PHYSICAL REVIEW B VOLUME 61, NUMBER 14 1 APRIL 2000-II

Electron correlation effects and magnetic ordering at the Gd(0001) surface

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(Received 29 September 1999)

Effects of electron correlation on the electronic structure and magnetic properties of the Gd(0001) surface are investigated using the full-potential linearized augmented plane-wave implementation of correlated band theory (''LDA+U''). The use of LDA+U instead of LDA (local-density approximation) total-energy calculations produces the correct ferromagnetic ground state for both bulk Gd and the Gd surface. Surface strain relaxation leads to a 90% enhancement of the interlayer surface-to-bulk effective exchange coupling. Application of a Landau-Ginzburg-type theory yields a 30% enhancement of the Curie temperature at the surface, in very good agreement with the experiment.

Many of the magnetic properties of Gd metal are well understood.[1] The half-filled $4f$ shell ($S=\frac{7}{2}, L=0$) of Gd leads to a formation of a well-localized spin-only magnetic moment. These localized spin moments couple through a Ruderman-Kittel-Kasuya-Yosida (RKKY)-type exchange interaction to form a ferromagnetic (FM) Heisenberg system with a bulk Curie temperature (T_C^b) of 293 K.[1] FM order polarizes the conduction electrons and leads to a total magnetic moment of $7.63\mu_B$/Gd atom.[2]

However, in spite of relatively simple bulk magnetic behavior, the magnetism of the Gd surface is rather unusual.[3] The results of different spectroscopic measurements suggest a significant enhancement of the surface Curie temperature (T_C^s) for Gd(0001). Gd is thus one of only three ferromagnets (including Tb and $FeNi_3$) for which such an increased T_C^s has been observed.[4] After a first observation of this effect in Gd by Rau *et al.*,[4] Weller *et al.* verified it for 400 Å thick Gd(0001) films grown on a W(110) substrate, by comparing spin-polarized low-energy electron diffraction (LEED) and the magneto-optic Kerr effect measurements,[5] and further suggested a possible antiferromagnetic (AFM) alignment of the surface layer(s) with respect to the bulk FM Gd. Further investigations with spin-polarized valence and core photoemission spectroscopy (PES) (Ref. 6) did not confirm an existence of this surface AFM coupling. Instead, the in-plane component of surface layer magnetization was observed to be parallel to the bulk,[6–8] although the possibility of canted or mixed in-plane and out-of-plane surface magnetic ordering was suggested. Very recent spin-polarized photoelectron diffraction experiments[9] for bulklike $\approx$300 Å thick epitaxial Gd/W(110) films clearly indicate temperature-dependent core-level spin asymmetries well above the bulk T_C^b, also suggesting surface enhancement of T_C^s of as much as 85 K. However, to date, there has been no quantitative theoretical explanation for this enhanced T_C^s.

The aim of this paper is to show that first-principles calculations which account for both electronic correlations of the $4f$ electrons and the relaxation of the surface atomic positions can provide such a quantitative description of the electronic and magnetic structure of the Gd(0001) surface. Using the results of total-energy calculations and the Landau-Ginzburg model we show that there is an increase of T_C at the Gd surface due to an enhanced surface-to-bulk effective exchange coupling that is in turn caused by the surface structure relaxation. We emphasize the substantial role of electron correlations for the Gd f electrons to obtain a correct FM ground state for both bulk Gd and the Gd surface. We also emphasize the role of structure relaxation as a ''driving force'' for the T_C enhancement.

I. DEFICIENCIES OF LDA AND GGA FOR Gd $4f$ ELECTRONS

Since the pioneering work of Dimmock and Freeman[10] there have been other attempts to describe the $4f$ states of Gd in terms of the localized ''$4f$-core'' electron model[11] (in which the $4f$ states of Gd are treated as a part of fully localized atomic core). Singh[12] performed a detailed analysis of the limitations of this ''$4f$-core'' model and achieved very good agreement with experiment for the ground-state lattice constant and the magnetic moment of FM bulk Gd by using a ''$4f$-band'' model and LDA, but he did not consider a possible AFM phase. Recent full potential linear ''muffin-tin'' orbitals (LMTO) calculations[13,14] show that both the LDA and the GGA yield an AFM phase that is lower in energy than the FM phase. This problem is solved by employing the LDA+U (Ref. 15) method to treat the electron correlations for the $4f$ electrons of Gd. It was demonstrated (Ref. 13) that the use of LDA+U (Ref. 15) instead of LDA yields a correct FM ground state and also provides $4f$ electron binding energies in good agreement with experiment. Recently we confirmed quantitatively the conclusions of Ref. 13 for bulk Gd using the LDA+U total-energy functional with the full-potential linearized augmented plane-wave (FLAPW) method.[16]

