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Authors

Falicov, L.M.
Victora, R.H.
Tersoff, J.

Publication Date

1984-08-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Presented at the First International Conference on the Structure of Surfaces, Berkeley, CA, August 13-16, 1984; and to be published in Structure of Surfaces, M. Van Hove, Ed., Springer-Verlag, 1985

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L.M. Falicov, R.H. Victora, and J. Tersoff

August 1984

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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ELECTRONIC AND MAGNETIC PROPERTIES OF TRANSITION-METAL SURFACES, INTERFACES AND OVERLAYERS

L.M.FALICOV and R.H.VICTORA

Department of Physics, University of California, and
Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California, 94720

and

J.TERSOFF

I.B.M. Thomas J.Watson Research Center
Yorktown Heights, New York, 10598

ABSTRACT

Results of calculations for the electronic and magnetic properties of transition-metal surfaces, interfaces and overlayers are presented for a variety of systems. They involve Ni, Co, Fe and Cr in a diversity of forms, including alloys, metastable configurations, and overlayers on non-magnetic metals. The overall behavior of these systems can be

interpreted in terms of four qualitative rules which are presented, analyzed, and illustrated.

INTRODUCTION

There is considerable current interest in the magnetism 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 incommensurable 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 [3-8]. We use 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 non-rigid exchange splitting. The interaction is treated selfconsistently in the Hartree-Fock approximation. Our scheme has been tested against experimental data [9,10] and against state-of-the-art first-principles calculations [11,12] on several occasions, and has produced consistently excellent agreement [5-7,13].

In this contribution we use our theoretical results, combined with experimental information, to develop systematically some qualitative rules for predicting the magnetization and density-of-state effects of these complicated systems. In addition we examine in more detail several systems where unusual or unexpected phenomena occur.

SURFACES

A particularly important system is body-centered-cubic Fe and its surfaces. The experimentally observed bulk spin polarization [7] (twice the magnetization divided by the g-factor) is 2.12. We have calculated the spin polarization of the (110) surface to be 2.55 and that of the (100) surface to be 2.90. These results are easily understood by considering the simple Stoner theory [14] which suggests that the magnetization of a ferromagnet increases with the electron-electron interaction and decreases with the bandwidth. An iron atom at the (100)

surface has four missing nearest neighbors as compared with a bulk atom. As a consequence the projected density-of-states bandwidth in such a surface atom is much narrower. The surface atom has an enhanced spin polarization relative to the bulk. An iron atom at the (110) surface has only two missing nearest neighbors; its projected bandwidth is intermediate between the bulk and the (100) surface atoms, and so is its magnetization. The conclusion to be drawn is that elemental surfaces increase the magnetic moment of atoms as compared with the bulk: the more missing neighbors, the higher the local magnetization.

The validity of the preceding argument can be tested by examining the behavior of other transition elements, e.g. Ni, Co and Cr. Nickel has a bulk spin polarization [5] of 0.56 and we have calculated the surface spin polarization to be 0.74 for the (100) surface, and 0.65 for the (111) surface. These results are in agreement with the nearest-neighbor argument because the face-centered-cubic (100) surface atom has four of the twelve bulk neighbors missing, while there are only three missing neighbors in the (111) surface. However, it is clear that the magnetization changes and the concomitant effects in the electronic spectrum such as the exchange splitting are smaller in Ni than in Fe. On the other hand we find [8] that the (100) surface of Cr has a spin polarization of 3.00, and increase by a factor of 4.4 from the antiferromagnetic bulk value. The magnetization of Cr is enhanced at the surface considerably more than that of Fe. We find [6] that for Co the influence of the surfaces is small, as in Ni.

A proper explanation of these disparate effects of the surfaces on these materials lies in the fact that two conditions are necessary for

the existence of d-electron magnetism: a sufficiently strong electron-electron interaction, as compared to the bandwidth, and an availability of holes (unoccupied d-states). Bulk Ni and Co are near saturation: almost all available holes are in the minority spin bands. Iron on the other hand has almost one additional unmagnetized d-hole. Chromium has four additional unmagnetized holes. Consequently an enhanced electron-electron-interaction to bandwidth ratio, as provided by the surfaces, can only influence those magnetic materials which have not reached saturation, i.e. there is a considerable increase of the magnetization at the surfaces of Fe and Cr, but small effects in Ni and Co.

