Surface ferromagnetism in transition metals in the Hubbard model

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We discuss the possibility of ferromagnetic ordering at the surface of transition metals whose interior layers are non-magnetic. A condition for the onset of surface ferromagnetism is derived. It is shown that the Curie temperature for the surface can exceed the Curie temperature of the interior metallic region at certain values of the Fermi energy and of the ratio of the intra-atomic Coulomb repulsion to the width of the conduction band. We analyze the influence of the intra-atomic Coulomb interaction on the Friedel oscillations of the electron density in atomic layers close to the metal surface, and compare our results with experimental data.

INTRODUCTION

In recent years, a number of works have been published in which observations were reported of magnetic order in the topmost clean surface layers of several transition metals whose interior layers were in a nonmagnetic state. For example, by measuring the magnetic susceptibility with the help of a magnetic balance, it was established that finely-dispersed particles of vanadium (100 to 1000 Å) exhibit a macroscopic moment proportional to their surface area.[1,2] Analogous results were obtained by the same method for small particles of chromium at temperatures $T > T_N$ ($T_N = 310$ °K is the Néel temperature for chromium).[3] The surface magnetic moment disappeared around a temperature $T \approx 800$ °K. Confirmation of the presence of magnetic order at the surface of the ⟨100⟩ faces of chromium was obtained for temperatures up to 780 °K by the method of angle-resolved photoelectron spectroscopy using synchrotron radiation.[4] Ferromagnetic order at the surface of the ⟨100⟩ faces of chromium for $T > T_N$ was also detected in experiments on grazing-angle scattering of deuterons accompanied by capture of electrons from the surface atoms.[5,6] Using these methods, the presence of at least near-ferromagnetic ordering was established for nickel on the (100), (110), (111) and (210) faces at temperatures $T > T_c$ ($T_c = 630$ °K is the Curie temperature for nickel), up to $2.05\,T_c$.[5] In Ref. 7, the temperature dependence of the black-body coefficient of cobalt is discussed: certain anomalies are found in this coefficient at the volume (second-order) magnetic phase transition temperature. At temperatures higher than T_c by 10–15 °K, however, additional (and analogous) anomalies were observed which, as suggested in Ref. 8, point to the presence of a surface magnetic phase transition at $T > T_c$. Very recently, by using the method of diffraction of slow spin-polarized electrons and a method based on the Kerr effect, it was observed that the Curie temperature of the (0001) crystal face of the rare-earth element gadolinium exceeds the volume Curie temperature by 22 °K.[9]

Previously, this problem was studied theoretically by Kaganov *et al.* within the framework of the thermodynamic Landau-Ginzburg model.[10–12] The possibility of ferromagnetic ordering at the surface of thin films with Curie temperatures exceeding bulk values is connected with a negative surface energy, which is caused by the presence at the sample boundary of various kinds of perturbations, i.e., perturbations which distinguish the surface from the bulk: the different anisotropy energy at the surface as compared to the bulk, the presence of a layer of oxide on a number of atomic layers, and surface deformation.[10] Other authors have studied the phenomenon of surface ferromagnetism in a strong-coupling model in which the parameters of the problem for surface and volume are considered to be essentially different.[13–16] Thus in Allan's work,[15,16] where the band structure of the metal is most completely taken into account, the magnitude of the intra-atomic Coulomb interaction between electrons for the surface atomic layer is assumed to be larger than that in the inner layers. In these works it was established that the cause of the appearance of surface ferromagnetism is the presence of oscillations in electron density as we move from the interior metallic layers to the surface. However, instead of solving the self-consistent problem of the influence of the oscillating electron density on the surface ferromagnetism, in these works a certain effective potential V_0 is introduced, which is taken to be different from zero only at the surface atomic layer and corresponds to the creation at the surface of a dipole layer due to charge transfer between the surface layers of the metal.

In the present work, we solve the problem of how a purely geometric property—the fact that the surface atoms differ from the interior atoms in that they have no "top" neighbors—can influence the possibility of surface magnetism. That is, we invoke only a general property possessed by all free surfaces. In accordance with this approach to the problem, we will let the atomic parameters for all metallic layers except the surface layer be the same. In particular, we do not introduce the Allan potential V_0. Thus, in the present work we solve the self-consistent problem for a metallic half-space in which electron density oscillations in the metallic surface, and in some cases the appearance of surface ferromagnetism, will take place purely because of the existence of a surface. In this way, we will show that the existence of new physical properties at the surface does not require for its explanation the introduction of adjustable parameters de-

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scribing, for example, a change in interatomic spacing near the surface, surface reconstruction, etc.

We have chosen the Hubbard model[17] as a model of the transition metal. Its usefulness as a crude model of transition metals was established in a series of works (see, e.g., Refs. 18–20), where in particular it was shown that the solution to the problem in the self-consistent layer approximation allows one to describe the magnetic state of the transition metals. As is well-known, the self-consistent field approximation is justified if the ratio $U/W<1$ (U is the intra-atomic Coulomb repulsion energy for electrons with different spins, and W is the band width of the metal). We show that surface ferromagnetism can occur when the ratio U/W is smaller than that which is required for the appearance of volume ferromagnetism.

