Exchange splitting of surface and bulk electronic states in excited magnetic states of Gd: First-principles study

L. M. Sandratskii
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany
(Received 11 June 2014; revised manuscript received 27 October 2014; published 5 November 2014)

Recent pump-probe experiments provide time evolution of the bulk and surface electronic states in Gd excited by the laser pulse. These experiments are in close connection with earlier spectroscopic experiments probing temperature dependence of the exchange splitting of the electronic states. We report first-principles study of the electronic states in excited Gd modeled by the noncollinearity of the $4f$ spin moments. In agreement with experiments we obtain a strong difference in the properties of the bulk and surface electronic states. To reveal the origin of this behavior we apply the concept of spin mixing to characterize the electronic states of the excited system. The surface states remain weakly spin mixed with respect to the local atomic spin axis of the surface layer that explains the persistence of the exchange splitting in highly excited Gd. On the other hand, a smaller part of the surface state localized in the second layer becomes strongly spin mixed leading to decreased value of the exchange splitting. In contrast to the surface states the bulk states are strongly spin mixed and average the influence of the atomic spin-up and spin-down potentials. This leads to the properties of the bulk states that are usually associated with the Stoner model. The good agreement between calculational results and the results of the pump-probe experiment support the assumption of ultrafast disordering of the $4f$ moments after laser irradiation.

DOI: 10.1103/PhysRevB.90.184406 PACS number(s): 73.20.At, 75.70.Rf, 75.50.Cc, 78.47.db

I. INTRODUCTION

Recently much effort was devoted to the study of ultrafast processes in Gd and its compounds [1–7]. The characteristic feature of Gd is large localized $4f$ spin moment polarizing by means of intra-atomic exchange interaction the states of the valence $5d6s$ electrons. The pump-probe experiments on Gd revealed strong drop of the magnetization within 1 ps after laser irradiation [2,4]. The physical mechanism of this ultrafast decrease of the spin magnetization remains the topic of controversial discussions. By itself, the drop of the magnetization is an expected consequence of the laser irradiation since the absorbed light increases the energy of the system. After relaxation to the thermal equilibrium the system has a higher temperature and, therefore, a lower magnetization than before irradiation. The problem is to understand the hierarchy of the processes governing the dynamics of the equilibration and to identify the process (or processes) leading to the subpicosecond demagnetization. One of the key points of the debates is the physical mechanism of the ultrafast reduction of the angular momentum of the electron system. Since the angular momentum is a conserved physical quantity its apparent decrease must be the result of the transfer of the angular momentum outside the measurement domain of a given experiment. Many researchers suggest that the leading mechanism of the ultrafast demagnetization is the transfer of the angular momentum from the electron system to the lattice [2,4] though alternative mechanisms were also proposed [1,8].

Accepting the lattice as a sink for the angular momentum one confronts the question whether this transfer takes place by single-electron scattering on lattice vibrations or is a result of the interaction of atomic spins and the lattice. For example, Koopmans *et al.* [2] suggest a phenomenological model assuming the decisive role of the electron-lattice interaction, whereas Wietstruk *et al.* [4] report a 50 times increase of the spin-lattice interaction under the influence of the laser irradiation. A first-principles description of time dependent processes in a nonequilibrium electron system including the dynamics of atomic magnetic moments and interaction with lattice is presently an unsolvable problem. Therefore, it is important to combine the development of phenomenological models characterizing the process as a whole with detailed first-principles investigation of the contributing subprocesses.

The first-principles study performed in this paper deals with the electronic structure of excited magnetic states of Gd. This study was partly motivated by a recent experiment by Carley *et al.* [3] reporting time dependence of the spin-up and spin-down bulk states and spin-up surface states near point Γ of the two-dimensional (2D) Brillouin zone (BZ). In particular, Carley *et al.* found that within the first 2 ps after laser irradiation the energies of the spin-up and spin-down bulk states change differently. The spin-up state increases monotonously up to about 0.14 eV (10 mRy) above the energy in an unperturbed system, whereas the corresponding spin-down state decreases first by about 0.09 eV (7 mRy) and then increases somewhat stabilizing at the energy about 0.05 eV (4 mRy) below the value before irradiation. The surface spin-up state is observed to shift to higher energies but by a substantially smaller value of about 0.04 eV (3 mRy) than the bulk spin-up state. In addition there is an apparent time delay in the variation of the bulk spin-up state that is absent in the cases of the bulk spin-down state and surface spin-up state.

This experimental work is in deep connection with the spectroscopic studies of the temperature dependence of the electronic states in Gd [9–12]. The experimental data for the bulk states are usually described within the Stoner picture assuming that the electron states preserve the spin projection as a good quantum number while the exchange splitting decreases with increasing temperature and vanishes at the Curie temperature. (It is worth noting that experimental reports claiming non-Stoner behavior of the bulk Gd states are also present [11].) The surface states behave differently preserving nonzero exchange splitting above the Curie temperature. Since

the spectroscopic experiments are the most direct probe of the electronic structure their understanding is crucial for the development of adequate microscopic models of temperature dependent properties and pump-probe experiments.

Several theoretical studies were performed aiming to understand the temperature dependence of the electronic structure of bulk Gd. References [13,14] are based on the first-principles investigation of the electronic structure of noncollinear configurations of the $4f$ moments, whereas Nolting *et al.* [15,16] suggest a theory based on the treatment of the many body Hamiltonian of interacting electrons. Despite a substantial difference in the theoretical machinery many conclusions of the studies correlate with each other. Both types of studies agree that the Stoner picture cannot provide an adequate general description of bulk hcp Gd at nonzero temperatures although the temperature dependence of some parts of the electron spectrum resembles the behavior expected from the Stoner model. A more adequate description is given by the account for spin hybridization (spin mixing) [13,16] of the electronic states.

We mention also the work by Khmelevskyi *et al.* [17] who used a disordered local moment (DLM) approach [18] to study the bulk hcp Gd at finite temperatures and came to the conclusion of the inapplicability of the Stoner model to this system. Khmelevskyi *et al.* focused on the consideration of the integrated quantities such as atomic moments and atomic potentials that is not sufficient for the description of the photoemission experiments dealing with particular electronic states.

To our knowledge, there was no attempt to extend the theoretical studies performed for the bulk electronic states in thermally excited Gd to the case of the surface states. Also, there were no attempts of the understanding of the time dependence of the electronic structure after laser irradiation on the basis of first-principles calculations.

In the given paper we consider both bulk and surface states within a common first-principles approach. The theoretical results are related to the results of older and recent experiments. Our physical model is based on the assumption that the disordering of the $4f$ moments is the main source of the variation of the electronic states. On this basis we model the demagnetized state with noncollinear configurations of the $4f$ spins and perform detailed calculations of the electronic structure for these configurations.

There are two issues that should be discussed concerning the modeling used in the paper. First, since we aim to address the experimental data obtained within 1–2 ps after laser irradiation do we have arguments in favor of considering the $4f$ spins disordering as an ultrafast process? The second issue concerns the $5d6s$ moments of the Gd atoms. Should the $5d6s$ moments be considered as separate degrees of freedom or should they be treated as determined by the $4f$ moments? These questions will be addressed in Sec. III.

In Sec. IV we discuss the properties of the electronic states of the 3D periodic hcp Gd. Section V reports slab calculations and focuses mostly on the properties of the surface states.