The preceding discussion is oversimplified: hybridization between the d and the sp-electrons somewhat blurs the angular momentum character of the electronic states. This means that there is no true value of the spin polarization which could be called "saturation". It just becomes progressively harder to increase the magnetization beyond a given value. This value is essentially reached in the bulk at the end of the series, and may be achieved for the other elements in other environments. In these "saturated" situations the available empty states of the majority spin do not have a large density at the Fermi level, i.e. they are essentially of sp-character. Despite these complexities, the basic idea is that the closer an element is to magnetic saturation, the less the effect that surfaces have in its magnetic properties.

The "healing length", i.e. the distance over which a given disturbance disappears, is also a strong function of the saturation of the spin polarization. This effect is clearly exemplified in our

calculations of the magnetic properties of the (100) surface of body-centered-cubic Cr. Here [8] the strongly enhanced local magnetization penetrates several layers into the bulk. The surface layer has a polarization of 3.00; the second layer has a polarization of 1.56; the third, 1.00. The whole structure is antiferromagnetic. The effect is a consequence of the extensive hybridization between states centered in neighboring atoms. In particular, the exchange splitting of a given atom is considerably enhanced by a larger exchange splitting of a nearest neighbor. This effect, striking in Cr, is observed to a lesser extent in Fe, but is negligible in Ni surfaces where saturation makes increases in polarization very difficult. (Third layers in Ni structures are almost completely "healed".)

A particularly interesting application of these concepts occurs in the ordered FeCo alloy and its surfaces. Ordered FeCo has a magnetization [7] of 4.85 per two-atom unit cell. This value is considerably higher than the sum of the two magnetizations of the constituent atoms: 1.72 + 2.22 = 3.94. Our calculations, in agreement with neutron diffraction data, find that almost all the increased moment occurs in the Fe atom. This is because the strong electron-electron interaction of Co helps increase the exchange splitting of the upper Fe bands and, since Fe is an unsaturated magnet, this perturbation increases the Fe magnetization to a value of approximately 3.0. The effect of Fe on Co on the other hand is much weaker, because the polarization of the d-holes in Co is essentially saturated. As a consequence the magnetization of Co decreases only slightly from what would be its bulk body-centered-cubic value.

The saturation of both the Fe and Co spin polarizations in the

ordered bulk FeCo alloy should make the magnetic moment relatively insensitive to the presence of surfaces. Our calculations show this to be the case: a Co atom at the (100) surface increases its spin polarization by only 0.25 to a value of 2.03, whereas an Fe atom increases its by 0.34, to a value of 2.95. Effects at the (110) surface are even smaller: the increases are 0.08 for Co and 0.09 for Fe. These are much smaller increases than that found for pure iron --0.78 for the (100) surface-- and clearly support our general arguments.

INTERFACES

Overlayers introduce complexities beyond that of the simple surfaces because of the effects of the film-substrate interface. In order to understand the magnetic properties of these overlayers we have first calculated the electronic and magnetic properties of some interfaces [3,5]. In particular we have examined [5] the nickel-copper (100) and (111) interfaces. We found that the sp-electrons of Cu hybridize considerably with the Ni d-electrons. This effect reduces the interface-projected density of states near the Fermi level and makes it difficult for the interface Ni atoms to achieve saturation. As a consequence the spin polarization of Ni at both the (100) and the (111) interfaces is found to be 0.38, a considerable reduction from the 0.56 bulk value. We also found that if the Ni-substrate coupling is increased above its Ni-Cu value, as should be the case for simple metals like lead and aluminum, then the interface layer is unmagnetized for the (100) case also. These results point out that the effect of a nonmagnetic substrate

such as Cu is to reduce the magnetic moment of the transition metal in direct contact with it to a value below that of the bulk.

ENVIRONMENTAL CHANGES IN THE MAGNETIZATION: QUALITATIVE RULES

We have thus far introduced four important observations, direct result of our calculations and of experimental results. We may call these observations qualitative rules:

1. The removal of nearest neighbors of its own kind reduces the projected bandwidth of a magnetic transition metal atom and thus increases the electron-electron-interaction to bandwidth ratio. This effect, most evident at surfaces, tends to enhance magnetism.

2. Magnetization enhancement is sizeable only in those elements where the bulk magnetization is not close to saturation, i.e. where there exist holes in the d-band which can still be polarized. Considerable enhancement is therefore expected for Cr and Fe; the effect is small for Co and Ni. It is also small for the surface enhancement of Fe in the FeCo alloy, where the alloying effect has already produced "saturation" of the Fe magnetization.

3. 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.

