of the MAE. Section III is devoted to the MAE of Gd, i.e.; we show the adequacy and the accuracy of the GGA$+U$ method for the calculation of the MAE by means of the force theorem, as well as Bruno's model applied to the MAE of rare-earth compounds. In Sec. IV the magnetic anisotropies of both GdN and $GdFe_2$ compounds are studied and the manner in which the 4*f* magnetization might affect the MAE of Gd compounds is discussed.

II. COMPUTATIONAL DETAILS

The calculations in the present work were made using the FLAPW method[27,28] as implemented in the FLEUR code.[29] The lattice-parameter constants used for the calculations are $a=6.858$ a.u. with a c/a ratio of 1.597 for hcp bulk Gd,[30] $a=9.52$ a.u. for the cubic rocksalt GdN,[31] and $a=13.96$ a.u. for the cubic Laves structure of $GdFe_2$.[32] In order to calculate the MAE using the force theorem, the SOC is calculated in a second-variational scheme.[25] For the exchange and correlation potentials, we used the GGA of Perdew-Burke-Ernzerhof.[33] The rotationally invariant GGA $+U$ method used in this study is similar to the implementation of Shick *et al.*[34] For the U and J parameters of the Gd sites required for GGA$+U$ calculations we have used: $U=7.7$ eV, $J=0.7$ eV,[25] and $U=9.9$ eV and $J=1.2$ eV (Ref. 26) for Gd bulk and GdN, respectively. For $GdFe_2$ we have used those of bulk Gd.[35] The muffin-tin radii $\mathbf{R}_{mt}$ is set to 2.8 a.u. for Gd, 2.19 a.u. for Fe, and 1.5 a.u. for N. The plane-wave cutoff for the basis functions is set to $K_{max}=3.0$ a.u.$^{-1}$ for Gd bulk, $K_{max}=4.4$ a.u.$^{-1}$ for GdN, and $K_{max}=3.5$ a.u.$^{-1}$ for $GdFe_2$, and the charge density and potential cutoff to $G_{max}=9.0$ a.u.$^{-1}$ for bulk Gd and GdN to $G_{max}=11.4$ a.u.$^{-1}$ for $GdFe_2$. The wave functions as well as the charge density and the potential inside the muffin-tin spheres were expanded on angular momentum up to $l_{max}=8$ for Gd bulk and GdN and up to $l_{max}=10$ for $GdFe_2$. For the Brillouin-zone (BZ) integration, we have used the standard Gaussian broadening method[36] (GBM) for the force-theorem-calculated MAE. The convergence of the MAE is obtained using about 16 000, 7000, and 10 000 **k** points in the full BZ for the case of Gd, GdN, and $GdFe_2$, respectively.

III. FORCE THEOREM DETERMINATION OF THE MAE FOR Gd METAL

The calculations carried out within the GGA$+U$ method[25,26] have provided a good description of the electronic properties of the 4*f* Gd and GdN materials. These results have motivated our present force-theorem calculations of the MAE. At the first stage, we show that the GGA$+U$ approach is much better than the GGA or GGA core for the description of MAE and that the force-theorem GGA$+U$ calculations are the closest to the observed MAE. Then we use the same method to predict the rotation that the magnetization might undergo in the case of GdN and $GdFe_2$ compounds.

A. GGA$+U$ adequacy for magnetic-anisotropy calculations

In the last two decades, the force theorem[24] has been an important and efficient tool for computing the MAE.[37–39] As proposed by Van Vleck,[40] the magnetocrystalline anisotropy originates mainly from the SOC. Its variation might lead to interesting tuning of the orbital magnetic moments and MAE of complex materials and may lead to the violation of Hund's third rule.[41] Indeed, the force-theorem-based calculations save an appreciable computational effort and CPU time because the simulation of the magnetization direction changes due to the SOC requires only one single iteration of the

