Magnetism of gadolinium: a first-principles perspective

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By calculating the spectral density of states in the ferromagnetic (FM) ground state and in the high temperature paramagnetic (PM) phase we provide the first concise study of finite temperature effects on the electronic structure of the bulk and the surface of gadolinium metal. The variation of calculated spectral properties of the Fermi surface and the density of states in the bulk and at the surface are in good agreement with recent photoemission experiments performed in both ferromagnetic and paramagnetic phases. In the paramagnetic state we find vanishing spin splitting of the conduction band, but finite local spin moments both in bulk and at the surface. We clearly demonstrate that the formation of these local spin moments in the conduction band is due to the asymmetry of the density of states in the two spin channels, suggesting a complex, non-Stoner behavior. We, therefore, suggest that the vanishing or nearly vanishing spin splitting of spectral features cannot be used as an indicator for Stoner-like magnetism.

Pure hcp Gd metal is perhaps the most investigated strongly correlated metallic system, where the well localized magnetic moment of the $4f$-shell interacts with the itinerant electrons of the conduction band.[1, 2] The half-filled $4f$-shell of Gd possesses a spin-moment of $7\mu_B$, and it is energetically well separated from the conduction band of the *spd*-electrons. In the FM ground state the ordered local moments induce a spin splitting of about 1 eV of the conduction band resulting in an additional spin magnetic moment of $0.6\,\mu_B$ [3].

Modern electronic structure theory describes adequately the ground state of Gd, if the strong correlation in the $4f$-shell is treated in some, even simple, manner. In pioneering works it has been shown that the LSDA+U method provides a good description of the Gd ground state in bulk [4, 5] and on the (0001) surface [6]. Later studies[7, 8] have confirmed this conclusion. Moreover, recent angle-resolved photoemission (ARPES) measurements of the Fermi surface in the FM phase of the bulk [9] have been successfully reproduced using the LSDA+U methodology[10]. Despite more sophisticated treatments of the correlated $4f$-shell in Gd [11–13], the considerable splitting of the Gd conduction band could also be obtained in a remarkably simple spin-polarized open-core approach.[14]

Owing to the strong localization of $4f$-states, the finite temperature magnetism in hcp Gd seems to be well described by the Heisenberg model, and it may be regarded as a model Heisenberg system among metallic ferromagnets. The magnetic critical temperature of hcp Gd can indeed be estimated reasonably well in terms of a Heisenberg model and calculating the exchange constants using either the open-core [15–17], the LSDA+U [18] or the self-interaction correction (SIC) approach [12].

However, despite the successful understanding of the ground state and finite temperature magnetism of Gd, the fundamental issue concerning the interaction between localized $4f$-moments and itinerant electrons has been the subject of a heated debate.[14, 19–22] Earlier photoemission (PES) experiments[23] have shown that the spin splitting of the conduction band vanishes near the Curie temperature. This gives rise to a simple interpretation that the *spd*-bands experience a spin polarization due to the (average) magnetization of the localized $4f$-electrons, a hallmark of Stoner magnetism [23–27]. However, more precise analyses of later PES measurements[28–30] seemed to provide clear evidence that the spin splitting of majority and minority spin channels remains finite in the PM state, although very small, being on the verge of the PES resolution. From this observation it was concluded that the Stoner model cannot describe the magnetism of bulk Gd.[21]

Contradictory theoretical interpretations were also given based on *ab initio* determined model parameters for the description of the interaction between the localized $4f$-moments and the conduction band. For example the authors of Ref. [31] derived a spin-mixing behavior of the conduction band in agreement with the experimental conclusions by Maiti *et al.* [21, 28], whereas later on the same authors proposed a theory predicting Stoner behavior [20] in line with old measurements by Kim *et al.* [23]. Fully *ab initio* attempts to resolve the above theoretical contradiction used the disordered local moment approximation (DLM) to model finite temperature magnetic disorder [22] or employed a study of non-collinear spin-configurations.[14] Although both of these studies were based on the open-core treatment of the $4f$-shell, they indicated a spin-mixing behavior of the conduction band. The DLM calculation [22] predicted a small but finite splitting of the majority and minority spin channels and a corresponding finite value of the local moment due to the *spd*-band in the paramagnetic state. The non-collinear calculation [14] clearly showed that the conduction band moment is strongly coupled to the direction of

the local $4f$-moment and cannot be treated as an independent magnetic degree of freedom.

