Condition for the existence of a permanent magnetic moment near transition-metal surfaces

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A condition for the existence of a magnetic instability localized near the surface of bulk paramagnetic transition metals is found in a one-electron band theory. Among the bcc transition metals of the first series, it is shown that this condition may be fulfilled near (100) vanadium surfaces. The same band model is applied to bulk magnetic transition metals. It describes the behavior of the magnetic moment near the surface of a crystal. Application is made to chromium and iron. Some recent experimental results on vanadium hyperfine particles and chromium surfaces are discussed.

I. INTRODUCTION

Surface experimental techniques like low-energy-electron diffraction,[1] field-emission microscopy[2] or photoemission[3] give information about surface magnetic properties. They are notably related to the spin populations on surface atoms. The value of the surface magnetic moment may also be obtained by measurement of hyperfine particle magnetic susceptibitily.[4] Mössbauer experiments also give direct access to the surface magnetic moment of ferromagnetic transition metals.[5] None of these experiments show the existence of dead layers[6] near the surface of ferromagnetic materials. The lack of magnetism observed for very thin film may be explained by the two-dimensional structure of the sample.[7] This is not the situation near the surface of a finite crystal. Moreover, we shall show below that a permanent magnetic moment may appear near the surface of a transition metal even if it is paramagnetic in the bulk.

A few attempts have been made to study surface magnetization within a free-electron scheme,[8] which is not well suited to describe the atomic d-electron character. This is not the case of the renormalization-atom approach and of the tight-binding approximation which have also been used[9] to study the influence of the surface on the magnetic moment. However, due to other approximations, the band structures used were not very good. Furthermore, the magnetization changes were limited to the surface atoms. All these very crude approximations could only lead to qualitative results. We shall try below to obtain more quantitative results using a better d-band scheme and a variation of the magnetization nonlocalized in the surface plane.

In Sec. II we find the condition for the existence of such a magnetic instability. We also calculate the variation of this magnetic moment as one goes into the bulk. The same model may also be ap-plied to bulk magnetic transition metals and gives near the surface, the deviation from the bulk value of the magnetic moment.

In Sec. III we apply these results to the transition metals of the first series. We show notably that the "Stoner" criterion obtained in Sec. II may easily be satisfied near vanadium (100) surfaces. We also compare our results with the few experimental results available.

II. MAGNETIC MOMENT NEAR A TRANSITION-METAL SURFACE

A. Bulk paramagnetic transition metals

We shall derive below a criterion for the existence of a surface magnetic instability that is similar to the one obtained by other authors.[10] However, our result depends upon already known bulk or surface properties, and the model may be extended to bulk magnetic crystals.

Let us call M_i the magnetic moment on the atom located at site $\vec{R}_i$:

$$M_i = N_{\uparrow i} - N_{\downarrow i} , \qquad (1)$$

where $N_{\uparrow i}$ and $N_{\downarrow i}$ are the spin-up and -down populations on atom i. We also define $\delta N_{\uparrow i}$, $\delta N_{\downarrow i}$, and δN_i as

$$M_i = \delta N_{\uparrow i} - \delta N_{\downarrow i} = 2\delta N_i ,$$

$$N_{\uparrow i} = N + \delta N_{\uparrow i} , \qquad (2)$$

$$N_{\downarrow i} = N + \delta N_{\downarrow i} ,$$

where N is the number of electrons per spin in the paramagnetic state. In the first-order perturbation theory we get

$$\delta N_{\uparrow i} = - \sum_j \chi_{ij} v_{\uparrow j} , \quad \delta N_{\downarrow i} = - \sum_j \chi_{ij} v_{\downarrow j} , \qquad (3)$$

where $v_{\uparrow j}$ and $v_{\downarrow j}$ are, in the Hartree-Fock scheme, the atomic exchange potentials and χ_{ij} is the paramagmetic interatomic susceptibility which defines