II. METHOD OF THE CALCULATIONS

The calculations are performed with the augmented spherical wave (ASW) method generalized to the case of noncollinear magnetic structures [19,20]. The local spin density approximation (LSDA) to the exchange-correlation functional is used [21]. The spin-polarized $4f$ electrons are treated as core electrons and do not hybridize with valence electrons. In the ASW method the electron states are presented as linear combinations of the atomic basis functions characterized by a given spin projection on the local atomic axis as well as by orbital and magnetic quantum numbers l and m. The knowledge of the coefficients of the linear combination allows us to determine for each electron state the partial atomic characteristics such as contribution to the moment of a given atom and the angle between the $5d6s$ and $4f$ spin moments [see Eq. (6) below].

The calculations are performed for the bulk hcp Gd and the slab consisting of a number of Gd layers and several layers of empty spheres simulating the vacuum (Figs. 2 and 7 present the corresponding unit cells).

We study the influence of the noncollinearity of the $4f$ moments on the electronic structure. The smearing of the Fermi-Dirac distribution function or other types of single-electron excitations are not considered.

III. THE MODEL OF DISORDERED $4f$ MOMENTS

A. Ultrafast character of the $4f$ disordering

It is usually assumed that the direct consequence of the absorption of the laser pulse is the spin-conserving transfer of the $5d6s$ electrons from the occupied states below the Fermi energy to the empty states above the Fermi energy. It is, however, important that the spin-down hot electrons can decay in energy creating deviations of the atomic spins from the direction of the net magnetization. Such spin-flip processes are the consequence of the electron-electron Coulomb interaction [16] and therefore should be fast. Indeed, there are experiments demonstrating the fast character of the $4f$ disordering initiated by the pump laser pulse. For example, in Refs. [4,22] it is shown that the demagnetization of both f and d electron subsystems in Gd and Gd/Fe multilayers takes place at the picosecond time scale (see also corresponding discussion in Ref. [2]). It is also worth mentioning that an experimental estimation of the magnon-emission time, that is a relevant quantity for the characterization of the process of the disordering of atomic spins by hot electrons, gives a value in the subpicosecond region [23]. On this basis we conclude that the transition from the collinear ferromagnetic (FM) orientation of the $4f$ moments to a noncollinear orientation under the influence of the hot electrons is an ultrafast process of a picosecond time scale.

On the other hand, the successful description of the results of the pump-probe experiment on Gd performed in this paper provides an additional strong argument supporting the ultrafast character of the $4f$ disordering.

B. $5d6s$ atomic moments as separate Heisenberg degrees of freedom

Different studies suggest different views of the relation between the atomic $4f$ and $5d6s$ spin moments of Gd atoms in excited states of Gd and Gd compounds. For example, Mekonnen *et al.* [6] in the paper published in 2013 treat the

$4f$ moment and the induced $5d6s$ moment of a Gd atom as a rigid entity. On the other hand, Wienholdt *et al.* [7] in the paper published in the same year argue that it is important to treat the moments as separate degrees of freedom that interact as two Heisenberg spins according to the Hamiltonian

$$H = J_{\text{int}}\mathbf{S}_{5d6s} \cdot \mathbf{S}_{4f}. \quad (1)$$

Wienholdt *et al.* remark that exchange parameter J_{int} was estimated by comparison of the energies of the configurations where $4f$ and $5d6s$ moments are parallel and antiparallel to each other. It is, indeed, a rather common practice in mapping an electron system onto a Heisenberg Hamiltonian of interacting spins to estimate exchange parameters by the comparison of energies of different collinear spin configurations. A necessary condition for the realization of this procedure is the possibility of performing first-principles calculations for spin configurations that are obtained from the ground state by reversal of the directions of some of the spins. In the present case this is the reversal of the $5d6s$ moments with respect to the $4f$ moments.

For performing such a calculation it is crucial that the moments whose directions are changed to opposite are sufficiently rigid to be well defined for the reversed directions. The condition of rigidity is satisfied if the change of the value of the moment needs distinctly more energy than the rotation of the moment by a large angle. The applicability of the rigid spin scenario can be verified by the calculation of the energy profile $E(m)$, where m is the value of the spin moment varied continuously. The direction of the spin remains collinear to the ground state direction. Positive (negative) m values correspond to the direction of the $5d6s$ moment parallel (antiparallel) to the direction of the $4f$ moment. In the case of rigid atomic spins $E(m)$ has a two-minima form (see an example in the inset in Fig. 1) where the deeper minimum corresponds to the ground state and the less deep minimum to the excited state. The energy difference between two minima can be used for the estimation of the effective Heisenberg exchange parameter as suggested by Wienholdt *et al.* The barrier between two minima corresponds to a high energy of the small-$|m|$ values

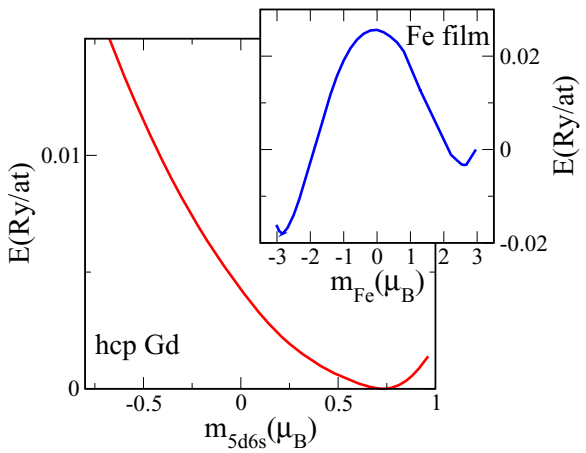

FIG. 1. (Color online) Energy of hcp Gd as a function of the value of spin moment of $5d6s$ electrons. In the inset the energy of the fcc Fe film as the function of the moment of the atoms of the first layer.

that makes the rotation of the spin energetically preferable compared to its decrease. The first-principles calculation of the $E(m)$ curve can be performed by applying a constraining effective magnetic field stabilizing a given m value.

The example of the two-minima $E(m)$ curve shown in Fig. 1 is obtained by varying the spin moment of the surface layer of the fcc-Fe film [24]. In the case of the $5d6s$ moments of the Gd atoms the situation is principally different. The calculated $E(m)$ curve has only one minimum corresponding to the ground state value of m (Fig. 1). Physically this situation is well understandable. In contrast to the Fe film where each atomic Fe spin moment is the result of the intra-atomic exchange interaction between $3d$ electrons, the $5d6s$ moment in Gd is induced by the exchange interaction of the $5d6s$ electrons with $4f$ electrons. The spin-up states of the $5d6s$ electrons are lower in energy than the corresponding spin-down states because the spin-up exchange-correlation potential is deeper than the spin-down exchange-correlation potential. This is the consequence of the presence of seven spin-up $4f$ electrons contributing to the spin-up electron density and of the absence of the spin-down $4f$ electrons [25].

The intra-atomic exchange interaction tends to form an atomic $5d6s$ moment that is parallel to the atomic $4f$ moment. A negative $5d6s$ moment can be obtained by a nonequilibrium occupation of the $5d6s$ states where the high-energy spin-down states are more strongly occupied than the lower-energy spin-up states. However, first, such an inversion in the occupation of the spin-up and spin-down states is not an expected result of the laser light absorption. Second, even if to assume, unrealistically, that such occupation inversion takes place there is no reason to expect that it will be well described by the Heisenberg Hamiltonian of rigid spin moments.

On the other hand, we will show that the noncollinearity of the $4f$ spins leads to the noncollinearity of the atomic $4f$ and $5d6s$ moments. This latter noncollinearity is the consequence of the interatomic hybridization between the electron states of different atoms. Through the hybridization the magnetic structure of the neighboring atoms influences the spin polarization of the electron states in the atomic sphere of a given atom and leads to the deviation of the $5d6s$ spin moment from the direction of the $4f$ moment. This noncollinearity is the property of the *lowest-energy state* corresponding to a given configuration of the $4f$ moments and is not an argument in favor of the treatment of the $5d6s$ moments as separate Heisenberg degrees of freedom [26].