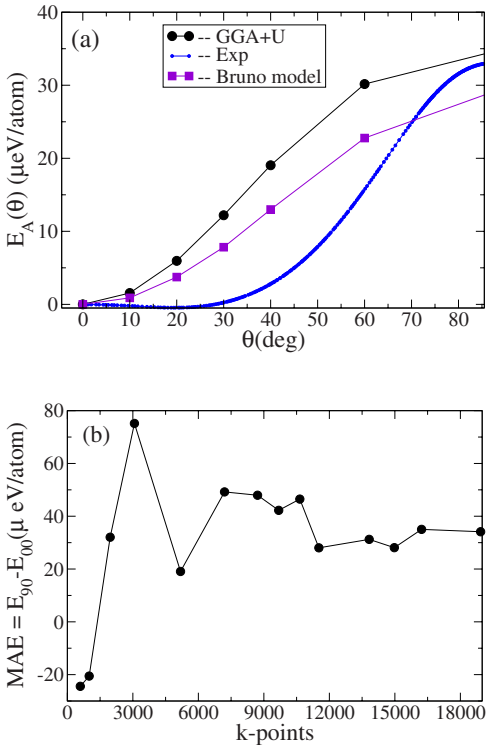

FIG. 1. (Color online) (a) The GGA+U calculated MAE of Gd as a function of the angle θ from the c axis (black circles) and for ϕ=0 and Bruno's model MAE [Eq. (1)] (violet squares) compared to the experimental one (thick blue curve) (Ref. 20). (b) Calculated MAE as a function of the number of **k** points in the whole Brillouin zone. The continuous curves are guides for the eyes. The dependence on the spherical angle ϕ, for a fixed θ value, is found to be very small and is not represented.

Kohn-Sham equations. The basic idea of the force theorem is to introduce the spin-orbit interaction as a perturbation to the scalar relativistic Hamiltonian. It is shown that the rotation of the spins is such a tiny perturbation that the electron-electron interaction hardly changes. We expect therefore that most of the contributions to the total energy remain unchanged. Using the frozen potential approximation, the total-energy difference between two spin configurations can be approximated by the difference between the sums of the eigenvalues up to the Fermi energy,[24] with both sums calculated with the SOC switched on. Since the SOC is only *switched* on during the last step, a considerable saving of computational effort is guaranteed. Indeed, we first make a self-consistent calculation with a scalar relativistic potential without spin-orbit interaction, and then we calculate the eigenvalues including the spin-orbit interaction for a given spin axis without allowing the self-consistent potential to change. Notice that one has to make sure that the scalar relativistic calculations are converged with the same number of **k** points as these used to determine the MAE [see Fig. 1(b)].

B. Gd (0001) magnetization easy axis

In this section, we discuss the Gd MAE within the GGA+U method. Figure 1(a) shows the MAE calculations

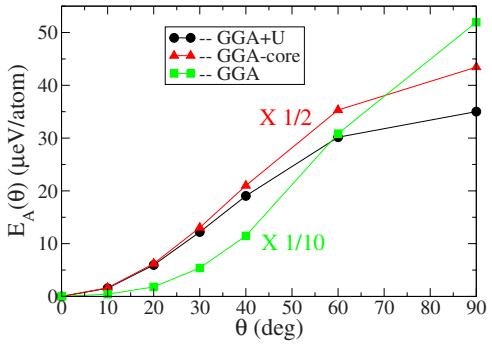

FIG. 2. (Color online) Calculated Gd MAE for the different treatments of the 4f states. The calculation within the GGA+U method is shown in black circles and is the same as that of Fig. 1. The GGA core, where the 4f states are treated as core electrons, is shown in red triangles, while the standard GGA, where the 4f electrons are allowed to relax as valence bands, is shown in green squares. Notice that the GGA and GGA-core curves are scaled, respectively, by a factor of 1/10 and 1/2 to fit into the graph. The continuous curves are guides for the eyes.