The appearance of surface ferromagnetism is detected in metals having various crystallographic structures, and can occur for a multiplicity of crystal faces. It is clear therefore that it depends only weakly on the crystal structure factor, and so we limit ourselves to investigating the (100) face of a simple cubic lattice.

In Section II, we calculate the electron density-of-states functions for the paramagnetic case, and determine the oscillating electron density to zeroth and first approximation in the parameter U/W for an arbitrary atomic layer. In particular, we will establish that when the Fermi level is located near the center of the band, the number of electrons per atom changes markedly not only in the surface layer, but also in the next few metallic layers. These results allow us to justify the approximations used to solve the surface ferromagnetism problem in this work.

In Section III, we obtain conditions for the appearance of surface ferromagnetism in the presence of a bulk paramagnetic state, i.e., paramagnetic metallic interior layers, for arbitrary temperatures. In particular, we show that the Curie temperature for the surface can exceed that of the interior metallic layers. We then present a comparison of the results with available experimental data.

II. ELECTRONIC STRUCTURE OF THE METALLIC HALF-SPACE (NON-MAGNETIC CASE)

Let us investigate a crystal with a simple cubic lattice, having a (100) surface and consisting of N atomic layers with coordinates $z=1,\dots,N$ (in units of the lattice parameter a). In order to study such a system using the Hubbard Hamiltonian, which in the standard notation takes the form

we will apply the Green's function method[21] in the self-consistent field approximation, which is correct for $U<W$ where $W=12B$ and B is the amplitude of the electron transport $B_{\mathbf{ff}'}$ from site $\mathbf{f}'$ to the nearest-neighbor site $\mathbf{f}$. Corresponding to what was said above, we will assume that the quantities ε_1, B, and U are the same for all atoms except the surface atoms. Furthermore, we will write down the equation for the Green's function $\langle\langle C_{\mathbf{f}\sigma}|C^+_{\mathbf{f}\sigma}\rangle\rangle$, which after the Hartree-Fock decoupling takes the form

$$H=\sum_{\mathbf{f}\sigma}\varepsilon_1 n_{\mathbf{f}\sigma}+\sum_{\mathbf{ff}'\sigma}B_{\mathbf{ff}'}c_{\mathbf{f}\sigma}{}^+c_{\mathbf{f}'\sigma}+U/2\sum_{\mathbf{f}\sigma}n_{\mathbf{f}\sigma}n_{\mathbf{f}-\sigma}$$

$$(\varepsilon-\varepsilon_1-Un_{\mathbf{f}-\sigma})\langle\langle c_{\mathbf{f}\sigma}|\overset{+}{c}_{\mathbf{f}'\sigma}\rangle\rangle=\frac{1}{2\pi}\delta_{\mathbf{ff}'}+\sum_{\mathbf{f}''}B_{\mathbf{ff}''}\langle\langle c_{\mathbf{f}''\sigma}|\overset{+}{c}_{\mathbf{f}'\sigma}\rangle\rangle. \quad (1)$$

Using the translation symmetry along the crystal surface, we are led from the Green's function in lattice-site representation to its Fourier transform $G^{\sigma}_{zz'}(\varepsilon,k)$ in x and y (ε is energy, $\mathbf{k}$ is the two-dimensional wave vector). Making all the energy parameters dimensionless relative to $2B$, we can write the equation for the Green's function in the compact form

$$\gamma G=\frac{1}{4\pi N_\perp B}I, \quad (2)$$

where $N_\perp=N_xN_y$ is the number of atoms in a layer, I is the $N\times N$-dimensional identity matrix, while the matrix γ is also $N\times N$ and has the form

$$\gamma_{zz'}=-{}^1/_2\delta_{z-1,z'}+(\omega_{\mathbf{k}}+gC_z)\delta_{z,z'}-{}^1/_2\delta_{z+1,z'}. \quad (3)$$

Here we introduce the following notation:

$$g=U/2B,\quad \omega_{\mathbf{k}}=\omega-S_{\mathbf{k}},\quad S_{\mathbf{k}}=\cos k_xa+\cos k_ya,$$
$$\omega=(\varepsilon-\varepsilon_1-Un_0/2)/2B,\quad C_z=(n_z-n_0)/2,$$

where n_z is the number of electrons per atom for a layer with index $z=1,\dots,N$ and n_0 is the number of electrons per atom when one is sufficiently far from the metallic surface layer ($N\gg z\gg 1$). We will henceforth denote energies by the quantity ω, and the Fermi energy by $\omega_f=(\varepsilon_f-\varepsilon_1-Un_0/2)/2B$. In this section, we will investigate the nonmagnetic case; thus, in going from (1) to (2) and (3) we will set $n_{z\sigma}=n_{z-\sigma}=n_z/2$. Our goal is to calculate the electron density-of-states function $\rho_z(\omega)$, and the amount of deviation C_z in the occupation number of electrons from its bulk value, as a function of the atomic-layer number z and the position of the Fermi level, to zeroth and first order in g. As we will see below, $\max|C_z|\sim 10^{-2}$, which points to smallness of the term gC_z in (3) and allows us to use an expansion in g even if $g\sim 1$. We will not keep track of electrical neutrality, since in transition metals electrical neutrality is provided by the s-electrons.

