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Presented at the Magnetic Properties of Low-Dimensional Systems, Taxco, Mexico, January 6-9, 1986; and published in the Proceedings, L.M. Falicov and J.L. Moran-Lopez, Eds., Springer-Verlag, New York, NY, 1986

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January 1986

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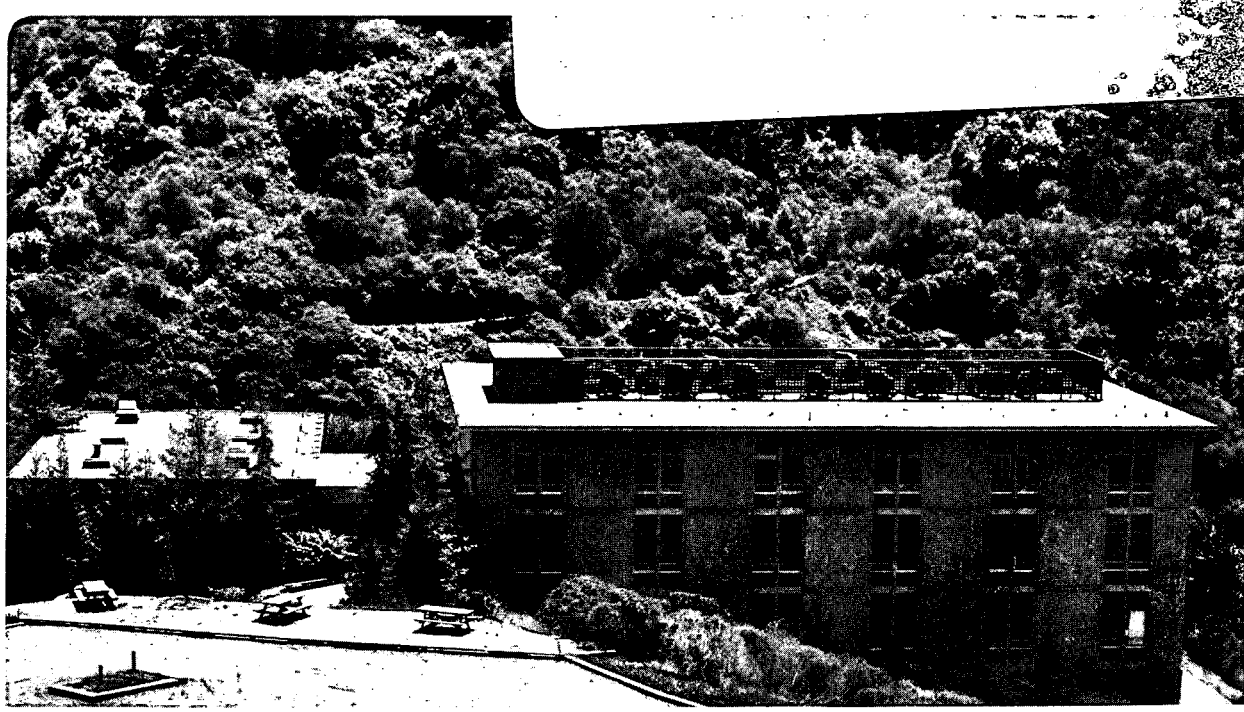

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MAGNETIC AND ELECTRONIC PROPERTIES OF TRANSITION-METAL SURFACES AND OVERLAYERS*

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January 1986

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*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Magnetic and Electronic Properties of Transition-Metal Surfaces and Overlayers

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Results of calculations for the magnetic and related electronic properties of transition-metal surfaces and overlayers are presented for a variety of systems. They involve Co, Fe, and Cr in a diversity of forms, including alloys, metastable configurations, and overlayers on nonmagnetic metals. The overall behavior of these systems is interpreted in terms of four qualitative rules which are presented, analyzed, and illustrated.

1. Introduction

There is considerable current interest in the magnetic and related electronic properties of 3d magnetic transition-metal surfaces and overlayers. These metals exhibit itinerant magnetism: Their magnetization derives from the spin polarization of the itinerant d electrons. In moving down the periodic table from Ni, there is a decrease in the number of these d electrons (an increase in the number of d holes), and a consequent increase in the bulk magnetization [1] from 0.61 Bohr magnetons in Ni, to 1.72 in Co, and 2.22 in Fe. Beyond Fe lie the more complicated magnetic structures of Mn and Cr. In particular Cr has an antiferromagnetic ground state [2] in which at the maximum of an incommensurate spin density wave there is a magnetization of 0.59 Bohr magnetons. In all these elements, the itinerant nature of the d electrons makes the magnetic properties a sensitive function of local environment. Consequently the presence of a dissimilar neighbor, as found in an interface, or the absence of some neighbors, as found at a surface, may cause considerable changes in the local magnetic properties.