for different angles θ, i.e., the difference of the eigenvalue sums as a function of the angle θ between the c axis and the magnetization axis. The reference energy is at θ=0°. The GGA+U MAE calculations are in black circles, and those calculated according to Bruno's model are in violet squares [Eq. (1)]. As it can be easily seen from this figure, the minimum of the difference of the eigenvalue sums is obtained for 0° and the maximum for 90°. These results show clearly that the easy axis of magnetization is lying at θ=0° and the hard one at θ=90°. These calculations were carried out using a sampling of around 16 000 **k** points in the whole Brillouin zone. In order to justify the convergence of this Gaussian broadening sampling,[36] we have performed MAE calculations up to 18 000 **k** points in the BZ. Figure 1(b) represents the MAE convergence according to the set of **k** points. This MAE is defined as the difference energy between the hard and easy axes of magnetization. The overall shape of the MAE presented in Fig. 1(b) shows that this latter is sensitive to the **k**-point numbers up to the set of 16 224 **k** points. The largest number considered is 18 928 **k** points, and it yields a MAE that deviates by less than 2% from the MAE using 16 224 **k** points. We have checked the force-theorem MAE by directly calculating the total energy including the spin-orbit coupling in a self-consistent manner. The results of the calculations showed that the MAE is about 32.14 μeV using 16 224 **k** points, in good agreement with the converged force-theorem calculation [see Fig. 1(b)]. We note here that although the force theorem allows a considerable saving of computational effort, it still requires a considerable computational time because of the fine grid of **k** points one should use to assess the converged tiny MAE.

Figure 2 summarizes the MAE calculations for the different ways in which the 4f electrons are treated. In order to compare the GGA+U [Fig. 1(a)] MAE to the other methods this latter is represented with the GGA and the GGA core. It is worth mentioning here the controversial debate concerning whether the Gd 4f states should be considered as localized core states or whether it should be allowed to hybridize as

band states (Ref. 25 and references therein). As it can be easily seen from Fig. 2, the Gd MAE calculated within the GGA+U scheme is in much better agreement with experiment [Fig. 1(a)]. The value of 520 μeV of our MAE, calculated using the standard GGA potential, is in good agreement with the full-potential linear muffin-tin orbital (FP-LMTO) calculation of 571 μeV by Colarieti-Tosti *et al.*[21] However, within our FLAPW framework, the core treatment of the 4f electrons leads to a MAE of 87 μeV, while within the FP-LMTO one[21] it is of about only 24 μeV in disagreement with our calculation. In order to understand the SOC magnetic anisotropy in more detail, we have applied Bruno's model[5] to calculate the Gd MAE. According to this model the MAE stems completely from the spin-orbit contribution and the anisotropy of orbital magnetic moments and is given by

$$E_A(\theta) = \Delta E(\theta) = -\frac{\xi}{4\mu_B}([\mu^{\uparrow}_{\mathrm{orb}}(\theta) - \mu^{\downarrow}_{\mathrm{orb}}(\theta)] - [\mu^{\uparrow}_{\mathrm{orb}}(0^\circ) - \mu^{\downarrow}_{\mathrm{orb}}(0^\circ)]), \quad (1)$$

where ξ is the spin-orbit parameter for 5d Gd orbitals and $\mu^{\sigma}_{\mathrm{orb}}$ is the orbital moment of the spin σ. We have presented in Fig. 1(a) (violet curve with squares) the corresponding calculations. The spin-orbit coupling parameter used in Bruno's model is that of the 5d orbitals and is found to be $\xi=\xi_d=71.2$ meV. As it can be seen from this figure, the overall behavior of the estimated MAE of the model is in good agreement with the GGA+U results. Bruno's model predicts a MAE maximum of 30 μeV and is a bit smaller than the experimental value. Gd is such a complex metal, and we have seen that the energy position of the 4f states is crucial for the strength of the MAE. The agreement of the full calculation with Bruno's model implies that the MAE is essentially due to the orbital anisotropy. Notice that the finding of the magnetization direction off the c axis by Colarieti-Tosti *et al.*[21] is questionable since their later calculation[42] has shown that both a full calculation (scalar self-consistent and force theorem) within either the GBM or the modified tetrahedron method (MTM) produce a magnetization easy axis along the c axis. Only when the GBM is used for the self-consistent calculation and the MTM for the force theorem do they find the magnetization direction off the c axis but dependent on the number of **k** points used up to 10^6. The MAE obtained by such an *ad hoc* manner is 40% smaller than that produced by the full calculation with the MTM. We therefore believe that the deviation of the magnetization easy axis of Gd metal from the c axis remains an open question for feature experimental and theoretical investigations.