In recent years the study of ultrafast magnetic processes induced by femtosecond laser pulses has been fueling a reinvigorated discussion concerning the nature of the interaction between $4f$-states and the conduction band moments in pure Gd and its compounds. [32–34] A crucial point in the simulations of these processes lies in the assumption of treating $5d$- and $4f$-moments as independent magnetic degrees of freedom.[35, 36] An elaborated discussion of this topic was recently given by Sandratskii.[14]

Recent ARPES [9, 37] and positron annihilation spectroscopy [38–40] experiments were able to observe differences of the Fermi surface topology between the FM and PM state. However, the current theoretical understanding of the PM electronic structure of the Gd conduction bands is far from being satisfactory. The Fermi surface of pure bulk Gd in the PM state has been calculated for several lattice constants using self-interaction correction to the LSDA [11]. The main features of the derived PM Fermi surface seem to be consistent with the later measured one [37]. However, so far there has been no consistent theoretical description of the Fermi surfaces in the FM and PM state and the evolution of spectroscopic properties from bulk to surface within the same framework.

An equivalently important issue is that the main experimental methods that provide us with precise information concerning the electronic structure of the Gd conduction band are surface sensitive. The presence of the surface leads to essential changes in the electronic structure of the terminating layers compared to the bulk. Moreover, the spin splitting of the surface states has been regarded as an important source of the information concerning the magnetic behavior of the conduction electrons. [19] It is therefore demanding to disentangle the signatures of the surface state from those of the bulk.

In this Letter we address both issues, namely the changes of the electronic structure of hcp Gd induced by finite temperature magnetic disorder and the variation of the Fermi surface near the Gd (0001) surface termination. We employ the well established LSDA+U methodology for the treatment of the half filled $4f$-shell and calculate bulk and layer resolved Fermi surfaces, as well as densities of states in the FM and the DLM state. We show that the high temperature behavior of the conduction band is governed by spin-mixing both in the bulk and near the surface. The comparison of our results with PES [21, 28] and ARPES studies [9, 37] suggests a good agreement for both FM and PM phases with regard to bulk and surface properties. We also find that electronic states associated with a presence of the surface decay faster towards the bulk in the paramagnetic phase than in the ferromagnetic state.

We performed self-consistent calculations by using the fully relativistic screened Korringa–Kohn–Rostoker (KKR) Green's function method with the atomic sphere approximation, that allows the study of layered systems and surfaces.[41] The strong correlation of the localized $4f$-states was treated within the framework of the LSDA+U approach[4, 5] as implemented within the KKR method.[42] The paramagnetic phase is treated in terms of the relativistic disordered local moment (R-DLM) method,[43, 44] in which the coherent potential approximation (CPA) is employed to model disorder in local spin orientations. [45] The application of these methods allows us to treat the correlations in the $4f$-shell on equal footing in FM ground state and finite temperature PM phase. The spectral density of states (SDOS) in the FM phase is directly related to the KKR Green's function, while in the PM phase the SDOS is evaluated from the configurationally averaged Green's function[41, 46]. For all the calculations we considered a hexagonal closed packed lattice with the experimental value of the c/a ratio of 1.5904, while the lattice constant was optimized to $a = 3.450$ Å. The optimization was performed with the commonly used $U = 6.7$ eV and $J = 0.7$ eV values, [4] and the LSDA parametrization from Ref. [47].

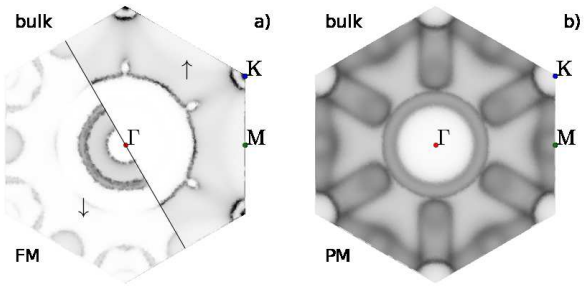

Figure 1. a) Spin resolved spectral DOS of the ferromagnetic phase and b) total spectral DOS of the paramagnetic phase of bulk gadolinium at the Fermi energy as projected to the 2D Brillouin zone. Darker colors represent larger values of the spectral DOS.