On the basis of the arguments suggested in this section, the calculations presented below do not consider the $5d6s$ moments as separate degrees of freedom. In the modeling of the excited states of the system, only the directions of the $4f$ moments are treated as the degrees of freedom making a decisive contribution in the formation of the electronic properties discussed in the paper.

C. Stoner model vs spin-mixing behavior

As mentioned above the properties of the electronic states in magnetically excited ferromagnets are usually discussed either in terms of the Stoner model or in terms of the spin-mixing model. The concept of spin mixing inevitably arises when noncollinear magnetic configurations are considered.

This property is general and valid for any choice of the spin quantization axes. However, the interpretation of the physical consequences of the spin mixing depends on the choice of the spin quantization axes.

There are two choices of the axes that are most often used in the analysis of the properties of the electron states of noncollinear magnetic configurations. First choice is the global axis parallel to the net magnetization of the system. For strong disorder of the atomic spins this axis is far from the directions of the individual atomic moments. If the properties of an electron state reflect an average of the potentials of different atoms the global axis is a proper reference system to characterize this state. Since in the Stoner theory only the value of the net magnetization is important, the spin quantization axis parallel to the net magnetization is always used. The second choice of the spin quantization axes are the local atomic axes parallel to the atomic moments, in the case of Gd parallel to the $4f$ moments. In this local system the spin-polarized atomic exchange-correlation potential due to the $4f$ electrons takes spin-diagonal form

$$V(r) = \begin{pmatrix} v_\uparrow(r) & 0 \\ 0 & v_\downarrow(r) \end{pmatrix}. \tag{2}$$

Within each atomic sphere the exchange field of the atom [Eq. (2)] tends to orient the electron spin either parallel or antiparallel to the direction of the atomic moments. If the influence of the neighboring atoms is negligible the spinor wave function of an electron state written with respect to the atomic axis is either $\binom{\psi_\uparrow(\mathbf{r})}{0}$ or $\binom{0}{\psi_\downarrow(\mathbf{r})}$ and has a definite spin projection on the local axis. The influence of the noncollinear environment disturbs this feature and leads to the spinor function of a general form $\binom{\psi_\uparrow(\mathbf{r})}{\psi_\downarrow(\mathbf{r})}$. The spin moment in the atomic sphere Ω corresponding to this state is given by the formulas

$$m_z = n_\uparrow - n_\downarrow, \tag{3}$$

where

$$n_\sigma = \int_\Omega d\mathbf{r}\psi_\sigma(\mathbf{r})\psi_\sigma(\mathbf{r})^*, \quad \sigma = \uparrow,\downarrow, \tag{4}$$

and

$$m_\perp = 2\int_\Omega d\mathbf{r}|\psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r})^*|. \tag{5}$$

Here m_z is the projection on the local z axis and $m_\perp$ is the component of the moment orthogonal to the local z axis. The deviation of the moment from the local z axis is given by the formula

$$\tan\theta_{\text{dev}} = \frac{m_z}{m_\perp}. \tag{6}$$

If for a given electron state $n_\uparrow \sim n_\downarrow$ the atomic spin-up and spin-down potentials average their influence on the state and we obtain the picture that resembles the Stoner model. If, however, the intra-atomic potential dominates over the influence of the noncollinear environment the states remain close to $\binom{\psi_\uparrow(\mathbf{r})}{0}$ and $\binom{0}{\psi_\downarrow(\mathbf{r})}$ form. Then the difference of the energies of the states reflects the difference of the atomic spin-up and spin-down potentials. Therefore, these states can be treated in terms of exchange splitting due to the intra-atomic exchange interaction independent of the extent of the disordering of the $4f$ spins.

To obtain values m_z and $m_\perp$ for the total atomic moment, the sum over occupied states must be performed.

IV. BULK HCP Gd

We start the discussion of the results of the calculations with bulk hcp Gd. We will consider noncollinear spin configurations of the $4f$ moments with varying angle 2Θ between neighboring noncollinear atomic $4f$ moments (Fig. 2). The analysis of the character of the changes in the electronic structure with increasing noncollinearity of the $4f$ moments will help us to understand the trends in the properties of the system disturbed from the ground state by heating or pump-pulse absorption.

A possible simple verification of overall validity of the Stoner picture in the case of Gd is the calculation of the values of the atomic $5d6s$ moments in the strongly noncollinear configurations of the $4f$ moments. In the Stoner-type picture in the limit of the antiferromagnetic (AFM) configuration of the $4f$ moments the extended $5d6s$ states average the influence of the nearest oppositely directed $4f$ moments leading to "nonmagnetic" itinerant-electron states that demonstrate no spin polarization and exchange splitting. The calculations (Fig. 3) reveal that the induced $5d6s$ atomic moment, although decreased compared to the ferromagnetic configuration, is still significant and has the value of $\sim 0.4\mu_B$. A similar estimation is obtained by Khmelevskyi *et al.* [17] with the DLM method in the limit of complete disorder.

With the deviation of the $4f$ moments from the parallel directions the induced $5d6s$ atomic moments become noncollinear to the corresponding atomic $4f$ moments. For $\Theta = 45^\circ$ (the angle between neighboring $4f$ spins of 90° corresponds to the maximal possible noncollinearity) the angle between atomic $4f$ and $5d6s$ moments is $\sim 5^\circ$. This angle is much smaller than the angle between noncollinear $4f$

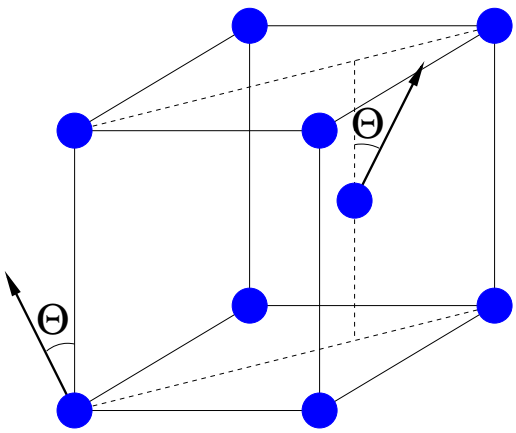

FIG. 2. (Color online) The unit cell of the hcp structure. The arrows show the directions of the $4f$ spin moments for two Gd atoms in the unit cell. The atoms connected by lattice translations have the same directions of the spin moments.

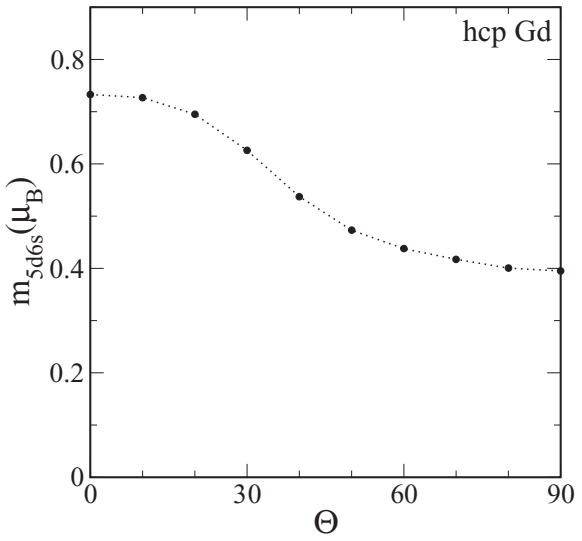

FIG. 3. Total (summed over all occupied electron states) atomic $5d6s$ spin moment as a function of Θ.

moments. Obviously the influence of the atomic spin-polarized potential on the formation of the direction of the atomic $5d6s$ moment is stronger than the influence of the environment. These calculational results show that the Stoner picture does not provide an adequate complete description of the physics of magnetic excited states of Gd. Why do some of the spectroscopic experiments seem to be well described by the Stoner picture? To answer this question it is not sufficient to consider the properties of the atomic moments that are an integral characteristic of all occupied states. Instead we should look closer at the properties of individual electronic states that can deviate strongly from the properties of the integrated quantities.