We have calculated the electronic and magnetic properties for many surface and overlayer systems [3-6]. We used a Slater-Koster parametrized tight-binding scheme in which the one- and two-center integrals are fitted to the bulk band structures of the elements; 4s, 4p and 3d electrons are included. The electron-electron interaction consists of single-site contributions and is sufficiently general to allow for realistic effects such as nonrigid exchange splitting. The interaction is treated self-consistently in the Hartree-Fock approximation. Our scheme (see Table 1) has been tested against experimental data [7,8] and against state-of-the-art first-principles calculations [9,10] on several occasions, and has produced consistently excellent agreement [3-6,11,12].

This contribution provides a summary of our most important predictions for the magnetic and related properties of a variety of surface and overlayer systems. Within each section, background information on the important issues and material properties is presented. Comparisons with experiment and other theories are made, and our most unusual or unexpected results are examined in detail.

Finally, the combination of our results with those of previous workers allows, in the concluding section, the derivation of a set of qualitative rules for the behavior of the magnetization in heterogeneous systems.

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TABLE 1
Hamiltonian Parameters.

Listed are the 24 Slater-Koster tight-binding matrix elements, the U necessary to produce the correct spin polarization, and the occupancies in the paramagnetic state. A slightly different (wider conduction band) set of bcc Co parameters was used in the Co on Cu calculation. The set listed was used for the FeCo calculations and is believed to be more accurate.

	bcc Cr	bccFe	fcc Fe	bcc Co	fcc Co
$(ss)_0$	.594	.514	.600	.507	.560
$(pp)_0$	1.173	1.118	1.384	1.111	1.344
$(dde_g)_0$	+.005	-.068	-.051	-.076	-.092
$(ddt_{2g})_0$	-.016	-.089	-.063	-.094	-.102
$(ss\sigma)_1$	-.10605	-.10605	-.07452	-.10605	-.07452
$(sp\sigma)_1$	-.19326	-.19326	+.14706	-.19326	+.14706
$(sd\sigma)_1$	-.08740	-.08018	+.08777	-.07537	+.08209
$(pp\sigma)_1$	+.26932	+.26932	+.30843	+.26932	+.30843
$(pp\pi)_1$	-.00672	-.00672	-.01129	-.00672	-.01129
$(pd\sigma)_1$	.10807	+.09915	+.11339	+.09320	+.10605
$(pd\pi)_1$	-.02689	-.02467	-.02049	-.02319	-.01917
$(dd\sigma)_1$	-.06735	-.05669	-.05217	-.05009	-.04563
$(dd\pi)_1$	+.04441	+.03738	+.02647	+.03303	+.02315
$(dd\delta)_1$	-.00795	-.00669	-.00290	-.00591	-.00254
$(ss\sigma)_2$	-.05276	-.05276	-.05495	-.05276	-.05495
$(sp\sigma)_2$	-.06725	-.06725	+.08064	-.06725	+.08064
$(sd\sigma)_2$	-.03308	-.03035	.00000	-.02853	.00000
$(pp\sigma)_2$	.17199	+.17199	+.15017	+.17199	+.15017
$(pp\pi)_2$	.03242	+.03242	-.05749	+.03242	-.05749
$(pd\sigma)_2$	.05670	+.05202	.00000	+.04890	.00000
$(pd\pi)_2$	-.00100	-.00092	.00000	-.00086	.00000
$(dd\sigma)_2$	-.04000	-.03367	.00000	-.02975	.00000
$(dd\pi)_2$	.01188	+.01000	.00000	+.00884	.00000
$(dd\delta)_2$	-.00089	-.00075	.00000	-.00066	.00000
U	.167	.220	.220	.296	.296
n^0_{sp}	1.175	1.185	1.154	1.174	1.150
n^0_{t2g}	3.258	4.223	3.954	4.478	4.448
n^0_{eg}	1.567	2.592	2.892	3.348	3.404
n^0_{total}	6.000	8.000	8.000	9.000	9.000

2. Surfaces of Ferromagnetic Iron and the Ferromagnetic Ordered Iron-Cobalt Alloy

The effort to understand surface behavior must start with an understanding of the bulk material. Iron is an element of great technological importance and its properties have been extensively examined. For our purposes, it is sufficient to note that Fe possesses a g factor [1] of approximately 2.10 and thus a spin polarization of 2.12. This means that Fe is ferromagnetically weak, i.e., not all available d holes contribute to the magnetization. This has been shown [11] to be a direct consequence of a relatively weak electron-electron interaction.