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the generalized susceptibility $\chi(\vec{q})$ in a perfect infinite lattice:

$$\chi(\vec{q}) = \sum_j \chi_{0j} \exp(i\vec{q} \cdot \vec{R}_j) . \tag{4}$$

The atomic exchange potentials $V_{\uparrow j}$ and $V_{\downarrow j}$ are simply related to δN_j:

$$V_{\uparrow j} = -U_j \delta N_j = -V_{\downarrow j} , \tag{5}$$

where U_j is the effective intra-atomic Coulomb integral on site $\vec{R}_j$. One can expect different values of this integral for bulk or surface atoms, for example. It seems reasonable to assume that the intratomic Coulomb integral differs from the bulk value U only for surface atoms where it is equal to U_s. Equations (3) and (5) lead to

$$\delta N_i = \sum_j \chi_{ij} U_j \delta N_j . \tag{6}$$

We recall that in (6) the summation over j is extended to all lattice sites. In a semi-infinite crystal, all the atoms in a given plane parallel to the surface are identical, therefore, $U_j \delta N_j$ takes the same value on all the atoms of this plane. Let us put

$$X_{ij} = \sum_k \chi_{ik} , \tag{7}$$

where the summation is extended to all the sites $\vec{R}_k$ belonging to the jth plane parallel to the surface. Then

$$\delta N_i = \sum_j X_{ij} U_j \delta N_j , \tag{8}$$

where the summation over j is over the planes parallel to the surface. Let us put $j = 0$ for this plane. The local density of states on atoms sitting in the plane 1 (just below the surface) is already very close to the bulk one.[11] It really does not present any surface feature, even if the perturbation due to the surface [like for the (100) plane of bcc metals] is strong. So we can assume that all the X_{ii} are equal excepted for $i = 0$. Moreover, we assume that there is some interaction between nearest-neighbor planes only. Then let us put X_b, X_s, and X_I as

$$X_{ii} = X_b, \quad i \neq 0$$

$$X_{00} = X_s , \tag{9}$$

$$X_{ij} = X_I(\delta_{i,j+1} + \delta_{i,j-1}) .$$

Then we get the following equations:

$$\delta N_0 \leqslant X_s U_s \delta N_0 + X_I U \delta N_1 , \tag{10a}$$

$$\delta N_1 = X_b U \delta N_1 + X_I U_s \delta N_0 + X_I U \delta N_2 , \tag{10b}$$

$$\delta N_i = X_b U \delta N_i + X_I U \delta N_{i-1} + X_I U \delta N_{i+1} . \tag{10c}$$

Higher-order terms in perturbation theory lead, in fact, to the inequality in (10a). We look for a solution of Eqs. (10) localized near the surface. It must have an exponential tail inside the bulk. We put

$$\delta N_i = \delta N_1 K^{i-1}, \quad i \geqslant 1, \quad |K| < 1 . \tag{11}$$

Equation (10c) is replaced by

$$1 = U[X_b + X_i(K + 1/K)] , \tag{12}$$

whose solutions are

$$K = \tfrac{1}{2}[A + (A^2 - 4)^{1/2}] \quad A \leqslant -2$$

$$K = \tfrac{1}{2}[A - (A^2 - 4)^{1/2}] \quad A \geqslant +2 \tag{13}$$

$$A = (1 - UX_b)/UX_I .$$

The other expressions, (10a) and (10b), give

$$\delta N_1 = (U_s/U)K\delta N_0 , \tag{14a}$$

$$1 \leqslant U_s(X_s + KX_I) . \tag{14b}$$

This last expression is the criterion for the existence of a magnetic solution near the surface of a bulk paramagnetic transition metal. If one wants to take into account terms like $X_{i,i\pm2}$, one slightly changes the value of K and introduces terms like $K^2 X_{i,i\pm2}$ in condition (14b). We shall show below that these terms are negligible, at least in the case of a (100) surface of the bcc lattice. We can relate the values of X_b and X_i to some values of $\chi(\vec{q})$. For example, if we consider the (100) surface of a bcc metal, we choose $\chi(0)$ and $\chi(\vec{Q})$ with $\vec{Q} = (2\pi/a)(0,0,1)$. Then one can easily show that

$$X_b \simeq \tfrac{1}{2}[\chi(0) + \chi(\vec{Q})] , \quad X_I \simeq \tfrac{1}{4}[\chi(0) - \chi(\vec{Q})] . \tag{15}$$

For other types of surfaces, one has to change the point $\vec{Q}$ in the reciprocal space. Let us recall that $\chi(0)$ is the bulk density of states at the Fermi level. When one knows the bulk paramagnetic electronic structure in the tight-binding approximation, the generalized susceptibility $\chi(\vec{q})$ can be easily calculated using, for example, the method of tetrahedrons.[12] Let us now look at the bulk magnetic crystals.

