Electron correlation effects at the Gd(0001) surface

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We have performed full-potential linearized augmented plane wave calculations of the Gd(0001) surface using the local density approximation (LDA) together with the Hubbard U (LDA+U) total energy functional. The use of LDA+U instead of LDA total energy calculations leads to a ferromagnetic ground state for both bulk Gd and the Gd surface, in agreement with experimental observation. The calculated downward shift of $4f$ eigenvalues for the Gd surface is in agreement with experimentally observed binding energies. 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. © *2000 American Institute of Physics.*
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The magnetic properties of Gd metal are well understood.[1] The half-filled $4f$ shell of Gd leads to a formation of well localized spin-only magnetic moments which are coupled through a RKKY exchange interaction to form a ferromagnetic (FM) Heisenberg system with a Curie temperature (T_c) of 293 K (Ref. 1) in the bulk.

However, the magnetism of the Gd surface is rather unusual.[1] The results of different spectroscopic measurements suggest a significant enhancement of the surface Curie temperature (T_c^s) for Gd(0001). Very recent spin-polarized photoelectron diffraction experiments[2] for bulklike ≈ 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.

The aim of this paper is to provide a quantitative description of the electronic structure and magnetic properties of the Gd(0001) surface using the results of first principles electronic structure calculations and taking into account electron correlations for $4f$ electrons. We emphasize the substantial role of electron correlations for the Gd f electrons to obtain a correct electronic structure and magnetic ordering for both bulk Gd and the Gd surface. A detailed description of the computational technique is given in Ref. 3.

(1) Bulk Gd: The recent full potential LMTO calculations[4,5] demonstrated that both LDA and generalized gradient approximation (GGA) fail to reproduce experimentally observed FM ground state for Gd: the AFM state was calculated to be lower in the total energy than FM state (Table I).

It was shown[4] that ''LDA+Hubbard U'' method (LDA+U) yields a correct FM ground state of Gd. We have performed LDA+U calculations for the bulk Gd with the full-potential LAPW method.[6] The spin magnetic moment for FM and AFM Gd are shown in Table I for both LDA and LDA+U calculations. The LDA result was in nearly perfect agreement with experiment, and the 2% increase given by LDA+U does not degrade the agreement much. The energy difference E(AFM)−E(FM) is negative in LDA calculations and positive in LDA+U calculations and in accord with the

conclusion of Ref. 4. The use of LDA+U instead of LDA produces significant changes in the energy positions of $4f$ states: there is a large (4.5 eV) shift of spin-majority f states below the Fermi level and removal of the unoccupied spin-minority f states from close vicinity of the Fermi level due to an upward shift of 1.5 eV.

(2) The Gd(0001) surface: The LDA $4f$-core model calculations[8] yield conflicting results (Refs. 5 and 9) for the magnetic ground state at the Gd surface: the full-potential LAPW calculations of Ref. 9 reported an AFM coupling of the surface layer with respect to the FM bulk; the full potential LMTO calculations of Ref. 5 did not reproduce the results of Ref. 9 and yielded FM coupling between the surface and bulk magnetization, in agreement with the recent experiments.[10] Since the LDA+U method works well to describe the electronic structure and magnetic ground state for bulk Gd, we applied it in the full-potential LAPW calculations of the Gd surface.

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 constants.[7] Two magnetic configurations for a Gd film with its surface layer magnetically coupled parallel ($\uparrow\uparrow$) and antiparallel ($\downarrow\uparrow$) to the FM bulk were considered (a detailed description of the calculations is given in Ref. 11). The bulk values[4] of the on-site repulsion $U=6.7$ eV and exchange $J=0.7$ eV were used in the calculations. These values of U and J[4] for the bulk Gd are in agreement with the values

TABLE I. The spin moments (in μ_B) and the total energy difference (in meV) between antiferromagnetic (AFM) and ferromagnetic (FM) phases for the bulk Gd.

	LDA	LDA+U	Exp.	
FM	7.659	7.818	7.63	
AFM	7.246	7.437		
E(AFM-FM)	LDA+U	LDA+U (Ref. 4)	LDA	LDA (Ref. 5)
per atom, meV	63	68	−2	−3
			GGA (Ref. 4)	GGA (Ref. 5)
			−17	−25

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TABLE II. Spin magnetic moments M_s (in μ_B) for a Gd film with surface layer coupled parallel to the FM bulk. For ''muffin-tin'' (MT), these values are integrals over a ''muffin-tin'' sphere of radius 3.2 a.u.

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

obtained in Ref. 12 from the experimental data for the Gd compounds. It shows that due to the highly localized character of the Gd f states the value of U is not affected by the screening contribution of a metallic environment, and allows to use the bulk values of U and J for the Gd surface.

The spin magnetic moments for a Gd film with surface layer magnetically coupled parallel to the FM bulk resulting from the LDA+U calculations are shown in Table II. There is an 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 $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$ (72 meV/atom) is positive and of the same order of magnitude as the result of the $4f$-core model (95 meV/atom).[5] 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 in accord with experimental observation.[2,10]

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 $4f$ states and a 1.5 eV upward shift of minority $4f$ states compared to the LDA calculation results. This latter shift makes the minority spin $4f$ band practically empty and corrects the fundamental error of LDA $4f$-band model. The exchange splitting for f states increases from 5 eV with LDA to 11 eV with LDA+U, close to the experimentally derived value (12 eV).[1] The formation of a surface state at the Gd surface clearly shows up as a peak of DOS in the vicinity of Fermi level (Fig. 1) due to majority d states. From the DOS it is clear that LDA+U method produces 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.