The first total-energy FLAPW calculations of the magnetic ordering at the Gd surface[17] using the $4f$-core model reported an AFM coupling of the surface layer with respect to the bulk, in agreement with early interpretation of experimental data.[5] The full potential LMTO calculations using the $4f$-core model[14] did not reproduce the results of Ref. 17 and yielded FM coupling between the surface and bulk magnetization, in agreement with the most recent experiments.[6–8] It is thus clear that (i) the $4f$-band model with LDA fails to

account for the correct magnetic ordering for bulk Gd, and the use of generalized gradient approximation (GGA) instead of LDA does not improve the situation and (ii) two LDA $4f$-core model calculations with LDA yield conflicting results (Refs. 14 and 17) for the magnetic ground state at the Gd surface.

Since the LDA+U method works well to describe the electronic structure and magnetic ground state for bulk Gd, we decided to apply it in electronic structure calculations and total-energy determinations of the magnetic behavior of the Gd surface.

II. SELF-CONSISTENT CALCULATIONS

The FLAPW method[18] is employed to perform scalar-relativistic self-consistent film calculations for Gd. The fully relativistic self-consistent version[19] of this method is then used to perform the final LDA calculations. The LDA+U calculations are based on the scalar-relativistic version of the FLAPW method.[16] The literature values[13] of the on-site repulsion $U=6.7$ eV and exchange $J=0.7$ eV were used in the calculations.

For the Gd(0001) surface, we choose the isolated slab model based on seven-layer Gd film (with z-reflection symmetry) and in the first set of calculations use the bulk lattice constant (3.634 Å) and c/a ratio (1.587).[20] Here, 32 special k points[21] in the irreducible 1/3 part of the two-dimensional (2D) Brillouin zone (BZ) (Ref. 22) were used, with Gaussian smearing for k points weighting. The ''muffin-tin'' radius values of $R_{MT}=3.2$ a.u. and $R_{MT}\times K_{max}=9.6$ (where, K_{max} is the cutoff for LAPW basis set) were used.

A. LDA results

The spin magnetic moments for a Gd film with its surface layer magnetically coupled parallel ($\uparrow\uparrow$) and antiparallel ($\downarrow\uparrow$) to the FM bulk resulting from the scalar-relativistic LDA calculations show that the magnetically active f states are almost fully polarized (with the magnetic moment $6.88\mu_B$ in the bulk and $6.82\mu_B$ at the surface) and induced spin polarization of $\approx 0.5\mu_B$/atom of conduction electrons (mainly d states). This magnetic coupling is a result of intra-atomic interband exchange interaction between conduction-band and localized f electrons as incorporated in the s-f exchange model[23] and can be understood to be due to a positive interband d-f exchange coupling.[24] There is a slight decrease of the $4f$ magnetic moment at the surface layer due to an increase of minority spin $4f$ occupation.

Starting from the results of scalar-relativistic calculations, we then performed self-consistent relativistic LDA calculations for a Gd film, assuming a [0001] spin axis direction. The spin moments are slightly decreased for f states in comparison with scalar-relativistic calculations, due to an increase of minority-spin occupation of the $4f$ states. The small spin-orbit induced orbital magnetic moments ($0.14\mu_B$ for the bulk and $0.33\mu_B$ for the surface atoms) are mainly due to the $4f$ minority-spin contribution. A parallel coupling between spin and orbital moments for $4f$ states is consistent with the third Hund rule. The orbital moments from $5d$ states are about $0.02\mu_B$ per Gd atom and coupled antiparallel to the spin moments, again consistent with the third Hund rule. The values of total magnetic moment (the sum of spin and orbital moments) are close to the values of spin moment from scalar-relativistic calculations.