Bruno's model validity for describing the spin-orbit magnetic anisotropy of Gd should reflect the fact that the magnetic anisotropy of Gd is too similar to that of a typical 3d transition metal such as hcp Co. However, there are additional terms which are related to the magnetic-dipole operator due to the anisotropy of the field of the spin. This additional contribution was derived by van der Laan.[18] The strong magnetic moment of the 4f electrons might give rise to this latter contribution. The resulting exchange field of that 4f spin is large enough to be sufficient to polarize significantly the remaining conduction electrons. In others words, the 4f magnetic field makes, in particular, the Gd 5d magnetic moment parallel to that of the 4f. Despite this high magnetic field, the contribution of van der Laan[18] for Gd is found to be negligible compared to that expected from Bruno's model. In fact, this contribution is only considerable for non-half-filled systems where spin flips among the 4f electrons occur.

However, even though the GGA+U calculations using the force theorem have reproduced the experimental magnitude of MAE of 34 μeV, it did not show that the easy axis of the magnetization makes 20° away from the c axis as experimentally observed, instead it shows that it is along the c direction. Our calculations which are in agreement with Bruno's model and in disagreement with the FP-LMTO calculation using 4f states as core states[21] suggest therefore that the deviation of the magnetization from the c axis could not be explained using bulk MAE calculations. We suggest that the experimental easy axis might be explained if we invoke symmetry-breaking lattice imperfections of the hcp structure of Gd, such as presence of intrinsic defects or impurities. We suspect the erroneous GGA energy positions of the 4f minority states[25] to be at the origin of the corresponding predicted large MAE. The presence of these states near the Fermi level leads to the erroneous MAE. The integration of the one-electron energies includes an *extra* contribution coming from a strong mixing of the 4f states with the others states at the Fermi level. Using the GGA+U method these 4f states are moved away from the Fermi level (U effect, for more details see Ref. 26) resulting in a more realistic assessment of the MAE. The MAE is therefore sensitive to the electronic structure around the Fermi level, and a better representation of the electronic structure leads to a precise evaluation of the MAE. Compared to the GGA and GGA core, the GGA+U method is once more the best method for the MAE calculations. Because the magnetic-anisotropy results from a tiny change in the total energy when the spin moment is changed from the hard axis to the easy one, the total density of states (DOS) hardly changes in the two spin configurations. Indeed, we tried to display the total DOS for the two spin configuration to show the MAE as a function of energy; however, we find them to be indistinguishable. We tried also representing the differences of the total DOS but since the Fermi levels for different magnetization directions are slightly different, any interpolation of the DOS in a single energy grid failed to produce the correct magnetic anisotropy. Given the adequacy of the GGA+U, we have proceeded in the same way to calculate the MAEs of two potential candidates for spintronics: GdN and $GdFe_2$.

IV. GdN AND $GdFe_2$ MAGNETIC ANISOTROPY

In order to get insight into the magnetic anisotropy of Gd compounds, we have applied the force theorem to calculate the MAE of the GdN pnictide and the metallic compound $GdFe_2$ in its Laves phase. Using the GGA+U method, we have recently shown that the GdN compound is a half metal for the experimental lattice constant.[26] A better understanding of the magnetic anisotropy of this compound would be useful for future spin-injection applications.