From (2) follows an obvious solution for $G\sim\gamma^{-1}$. Let us expand G in a series in g ($G=G^0+gG^1$). The diagonal matrix elements of the Green's function, which are all that is of interest to us, are expressible in terms of the determinants d_l of the matrix $\gamma(l\times l)$ at $g=0$:

$$G_{zz}=\frac{1}{4\pi N_\perp B}\Big[d_{z-1}d_{N-z}/d_N+g\Big(d_{z-1}d_{N-z}\sum_{m=1}^{N}C_md_{m-1}d_{N-m}$$
$$-d_{N-z}d_N\sum_{m=1}^{z-1}C_md_{m-1}d_{z-1-m}-d_{z-1}d_N \quad (4)$$
$$\times\sum_{m=z+1}^{N}C_md_{m-z-1}d_{N-m}\Big)\Big/d_N{}^2\Big].$$

The determinants d_l can be calculated by the recursion-relation method. For the condition $|\omega_k|<1$, the answer for d_l has the form

$$d_l=\frac{1}{2^l}\frac{\sin\varphi(l+1)}{\sin\varphi}, \quad (5)$$

where the angle φ is determined from the relations $\sin\varphi = (1-\omega_k^2)^{1/2}$, $\cos\varphi = \omega_k$. We can show that if we use the opposite condition $|\omega_k| > 1$ we are led to a value of zero for the electronic density of states both in zeroth and first approximation in g. From this it follows that in the problem under discussion here there are no extra allowed energy intervals, i.e., no surface bands. This result is in agreement with the results obtained in Ref. 22, in which the (100) face of a simple cubic lattice was also treated (although calculations were carried out there only for the case $g=0$).

From (4), we can, by taking (5) into account, obtain expressions for the retarded and advanced Green's functions of an atom in the zth layer in the semi-infinite ($N\to\infty$) metal:

$$G_{zz}(\omega\pm i0,\mathbf{k}) = \frac{1}{4\pi N_\perp B}\Big[2^z e^{\mp i\varphi z} + g\Big(d_{z-1}2^z e^{\mp i\varphi z}\sum_{m=1}^{\infty} C_m d_{m-1}2^m e^{\mp i\varphi m} - 2^z e^{\mp i\varphi z}\sum_{m=1}^{z-1} C_m d_{m-1} d_{z-1-m} - d_{z-1}\sum_{m=z+1}^{\infty} C_m d_{m-z-1}2^m e^{\mp i\varphi m}\Big)\Big] \tag{6}$$

and corresponding to it the electron density-of-states function

$$\rho_z(\omega) = \frac{1}{\pi N_\perp B}\sum_{\mathbf{k}}\Big\{\frac{\sin^2\varphi z}{\sin\varphi} - 2g\frac{\sin\varphi z}{\sin^2\varphi} \times \Big[\sum_{m=1}^{z-1} C_m \sin\varphi m \sin\varphi(z-m) + \sum_{m=z+1}^{\infty} C_m \sin\varphi(m-z)\sin\varphi m - \sum_{m=1}^{\infty} C_m \sin\varphi m \sin\varphi(z+m)\Big]\Big\}. \tag{7}$$

Analogously, we obtain the bulk Green's functions and electron density of states for atoms in a layer sufficiently far from the surface ($N\to\infty$, $z\to\infty$):

$$G_0(\omega\pm i0,\mathbf{k}) = \frac{1}{4\pi N_\perp B}\frac{\mp i}{\sin\varphi}, \qquad \rho_0(\omega) = \frac{1}{\pi N_\perp B}\sum_{\mathbf{k}}\frac{1}{2\sin\varphi}. \tag{8}$$

The Green's function G_0 and electronic density of states ρ_0, as one can convince oneself, coincide with the analogous (and well-known) expressions for the bulk metal integrated over k_z.[20] We can also show that expressions (6) and (7) for $g=0$ coincide with the analogous expressions obtained in Ref. 22 by other techniques, if the perturbation U_0 introduced in this work for a surface atomic layer is set equal to zero in the spirit of our work here. Corrections to the interaction in (6) and (7) are calculated in the present work for the first time.