TABLE I. Spin magnetic moments (M_s in μ_B) for a Gd film with surface layer coupled parallel to the FM bulk resulting from scalar-relativistic LDA+U calculations with experimental lattice constants.

M_s	layer	s	p	d	f	total
MT	C	0.016	0.079	0.46	6.97	7.536
MT	S-2	0.019	0.081	0.49	6.97	7.576
MT	S-1	0.011	0.093	0.50	6.97	7.588
MT	S	0.041	0.074	0.67	6.975	7.773
Interstitial:		2.076	Vacuum:		0.088	

The total-energy difference $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$ between the two surface magnetic configurations $\uparrow\uparrow$ and $\downarrow\uparrow$ defined above is positive (36 meV/atom in scalar-relativistic calculations) and does not change appreciably when spin-orbit coupling is included (40 meV/atom). The effect of the spin-orbit interaction is seen to be very small for the energetics of Gd due to the fact that the $4f$ spin-majority band is fully occupied and the $4f$ spin-minority band is almost empty. Therefore, the spin-orbit coupling does not affect the calculated values of magnetic and total-energy properties of Gd and does not assist in resolving the limitations of LDA.

B. LDA+U results

The spin magnetic moments for a Gd film with surface layer magnetically coupled parallel to the FM bulk resulting from the scalar-relativistic LDA+U calculations are shown in Table I. There is a moderate enhancement of the magnetic moment of $4f$ states compared to LDA values ($\approx 0.1\mu_B$/atom) due to an upward shift of 1.5 eV of minority-spin $4f$ states. There is practically no difference between surface and bulk f-state magnetic moments. The total magnetic moment at the surface layer is enhanced compared to the bulk mainly due to an increase of the d-state contribution.

The total-energy difference $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$ (71 meV/atom) is positive and of the same order of magnitude as the result of the $4f$-core model.[14] The results of the present LDA+U calculations for both bulk $\Delta E_{(AFM-FM)}$ (63 meV/atom[16]–the difference in energies between bulk AFM and FM spin configurations) and surface $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$ (71 meV/atom) are in reasonable agreement with the results of $4f$-core model calculations (85 meV/atom for the bulk and 95 meV/atom for the surface).[14] It shows that parallel coupling between surface and bulk magnetization is energetically preferable and there is no antiparallel surface-to-bulk magnetic coupling for the Gd surface. This conclusion is consistent with experimental observations of the in-plane component of surface layer magnetization to be parallel to the bulk.[6–8]

The electron density of states (DOS) for the case of (energetically preferred) $\uparrow\uparrow$ coupled surface layer are shown in Fig. 1. There is a 4.5 eV downward shift of the majority-spin $4f$ states and a 1.5 eV upward shift of minority-spin $4f$ states compared to the LDA calculation results. This latter shift makes the minority-spin $4f$ band practically empty and