Let us focus first on the ΓA interval in the BZ of the hcp lattice (Fig. 4). In the ferromagnetic structure (Fig. 4, left panel) there are two pairs of the occupied exchange split bands. In the collinear structure the spin-up and spin-down states do not hybridize and the spin-down subband of the first pair intersects with spin up subband of the second pair at $k \sim 0.75\Gamma A$. With increasing Θ two types of changes in the band structure can be distinguished. In the main part of the ΓA interval from Γ to about $0.65\Gamma A$ the bands within each of the two pairs are getting closer to each other and become degenerate at $\Theta = 90^\circ$. This behavior reminds us of the Stoner picture where energy distance between exchange-split states decreases with increasing temperature and the states become degenerate when the net magnetization of the system vanishes. The calculated projection of the spin moment of individual electronic states on the local atomic axis decreases with increasing Θ. In Fig. 4 these projections are presented by "errorbars" where the length of the bar shows the absolute value of the projection and the upper or lower position of the bar with respect to the energy point corresponds to, respectively, the positive or negative sign of the projection. The projection with respect to the local atomic axis decreases because the states become spin mixed with respect to this axis. The angle between the vector of the $5d6s$ moment of the states and the local atomic axis is given by Eq. (6). If the projection of the vector on the local axis is small the angle between the moment and local axis is large.

In Fig. 5 we present the calculated angles between the $5d6s$ moment and the spin quantization axis for the electron states of the four occupied bands in the interval ΓA (Fig. 4). The data are shown for the noncollinear structure with $\Theta = 45^\circ$. For convenience the values of the angle are given with respect to both local (θ_{local}) and global (θ_{global}) spin-quantization axes. The two angles differ by 45°. (We use lowercase letter θ to distinguish the characteristics of individual electron states from the characteristics of the total atomic moments where we employ capital Θ.) The behavior of the angles is remarkable. For bands 1 and 4 the k dependence of the angles is rather weak in the whole ΓA interval. The analysis from the point of view of the global axis is more informative. It shows that despite large noncollinearity of the $4f$ moments the $5d6s$ moment of the electronic states remains almost parallel to the global z axis for the first band and almost antiparallel to it for the fourth band. This is the behavior expected for the Stoner model. For bands 2 and 3 the angle θ_{global} varies weakly in the first part of the ΓA interval. It is close to 180° for band 2 and close to 0° for band 3. Thus the energy positions and the directions of the

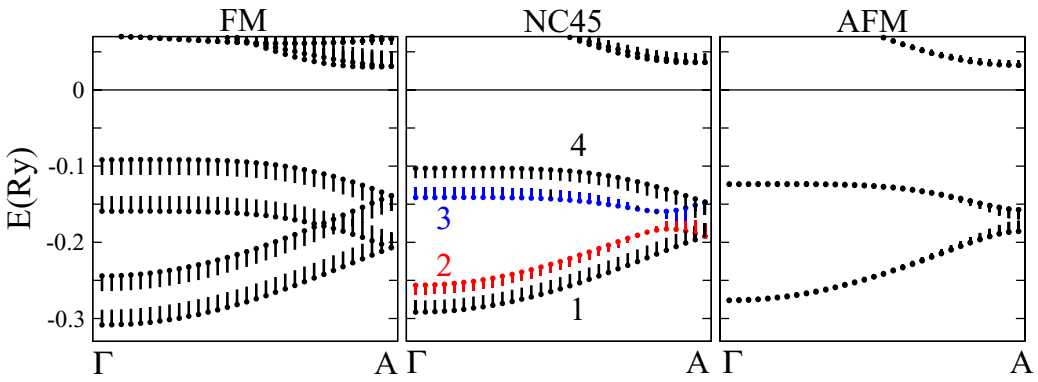

FIG. 4. (Color online) The band structure of hcp Gd for the ΓA interval of the three-dimensional (3D) BZ. Left panel: FM structure. Middle panel: Noncollinear structure with $\Theta = 45^\circ$. Right panel: Antiferromagnetic structure ($\Theta = 90^\circ$). The lengths of the errorbars show the absolute value of the projection of the $5d6s$ moment of the electron state on the local atomic axis. The upper or lower position of the bar with respect to the energy point corresponds to, respectively, the positive or negative sign of the projection.

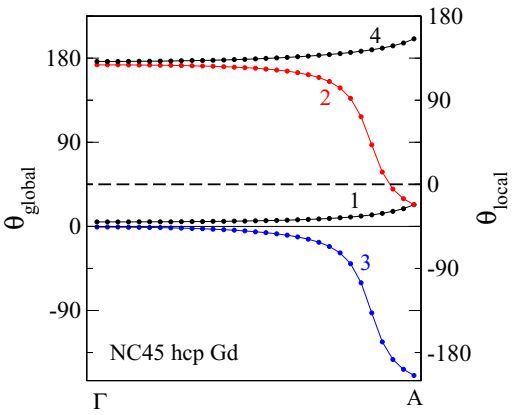

FIG. 5. (Color online) The angle between $5d6s$ moment and global and local axes for the electron states of the four occupied bands of hcp Gd in interval ΓA. Calculation for the noncollinear configuration with $\Theta = 45^\circ$. The numbering and the color scheme correspond to those from the middle panel of Fig. 4.

spin moments resemble the behavior expected on the basis of the Stoner theory. However, in the second part of the interval the angle θ_{global} changes strongly for both the second and third bands. At the end of the interval the states of the second band are close to the global spin-up, whereas the states of the third band are close to the global spin-down. Therefore, the spin character of the states of the second and third bands changes to the opposite.

The strong spin-hybridization effect in the second part of the ΓA interval is explained by the increased number of the interacting states lying close in energy to each other. In the limit of $\Theta = 90^\circ$ we obtain at the A point a gap of about 0.03 Ry between pairs of partly spin-polarized states. The gap and the spin polarization are the result of the hybridizational redistribution of the spin projections between interacting states. In the Stoner picture, the energy gap between pairs of bands at the A point closes and the states of both pairs of bands give no contribution to the atomic moment. So, the states at the A point cannot be described within the Stoner model. On the other hand, at the Γ point the redistribution process is weak since the energy distance between pairs of interacting states is large compared with the characteristic exchange splitting. In this case the Stoner model is applicable.

Qualitatively similar properties were obtained also for the ΓM and ΓK intervals (Fig. 6). The noncollinearity of the $4f$ moments leads to the spin mixing and decreased projection of the spin moment of the states on the local atomic axis. In the limit $\Theta \to 90^\circ$ some of the states make sizable contribution to the local atomic moment, whereas others behave like Stoner states.

To summarize, in the study of the 3D periodic hcp Gd we found two types of behavior of the electronic states. If the pair of the exchange-split states of the ferromagnetic structure is isolated from the other states by energy exceeding the characteristic exchange splitting the states behave according to the Stoner scenario. If however, a larger number of the states is close in energy the spin hybridization of the states leads to a complex redistribution of the spin projections and results in the behavior that cannot be described within the Stoner picture. It is important that, from the viewpoint of the local atomic axes, both types of behavior correspond to the strong spin mixing. Completely different situation was obtained in the case of surface states studied in the next section.