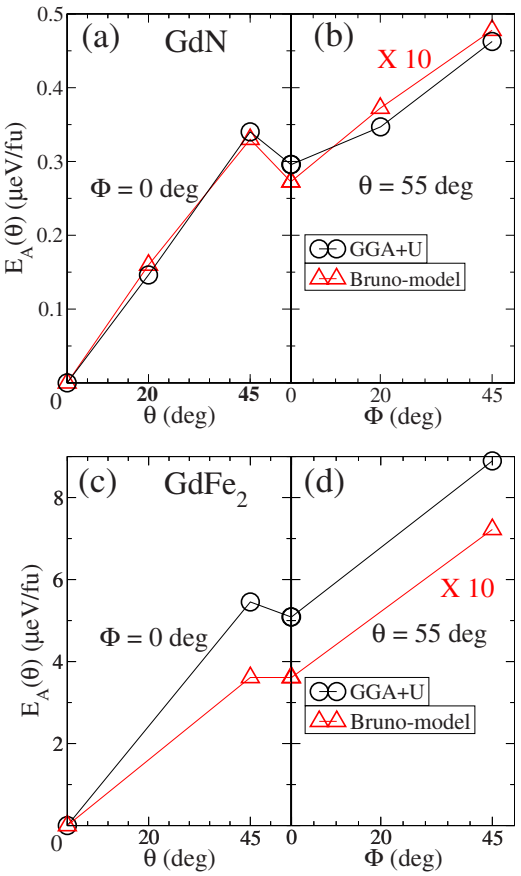

FIG. 3. (Color online) Calculated MAE of GdN and $GdFe_2$ per formula unit (f.u.): the circles represent the GGA+U calculations and triangles the corresponding Bruno's model estimations. Panels (a) and (b) summarize the GdN MAE. These MAEs are calculated as a function of the angles θ, ϕ for: varying θ while keeping $\phi=0°$ in panel (a) and varying ϕ while keeping $\theta=55°$ in panel (b). The $GdFe_2$ MAE is shown in panels (c) and (d) similarly. The Bruno-model curves are scaled by a factor of 10 to fit into the graph. The continuous curves are guides for the eyes.

In this section the MAE, $E_A(\theta)$, is defined as in Sec. III: $E_A(\theta)=E_{\theta,\phi}-E_{0°,0°}$. Unlike Gd, the GdN compound crystallizes in the cubic rocksalt structure and its magnetic anisotropy will depend not only on θ but also on ϕ. In order to determine the easy and the hard axes of magnetization, we have calculated the MAE as a function of spherical coordinate angle θ or ϕ by keeping one of them fixed and varying the other one.

Figure 3 shows the MAEs of GdN and $GdFe_2$ as a function of the spherical coordinates angle θ or ϕ. The curve with circles in Fig. 3(a) represents the GdN MAE versus θ for $\phi=0°$, and the curve with circles [Fig. 3(b)] represents the GdN MAE versus ϕ for $\theta=55°$. According to the curve with circles, the easy axis of magnetization is along the direction (001) defined by ($\theta=0°$, $\phi=0°$), and the hard axis of magnetization is along the direction (111) defined by ($\theta=55°$, $\phi=45°$).

Figures 3(a) and 3(b) contain also Bruno's model estimations of the GdN MAE. Though the magnitude of the magnetic anisotropy is one order smaller than that of the GGA+U (curves with circles), Bruno's model predicts the same directions of easy and hard magnetization axes. This discrepancy can be ascribed to the strong hybridization of the 2p N orbitals with the 5d Gd orbitals in GdN. One should however keep in mind that Bruno's model[5] was derived for 3d magnetic-anisotropy energy, and its application should be, in principle, restricted to *pure d* magnetic anisotropy. Its use in other complicated MAE such as that of rare-earth materials will lead only to qualitative results.