B. Bulk magnetic transition metals

Let us now define $\delta N_{\uparrow i}$ and $\delta N_{\downarrow i}$ as

$$N_{\uparrow i} = N^0_{\uparrow i} + \delta N_{\uparrow i}, \quad N_{\downarrow i} = N^0_{\downarrow i} + \delta N_{\downarrow i}, \tag{16}$$

where $N^0_{\uparrow i}$ and $N^0_{\downarrow i}$ are the spin populations on site $\vec{R}_i$ in a perfect crystal. $N_{\uparrow i}$ and $N_{\downarrow i}$ are the same quantities in a perturbed crytsal. In the

first-order perturbation theory, we get

$$\delta N_{\uparrow i} = -\sum_j \chi^{\uparrow}_{ij} \delta V_{\uparrow j}, \quad \delta N_{\downarrow i} = -\sum_j \chi^{\downarrow}_{ij} \delta V_{\downarrow j} , \quad (17)$$

where $\delta V_{\uparrow j}$ and $\delta V_{\downarrow j}$ are the differences between Hartree-Fock exchange potentials on site $\vec{R}_j$ of perturbed and perfect crystals, respectively. The variations of the spin polarization on site $\vec{R}_i$ is

$$2\delta N_i = \delta N_{\uparrow i} - \delta N_{\downarrow i}, \quad \delta V_{\uparrow j} = -U_j \delta N_j = -\delta V_{\downarrow j} . \quad (18)$$

Instead of (6), we obtain

$$\delta N_i = \sum_j \frac{\chi^{\uparrow}_{ij} + \chi^{\downarrow}_{ij}}{2} U_j \delta N_j . \quad (19)$$

All the atoms sitting in planes parallel to the surface of a semi-infinite ferromagnetic crystal are still equivalent. In an antiferromagnetic crystal, this is no longer true except for a surface normal to the bulk spin wave vector $\vec{Q}$. But we recall that $\vec{Q}$ is close or equal to $(2\pi/a)(0,0,1)$ for bcc chromium and fcc γ-manganese. Therefore all the atoms of these antiferromagnetic metals lying in a (100) plane carry the same magnetic moment. Equation (8) is still valid in this case if we put

$$X_{ij} = \sum_k \frac{\chi^{\uparrow}_{ik} + \chi^{\downarrow}_{ik}}{2} , \quad (20)$$

where the summation over k is extended to all lattice sites that belong to the same plane j. We also get the same expression as (11), but K now describes the decrease of the spin population deviation near the surface. However, X_b and X_{ij}, like the generalized susceptibility $\chi(0)$ and $\chi(\vec{Q})$, have to be calculated in the magnetic states.

III. APPLICATION TO THE (100) SURFACE OF bcc TRANSITION METALS

A. Bulk electronic structure

We have used the tight-binding approximation to describe the d band of the bcc transition metals. We neglect the s electrons, since all the properties we calculate are related to the density of states, which is much larger for the d electrons than for the s or p electron. Their main effect that on the band structure is the s-d interaction, which we also neglect. Along the first transition series, we keep constant the values of the hopping integrals between first, and second-nearest neighbors. We take the values calculated for chromium[13] (Table I). The bandwidth slightly decreases as one goes along a series from chromium to iron.[14] This does not affect our results much, for

TABLE I. Bulk band parameters (eV) (Ref. 13).

	$dd\sigma$	$dd\pi$	$dd\delta$
First neighbor	−1.13	0.62	−0.10
Second neighbor	−0.52	0.24	0.0

it is rather the ratio of the effective Coulomb integral U to the bandwidth W that is involved in the calculation of K. At least for chromium and iron, this quantity will be fixed by experimental results.