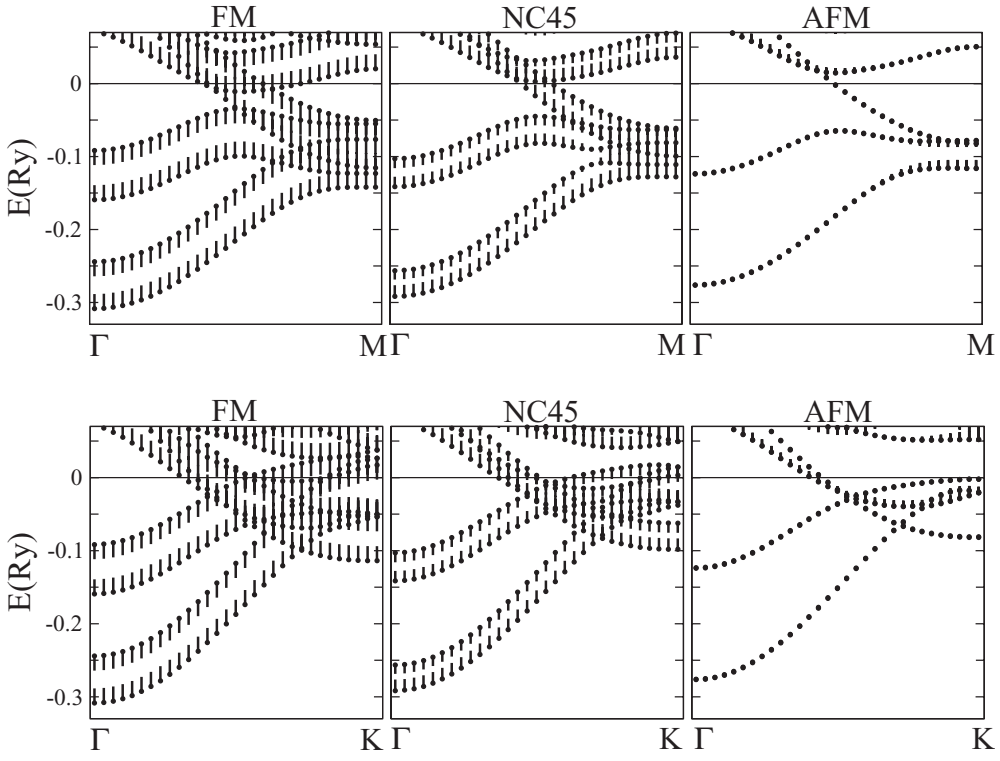

FIG. 6. The same as in Fig. 4 but for the ΓM and ΓK intervals.

V. SLAB CALCULATION: PROPERTIES OF THE SURFACE STATES

To study the surface properties of Gd we performed the slab calculation for a periodically repeated block of Gd layers in hcp structure and several layers of empty spheres simulating vacuum. Most of the results presented in the paper are obtained for 12 Gd layers and 4 layers of the empty spheres. Test calculations for larger slabs show that all the conclusions of the paper remain intact.

An important consequence of the presence of the surface is inequivalence of the Gd atoms belonging to different layers. In particular, the atoms of the first surface layer have a strongly different atomic environment compared to the atoms of deeper layers. One of the consequences of this inequivalence is the formation of the surface electronic states that are localized mostly in the surface layer and quickly decay with increasing depth of the layer. The surface states were detected in many experiments and were also obtained in the first-principles calculations for the ferromagnetic ground state [27,28]. Our purpose is to study the influence of the noncollinearity of the $4f$ moments on the properties of the surface states.

We will consider the noncollinear magnetic configurations (Fig. 7) similar to those used above in the study of the bulk Gd (Fig. 2). First, we focus on the integrated quantities obtained

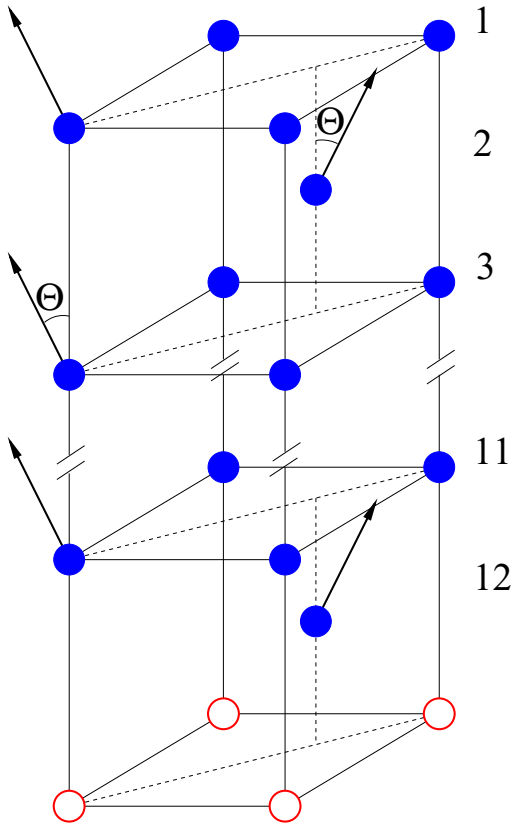

FIG. 7. (Color online) The slab unit cell. Most of the results presented in the paper are obtained for 12 Gd layers and 4 layers of the empty spheres. The arrows show the directions of the atomic $4f$ moments. The empty red circles show the first layer of the empty spheres. The atoms belonging to the same plane have the same direction of the spin moments.

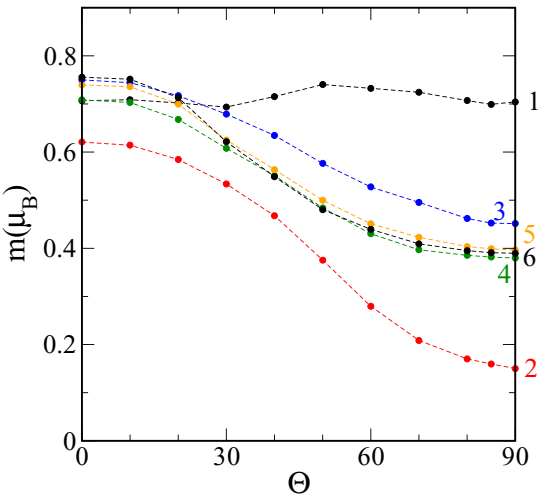

FIG. 8. (Color online) The Θ dependence of the $5d6s$ moments of different atomic layers. The layers are numbered starting from the surface layer. The moments are obtained by summing over all occupied states.

by summing over all occupied electron states. The values of the atomic spin moments for different layers as a function of angle Θ are presented in Fig. 8.

In all layers excluding the surface layer the spin moment monotonously decreases with increasing angle. In the surface layer the spin moment depends rather weakly on the variation of Θ. At both ends of the angle interval, $\Theta = 0^\circ$ and $\Theta = 90^\circ$, the atomic moment of the surface layer is close to $0.7\mu_B$. On the other hand, the spin moment of the second layer is smaller than the spin moments of all other layers. In the limit of $\Theta = 90^\circ$ the spin moment of the atoms of the second layer decreases down to $0.15\mu_B$ that is much smaller than the corresponding value of $0.45\mu_B$ for the atoms of the third layer. Obviously the specific structural properties of the surface layer influence strongly the electronic properties of the next layer.