Using (7) and (8), we can obtain expressions for the occupation numbers n_z and n_0, and consequently for C_z:

$$C_z = -\frac{2}{\pi N_\perp}\sum_{\mathbf{k}}\int_{-\infty}^{\omega_f} d\omega\Big\{\frac{\cos\varphi 2z}{2\sin\varphi} + g\frac{\sin\varphi z}{\sin^2\varphi}\Big[\sum_{m=1}^{z-1} C_m \sin\varphi m \sin\varphi(z-m) + \sum_{m=z+1}^{\infty} C_m \sin\varphi(m-z)\sin\varphi m - \sum_{m=1}^{\infty} C_m \sin\varphi m \sin\varphi(z+m)\Big]\Big\}. \tag{9}$$

Relation (9) gives a set of simultaneous equations for the quantity C_z, which we will solve by the method of perturbation theory in the small parameter $j = U/W = g/6$. We expand the quantity C_z as a series in j ($C_z = C_z^0 + jC_z^1$) and substitute it into (9). Equating coefficients of equal powers of j, we obtain in zero-order approximation

$$C_z^0 = -\frac{2}{\pi N_\perp}\sum_{\mathbf{k}}\int_{-\infty}^{\omega_f} d\omega\frac{\cos\varphi 2z}{2\sin\varphi}. \tag{10}$$

The quantity C_z^1 can be expressed in terms of C_z^0. After some straightforward but tedious calculations, consisting essentially of a summation of the series in (9), we obtain with allowance for (10) an expression for C_z^1 in the compact form

$$C_z^1 = -\frac{3}{2}\Big(\frac{2}{\pi N_\perp}\Big)^2\sum_{\mathbf{k}\mathbf{k}'}\int_{-\infty}^{\omega_f} d\omega\int_{-\infty}^{\omega_f} d\omega'\,\frac{\sin\varphi z[\sin\varphi'(2z-1)\sin\varphi(z+1) - \sin\varphi'(2z+1)\sin\varphi(z-1)]}{\sin\varphi\sin^2\varphi'(\sin^2\varphi - \sin^2\varphi')}. \tag{11}$$

In analogous fashion, we obtain an expression for $\Delta\rho_z$ ($\rho_z = \rho_z^0 + j\Delta\rho_z$), which differs from equation (11) only in the absence of an integration over energy ω and the dimensional multiplier $2B$.

The quantities C_z^0 oscillate, and decrease as the layer index increases—these are Friedel oscillations in the electron density. The dependence of the quantities C_z^1 on z are rather difficult to extract from (11). However, the integrals in ω and ω' in (11) can be evaluated for $z = 1, 2, 3$ (see the Appendix). A graph of the dependences of C_z^0 and C_z^1 on the Fermi energy ω_f is shown in Fig. 1. From this figure, it is clear that the quantities C_z^1 also oscillate and decrease with

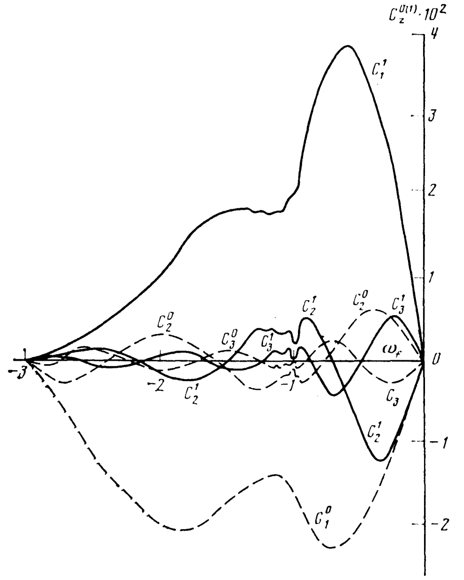

FIG. 1

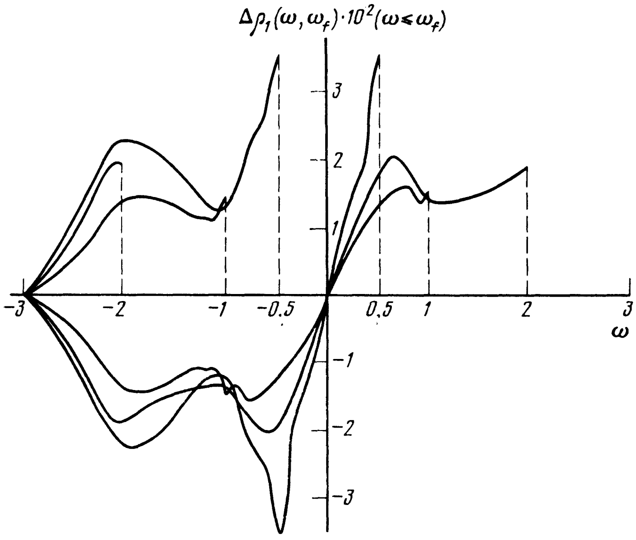

FIG. 2

increasing z, i.e., the Friedel oscillations are strongly screened as we pass into the metal interior. It is also clear that $\max|C_z^{0(1)}|\sim 10^{-2}$, which justifies our expansion of the Green's function in a series in g (see (3) and below). The dependences of the quantities $C_z^{0(1)}$ on ω_f have an oscillatory character and are of odd parity in ω_f. This latter fact is connected with the electron-hole symmetry which occurs in the Hubbard model for non-degenerate bands.[23] The largest values of $C_z^{0(1)}$ are achieved at the first atomic layer. This justifies our using the usual approximation, in which it is assumed that when a surface is created, a strong change in the number of electrons per atom occurs only for the surface atomic layers. An exception to this is the energy region directly adjacent to the center of the band, where the magnitudes of the peaks of C_2^0 and C_2^1 are comparable to C_1^0. Consequently, for transition metals located in the center of the d-series, it is in general also necessary to take into account the change in electron number at atoms located in the next few atomic layers below the surface. This situation clearly obtains for chromium, which is located at the center of the $3d$ series. This inference agrees with the considerations expressed in Ref. 15 relating to the electronic structure of the near-surface layers of chromium.