(3) $4f$ states binding energies at the Gd surface: The experimental data for majority and minority $4f$ state binding energies for bulk and surface are shown in Table III.[13] The energy positions of majority f states are in reasonable agreement with XPS measured binding energies when LDA+U instead LDA is used. The comparison between present LAPW results, the results of previous LMTO-ASA[16] and LMTO[4] calculations show that all LDA+U calculations agree within 10% with experimental data.
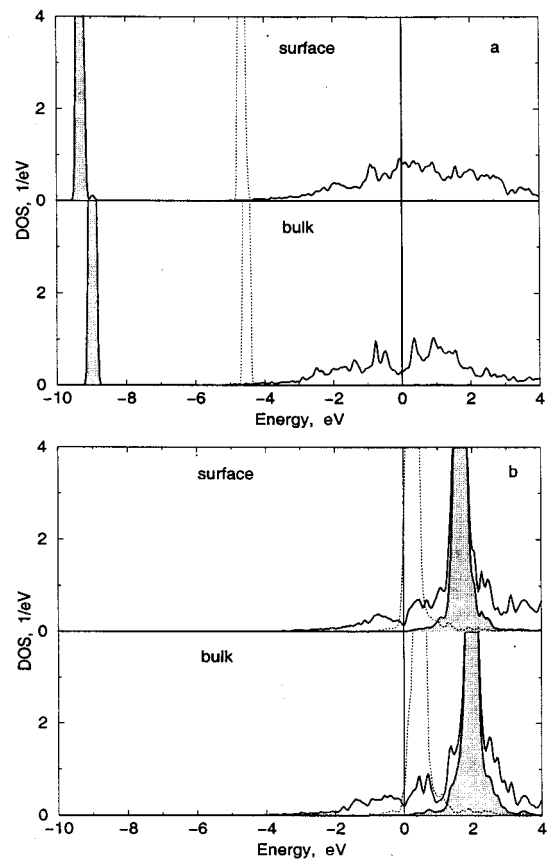

FIG. 1. DOS for Gd film: LDA+U spin-up (a); spin-down (b) $4f$ states (filled); LDA $4f$-states (dotted)

For minority f states (cf. Table III) there is some disagreement between LAPW and LMTO results. Both methods yield an upward shift for eigenvalues but LMTO eigenvalues are 1–1.5 eV higher than LAPW. At present the reason for the difference is not clear. The comparison of unoccupied $4f$ minority eigenvalues with experimental excitation energies does not resolve the question, since calculated eigenvalues do not quantitatively represent excited states.

Recent experiment (XPS and BIS) on strained Gd films on W(110)[17] show that there is a downward shift (≈ 0.4 eV) at the surface for both occupied and unoccupied $4f$ states binding energies. The LMTO-ASA LDA+U supercell calculations[16] confirm this prediction theoretically. Our

TABLE III. Binding energies (eV) for surface and bulk Gd for occupied spin-majority $\uparrow$ and unoccupied spin-minority $\downarrow$ $4f$ states

Bulk		$\uparrow$		$\downarrow$
	LDA	LDA+U	LDA	LDA+U
LAPW	−4.5	−8.8	0.5	2
LMTO (Ref. 4)	−4.3	−8.2	0.7	3.5
Exp.		−8.05 (Ref. 17),		4.5 (Ref. 17),
		−8.5 (Ref. 14)		3.5 (Ref. 16)
Surface		$\uparrow$		$\downarrow$
LAPW	−4.7	−9.1	0.3	1.7
Exp.		−8.5 (Ref. 15),		4.1 (Ref. 17)
		−8.8 (Ref. 15)		

LAPW LDA+U calculations yield very similar results (cf. Table III). We calculate a 0.3 eV downward shift for both occupied majority and unoccupied minority states, in agreement with previous calculations and experiment. In spite of this surface shift, the exchange splitting between occupied majority and unoccupied minority $4f$ states is calculated to be the same for bulk and surface.

(4) Strain relaxation and magnetic ordering at the Gd surface: LEED measurements[18] 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 experiment[18] and (ii) with interlayer relaxations taken to be halfway 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 ($\uparrow\uparrow$, $\downarrow\uparrow$) for the surface layer coupled to the FM bulk Gd.

There is a surprisingly large enhancement of the magnetic coupling energy $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}$ due to the surface relaxation: the calculated energy difference of 135 meV for relaxed structure from experiment, and of 136 meV for an ''average'' structure (between bulk and relaxed surface interlayer distances) increases by 90% in comparison to the unrelaxed structure (72 meV). We then assume the Heisenberg-type of spin Hamiltonian with the nearest-neighbor exchange interactions and determine the change of exchange interaction parameters at the surface from the ratio $\Delta E_{(\downarrow\uparrow-\uparrow\uparrow)}/\Delta E(\text{AFM}-\text{FM})$. Applying then the Landau–Ginzburg model of Ref. 19 for the temperature dependence of the magnetization, we obtain the result that in the case of an ideal surface the enhancement of exchange coupling is not sufficient to produce an additional surface T_c^s. However, when the surface relaxation is taken into account, the model yields $T_c^s = 1.33T_c^b$ in very good quantitative agreement with the recent experimental data[2] ($T_c^s \approx 1.29T_c^b$).

To summarize, 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. The LDA+U calculations reproduce quantitatively the exchange splitting between occupied majority and unoccupied minority $4f$ states and downward shift for $4f$ states binding energies. 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.

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