All the bulk or surface densities of states have been expressed as a continued fraction expansion.[15] The expansion coefficients are calculated from 16 exact moments of the density of states.[15] These moments are easily obtained by summation of the trace of the one-electron tight-binding matrix Hamiltonian over special points in the Brillouin zone.[16] The Coulomb integral is fitted to obtain the bulk experimental value of the magnetic moment. This determines the ratio U/W and then U:

$$\begin{aligned} U &\sim 0.6 \text{ eV} \quad \text{for chromium,} \\ U &\sim 0.9 \text{ eV} \quad \text{for iron.} \end{aligned} \quad (21)$$

These values agree very well with previous estimations[17] and measurements.[18]

Figure 1 gives the generalized susceptibilities $\chi(0)$ and $\chi(\vec{Q})$ as a function of the d-electron number N_d. The limit between antiferromagnetism and ferromagnetism is close to the crossing point of $\chi(0)$ and $\chi(\vec{Q})$, with $U = 0.6$ eV. When both $\chi(0)$ and $\chi(\vec{Q})$ are larger than $1/U$, the limit must be determined by the calculation of the energy. The results for K are plotted in Fig. 2. We note some
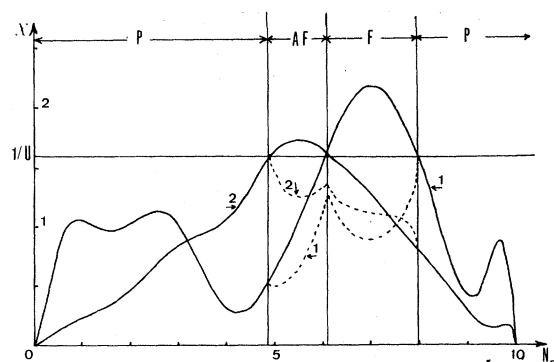

FIG. 1. Generalized susceptibilities $\chi(0)$ (curve 1) and $\chi(\vec{Q})$ (curve 2) in the paramagnetic state (full lines) and in the magnetic state (dotted lines) as a function of the number of d electrons N_d. The horizontal line corresponds to the bulk Stoner condition $1/U$, with $U = 0.6$ eV.
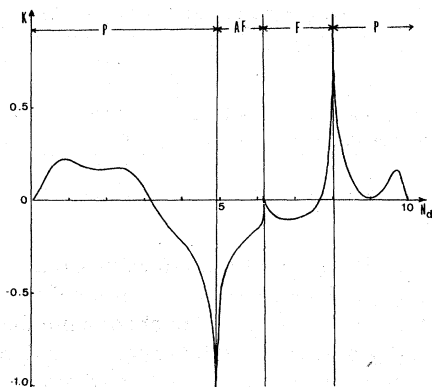
FIG. 2. Values of K vs the number of d electrons ($U = 0.6$ eV). (Recall that $\delta N_i = \delta N_1 K^{i-1}$.)

values we need below, for example, K close to -0.2 (V) or -0.5 (Cr). For iron, K is close to -0.3, with $U = 0.9$ eV. Such negative values of K are due to a negative value of X_i in the middle of the series. For smaller values of U, (since we keep a constant bandwidth, this would correspond to bcc metals of the second or third transition series), K approaches a limit equal to UX_i.