The Fe-Co alloy is also technologically important [13]. This alloy possesses several useful characteristics such as the largest known magnetization per atom and an extremely high Curie temperature. In particular, the ordered FeCo alloy, which consists of Fe and Co atoms arranged at the corner and body-centered positions of a simple-cubic lattice, has a magnetization of 2.42 μ_B per atom [14]. This is 0.45 μ_B higher than the average of its constituent elements. Neutron-diffraction studies [15] indicate that the vast majority of the anomalous increase in the magnetization is caused by an increase in the Fe magnetic moment from 2.2 μ_B to

approximately 3.0 μ_B, while the Co magnetic moment increases only slightly. MEYER and ASCH [16] found the g factor of the equiatomic alloy to be approximately 2.15, thus suggesting that the spin polarization is 2.25 ± 0.01. Victora and Falicov demonstrated [11] that, at least for the disordered equiatomic alloy, the increased magnetization is caused by magnetic saturation made possible by the presence of the strong Co electron-electron interaction.

A wide variety of experimental techniques [7-8,17-22] show that the surface layer of a magnetic 3d transition metal is magnetic, while recent theoretical studies demonstrate that the surface magnetization is, in fact, enhanced relative to the bulk value [10,12,23]. In particular, theory predicts a spin polarization of 2.98 electrons for the Fe(100) surface [10] and approximately 0.70 electrons for the Ni surfaces [12,23]. The experimental evidence of GRADMANN et al. [7] suggests that the magnetization of the Fe(110) surface is enhanced by approximately 30%. It is found [24] that Fe atoms segregate to the surface of the Fe-Co alloy.

Our calculation gives a surface spin polarization for the Fe(100) surface of 2.90 electrons. The enhanced magnetization penetrates some distance into the bulk: The second, third, and center layers have spin polarizations of 2.30, 2.24, and 2.18 electrons, respectively. These results are very similar to those of OHNISHI et al. [10]. In particular, their surface spin polarization is 2.98 electrons and their calculated DOSs also resemble ours, although 5-10% narrower. This excellent agreement between two different calculational techniques confirms the accuracy of our methods. We find that the spin polarization also increases at the Fe(110) surface, where it reaches a value of 2.55. This is in agreement with the experimental results of GRADMANN et al. [7]. The relative magnetizations of bulk Fe and the two surfaces are easily explained by noting that nearest-neighbor interactions dominate the d-band width (matrix elements are proportional [25] to $(\text{distance})^{-5}$ and the first-nearest-neighbor distance is $(1/2)\sqrt{3}$ smaller than the second-nearest-neighbor (distance)). The bulk atom in the bcc structure has eight nearest neighbors, an atom on the (110) surface has six, and an atom on the (100) surface has four. Thus the (100) surface has the fewest neighbors, smallest bandwidth, the same electron-electron interaction as the other geometries, and consequently the highest magnetization. The atom on the (110) surface has an intermediate number of neighbors and consequently will have an intermediate magnetization.

A necessary prerequisite to the study of the FeCo surface properties is a proper understanding of the bulk material itself. We calculate the spin polarization of bulk FeCo to be 4.44 electrons per unit cell, thus capturing more than 90% of the experimental enhancement observed in the alloy relative to the average of the pure elemental magnetization. Most of the increase is found to occur on the Fe atom, where the presence of eight neighboring Co atoms helps increase the effective electron-electron interaction and saturates the moment. The much smaller magnetic enhancement found on the Co atom is caused by the shift from fcc to bcc structures and possibly a slight swelling in the lattice constant as iron is added.

The simple-cubic FeCo structure may be cut by the (100) plane, leaving either all Fe atoms at the surface or all Co atoms. The DOS of the Fe surface bears a strong resemblance to the DOS at the elemental Fe(100) surface. The spin polarization is 2.95 electrons, which is also very similar to the Fe(100) result of 2.90 electrons. These results suggest that the presence of the (100) surface is the dominant effect and that the precise nature of the second layer is not too important for the surface Fe layer. This is reasonable since, as previously observed, the effect of Co is to increase the effective electron-electron-interaction to bandwidth ratio at the Fe atom and it is clear from Fe(100) results that a (100) surface can do this much more effectively. Consequently, the presence of Co instead of Fe is somewhat unimportant. The one major difference is that the surface effects are not able to penetrate even one layer deep into the bulk. This is presumably because Co, unlike Fe, has a saturated magnetization. Consequently, spin polarization and related properties are less susceptible to perturbation.

The all-Co surface has slightly larger exchange splitting and spin polarization than the bulk (2.03 vs. 1.78 electrons). Interestingly, there is a very slight (0.1 electron) decrease in the spin polarization of the underlying Fe layer. However, even this effect vanishes at the next Co layer and deeper. Overall, the surface behaves like Ni surfaces [12,23] in that the surface DOS is narrowed and new features appear, but the magnetic saturation allows only small increases in the magnetization.

The (110) surface of FeCo contains both Fe and Co atoms arranged in a two-atom unit surface cell. As expected from the nearest-neighbor arguments given previously, the (110) surface displays behavior intermediate between bulk FeCo and the (100) FeCo surfaces. The calculated spin polarizations at the surface are 2.75 electrons for Fe and 1.86 electrons for Co. There is very little penetration of surface effects into the bulk.