4. The presence of a nonmagnetic unpolarizable atom next to --and coupled to-- a magnetic transition-element atom tends to decrease or fully destroy the magnetization of the latter.

OVERLAYERS

The above rules are conceptually very important but unfortunately only qualitative. In systems like overlayers, where all four rules apply simultaneously and where they act in opposite directions, only a full selfconsistent calculation can yield the final result: no a priori prediction is possible.

Monoatomic overlayers of Ni on Cu (100) and on Cu (111) surfaces provide a clear example of this point. As discussed previously, the effect of the Cu interface is to decrease the Ni magnetization. On the other hand the effect of the free surface is to enhance it. Our calculations [5] show that the magnetization of the (111) Ni monolayer is nearly zero, whereas the (100) monolayer has essentially the bulk magnetization. These results correspond well with our previous arguments that face-centered-cubic (100) surfaces have higher magnetization than (111) surfaces.

Comparison with the interface results is however not so straightforward. As previously noted, the spin polarization of both interfaces is 0.38, a decrease by a factor of 1.47 from the bulk value. Clearly the exchange splitting of the bulk atoms helps to maintain a sizeable magnetization at the interface. On the other hand, the presence of a surface ("the other side" of a monolayer) also tends to enhance the magnetization. Which effect is more important --hybridization with the strongly magnetized bulk atoms or the enhancement caused by the free surface-- is clearly a sensitive function of environmental variables such

as surface orientation and chemical composition, and not susceptible to simple qualitative arguments.

The extent of this sensitivity is demonstrated by our calculations [6] for Co overlayers on the Cu (111) surface. Here the monolayer has a spin polarization of 1.63, greater than the values for the inner atoms of the dilayer: 1.58. In other words, the surface enhancement of the magnetization is more important in this case than the enhancement caused by the nearest neighbor exchange splitting. It is probably the result of Co having more holes than Ni, and a monolayer moment close to the bulk value, a case similar to the monolayer of Ni on Cu (100).

A more predictable system is that consisting of an Fe monolayer on the (110) surface of the ordered FeCo alloy. Here the Fe magnetization is expected to be higher than its ordinary value at the (110) surface of body-centered-cubic Fe: the substrate has a larger exchange splitting in the alloy than in pure Fe. Our calculation [7] finds the additional enhancement to be 0.08 and 0.12, depending on the Fe atom position, relative to the spin polarizaion of 2.55 found at the Fe (110) free surface.

Another result of considerable interest [5] is the fact that in the extreme strong coupling limit, when the magnetic transition metal hybridizes infinitely strongly to the conduction states of the substrate, both a monolayer and a dilayer of Ni (100) show no magnetization whatsoever --two "dead" magnetic layers-- whereas a triatomic layer shows considerable spin polarization (0.61 at the surface, 0.45 for the intermediate atoms) even though the interface Ni atoms are magnetically dead.

So far the discussion has centered on the local values of the spin polarization. In fact many other interesting properties involving, inter alia, the electronic density of states, the total electronic energies and the spatial distribution of charge and spin polarization can be investigated at the same time. The system consisting of a monolayer of Co on the Cu (111) surface provides a particularly interesting example [6] because of the richness of its low energy configurations. In particular an antiferromagnetic two-atom unit surface cell is found to have a total electronic energy 2.04 eV per surface atom higher than the ferromagnetic ground state. Even more interesting is the existence of a spatially modulated two-atom surface cell state, with an energy only 0.41 eV per surface atom higher than the ferromagnetic ground state. The spatially modulated state, which should be easily accessible, consists of equal charge and magnetization in the two atoms of the unit cell, but different distribution of the magnetization among the various d-orbitals. It possesses a surface projected density of states very similar to that of the ferromagnetic ground state.

The type of calculation discussed here is not necessarily restricted to smooth, uniform surfaces. By enlarging the surface unit cell it is possible, albeit computationally expensive, to include surface defects such as steps, terraces, kinks and partial overlayers, all structures of considerable importance in heterogeneous catalysis [15-20]. Our calculation [21] of the electronic properties of a paramagnetic partial layer (two-third coverage) of either Cu or Ni on paramagnetic Ni proves that the calculations are feasible and their results provide useful information on chemical as well as electronic properties of these

interesting and practical systems.

ACKNOWLEDGMENTS

One of us (R.H.V.) would like to acknowledge an A.T.T. Bell Laboratories predoctoral fellowship, under whose sponsorship this work was done.

This work was supported at the Lawrence Berkeley Laboratory by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the Department of Energy under Contract Number DE-AC03-76SF00098.

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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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