B. (100) paramagnetic surface electronic structure

The same approximations are used to calculate the electronic structure near the (100) surface of bcc transition metals. This surface has been choosen because of the large peak in the surface density of states near the middle of the d band. One may expect that the local surface susceptibility will be increased and that the surface Stoner criterion found above will be satisfied. The surface acts as a perturbation on a perfect infinite crystal. It induces Friedel charge oscillations which are screened as one goes into the bulk. These oscillations induce a potential which must be calculated self-consistently. This potential includes not only the intra-atomic Coulomb potential, but also interatomic terms. These are very important in a surface problem.[19] We also recall that they give a $1/q^2$ divergence in the dielectric function $\epsilon(\vec{q})$ for small-q values. This ensures a complete screening of a defect and leads to the Friedel sum rule.[20] All these intra-atomic and interatomic terms are difficult to evaluate, for they are reduced by the electron-electron correlations or by s-electron screening. The usual approximation, used since an earlier model band calculation,[21] is to retain only one matrix element V_0 of this potential for atoms sitting in the surface plane. Then V_0 is fitted to satisfy the Friedel sum
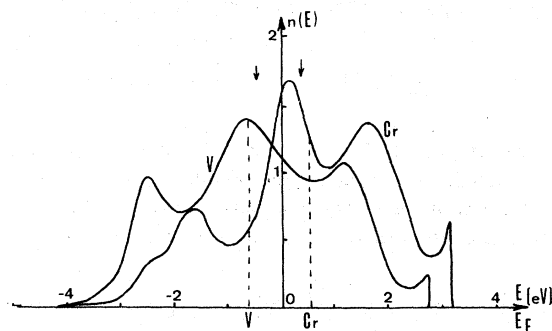

FIG. 3. (100) surface density of states of vanadium ($V_0 \sim -0.36$ eV) and chromium ($V_0 \sim 0.6$ eV). Note the position of the surface peak which is close to V_0.

rule. Such a potential corresponds to the dipole layer which is issued by a charge transfer from the surface plane to the plane just below the surface. The position at the peak in the surface density of states is very sensitive to this potential. For example, let us consider the cases of paramagnetic vanadium and chromium (Fig. 3). The only difference between the plotted densities of states is the value of the self-consistent potential that would correspond to vanadium and chromium. Keeping the same d-band parameters for chromium and vanadium is a good approximation, since the band structures calculated with the augmented-plane-wave approximation are very close.[22] One can see that the surface peak that appears near the middle of the (100) surface band[23] is located near the value of V_0, so the surface density of states at the Fermi level of vanadium strongly depends on V_0. The surface density of states at the Fermi level along the whole series remains almost constant (Fig. 4). The susceptibilities X_{0j} are easily calculated since one needs only the
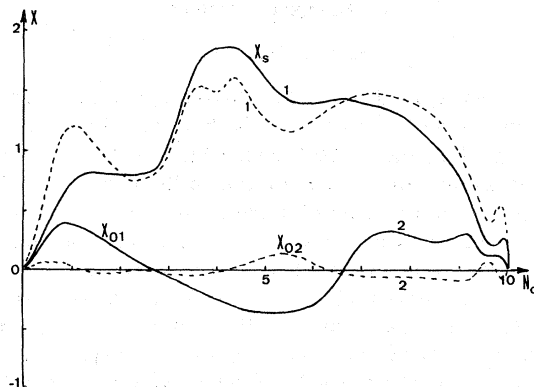

FIG. 4. (100) surface density of states (dotted line 1) compared with X_s (full line 1). The other curves correspond to X_{01} (full line 2) and to X_{02} (dotted line 2).

number of states N_j below the Fermi level for atoms sitting in the jth plane below the surface:

$$X_{0j} = -\frac{dN_j}{dV_0}\Big|_{V_0(\epsilon_F)} . \qquad (22)$$

The results are given in Fig. 1 for $j = 0, 1, 2$. The susceptibility X_{02} is quite small. This is not due to the proximity of the surface, for we shall see the exact X_{01} already is close to the bulk value X_I. This fully justifies the approximation used above to calculate K.

The most striking result concerns vanadium $(n_d = 4)$. X_s, which is already large for this metal, is still increased by KX_I, which is positive. The surface Stoner criterion is satisfied if U_s is larger than 0.5 eV. One can expect that U_s is larger than the bulk value U, for the properties of a surface atom are certainly between those of a bulk atom and those of a free one. The surface magnetic moment is plotted in Fig. 5 as a function of the surface Coulomb exchange integral U_s. We have neglected the magnetization of the atoms below the surface, since KX_I is small compared with X_s. The error introduced by this approximation is of the order of 10%. We can compare these results with the surface magnetic moment deduced from the measurements of the vanadium hyperfine particle susceptibility. Akoh and Tasaki[4] have assumed an equal magnetic moment $1.2\mu_B$ on atoms sitting in the surface plane and in the plane just below. We have seen that the magnetic moment rapidly decreases $(K \sim -0.2)$ as one goes into