The $GdFe_2$ MAE [see Figs. 3(c) and 3(d)] is found to exhibit a similar behavior to that of GdN MAE with the same axis of easy and hard magnetizations, but with a higher MAE. The GdN MAE is only of 0.45 μeV while that of the $GdFe_2$ is of about 9 μeV. It is worth mentioning here that although Gd monocrystal MAE is similar to that of a 3d transition metal, the MAEs of its GdN and $GdFe_2$ compounds seem to be different from that of a cubic transition metal, such as Ni. It is well known that in a fcc transition metal such as Ni, the (111) direction is that of the easy axis of magnetization and the hard axis is found to lie along one of the symmetry equivalent (001), (010), and (100) directions. Our results suggest the opposite for GdN and $GdFe_2$ compounds. This peculiar behavior of the magnetic anisotropy of the Gd compounds show that, even in the presence of another nonmagnetic (N) or magnetic (Fe) atoms, it is the Gd strong magnetism which manages indirectly the magnetic anisotropy in these compounds. Indeed, because of the zero-spin-orbit coupling of the 4f half-filled shell, the 4f magnetic moment should not be involved directly in the MAE but only through hybridization and polarization of the other valence orbitals. One notices that the 4f strong spin magnetic moment is to some extent *decoupled* from the crystal structure. However, due to the strongly localized character of these orbitals, the 4f states carry a strong magnetic moment that polarizes strongly the remaining valence orbitals. Therefore, despite their strong localized character and zero orbital moment, their energy positions in the band structure are directly related to the strength of MAE.

As it was discussed in Sec. III, there is a big difference between the GGA+U MAE and the GGA or the GGA-core MAEs; i.e., one is left with a wrong magnetic anisotropy of three times that of the GGA+U if the 4f orbitals are *prevented* to hybridize correctly with the other orbitals, and 1 order of magnitude if they hybridize too much, like in the GGA calculation. In the case of the GdN compound not only the 5d Gd orbital would be affected by the 4f exchange magnetic field but also the 2p N orbitals. This happens because of the hybridization effect of the 5d-Gd orbitals with 2p-N orbitals.[26] For the $GdFe_2$ compound the same scenario happens to the 3d Fe orbitals. This interesting property would make Gd a good candidate for high performance ferromagnets. Indeed, if we could make materials with different 4f energy positions in order to change the hybridization to induce large spin polarization in other orbitals, it will be possible to tune their MAE.

In order to simulate the effect of the crystal symmetry and the presence of nitrogen on the magnetic anisotropy of Gd we have carried out a GGA+U calculation for the MAE of the Gd fcc crystal. The calculations are performed using the same lattice parameter of GdN and the same GGA+U parameters (U and J) used for Gd. Figures 4(a) and 4(b) rep-

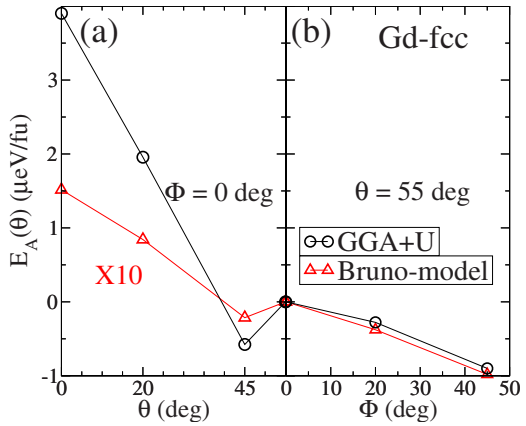

FIG. 4. (Color online) (a) GGA+U calculated MAE of Gd using the GdN experimental lattice parameter of the fcc structure. The circles represent the GGA+U calculations and the triangles represent the corresponding estimations from Bruno's model (Ref. 5). Panel (a): the MAE versus θ; panel (b): the MAE versus ϕ. In both cases the energy is calculated per formula unit (f.u.). The Bruno-model curves are scaled by a factor of 10 to fit into the graph. The continuous curves are guides for the eyes.