An increase of the number of Gd layers changes only weakly the properties of the surface and subsurface layers. Additional layers behave like inner fourth to sixth layers in Fig. 8. To a good approximation the atoms of these additional layers can be considered as bulk atoms that experience only weak influence of the surface.

The calculated angles between $4f$ and $5d6s$ atomic moments are also layer dependent. For the surface layer the angle between two moments is very small for all values of Θ. For $\Theta = 45^\circ$ the angle between atomic $4f$ and $5d6s$ moments of the surface layer is as small as 1.5°. On the other hand, for the second layer it reaches a relatively large value of $\sim 17^\circ$. For the third layer it decreases again to the value of $\sim 8^\circ$ and remains on this level for further layers.

In Fig. 9 we present the band structure of the slab in the interval ΓM of the 2D BZ. In the ferromagnetic structure the electronic states can be exactly classified by their spin projection and plotted separately. For both spin-up and spin-down states we clearly see a specific isolated band lying in the energy gap formed by the other bands. These isolated bands are formed by the surface states. The layer distribution of the spin-up and spin-down surface states of ferromagnetic Gd slab

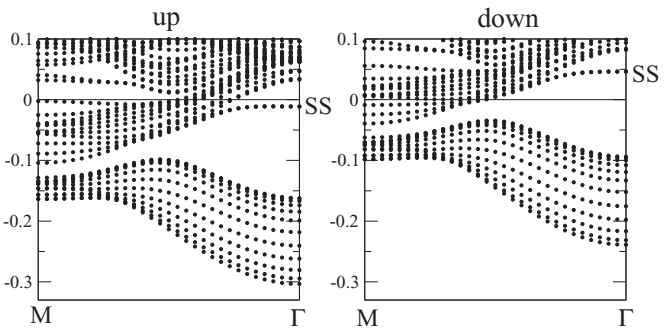

FIG. 9. The spin-projection resolved band structure of the ferromagnetic Gd in ΓM interval of the 2D Brillouin zone. Slab calculation. Left panel: Spin-up. Right panel: Spin-down. SS marks the surface states.

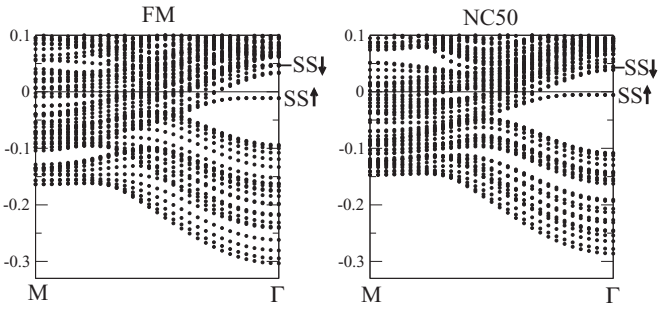

FIG. 11. The band structure of the Gd slab in ΓM interval of the 2D Brillouin zone. Left panel: Ferromagnetic configuration of the $4f$ moments ($\Theta = 0^\circ$). Right panel: Noncollinear configuration ($\Theta = 50^\circ$). The positions of the spin-up and spin-down surface states at the Γ point are marked with letters SS.

at the Γ point of 2D BZ is presented in Fig. 10. More than 50% of the states are in the surface layer. The contribution of the second layer drops to about 20% with further fast decrease for deeper layers. Since in the FM structure the spin projection is a good quantum number the spin-down contribution in the left panel (black dashed curve) and spin-up contribution in the right panel (black solid curve) are zero.

In Fig. 11 we compare the band structures for the ferromagnetic configuration of the $4f$ spin moments and the noncollinear configuration with $\Theta = 50^\circ$. Many quantitative changes can be noticed. For example, in the noncollinear case the lowest-energy band shifts by 0.02 Ry to higher energy. The energy gap at the M point of the FM spectrum just below -0.1 Ry is closed in the noncollinear case, whereas a similar energy gap appears at the Γ point in the energy interval between -0.15 and -0.2 Ry. The band of the spin-up surface states is clearly seen also in the noncollinear case. The states have somewhat higher energy and are closer to the Fermi level. Note that although the band of the spin-down surface states cannot be distinguished visually on the band structure plot

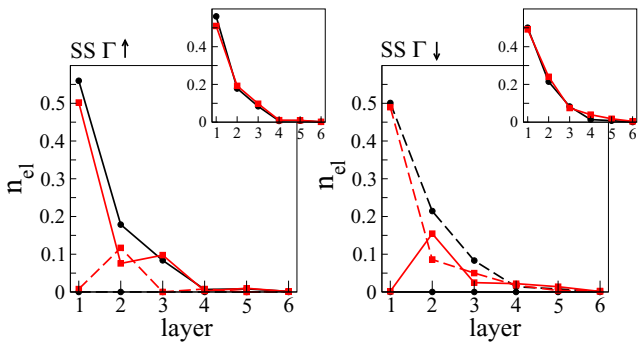

FIG. 10. (Color online) Distribution of the surface state at the Γ point over layers. Left panel: Spin-up surface state for the FM configuration (black curves) and for the configuration with $\Theta = 50^\circ$ (red curves). The solid lines give the partial spin-up contribution with respect to the local atomic axes, the broken lines give partial spin-down contribution. In the inset, the sum of the partial spin contributions for both spin configurations. Left panel: The same as in the right panel but for the spin-down surface states.

(Fig. 11) the analysis of the wave functions of the electronic states allows us to uniquely establish the properties of these states.

Since for nonzero Θ the spin projection ceases to be a good quantum number we need to analyze spin mixing of the states to understand the Θ dependence of the energy. For this purpose we come back to Fig. 10 and consider the results obtained for the noncollinear configuration with $\Theta = 50^\circ$. In contrast to the ferromagnetic case (black curves) both spin contributions become nonzero: in the left panel the spin-down contribution, in the right panel the spin-up contribution. The comparison of the calculations for $\Theta = 0^\circ$ and $\Theta = 50^\circ$ gives a number of interesting results. First, the sum of the spin-up and spin-down contributions depends very weakly on Θ (see insets in Fig. 10). This means that the noncollinearity does not lead to the delocalization of the states from the surface layer. Second, in the surface layer the spin mixture due to the noncollinearity is very weak. For the second layer the situation becomes strongly different. Here for the nominally spin-up surface state the spin-down contribution considerably exceeds the spin-up contribution (left panel of Fig. 10) with similar property of the nominally spin-down surface state (right panel of Fig. 10). For deeper layers the spin mixing drops again.

In Fig. 12 we present the calculated angles between the atomic $5d6s$ moment and the local atomic axis for the spin-up surface states in the noncollinear structure with $\Theta = 50^\circ$. Since the layers are inequivalent the angles θ_{local} are layer dependent. In Fig. 12 we show the θ_{local} for the surface and first subsurface layers numbered, respectively, with 1 and 2. In correlation with spin-mixing data (Fig. 10) we obtain for the surface layer an angle of about 12° that is much smaller than the angle 100° between the $4f$ moments of the neighboring layers. In the second layer the large spin mixing leads to a large angle between atomic $5d6s$ and $4f$ moments. Since the spin-down component exceeds the spin-up component (Fig. 10) the angle is larger than 90°.