The spin resolved SDOS of the FM bulk and the total SDOS of the PM bulk is depicted in Fig. 1, projected onto the hexagonal two-dimensional (2D) Brillouin zone. As can be clearly seen in Fig. 1 a), the Fermi surface in the case of the FM phase shows a significant spin splitting in momentum space with concentric features around both the Γ and K points of the Brillouin zone, in agreement with ARPES experiments.[37] The minority (↓) components form a tight cylinder around the Γ point surrounded by a second cylinder consisting entirely of majority (↑) spin-states. A similar, but much narrower feature can be observed around the K points with the order of the spin channels reversed, that is the majority states form the inner and the minority components the outer cylinder. In the paramagnetic phase the splitting

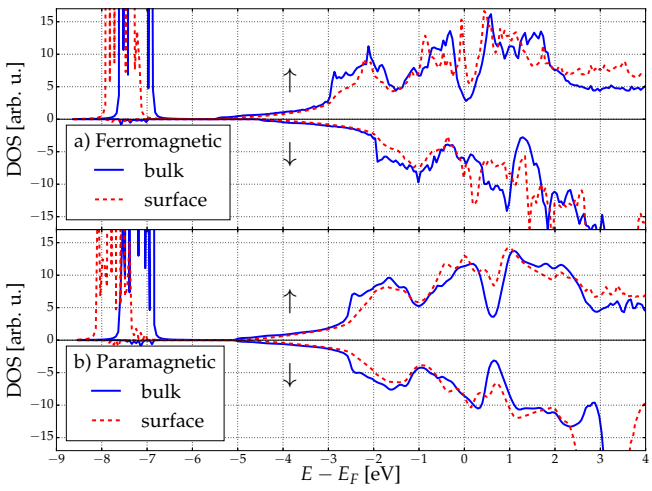

Figure 2. Spin resolved densities of states in Gd bulk and in the top layer of Gd(0001) surface in the a) ferromagnetic and b) paramagnetic phase.

disappears, only a single cylindrical feature is present around the Γ and K points, nicely recovering the experimental observations.[37] These experimental and theoretical findings seem to lead to the simple conclusion that a vanishing spin splitting in the paramagnetic phase is an indication of Stoner behavior, where the spin splitting depends on the total magnetization of Gd.

The densities of states for the bulk and surface in the FM and PM phases are depicted in Fig. 2. In the FM phase, similarly to the results of previous works [4–6, 10], the $4f$-electrons move away from the Fermi level with an exchange splitting of $\sim 11\,\mathrm{eV}$. Note that the relatively large dispersion of about 0.8 eV of the majority $4f$-states is due to spin-orbit splitting of these states. Clearly, in the PM phase very similar features of the density of $4f$-states can be found. The conduction electrons, dominated by $5d$-states, are characterized by a spin splitting on the order of 1 eV in the FM state. The magnitude of this splitting can be inferred from Fig. 2a), for example by comparing the onset of the majority d electrons at roughly $-3\,\mathrm{eV}$ below the Fermi energy to the onset of minority d-electrons at $-2\,\mathrm{eV}$. Another measure of the spin splitting would be to consider the shift of the minimum in the majority-spin DOS at the Fermi energy to roughly 1.2 eV above the Fermi level in the minority-spin DOS. The spin splitting of bulk states in the PM phase is somewhat harder to quantify with the above measures. A comparison of the position of the peak near the Fermi energy for the two spin channels suggests a largely reduced splitting of the order of 0.1 eV, as can be assessed from Fig. 2 b). At this point one might again conclude that an almost vanishing spin splitting in the PM phase indicates Stoner behavior.

In the FM phase we calculated a total spin moment of $7.77\,\mu_B$, that is, the polarization of the *spd*-band amounts to $0.77\,\mu_B$. In the PM phase the total spin magnetic moment is reduced to $7.41\,\mu_B$, which means that a considerable polarization of the conduction band still persists. These values are in agreement with recent disordered local moment calculations[11, 22] and also with studies performed for non-collinear magnetic configurations [14], where the $4f$-electrons are treated as part of the core. The finite value of the local moment related to the conduction band in the PM phase is indeed at the heart of the controversy, since there is (nearly) no splitting in the spin channels either in momentum space or in the energy resolved spectra.