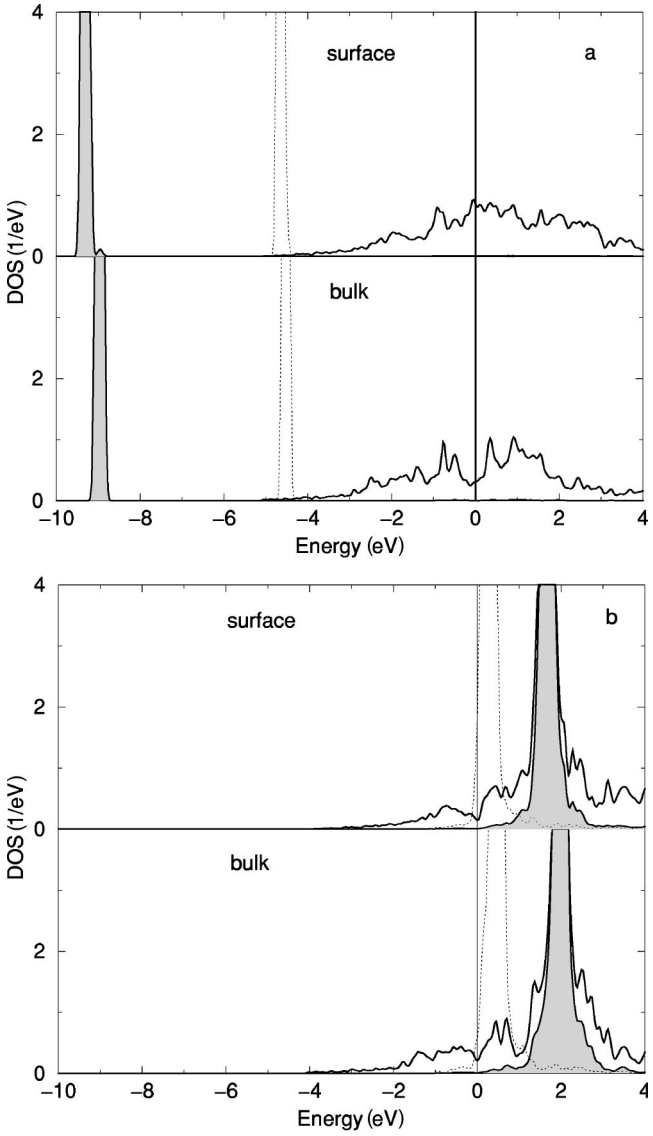

FIG. 1. DOS for Gd film: LDA+U spin up (a); spin down (b); $4f$ states (filled); LDA $4f$ states (dotted).

corrects the fundamental error of LDA $4f$-band model. The exchange splitting of 4f states is enhanced in LDA+U calculations by the amount of the Hubbard U (Ref. 16) resulting in an 11 eV splitting of majority and minority $4f$ states, close to the experimentally derived value (12 eV).[3] The formation of a surface state at the Gd surface clearly shows up as a peak of DOS in the vicinity of Fermi level (cf. Fig. 1) due to majority d states. From the DOS it is clear that LDA+U yields strongly localized character of $4f$ states for both bulk and surface. However, the response of the $4f$ states to their environment does not allow them to be considered as true core states.

In order to check numerical convergence of our results with respect to k-space integration, we increased the number of special k points in the irreducible part of 2D BZ (Ref. 22) from 32 to 50 in self-consistent calculations and found very little change in magnetic moment for both $\downarrow\uparrow$ and $\uparrow\uparrow$ magnetic configurations ($\leqslant 0.04\mu_B$). The calculated total-energy difference $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}=$ 72 meV per surface atom agrees very well with its value of 71 meV for a smaller number of k points.

TABLE II. Total-energy difference between two magnetic configurations with the surface layer magnetically coupled ($\downarrow\uparrow$) and ($\uparrow\uparrow$) to the FM bulk, $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$ (meV/atom), for a Gd surface with (a) an ideal bulk atomic structure, (b) a relaxed structure from experiment, and (c) an ''average'' structure and its ratio to the total-energy difference between AFM and FM bulk [ΔE(AFM-FM) $=63$ meV/atom]: $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}/\Delta E(\text{AFM-FM})=J_s/J_b$.

	$\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$	$\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}/\Delta E$(AFM-FM)
a	72	1.14
b	135	2.14
c	136	2.16

III. STRAIN RELAXATION AND MAGNETIC ORDERING AT THE Gd SURFACE

LEED measurements[25] show that there is atomic structural relaxation near the Gd surface: the interlayer distance between surface and subsurface Gd layers is about 2.6% smaller than its bulk value and the subsurface-to-bulk layer distance is about 1% bigger than its bulk value. We have performed LDA+U calculations with the surface and subsurface layers (i) with interlayer distances taken from the experiment[25] and (ii) with interlayer relaxations taken to be half way between the experimental surface values and the bulk values. As in the case of an ideal Gd surface we have considered two possible magnetic configurations ($\uparrow\uparrow$, $\downarrow\uparrow$) with the surface layer coupled parallel and antiparallel to the FM bulk Gd. Here, 50 special k points in the irreducible 1/3 part of the 2D BZ were used.

The surface relaxation affects very little the values of the magnetic moment in comparison with the ideal surface: for both cases of $\uparrow\uparrow$ and $\downarrow\uparrow$ coupled surface layer there is a slight decrease in the values of the surface and subsurface layers magnetic moment due to the change of conduction-band magnetization caused by reduced interlayer distance. There is, on the other hand, a surprisingly large enhancement of the magnetic coupling energy $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$ (cf. Table II) due to the surface relaxation: the energy difference increases by 90% in the comparison with the unrelaxed structure.