Experimental and theoretical studies indicate that Fe tends to segregate to the surface of the FeCo alloy. To represent this, we have calculated the electronic properties of a Fe(110) overlayer, one atom thick, atop the FeCo alloy. The spin polarizations are 2.63 electrons for the Fe atom occupying the Co position and 2.67 electrons for the Fe atom occupying the normal position. Clearly, the two Fe atoms have very similar electronic properties. It is to be noted that their properties are intermediate between the Fe(110) surface and the FeCo(110) surface.

This section has examined two Fe surfaces, bulk FeCo, three FeCo surfaces, and the segregated surface. These systems have served to exemplify two very important ideas: (1) Surfaces tend to increase magnetization; and (2) Co is magnetically saturated; Fe is magnetically weak. These two ideas will reappear in later sections and, finally, be made more specific in the conclusion.

3. Cobalt Overlayers on Copper (111)

Recently, there has been renewed interest in the magnetism and related properties of thin magnetic transition-metal layers deposited on non-magnetic substrates. Experimental evidence shows that two layers of Ni on Cu form a magnetic system [22,26], but Ni on a Pb-Bi alloy substrate or on an Al substrate is paramagnetic below 2.5-3 atomic layers [27,28]. However, Co and Fe retained their magnetic moment on these same substrates, even when deposited in subatomic layers [27,28]. Theoretical investigation shows that one layer of Ni on Cu(100) is substantially magnetic [9,12] while the same system on the (111) surface is not [12]. As discussed in the previous section, the effect of a surface is to increase the magnetization. This suggests that any possible reduction in magnetization is caused by the substrate. In fact, it is believed [12] that the crucial mechanism acting to suppress Ni magnetization at the Ni-Cu interface is hybridization of the Ni d band with the Cu sp band, which changes the shape of the band edge and reduces the "effective" number of d holes. Both Fe and Co, which have many more holes, should be relatively immune to this effect.

The particular system addressed in this section [Co on Cu(111)] has also been studied previously. GONZALEZ et al. [29] and MIRANDA et al. [30] used angle-resolved photoemission spectroscopy to determine a surface density of states for one and two layers of Co deposited on a clean, well-ordered Cu(111) surface. Observations at the surface Brillouin-zone center produced several large peaks, one of which is near the Fermi energy and thus not normally associated with the Cu density of states (DOS). The similarity between this peak and a bulk Co DOS, interpreted as ferromagnetic by HIMPSEL and EASTMAN [31], suggested to them that Co is magnetic with an exchange splitting of 0.7 eV at the T point of the surface Brillouin zone. Further support for the ferromagnetism of this system arises from Mossbauer spectroscopy which shows that two and four layers of Co are magnetic when epitaxially grown on Cu(111) surfaces [32].

In this section I present results of calculations for the magnetic properties of thin (one- and two-layer) Co films deposited on the Cu(111) surface. Calculations

are performed using both a one-atom hexagonal unit surface cell (symmetry C_{3V}) and a two-atom rectangular unit cell. This latter cell permits possible breaking of spatial symmetry such as antiferromagnetism, ferrimagnetism, etc.

Our calculations show that for one layer Co on the Cu(111) surface, the spin polarization of the Co atom equals 1.63. However, approximations within the calculation may slightly exaggerate this polarization which suggests that the true value is essentially unchanged from the bulk value: 1.56. This is in interesting contrast to the case of Ni on the Cu(111) surface in which the Ni magnetization is greatly suppressed. Of course, there is no contradiction present since previous calculations [12] have shown that small changes in substrate orientation or material composition can produce large effects. This is attributable to the delicate balance between two competing effects: enhancement by the surface and suppression by the substrate hybridization.

The d orbitals of the Co layer can be classified uniquely by specifying their bulk and surface symmetries. This facilitates detailed examination of the distribution of magnetization among orbitals. One finds that the orbital of symmetry Λ_1 has significantly less spin polarization and exchange splitting than the orbitals of symmetry Λ_3. This is presumably due to its geometric orientation perpendicular to the (111) plane, which means that it points directly into the Cu substrate. In addition, its symmetry is the same as most of the Cu sp electrons, which facilitates hybridization. One interesting conclusion to be drawn is that rigid-band exchange splitting is only approximately obeyed in this Co-on-Cu(111) system. This contrasts to the bulk system, where our calculations found only negligible (less than 1%) exchange-splitting difference between orbitals.

We also performed our calculations for two layers of Co-on-Cu(111). The top and second layers have spin polarizations of 1.65 and 1.58, respectively. The spin polarization is distributed much more evenly between orbitals although, relative to the Λ_3 states, the Λ_1 orbital has a slightly enhanced (~0.06) value in the surface layer and a slightly suppressed (~0.05) value in the second layer. The Cu atoms have negligible spin polarization (~0.01) independent of the number of Co overlayers.