resent the GGA+U MAE together with that of Bruno's model. From this figure one can easily recognize a magnetic anisotropy with the same characteristics of a typical 3d material such as Ni. Both Figs. 4(a) and 4(b) show that the easy axis of magnetization for an fcc Gd crystal is along the (111) direction much similar to that of a transition metal. This calculation shows also that the easy magnetization axis of GdN is due to the Gd 5d and N 2p hybridization; i.e., the magnetization vector rotates from the (111) direction to the (100) direction due to this hybridization. Therefore, the GdN MAE can be tuned by varying the nitrogen content and would be a good candidate for industrial applications with the advantage of a strong spin magnetic moment. We have also checked that a calculation done using an hcp structure with the same volume per atom as the fcc structure but with an ideal $c/a=\sqrt{8/3}$ produced a high MAE of 32 μRy compared to the 5 μRy of the fcc structure. We conclude therefore that the high MAE of hcp Gd is due to its hcp structure [an $ABAB$ atomic plane packing along the (111) direction instead of an $ABCABC$ packing like in the fcc structure].

V. CONCLUSION

In conclusion, we have carried out first-principles calculations of the MAE within the GGA, GGA core, and GGA +U methods for the purpose of representing accurately the 4f electrons of Gd. It is shown that the MAE is sensitive to the electronic structure details at the Fermi level; i.e., the failure of the GGA method to account for the correct 4f energy position results in an overestimation of the Gd MAE. On the contrary, the GGA+U, which produced the best position of the 4f states of Gd, reproduced the best MAE of Gd. Indeed, the force-theorem MAE results of the GGA+U produced the best agreement with the experimental MAE magnitude. The results of GGA+U are also in good agreement with Bruno's model, where the MAE is obtained from the anisotropy of the orbital magnetic moments. Our calculation did not, however, find any deviation of the easy axis from the crystal c direction as shown in the experiment and in the calculation of Colarieti-Tosti *et al.*[21] Based on our GGA+U calculations, Bruno's model, and symmetry of the hcp lattice, we did not find any good argument for the deviation of the easy axis from the hcp crystal c direction. We can only speculate that this deviation might be the result of symmetry-breaking imperfections in the hcp structure.

Notice that the calculations of Colarieti-Tosti *et al.*[21] are questionable since in a paper[42] following their Letter,[21] they showed that the use of the MTM for both the scalar self-consistent calculation and the force theorem produce a magnetization easy axis along the c direction. The only way to produce an easy axis with an angle of 20° off the c axis is when the scalar self-consistent calculation is done using the GBM and the force theorem using the MTM. This is really *ad hoc* and not justified. In addition, as it is shown in their Fig. 2, the results of the latter approach are very dependent on the number of k points used in the calculation for up to 10^6 **k** points and produced a MAE 40% smaller than the one calculated using the MTM method. Indeed their Fig. 2 shows an oscillation of the difference of energy used for the off setting the easy axis from the c axis. One can only conclude from their study that an accurate calculation done either with the MTM or the GBM will find the easy axis along the c direction in agreement with our conclusion. We therefore believe that the deviation of the magnetization easy axis of Gd metal from the c axis remains an open question for future experimental and theoretical investigations.

The comparison of the GGA-core MAE and the GGA +U MAE with experiment has indirectly demonstrated that the 4f hybridization with the rest of the valence orbitals, resulting in an induced polarization, is the key parameter for the tuning of the MAE of Gd- or Gd-based compounds. This parameter is tuned by the energy position of the 4f states in each compound. Indeed, within the GGA+U scheme we have shown that for both GdN and $GdFe_2$ compounds, the Gd 4f states through hybridization and induced strong polarization of, respectively, the nitrogen p and Fe 3d states change drastically the MAE. Unlike 3d transition-metal fcc structures such as Ni, GdN, and $GdFe_2$ magnetizations are found to lie along one of the symmetry equivalent (100), (010), or (001) directions. It will be of great interest to perform experimental measurements of MAE for GdN or $GdFe_2$ to check our theoretical predictions.

ACKNOWLEDGMENTS

The calculations were performed using the CINES IBM SP4 supercomputer under Computer Grant No. gem1100. This work was supported by ANR under Grant No. ANR-06-NANO-053-01.

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