These results are very important for the understanding of the properties of the surface states. In Fig. 13 we present the Θ dependence of the energies of the spin-up and spin-down surface states. The energy shift of the states with increasing noncollinearity is small compared with the characteristic exchange splitting of $\sim$0.058 Ry between corresponding

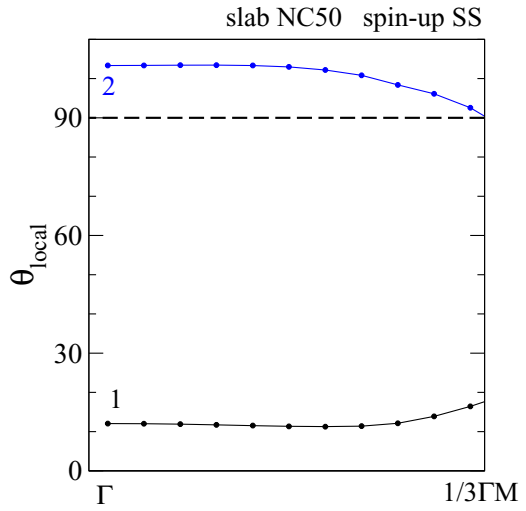

FIG. 12. (Color online) The angle between atomic $5d6s$ moment and the local atomic axis for the band of the spin-up surface states. Calculation for the noncollinear configuration with $\Theta = 50^\circ$. The curve labeled with "1" gives the angle for the surface layer, the curve labeled with "2" corresponds to the first subsurface layer.

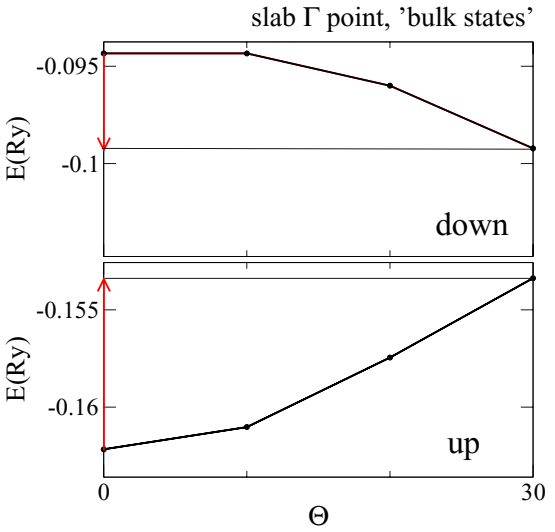

FIG. 14. (Color online) The θ dependence of the bulk states at the Γ point obtained in the slab calculations.

spin-up and spin-down states in the ferromagnetic case. Since these states are localized predominantly in the surface layer where the spin mixing is very weak the main part of the state, also in the noncollinear configuration, experiences the atomic potential of either spin-up (left panel) or spin-down (right panel) character. This naturally leads to the preserving of the spin splitting in the excited system since the spin splitting of the electronic states reflects the difference between atomic spin-up and spin-down potentials. Therefore, even in the case of very strong noncollinearity of the $4f$ moments the surface states can be approximately characterized as spin-up or spin-down referring to the local atomic axis. On the other hand, a smaller part of the surface state localized in the second layer produces a different trend. The influence of the spin-down potential of the second layer on the nominally spin-up surface state leads to the increase of the energy of this state. Respectively, the influence of the spin-up potential of the second layer on the nominally spin-down surface state leads to the decrease of the energy of this state. Therefore, in agreement with experiment the states move in energy towards each other keeping however a large part of the spin splitting preserved.

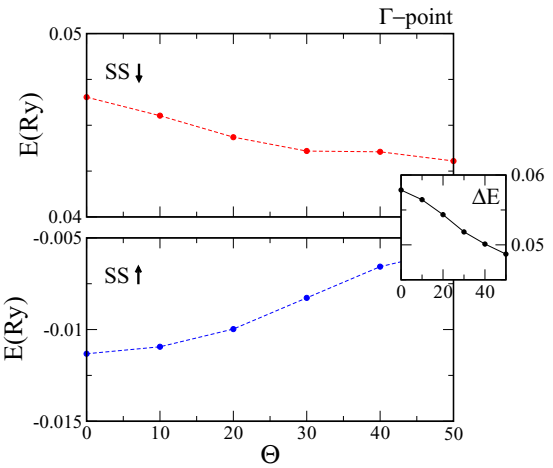

FIG. 13. (Color online) The Θ dependencies of the spin-up (upper panel) and spin-down (lower panel) surface states at the Γ point. The inset presents the Θ dependence of the exchange splitting.

Very low spin mixing in the first layer distinguishes the surface states with respect to the bulk states considered above and explains their highly non-Stoner behavior in the spectroscopic experiments.

Next we turn to the properties of the bulk states observed by Carley *et al.* [3]. As mentioned in the Introduction they report a stronger change of the energy of the bulk spin-up states compared to the spin-down states. In the consideration of the states at the Γ point of the hcp bulk Gd crystal performed above (Sec. IV) we did not obtain this effect. The shift of the spin-down state to lower energy was approximately equal to the shift of the spin-up state to the higher energy. However, in the slab calculations we find the behavior of the "bulk" bands that is similar to the properties observed by Carley *et al.* In Fig. 14 we show the dependence of the two states at the Γ point on the angle Θ between atomic moments of the adjacent layers. In contrast to the surface states these states are predominantly located in the inner part of the slab. In the FM, where spin mixing is absent the lower state is of the spin-up type, whereas the upper state is of the spin-down type. For nonzero Θ the states become spin mixed. With increasing Θ the spin-up state shifts to higher energies while the spin-down state shifts to lower energies. The values of the shifts are however different. For instance, for $\Theta = 30^\circ$ we obtain, respectively, 0.12 eV (9 mRy) and 0.07 eV (5 mRy) that is good correlation with the values reported by Carley *et al.* (see Introduction). The shift of the spin-up bulk state is much larger than for the surface state. For instance the spin-up surface state shifts for $\Theta = 30^\circ$ by 0.04 eV (3 mRy) that is also in good agreement with experiment.

The reason for the difference between 3D-periodic calculation for the hcp crystal and the calculation for the 2D-periodic slab is clear. In the 3D periodic case we also obtained different shifts of the corresponding spin-up and spin-down states for the k points at the end of the ΓM and ΓK intervals where the number of interacting bands lying close to each other increases. In this part of the electronic structure the influence of the noncollinearity of the $4f$ moments on the energy bands becomes more complex because of the complex influence of the states on each other. In the 2D case such complex influence takes place already at the Γ point since the k_z projection of the crystal momentum is no longer a good quantum number and all states corresponding to different k_z for a given $k_{||}$ are now involved in the interaction. The slab calculation is closer to the experimental situation since it takes into account the presence of the surface exerting strong influence on the electronic structure.

There is another interesting observation reported by Carley *et al.* They obtained a time delay in the variation of the energy of the bulk spin-up state compared to the bulk spin-down state where no delay was noticed. In the picture discussed in this paper the noncollinearity of the atomic exchange fields influences all states without time delay. We also remark that in the experiment by Carley *et al.* the dynamics of the spin-up *surface* state has no time delay. This means the sign of the spin projection by itself does not lead to the observed effect. The possible reason for the apparent delay is the following. Besides the noncollinearity of the $4f$ moments the energies of the electron states are influenced by the values of the induced $5d6s$ moments. These moments contribute to the difference of atomic spin-up and spin-down electron densities and, therefore, to the difference between atomic spin-up and spin-down potentials. In our present calculations we considered the self-consistent solution for the system with given noncollinear configuration of the $4f$ moments. But in the laser excited system the occupation of the electronic states must not correspond to the equilibrium occupation. The time-dependent nonequilibrium redistribution of the electrons between surface and bulk states can differently influence the surface layer and the inner layers of the slab. We propose that these additional effects influencing the contribution to the spin-polarized potential from the $5d6s$ states compensates the influence of the noncollinearity of the $4f$ moments leading to an apparent delay in the response of the part of the states. The quantitative description of such competing processes needs a detailed picture of the nonequilibrium electron distribution over the states of the excited system. This problem is not the topic of the present work.