The quantities C_z^0 and C_z^1 for the same atomic layer have opposite signs over a wide range of values of the Fermi energy ω_f. From this it can be inferred that switching on the interaction ($U/W\neq 0$) should lead to a smoothing out of the Friedel oscillations in the electron density, i.e., to a decrease in the thickness of the transition layer at the metal surface. Such a situation should occur as we go from simple to transition metals.

In Fig. 2 we present the dependence of $\Delta\rho_1$ on the energy ω for various values of the Fermi energy ω_f. It is important to note that the value of the quantity $\Delta\rho_1$ at the Fermi level ω_f is always positive. This has direct bearing on our description of the appearance of surface ferromagnetism: an increase in the value of the electronic density of states of a surface atom at the Fermi level, as will be shown below, leads to relaxation of the criterion for Stoner ferromagnetism, i.e., at the surface this criterion is fulfilled at a smaller value of the parameter U/W than for the volume. For $\Delta\rho_1$ we have

III. SURFACE FERROMAGNETISM

Clearly, surface ferromagnetism is a property of a small number of atomic layers near the surface. We approximate the problem by assuming that for $z>1$ all the metallic layers coincide with the bulk layers, which we assume to be nonmagnetic, and that only for the surface atoms can the electron occupation numbers for different spins be unequal, i.e., $n_+\neq n_-$. This implies that the surface atomic layer is different from the remaining layers, and is equivalent to a self-consistent renormalization of the model parameters as we go from the inner metallic layers to the surface. However, as we will see below, surface ferromagnetism occurs for certain values of the Fermi energy for which, according to the results of the previous section, the layers immediately below the surface can actually be considered as no different from the infinite bulk metallic layers. In keeping with these statements, we return to equation (1) and pass from the Green's functions in the lattice-site representation to their Fourier transforms in x and y, just as was done in the previous section. Now there is one difference, however: we retain the spin index σ of the electron occupation numbers for the surface atoms. The equation for the Green's function G^σ again takes the form (2), while the matrix γ^σ is determined by expression (3), but now the matrix element γ_{11}^σ is

$$\gamma_{11}{}^{\sigma}=\omega_{\mathbf{k}}-g\delta n_{-\sigma},\quad \delta n_{-\sigma}=n_{-\sigma}-n_0/2,$$

where n_σ is the electron occupation number for spins $\sigma=+,-$, for an atom on the surface layer ($z=1$). We will try to evaluate the occupation numbers n_+ and n_- in a self-consistent way; again, we will not keep track of charge neutrality, since in transition metals this is supplied by the s-electrons, which do not take part in the formation of surface ferromagnetism.

The Green's function G_{11}^{σ} can be expressed in terms of the determinants d_l (see (5)):

$$G_{11}^{\sigma}=\frac{1}{4\pi N_{\perp}B}\frac{d_{N-1}}{(\omega_{\mathbf{k}}-g\delta n_{-\sigma})d_{N-1}-{}^1/_4 d_{N-2}}. \tag{12}$$

In this work, the appearance of surface ferromagnetism is not connected with the appearance of additional allowed energy regions, i.e., surface bands. (As was shown in Section II, the density-of-states for surface atoms for energies outside the band is zero.) Using (12), we find the retarded and advanced Green's functions for a surface atom in the semi-infinite ($N\to\infty$) metal:

$$\begin{aligned}G_{11}^{\sigma}(\omega\pm i0,\mathbf{k})&=\lim_{s\to+0}\lim_{N\to\infty}G_{11}^{\sigma}(\omega\pm is,\mathbf{k})\\&=\frac{1}{4\pi N_{\perp}B}\frac{2}{\omega_{\mathbf{k}}\pm i(1-\omega_{\mathbf{k}}^2)^{1/2}-2g\delta n_{-\sigma}}.\end{aligned}$$

Furthermore, after expanding $G_{11}^{\sigma}(\omega\pm i0,k)$ in a series in the parameter $2g\delta n_{-\sigma}$ and limiting ourselves to second order terms, we find by standard methods the density-of-states functions ρ_1^{σ} for the surface layer. Integrating ρ_1^{σ} multiplied by the Fermi distribution, we obtain equations for the occupation numbers n_+ and n_-, or for the quantities $\delta n=\delta n_+ + \delta n_-$, $m=n_+ - n_-$, i.e., the difference between the numbers of electrons per atom in the surface layer and in an interior layer, and the magnetic moment of a surface atom, respectively:

$$\begin{aligned}\delta n&=-{}^1/_4R_1-g\delta nQ+{}^1/_2g^2[(\delta n)^2+m^2]R,\\ m&=gmQ-g^2m\delta nR.\end{aligned}\tag{13}$$