Agreement between our theory and the experiment of Miranda and co-workers is considerable, but discrepancies do exist. The quantitative correspondence between theoretical and experimental peak locations for one layer Co-on-Cu is excellent. The photoemission spectra at the K point for both this system and for the clean Cu(111) surface can be consistently explained by theoretical states which transform according to Λ_1, the identity representation. More disappointing is the experimentally observed absence of the theoretically predicted shift in peak locations as an additional layer of Co is added. The experimentally observed displacement in Co peak location with photon energy is also puzzling, since monolayer states can have no dispersion.

Through the employment of the two-atom rectangular unit surface cell discussed previously, we have found three locally stable configurations for the system consisting of one layer of Co-on-Cu(111). The simplest of these is the ferromagnetic arrangement discussed earlier. In this state both of the atoms in the unit cell possess equal polarizations and are identical in all respects.

We also examine an antiferromagnetic state in which the spin polarizations of the two atoms in the unit cell have equal magnitude (1.51 per atom) but opposite orientation. Those states which possess a positive reflection symmetry are found to have the lowest spin polarization, presumably due to their hybridization with the Cu s states. The total energy of this configuration is found to be considerably higher (0.15 Ry per surface atom) than that of the ferromagnetic system, which implies that it is not the ground state.

Our third configuration is a new kind of state which we call "spatially modulated." This state possesses an approximately equal polarization of 1.60 on

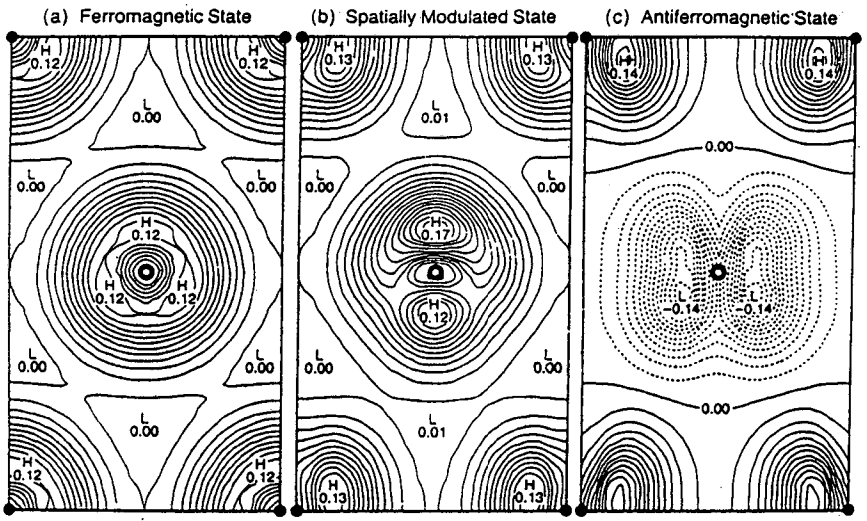

Fig. 1. Real-space magnetization density of a Co monolayer on Cu(111): the Co surface layer for (a) ferromagnetic state; (b) spatially modulated state; (c) antiferromagnetic state. Spin-up density contours are plotted in full lines; spin-down density contours in dashed lines. All graphs are projections on the Co(111) plane of the magnetization of the "vacuum" half-space.

each atom of the unit cell, but it is distributed differently between the orbitals. The first three orbitals, which form the t_{2g} representation in the bulk, have equal polarization on both atoms; but the last two orbitals, the "e_g orbitals," switch the polarization between them as one moves from one atom to the other. This redistribution in space leads to the expression "spatially modulated." It is not to be confused with ferrimagnetic states which possess opposite and unequal spins on the two atoms of the unit cell. The total energy of the spatially modulated state is calculated to be 0.03 Ry per surface atom above the ferromagnetic state. Distinctions of this small magnitude are probably not within the accuracy of our approximations. Consequently, we conclude that either the ferromagnetic or spatially modulated state could be the ground state.

Figure 1 illustrates the spatial distribution of magnetization. The plots were calculated by multiplying the spin polarization by the correct spherical harmonic and an atomic radial function. Most trivially, the figures exhibit the C_{3v} symmetry of the ferromagnetic configuration (one reflection line is vertical, the other two at 120° to it) and the single vertical reflection line of the other two configurations. The wavelike modulation of the spin polarization in the antiferromagnetic case is also clearly visible. More interesting is the asymmetric accumulation of magnetization density above the middle Co atom in the spatially modulated state, leading to the concept of a small wave of periodicity equal to two atoms, superposed on a more constant background.

In concluding this section, attention is drawn to three distinct results: (1) Both one and two layers of Co on a Cu(111) surface are magnetized with a spin polarization close to the bulk value. (2) There exists a new kind of broken symmetry state which we have called spatially modulated. (3) Interface magnetization is reduced by the paramagnetic substrate. This latter result will reappear in the concluding section.