The density of states at the surface, shown in Fig. 2, has two main characteristics. First, in accordance with previous results [6] and experimental observation,[48] the localized $4f$-states experience a down-shift in energy. This feature is slightly more pronounced in the PM phase than in the FM phase. The second feature, again in line with experiments, [21, 28, 30] is the appearance of new states absent in the bulk. The surface states in the FM phase near the Fermi energy are highly of majority-spin character. In the PM phase, we still detect a track of such surface states near the Fermi energy, but with a reduced spin polarization as observed in experiments.[21, 28] The spin magnetic moment per atom on the surface in the FM phase is found to be slightly reduced, compared to the bulk value, to $7.74\,\mu_B$. On the other hand, in the PM phase the magnetization slightly increases to $7.48\,\mu_B$ on the surface. Therefore, similarly to the case of bulk, the vanishing splitting of the spectral density of the surface states in the PM phase can not be regarded as a herald of Stoner magnetism. It is the asymmetry of the spectral weight for the two spin channels that is responsible for the finite residual local moment of the conduction band in the PM phase, suggesting a spin-mixing non-Stoner behavior.

As we stated before, most spectroscopic methods are surface sensitive. So far it is not clear how deep the effects of surface termination on the electronic spectra extend in to the bulk. To elucidate an answer for this question, in Fig. 3 we present the layer resolved spectral DOS at the Fermi energy for the first six layers below the (0001) surface and compare them with the bulk spectral function. The most pronounced effects of the surface can be seen on the first (surface) layer. In both phases a high intensity feature is present in the vicinity of the Γ point which is absent in the subsequent layers. In the FM phase an enhancement of the spectral density around the K points and along the lines connecting equivalent K points, forming a hexagram like structure, can also be attributed to the surface states. These highly spin polarized features gradually fade in deeper layers. In the PM phase no such distinctive spectral features are present near the surface. We merely observe a slight modulation in the SDOS along the $\Gamma - K$ direction in the region out of the disk of zero weight characterizing the bulk. Our

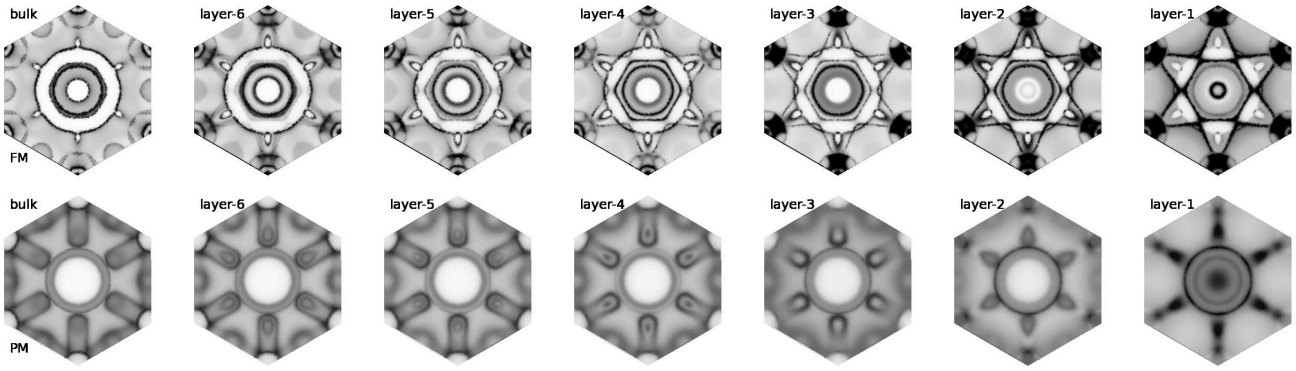

Figure 3. Spectral densities of states evaluated at the Fermi energy in the ferromagnetic (top row) and paramagnetic (bottom row) phases for Gd bulk and the first six layers below a Gd(0001) surface.

calculations show that the penetration depth of the surface states is different in the two phases. A bulk like spectral density is nearly recovered in the 3rd layer from the surface in the PM phase, while in the FM phase the SDOS even at the 5th-6th layers below the surface contain surface associated features. Thus one can deduce that the surface effects are more pronounced in the FM phase than in the high temperature PM state.

In conclusion, we provided a coherent first-principles study of the electronic and magnetic properties of the bulk and the surface of Gd metal, both in the ferromagnetic ground state and in the high temperature paramagnetic phase. Our results reveal the root of the existing controversy concerning the nature of magnetism related to the conduction band of Gd. A finite, though reduced, value of the spin moment related to the conduction band in the paramagnetic phase both in the bulk and for the surface implies a non-Stoner magnetism for these electrons. We argue that the asymmetry of the density of states with respect to different spin channels can be regarded as an indicator for this behavior rather than the spin splitting of the bulk conduction band or of the surface states, as it has been judged in many previous investigations. The asymmetry of the conduction spin-bands is generated by stable local $4f$-moments irrespective of their directions and it is the consequence of the formation of a common band, i.e. of a spin-mixing state.

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