The coefficients R, R_1 and Q depend on the Fermi energy ω_f and the temperature $t=T/2B$; expressions for them are given in the Appendix. The system of equations (13) has both magnetic and nonmagnetic solutions. Setting $m=0$ in (13), we obtain from the first equation the quantity $\delta n=\delta n_{\rm PM}$

$$\delta n_{\rm PM}=\{1+gQ-[(1+gQ)^2+g^2RR_1/2]^{1/2}\}/Rg^2. \tag{14}$$

The magnetic solution is given by the result

$$\begin{aligned}\delta n_{\rm FM}&=-(1-gQ)/Rg^2\\ m^2&=[g^2(2Q^2+RR_1)+4gQ-6]/2g^4R^2.\end{aligned}\tag{15}$$

From the expression for m^2 follows a condition for the appearance of surface ferromagnetism: we will have $m^2>0$ if

$$\begin{aligned}j=U/W>j_s(\omega_f,\ t)&=g_s/6\\&=[-Q+(4Q^2+3RR_1/2)^{1/2}]/(6Q^2+3RR_1).\end{aligned}\tag{16}$$

For $t=0$, we can find from formula (16) a region of values of the parameters ω_f and $j=U/W$ for which the surface atomic layer is ferromagnetic, while the interior is nonmagnetic. The region where surface ferromagnetism (SFM) exists is depicted in Fig. 3, where a magnetic phase diagram in the variables (ω_f, j) is presented for the surface and bulk, for $\omega_f<0$. The portion of the diagram for $\omega_f>0$ is obtained by mirror reflection of the $\omega_f<0$ diagram relative to the $\omega_f=0$ axis, by virtue of the even parity of all dependences shown in Fig. 3 on ω_f.

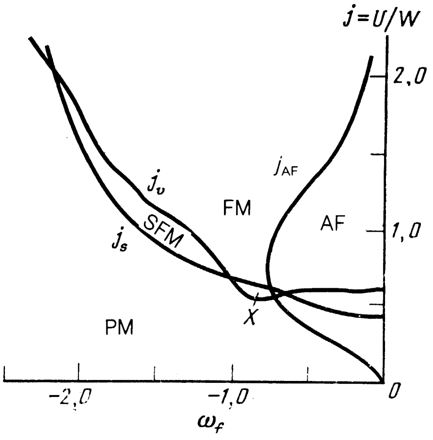

FIG. 3

In Fig. 3, the phase boundary for volume ferromagnetism j_v is obtained from the Stoner criterion, while the surface phase boundary j_s is found from condition (16). From this figure, it is apparent that surface ferromagnetism arises for smaller values of the parameter $j=U/W$ than are needed for volume ferromagnetism at the same value of ω_f. Comparing Figs. 1 and 3, we see that surface ferromagnetism occurs for those values of ω_f for which the change in electron occupation number for an atom in the layers *next* to the surface can be neglected. For $|\omega_f|>1.6$, the quantities j_v and j_s are >1, and therefore lie beyond the limits of the self-consistent field approximation; hence, we will not investigate these values of ω_f. To complete the picture of the (ω_f, j) diagram, we also present the phase boundary $j_{\rm AF}$ for volume antiferromagnetism (AF). The presence of surface ferromagnetism in the problem under investigation here is connected with an "effective narrowing" of the band, due to the smaller number of nearest neighbor lattice sites as we go from the interior metallic layers to the surface; this implies that the density-of-states functions for a surface atom ρ_1 and a bulk atom ρ_0 near the top and bottom of the band are in the relation $\rho_1\ll\rho_0$, since $\rho_1\sim|3-|\omega||^{3/2}$ while $\rho_0\sim|3-|\omega||^{1/2}$ (see e.g., Ref. 24). Taking into account the normalization of ρ_0 and ρ_1 (on one atom there can be a maximum of two electrons), this distortion in the density-of states functions for the transition from bulk atoms to surface atoms leads to the existence of intermediate values of the quantity ω_f, for which $U\rho_1>1>U\rho_0$, i.e., at the surface the Stoner criterion is satisfied while in the volume layers it is not.