VI. CONCLUSION

We studied the properties of electronic states in excited states of Gd. The calculations were performed for both bulk hcp crystal and slabs of Gd layers separated by layers of empty spheres. We simulated magnetically excited states by noncollinear configurations of the $4f$ moments. We found strong difference in the response of the bulk and surface states on the noncollinearity of the $4f$ spin moments. Also different bulk states show substantially different behavior. We explain the difference in the behavior by analyzing the character of the spin mixing with respect to the local atomic spin quantization axes. In most of the bulk states this spin mixing is strong, which leads to the property that some groups of the bulk states behave like Stoner states. On the other hand, the properties of the surface states are different. Since the presence of the surface makes different layers inequivalent the spin mixing becomes layer dependent. In the surface layer where more than 50% of the surface state is localized the spin mixing is very weak and this part of the surface state experience predominantly either local spin-up or local spin-down potential. On the other hand, the part of the surface state corresponding to the second layer becomes strongly spin mixed and experiences strong influence of the opposite-spin exchange-correlation potential. Thus the surface state preserving mostly its local spin character changes its energy because of the spin mixing in the second layer. The results of the calculations are in good agreement with available experiments.

An interesting result we obtained by the study of the bulk states in the case of slab calculations. In particular, at the Γ point of the 2D BZ we obtained different energy shifts of the spin-up and spin-down states. This property is in agreement with recent measurement by Carley *et al.* In the case of the slab because of the absence of the periodicity along the z direction the involvement of a large number of close-in-energy states into a spin-mixing process leads to different shifts of the spin-up and spin-down states.

Good correlation between our theoretical results and the experimental data obtained in the pump-probe experiment within the first 1–2 ps gives an additional argument in favor of the ultrafast character of disordering of the $4f$ moments in Gd.

[1] U. Bovensiepen, J. Phys.: Condens. Matter **19**, 083201 (2007).
[2] B. Koopmans, G. Malinowski, F. Dalla Longa, D. Steiauf, M. Fähnle, T. Roth, M. Cinchetti, and M. Aeschlimann, Nat. Mater. **9**, 259 (2010).
[3] R. Carley, K. Döbrich, B. Frietsch, C. Gahl, M. Teichmann, O. Schwarzkopf, P. Wernet, and M. Weinelt, Phys. Rev. Lett. **109**, 057401 (2012).
[4] M. Wietstruk, A. Melnikov, C. Stamm, T. Kachel, N. Pontius, M. Sultan, C. Gahl, M. Weinelt, H. A. Dürr, and U. Bovensiepen, Phys. Rev. Lett. **106**, 127401 (2011).
[5] C. D. Stanciu, F. Hansteen, A. V. Kimel, A. Kirilyuk, A. Tsukamoto, A. Itoh, and Th. Rasing, Phys. Rev. Lett. **99**, 047601 (2007).
[6] A. Mekonnen, A. R. Khorsand, M. Cormier, A. V. Kimel, A. Kirilyuk, A. Hrabec, L. Ranno, A. Tsukamoto, A. Itoh, and Th. Rasing, Phys. Rev. B **87**, 180406(R) (2013).
[7] A. Suslov, J. B. Ketterson, D. G. Hinks, D. F. Agterberg, and B. K. Sarma, Phys. Rev. B **68**, 020406(R) (2003).
[8] M. Battiaro, K. Carva, and P. M. Oppeneer, Phys. Rev. Lett. **105**, 027203 (2010).

[9] D. Li, J. Pearson, S. D. Bader, D. N. McIlroy, C. Waldfried, and P. A. Dowben, Phys. Rev. B **51**, 13895 (1995).
[10] M. Bode, M. Getzlaff, S. Heinze, R. Pascal, and R. Wiesendanger, Appl. Phys. A **66**, S121 (1998).
[11] K. Maiti, M. C. Malagoli, A. Dallmeyer, and C. Carbone, Pramana **58**, 725 (2002).
[12] N. Beaulieu, G. Malinowski, A. Bendounan, M. G. Silly, C. Chauvet, D. Krizmancic, and F. Sirotti, J. Electron Spectrosc. Relat. Phenom.a **189**, 40 (2013).
[13] L. M. Sandratskii and J. Kübler, Europhys. Lett. **23**, 661 (1993).
[14] L. M. Sandratskii and J. Kübler, in *Magnetism and Electronic Correlations in Local-Moment Systems: Rare-Earth Elements and Compounds*, edited by M. Donath, P. A. Dowben, and W. Nolting (World Scientific, Singapore, 1998).
[15] W. Nolting, S. Rex, and S. Mathi Jaya, J. Phys.: Condens. Matter **9**, 1301 (1997).
[16] C. Santos, W. Nolting, and V. Eyert, Phys. Rev. B **69**, 214412 (2004).
[17] S. Khmelevskyi, I. Turek, and P. Mohn, Phys. Rev. B **70**, 132401 (2004).
[18] B. L. Gyorffy, A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. **15**, 1337 (1985).
[19] L. M. Sandratskii, Adv. Phys. **47**, 91 (1998).
[20] J. Kübler, *Theory of Itinerant Electron Magnetism* (Oxford University Press, Oxford, 2000).
[21] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[22] A. F. Bartelt, A. Comin, J. Feng, J. R. Nasiatka, T. Eimüller, B. Ludescher, G. Schütz, H. A. Padmore, A. T. Young, and A. Scholl, Appl. Phys. Lett. **90**, 162503 (2007).
[23] A. B. Schmidt, M. Pickel, M. Donath, P. Buczek, A. Ernst, V. P. Zhukov, P. M. Echenique, L. M. Sandratskii, E. V. Chulkov, and M. Weinelt, Phys. Rev. Lett. **105**, 197401 (2010).
[24] L. M. Sandratskii, Phys. Rev. B **81**, 064417 (2010).
[25] The trend to the spin splitting of the electron states due to the spin polarization of the atomic potential is often described by exchange parameters j_{4f5d} whose physical nature is principally different from the Heisenberg exchange parameter J_{int} describing the interaction between atomic moments [Eq. (1)]. Estimations of j_{4f5d} are provided, for instance, by Ahuja *et al.* [R. Ahuja, S. Auluck, B. Johansson, and M. S. S. Brooks, Phys. Rev. B **50**, 5147 (1994)] and Khmelevskyi *et al.* [17]. The reported values are, respectively, 94 meV and $\sim$1 eV/7 = 143 meV. The ASW method employed in the present work also allows the estimation of this parameter: The analysis of the solutions of the radial Schrödinger equations for the spin-up and spin-down electrons performed in the atomic sphere of a Gd atom results in the parameter that is in the same energy range as those of Ahuja *et al.* and Khmelevskyi *et al.* Since this parameter is not used in the rest of the paper we do not provide the details of its estimation.
[26] If one considers fluctuations of the 5*d* moment about its induced "ground state" value it is logical to consider both transversal and longitudinal fluctuations since they strongly compete in the case of induced moments. In principle one can try to reduce the consideration to the weak transversal fluctuations and describe their energies by means of the Heisenberg-type Hamiltonian obtained by the study of the energetics of the small transversal perturbation of the 5*d*6*s* moments. Such fluctuations are not considered in the paper and have weak influence of the electronic properties studied here.
[27] R. Wu, C. Li, A. J. Freeman, and C. L. Fu, Phys. Rev. B **44**, 9400 (1991).
[28] Ph. Kurz, G. Bihlmayer, and S. Blügel, J. Phys.: Condens. Matter **14**, 6353 (2002).