4. Chromium Surfaces and Chromium Monolayers on Iron

Bulk chromium occurs in the body-centered cubic structure with an antiferromagnetic (AF) ground state [2] modulated by an incommensurate spin density wave

(SDW). The SDW is in one of the (100) directions with a wavelength of approximately 21 lattice spacings. The magnetization at the maximum is 0.59 Bohr magnetons. Experimentally it is found that the addition of small amounts (approximately 1%) of group VII impurities such as Mn produces a simple AF structure with a magnetic moment of approximately 0.67 Bohr magnetons. In this structure atoms in the body-centered positions of the bcc lattice have spins pointing only in on direction; atoms in the corner positions have spins in the opposite direction.

This simple AF structure demands that (100) planes contain atoms of only one spin direction. Consequently, the (100) surface is expected to possess ferromagnetic order. Evidence of this planar ferromagnetism is found in the electron-capture spectroscopy results of RAU and EICHNER [8]. Their sample, however, displayed a c(2x2) structure indicative of impurities, which may have affected their results. The (100) surface has been examined also by two angle-resolved photoemission experiments [34,35]; both find a surface state or resonance at an energy approximately 0.70 eV below the Fermi level. The measured temperature dependence of this resonance in the latter experiment is taken as evidence for a ferromagnetic surface [35].

The (100) surface of chromium has also been examined theoretically [36,37] by means of a simple exchange interaction and a tight-binding approach which neglected the sp conduction electrons. ALLAN [36] finds that the surface magnetization is very large (2.8 Bohr magnetons) relative to the bulk and argues that this enhancement should penetrate into the bulk, decreasing by a factor (-0.5) per layer. (The negative sign refers to the AF.) GREMPEL [37] finds a surface spin polarization of 2.6 Bohr magnetons and a very high surface Curie temperature. FU, FREEMAN and OGUCHI, in a very recent paper [38], cite a value of 2.49 μ_B for the surface magnetization.

The (110) planes cut the simple AF bcc lattice so that an equal number of up and down spins are encountered. The (110) surface should therefore be an AF one. There have been two photoemission experiments on the Cr(110) surface. The experiment of JOHANSSON et al. [39] found no evidence of surface states; the later experiment of WINCOTT et al. [40] measured the dispersion of a surface state (binding energy of approximately 0.2 eV) along $\bar{\Gamma}$. The periodicity of their spectra suggests an AF surface.

Stainless steel is the name given to a family of iron based alloys which contain at least 12% chromium. Auger electron spectroscopy [41] shows that when a 304 stainless steel sample (a common type) is heated, there is a strong enhancement of the Cr concentration at the surface. This is in agreement with chromium's lower heat of crystal formation [42]. It is this enhanced concentration of Cr at the surface which, when oxidized, is influential in preventing the rusting of the steel.

We find the surface spin polarization at the Cr(100) surface to be 3.00 electrons. This enhancement relative to the bulk, a factor of 5.1 from the SDW maximum, is much larger than that [4,12] found in Fe and Ni. The magnitude of the enhancement can be attributed to the large number of unpolarized d-holes present in the bulk. Consequently, the decreased bandwidth found at the Cr surface, which leads to a stronger effective magnetic interaction, can greatly increase the surface spin polarization. Elements like Fe or Ni, with fewer available unpolarized holes, experience smaller changes in the same local environment.

The narrowing of the Cr DOS at the (100) surface is shown in Figure 2. It is clear that most d-holes occur in the minority subband. This subband is essentially concentrated in a single peak structure entirely above the Fermi level. The surface DOS can be compared with the bulk DOS given in [5]. There the d-holes are almost evenly distributed between the two subbands. Furthermore, it is clear that both subbands have sizable strength on either side of the Fermi energy, which falls in a valley of the bcc DOS.

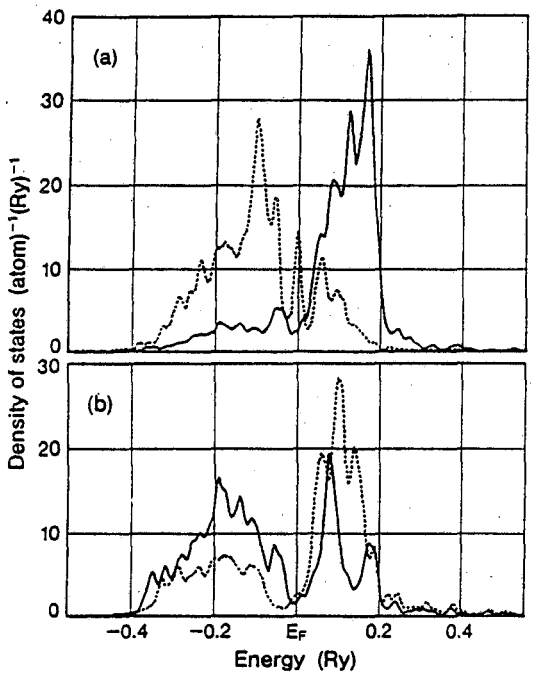

Fig. 2. The d-orbital component of the projected density of states. (a) The chromium (100) surface layer. (b) The chromium (100) second layer. Solid lines are states with the spin orientation of the surface minority states; dashed lines correspond to the majority states.