For fixed values of ω_f, in the region where surface ferromagnetism exists (see Fig. 3), an increase in the parameter $j=U/W$ leads at some point to the appearance first of a surface magnetic moment and then for a further increase in j to the appearance of a moment on the interior layers. Both of these phase transitions are second-order phase transitions, since it is easily established that the expression for $\delta n_{\rm PM}$ (14) at the point of the surface phase transition matches smoothly with expression (15) for $\delta n_{\rm FM}$, i.e., without a discontinuity. For values of ω_f corresponding to the region X on the (ω_f, j) phase diagram, surface ferromagnetism on a nonmagnetic volume is impossible for the $t=0$ case assumed here, since in this case $j_v(\omega_f) < j_s(\omega_f)$. A comparison of the energies of the paramagnetic and ferromagnetic phases for the surface layer shows that the ferromagnetic state is more advantageous for values of ω_f and j in the region of surface ferromagnetism on the (ω_f, j) diagram (Fig. 3).

In Ref. 18, a correspondence results of magnetic solutions to the Hubbard model were set in correspondence with the magnetic properties of transition metals. On the basis of qualitative considerations regarding the values of U and W, it was shown that the parameter $j = U/W$ increases as the d-shell of the transition metals becomes filled, both for $5d$ and $3d$ transition metals. Assuming that there is close to a direct proportionality between the number of d electrons of an element in the periodic table and the Fermi energy ω_f (for a change in ω_f from -3 to 3, the number of electrons per atom goes from 0 to 2), we can expect that surface ferromagnetism is most likely to be observed for elements located at the beginning of the $3d$ series and at the end of the $4d$ series, which do not exhibit volume magnetism. The results of measurements of the magnetic susceptibility of finely-dispersed particles of vanadium,[1,3] which is located at the beginning of the $3d$ series, can be clearly explained by the presence of surface ferromagnetism in correspondence with the results obtained here. If the model parameters for the surface U_s and B_s and for the bulk U and B are chosen so that $U_s > U$ or $B_s < B$, we can then expect that the phase boundary j_s on the (ω_f, j) diagram will be lowered, and that the region of surface ferromagnetism will be widened.

Let us now investigate the $t \neq 0$ case. Here, the coefficients R, R_1 and Q in (13)–(16) depend not only on the Fermi energy but also on the temperature t (see Appendix). Let us fix the value of ω_f so that it corresponds to the region of surface ferromagnetism at $t = 0$ (i.e., $-1.6 < \omega_f < -1.0$) in Fig. 3, and elucidate the way that the phase boundaries for volume and surface ferromagnetism $j_v(t)$ and $j_s(t)$ change with temperature. It turns out that the function $j_v(t)$ goes through a minimum while $j_s(t)$ increases smoothly with temperature, as shown in Fig. 4. The minimum in the curve $j_v(t)$ leads to a pair of solutions for the Curie temperature t_{Cv} of a volume layer of metal. This effect was established earlier in Ref. 25. The curves for $j_v(t)$ and $j_s(t)$ do not intersect for all numerical choices of the Fermi energy ω_f (see above) and temperature t. From the plots of $j_v(t)$ and $j_s(t)$, it is clear that for the region of values of ω_f under investigation, surface ferromagnetism vanishes at temperatures higher than those at which volume ferromagnetism, i.e., $t_{Cs} > t_{Cv}$. It is also clear from Fig. 4 that a situation can occur where, as the temperature increases, no volume magnetic moment is present, while a surface magnetic moment which is present at $t = 0$ vanishes at some finite temperature t_{Cs}. That is to say, the Curie temperature t_{Cs} of the surface can be higher than the Curie temperature of a bulk layer t_{Cv}, which is in direct correspondence with existing experimental data for transition metals. By virtue of the even-parity dependence of all quantities on ω_f, as exhibited on the (ω_f, j) diagram (see Fig. 3), these results also obtain for the region of values $\omega_f = (1.0–1.6)$, which allows us to correlate our results with experimental data on nickel and cobalt. In order to describe the magnetic behavior of the chromium surface, it is necessary to know the dependence of the Néel temperature t_N on the values of ω_f and j. However, the fact of possible ferromagnetic order at the surface of a nonmagnetic metal has been established, which qualitatively corresponds to the situation with chromium for $t > t_N$.

If the value of the Fermi energy ω_f is fixed so that it corresponds to the region X (see Fig. 3), it turns out that the curves $j_v(t)$ and $j_s(t)$ intersect, as shown in Fig. 5. Here, there are two possible cases. If $j_v(t=0) < j < j_s$, then as the temperature increases, the volume ferromagnetism vanishes at the Curie temperature t_{Cv}. If $j > j_s(t=0)$, however, then for $t < t_{Cv}$ we have a volume ferromagnet, while for $t > t_{Cv}$ the nonmagnetic metal has a ferromagnetic surface up to the surface Curie temperature $t_{Cs} > t_{Cv}$. However, one must keep in mind that the region X in the (ω_f, j) diagram corresponds to values of the parameters ω_f and j which give rise to the magnetic state in the interior layers of metal (a magnetic state with an order parameter close to the ferromagnetic state).[26] Thus, a more detailed investigation of magnetism in the region X of the parameters ω_f and j may lead to the result that the assumptions made in the present work about the bulk non-magnetic state of the interior layers of metal break down.