the bulk. It is easy to show that the total magnetic moment per surface atoms is equal to

$$m_T = 2\delta N_0\left(1 + \frac{(U_s/U)K}{1-K}\right) . \qquad (23)$$

A Coulomb exchange integral U_s close to 1 eV gives a total magnetic moment of $2.4\mu_B$ per (100) surface atom.

In the case of iron, the term KX_I is negative, and reduces the surface susceptibility. Nevertheless the surface remains ferromagnetic even if $U_s = U$. Then the surface magnetic moment is close to the bulk value.[5,11] The iron surface peaks are also located near $V_0 + V_s$ and $V_0 - V_s$, with $V_s = U_s\delta N_0$. It would be interesting to follow by photoemission the shift of the surface levels as one varies the temperature through the Curie point. Since one knows the iron surface magnetic moment,[5] this would lead to a measurement of U_s.

The influence of the (100) surface peak is still more striking for chromium. The Cr surface magnetic moment seems to be larger $(2.8\mu_B)$.[24] One could also see the corresponding surface peak shift when the temperature varies. This would also give some information about the product $U_s\delta N_0$. The measurements of chromium thin-film resistivity suggest that the grain boundaries have some effect like that of iron localized moments.[25] Near a grain boundary, there are dangling bonds which may have the same effect as near a surface, and induce a magnetic surface layer. We also note that the existence of a ferromagnetic layer has been observed near chromium surfaces.[26]
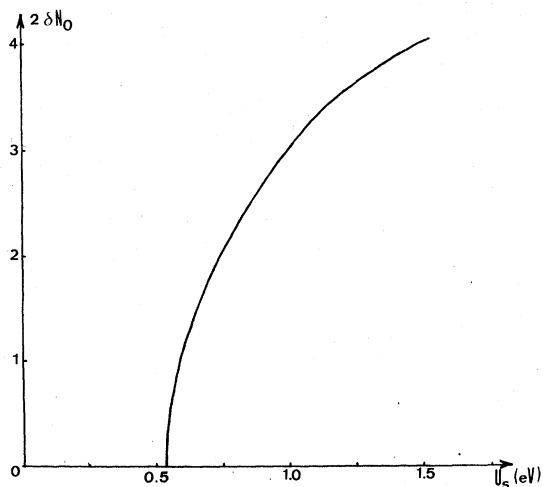
IV. CONCLUSION

In the tight-binding approximation, we have derived a criterion for the existence of a magnetic layer near the transition-metal surfaces. This criterion seems to be easily satisfied near (100) vanadium surfaces. We propose a photoemission measurement of the surface peak energy as a function of temperature to obtain information about the surface Coulomb exchange integral and the surface magnetic moment. A systematic study of the (100) surface peak position for bcc metals of the same transition series would also give information about the self-consistent potential.

For bulk magnetic transition metals, the same model shows that only a few planes close to the surface have their magnetic moment quite different from the bulk value. It seems that such a variation is not negligible near chromium (100) surfaces.

The (110) surface electronic structure of transition metals does not show any surface peak that

FIG. 5. Surface magnetic moment $2\delta N_0$ of vanadium as a function of the surface Coulomb exchange integral U_s. The magnetization in all the planes, except that in the surface one, has been neglected. This slightly underestimates the surface magnetic moment.

can strongly increase the surface susceptibility and lead to a surface magnetic layer. However, the appearance of localized surface states in the antiferromagnetic gap near the surface has been noted.[27] A surface peak also occurs near the (111) surface of bcc transition metals. As the number of dangling bonds per surface atom is slightly smaller that for the (100) surface, the effect is less important. A comparison with the results concerning (100) surface is interesting, however.

As the Fermi level must be close to the sur-face peak, the case of fcc transition metals seems less striking even if localized surface peaks appear in the local surface density of states.

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