Figure 2(b) shows the DOS projected at the layer immediately below the surface. The width of each subband is approximately equal to the bulk value, which is consistent with the presence of all nearest, and most second-nearest, neighbors. The spin polarization is opposite to that of the surface layer, which is consistent with the AF of chromium. However, it is clear that there is a substantial difference between the minority and the majority DOS, suggesting that the spin polarization is not bulklike.

The spin polarization of the second layer is (-1.56), substantially different from the bulk. The spin polarizations of the third through sixth layers are 1.00, (-0.93), 0.86, and (-0.85), respectively. A similar penetration of the enhanced surface magnetization was predicted in Section 2 for the Fe(100) surface, although there the effect is much smaller. This penetration appears to be a direct consequence of the easy availability of unpolarized d-holes in bulk Cr. Each atoms feels the larger exchange splitting of its neighbor towards the surface and responds by increasing its own; this is, in the case of Cr, an energetically very inexpensive process.

We find a very large pair of surface states at the $\bar{\Gamma}$ point. Both their symmetry and dispersion characteristics are in agreement with that feature found by KLEBANOFF et al. [35]. Furthermore, we find the states to be spin-polarized. This then supports the experimentally proposed arguments [35] for the Cr(100) surface ferromagnetism.

Our (110) surface calculation gives a two-atom unit surface cell with AF ordering as the ground-state configuration. We also find a surface feature with AF periodicity which disperses similarly to that found by WINCOTT et al. [40], thus reinforcing their experimental deduction of AF surface ordering. This ordering is in agreement with a simple saw cut of the bulk along the (110) plane. We were unable to find a ferromagnetic locally stable minimum in the ground-state energy.

The surface spin polarization in the AF configuration is 2.31 electrons. This value is smaller than that for the (100) surface as one would expect, since the

(110) surface atom has six nearest neighbors, as opposed to four in the (100) surface. The spin polarization in the second layer, 1.00 electrons, is considerably smaller than that of a second-layer (100) atom, 1.56. This is a consequence not only of the smaller (110) surface perturbation, but also of the larger interlayer distance in the (110) direction. In particular, (100) layers are separated by 0.5 a (where a is the lattice constant), whereas (110) layers are separated by 0.707 a, with a consequent smaller coupling between layers.

We have calculated the spin polarization of a Cr monolayer atop the Fe(100) surface to be 3.63 electrons, with a ferromagnetic arrangement pointing oppositely to the underlying Fe substrate. This surprising prediction has been supported by the recent results of FU et al. [38] who also predict a large monolayer polarization (3.1 electrons). It is interesting that this large magnetization occurs for a system as important as the pre-oxidized stainless-steel surface. We were unable to obtain a local stable minimum for a Cr ferromagnetic layer, ferromagnetically ordered with respect to the iron.

Insight into this result may be gained by comparing it with the dilute FeCr alloy. Neutron scattering [43] results show that the isolated Cr atoms point oppositely to the surrounding Fe bulk and have a spin polarization of 1.2 electrons, twice the maximum bulk value of the SDW. This latter result presumably stems from the stronger electron-electron interaction in Fe, and a consequent stronger exchange splitting which helps Cr increase its own splitting and magnetization. This is the same argument explored in great detail for the iron-cobalt alloy [4], where Co has the stronger electron-electron interaction. The combined effect of diminished number of neighbors and stronger Fe exchange results in the calculated large Cr moment. We may understand the AF coupling by noting that Mn is the element intermediate between Fe and Cr, which suggests that the Fe-Cr interaction may be similar to the Mn-Mn interaction. Manganese exhibits localized moments but no ferromagnetism, implying that Fe and Cr would not couple ferromagnetically either.

Consideration of a Cr monolayer atop the Fe(110) surface suggests several alternative configurations. One might expect the monolayer to be AF because of the AF interaction of each Cr atom with its four Cr neighbors. This arrangement forces half the Cr atoms to have a ferromagnetic interaction with the four underlying nearest Fe atoms. As already discussed, Fe has a very strong effect on the Cr spin polarization (it doubles the value of the Cr polarization in the dilute alloy). The Fe substrate therefore would favor a ferromagnetic Cr monolayer, with AF order with respect to the bulk. Clearly there are two competing effects, and the nature of the ground state can be determined only after a detailed calculation.