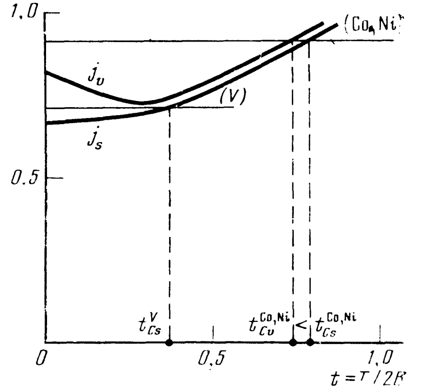

FIG. 4

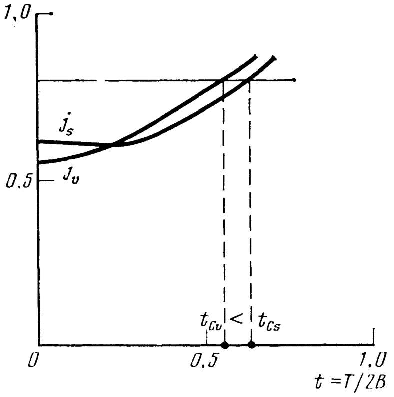

FIG. 5

In conclusion, we want to thank S. Yu. Davydov for discussing these results.

APPENDIX

For $z = 1,2,3$, the integrals over energies ω and ω' in (11) can be evaluated under the condition that $|\omega_k| < 1$, which must be used to determine the value of the original function at the lower limit of integration (and at the upper limit, if the Fermi energy corresponds to the top of the band):

$$C_1^1(\omega_f) = \frac{3}{2}\left(\frac{2}{\pi N_\perp}\right)^2 \sum_{\mathbf{k}\mathbf{k}'}\left[\cos\varphi_f \ln\left|\frac{\sin(\varphi_f+\varphi_f')}{\sin(\varphi_f-\varphi_f')}\right| + \cos\varphi_f' \ln\left|\frac{\sin\varphi_f - \sin\varphi_f'}{\sin\varphi_f + \sin\varphi_f'}\right|\right],$$

$$C_2^1(\omega_f) = 2\left(\frac{2}{\pi N_\perp}\right)^2 \sum_{\mathbf{k}\mathbf{k}'}\left[\sin 2\varphi_f' \sin\varphi_f \cos 2\varphi_f + \cos^3\varphi_f \ln\left|\frac{\sin(\varphi_f+\varphi_f')}{\sin(\varphi_f-\varphi_f')}\right| + \cos^3\varphi_f' \ln\left|\frac{\sin\varphi_f - \sin\varphi_f'}{\sin\varphi_f + \sin\varphi_f'}\right|\right],$$

$$\begin{aligned} C_3^1(\omega_f) &= \frac{1}{10}\left(\frac{2}{\pi N_\perp}\right)^2 \sum_{\mathbf{k}\mathbf{k}'}\Big[-48\sin^5\varphi_f(2\sin 2\varphi_f' + \sin 4\varphi_f') \\ &+ 4\sin^3\varphi_f(34\sin 2\varphi_f' + 15\sin 4\varphi_f') \\ &- 4\sin\varphi_f(8\sin 2\varphi_f' + 3\sin 4\varphi_f') \\ &+ (48\cos^5\varphi_f' - 40\cos^3\varphi_f' + 15\cos\varphi_f') \\ &\times \ln\left|\frac{\sin\varphi_f - \sin\varphi_f'}{\sin\varphi_f + \sin\varphi_f'}\right| \\ &+ (48\cos^5\varphi_f - 40\cos^3\varphi_f + 15\cos\varphi_f) \\ &\times \ln\left|\frac{\sin(\varphi_f+\varphi_f')}{\sin(\varphi_f-\varphi_f')}\right|\Big], \end{aligned}$$

where $\varphi_f^{(\prime)} = \arccos(\omega_f - S_{\mathbf{k}^{(\prime)}})$. The summation over **k** and **k**′ is in the first Brillouin zone of a square lattice.

The coefficients R, R_1 and Q depend on ω_f and t, and are determined from the expressions

$$R = \frac{2}{\pi N_\perp}\sum_{\mathbf{k}}\int_{-\infty}^{+\infty} d\omega\, 8(4\omega_{\mathbf{k}}^2-1)(1-\omega_{\mathbf{k}}^2)^{1/2} \times [\exp((\omega-\omega_f)/t)+1]^{-1},$$

$$R_1 = \frac{2}{\pi N_\perp}\sum_{\mathbf{k}}\int_{-\infty}^{+\infty} d\omega\, 2(2\omega_{\mathbf{k}}^2-1)(1-\omega_{\mathbf{k}}^2)^{-1/2} \times [\exp((\omega-\omega_f)/t)+1]^{-1},$$

$$Q = -\frac{2}{\pi N_\perp}\sum_{\mathbf{k}}\int_{-\infty}^{+\infty} d\omega\, 4\omega_{\mathbf{k}}(1-\omega_{\mathbf{k}}^2)^{1/2}[\exp((\omega-\omega_f)/t)+1]^{-1},$$

$$t = T/2B.$$

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