As was already mentioned, there is considerable experimental evidence of T_C enhancement at the Gd surface. Since $4f$-magnetic moments are well localized and interact due to RKKY type exchange interactions, the use of the Heisenberg-type Hamiltonian for the dependence of energy on spin configuration is physically justified for Gd. For the sake of simplicity, we neglect the long-range behavior of exchange interactions for the Gd bulk and surface, assuming that significant physics can be discussed in terms of nearest-neighbor (NN) interactions and neglect anisotropy in exchange interaction between a Gd atom and its six in-plane and six interplane NN in the bulk and three interplane NN at the surface. The spin Hamiltonian is then given by

$$H=-B_0\sum_i \hat{S}_i-\sum_i\sum_\delta J_{i,i+\delta}\hat{S}_i\hat{S}_{i+\delta}, \qquad (1)$$

where B_0 is an external field, $J_{i,i+\delta}$ is an exchange coupling constant between the spin i and its δ NN (J^b in the bulk and J^s at the surface) and $\hat{S}_i$ is a spin operator. We then apply ''molecular-field'' theory[26] to Eq. (1). It leads to different

molecular fields acting on the spin at the surface and in the bulk, due to the different number of the interplane NN (six in the bulk, three at the surface), and the difference between bulk and surface exchange coupling constants J_b and J_s. In the vicinity of the Curie temperature, when the value of the average spin moment $\langle S(T)\rangle$ is small, it is possible to introduce a Landau-Ginzburg-type model for the temperature dependence of $\langle S(T)\rangle$ (Ref. 27) using the continuum limit of the molecular field theory. Applying the procedure of Ref. 27 to the case of the hcp(0001) surface, we obtain the result that, for an exchange coupling ratio that satisfies

$$1.5-2\frac{J_b}{J_s}\geqslant 0 \quad \text{or} \quad \frac{J^s}{J^b}\geqslant 4/3, \tag{2}$$

there is in addition to the bulk Curie temperature T_C^b an additional pole in the static magnetic susceptibility corresponding to a surface Curie temperature T_C^s which is connected to the bulk T_C as

$$T_C^s=[1+(1.5-2J_b/J_s)^2]T_C^b, \quad T_C^b=\frac{12J_bS(S+1)}{3k_B}. \tag{3}$$

It is seen from the condition Eq. (2) that the additional surface T_C^s can appear when the exchange coupling at the surface is bigger than it is in the bulk. The ratio $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}/\Delta E(\text{AFM-FM})$ (cf. Table II) is then used to determine J^s/J^b in Eq. (2).[28] In the case of an ideal surface the condition Eq. (2) is not satisfied and there is no additional T_C^s. However, when the surface relaxation is taken into account, the condition Eq. (2) is satisfied and Eq. (3) yields $T_C^s=1.33T_C^b$ in very good quantitative agreement with the recent experimental data[9] ($T_C^s\approx 1.29T_C^b$). The use of the total-energy differences (cf. Table II) leads to overestimated values for the exchange interaction parameters in metallic magnetic systems.[13] The ratio of the surface and the bulk T_C should however be much more reliable than their absolute values. Further justification of the magnetic order near the Gd surface will require the consideration of the long-range behavior of exchange interactions in Eqs. (1) and (2) and the use of Monte Carlo numerical simulations.[29]

To summarize, we have presented the results of one of the first applications of the LDA+U total-energy method to study the magnetic and electronic properties of a correlated metal. We have found that the use of LDA+U instead of LDA yields FM alignment between surface and bulk magnetic moments, in agreement with experiment. An interlayer surface-to-bulk effective exchange coupling is calculated to be close to its bulk value for an ideal surface, but is enhanced by 90% by surface relaxation. This enhancement is sufficiently strong to produce an elevated Curie temperature at the surface, as observed experimentally.

ACKNOWLEDGMENTS

This research was supported by National Science Foundation Grant No. DMR-9802076 and U.S. Department of Energy, under Contract No. DE-AC03-76F00098.

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