We find that the ground state consists of a ferromagnetic Cr monolayer with its spins oriented in the direction opposite to the Fe substrate, similar to the Cr on Fe(100) arrangement. The spin polarization of the Cr is 2.25 electrons, smaller than the pure Cr surface. There is, as in the (100) monolayer, a small decrease in the spin polarization of the underlying Fe layer to a value of 2.03 electrons. Changes in the Cr monolayer DOS relative to the bulk DOS are not spectacular and mostly they reflect just the increased spin polarization.

We find that a structure consisting of an AF chromium layer is metastable: It produces a local minimum in the total energy curve, 0.05 Ry/surface atom above the ground state. The spin polarization of the two different Cr atoms are 3.03 and (-3.31) electrons, with the larger magnitude corresponding to the atom with AF arrangement to both its Cr and Fe nearest neighbors. It is clear that because of the different magnitudes of the spin polarizations the Cr monolayer is not truly AF, but rather ferrimagnetic.

5. Conclusion

This paper has described calculations for the magnetic and related electronic properties of a variety of transition metal systems (see Table 2). Some of the

Table 2

Spin-Polarization Results for All Ordered Systems

System	Spin Polarization
fcc Co	1.56
bcc Co	1.80
bcc Fe	2.12
bcc Cr	0.67
sc FeCo - Fe atom	2.66
sc FeCo - Co atom	1.78
(100) Fe surface	2.90
(110) Fe surface	2.55
(100) Cr surface - surface layer	3.00
(100) Cr surface - second layer	-1.56
(110) Cr surface	2.31
(100) FeCo surfaces - Fe surface layer	2.95
(100) FeCo surfaces - Co surface layer	2.03
(110) FeCo surface - Fe atom	2.75
(110) FeCo surface - Co atom	1.86
(110) Fe monolayer on FeCo - Co position	2.63
(110) Fe monolayer on FeCo - Fe position	2.67
(100) Cr monolayer on Fe	3.63
(110) Cr monolayer on Fe	2.25
(111) Co monolayer on Cu	1.63
(111) Co dilayer on Cu - surface layer	1.65
(111) Co dilayer on Cu - interface layer	1.58

more unusual results were the huge magnetizations found in the Cr(100) systems and the possibility of a new kind of magnetic order in the Co monolayer on Cu. The large variety of our results also suggests the possibility of a set of summarizing rules.

Four of the calculations have been made for pure transition metal surfaces. These calculations [Cr(100), Cr(110), Fe(100), and Fe(110)] all demonstrate that the removal of neighboring atoms decreases the projected bandwidth on the surface. Consequently, the electron-electron interaction to bandwidth ratio increases and so does the magnetism. In short, removal of the nearest neighbor atoms of its own kind tends to enhance magnetism.

These four surface calculations also help justify the next rule. It is recalled that the Cr surface enhancement of the magnetization is enormous; four to five times over bulk values. The enhancement at the Fe surface is smaller (20% to 40%) but still significant. The enhancement at the FeCo surfaces is quite small: less than 15%. The relevant difference between these systems is the number of available unpolarized d holes. FeCo has very few; Fe has approximately 0.7 per atom, and Cr has more than 4 per atom. (The concept of d-holes is not entirely concrete due to the presence of sp-d hybridization; it is the qualitative idea that is important.) Consequently, magnetization enhancement is most pronounced in those elements where the bulk magnetization is not close to saturation.

Bulk FeCo displays an interesting principle in itself. Section 2 argued that the strongly exchanged split Co can help increase the Fe magnetization. This same effect occurs in the Cr near surface region where the strongly exchange split surface Cr atoms help increase the spin polarization of the lower Cr layers. In general, we conclude that the presence of a strongly magnetized atom with a large exchange splitting near a weakly magnetic but polarizable atom with a smaller splitting considerably enhances the magnetization of the latter.

The final rule is exemplified by the calculations for the Co overlayers on Cu, in which it is found that a Co surface layer in contact with Cu has a lower spin polarization than a surface layer only in contact with Co. This suppression of magnetization by a nonmagnetic substrate has been explored in a number of experimental and theoretical studies as described in the introduction to Section 3. Examination of all these results suggests that the presence of a nonmagnetic unpolarizable atom next to - and coupled to - a magnetic transition metal element tends to decrease the magnetization of the latter.

It is hoped that these four qualitative rules bring some additional order to the systematics of heterogeneous systems displaying itinerant magnetism.

Acknowledgments

All calculational results reviewed in this paper were originally derived while the author was at U.C. Berkeley, collaborating with L. M. Falicov. The work was supported at the Lawrence Berkeley Laboratory by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the Department of Energy under Contract No. DE-AC03-76SF00098. I would also like to acknowledge an A.T.&T. Bell Laboratories predoctoral fellowship, under whose sponsorship much of this work was done.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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