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# Surface Effects on the Spin Susceptibility of Paramagnetic Metals; A Simple Model

D. L. Mills*
*Department of Physics, University of California, Irvine, California* 92664

and

M. T. Béal-Monod
*Physique des Solides, Laboratoire associé au Centre National de la Recherche Scientifique,*
*Université de Paris-Sud, Centre d'Orsay, 91-Orsay, France*

and

R. A. Weiner
*Department of Physics, Carnegie-Mellon University, Pittsburgh, Pennsylvania* 15213

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The purpose of this paper is to study the effect of a surface on the spin susceptibility of simple models of paramagnetic metals. We first formally derive the form of the random-phase-approximation (RPA) equation satisfied by the dynamic susceptibility of a single tight-binding band of electrons that interact via a local intra-atomic Coulomb interaction. We then find an explicit expression for the dynamic susceptibility appropriate to a simple cubic metal with a (100) surface, in the absence of interactions. Special limiting forms of this function are studied, and in particular the magnitude of the magnetic moment induced in the surface layer by a static, spatially uniform field is calculated as a function of the position of the Fermi level. In a final section, we use a simplified form of the RPA equations to obtain analytic expressions for the static, wave-vector-dependent susceptibility in the limit that exchange enhancement of the host becomes large. The static correlation length between spins in the surface layer remains finite in our model even when the Stoner factor $1-\overline{I}$ vanishes. The form of the static correlation function is weakly dependent on $(1-\overline{I})$ when this parameter is small, but we find a rather strong dependence on the strength of the intra-atomic Coulomb interaction in the surface layer. A number of features of this result are discussed and compared with an earlier molecular-field theory of static spin correlations near the surface of the Heisenberg paramagnet.

## I. INTRODUCTION

A number of theoretical studies of the effect of a surface on the magnetic properties of crystals have been carried out. With one exception,[1] these papers have confined their attention to materials described by the Heisenberg model of ferromagnetism and antiferromagnetism.[2]

At low temperatures, spin-wave theory may be employed to explore the effect of a surface on the excitation spectrum and the thermodynamic properties of the crystal. More recently,[3] molecular-field theory has been used to obtain an approximate description of the temperature dependence of the magnetization near the surface when the temperature is close to the ordering temperature, and also the behavior of the static spin-correlation function $\langle S_z(\vec{1})S_z(\vec{1}')\rangle$ when $\vec{1}$ and $\vec{1}'$ are in or near the surface. These studies show that the presence of the surface modifies the behavior of the spins in or near the surface in important qualitative ways. For example, as the temperature $T$ approaches the ordering temperature $T_0$ of the bulk material, it is well known that the static correlation length in the bulk becomes infinite. However, at least within the framework of the molecular-field theory, the static correlation length associated with the function $\langle S_z(\vec{1})S(\vec{1}')\rangle$ remains microscopic and insensitive to temperature as $T \rightarrow T_0$ from above.[3] The spins in the surface are forced into order by the effective field which arises from the ordering of the bulk spins, and no long-range spatial correlations appear within the surface layer near $T_0$. At low temperatures, as well as just below the ordering temperature $T_0$,[2,3] the magnetization in and near the surface is much smaller than in the bulk of the crystal.

So far, we know of no study of the effect of a surface on the magnetic response of an itinerant-electron gas. In particular, in itinerant-electron materials that are strongly paramagnetic either because the exchange enhancement is large, or because the temperature is near the magnetic ordering temperature $T_0$, one might expect the behavior of the material near the surface to be very different from that in the bulk, if the itinerant-electron gas exhibits behavior similar to that described above for the Heisenberg model.

The purpose of this paper is to explore the effect of a surface on the properties of an itinerant-electron material that is strongly paramagnetic by virtue of strong exchange enhancement in the bulk of the material. We begin by deriving an equation for the dynamic susceptibility of the system by means of a random-phase-approximation (RPA) decoupling scheme. This is done for a model which describes a single narrow band of electrons, which may be described by the tight-binding picture in the one-electron approximation. Two electrons interact only when they are in the same unit cell of the crystal. For the case where the interactions between the electrons are ignored, and the crystal is taken to be simple cubic with a (100) surface, we derive a form for the dynamic susceptibility. If a static, spatially uniform magnetic field is imposed on the system, the magnetization induced by the field, as a function of distance from the surface, is given by a simple analytic expression that may be calculated readily from tabulated functions. We then turn to the case where the exchange enhancement in the bulk is large. We are not able to solve the full RPA equations for the dynamic response. However, we modify these equations and produce an integral equation which may be solved in closed form for the static correlation function. We allow the strength of the interaction between electrons to differ from the bulk value when they are in the surface.

The form of the static correlation function we obtain from our model bears a close resemblance to the results obtained earlier for the Heisenberg ferromagnet and antiferromagnet, when the temperature is close to the ordering temperature. The surface has a pronounced and qualitative effect on the nature of the static correlation function and on the response of the surface region to an external field. As the quantity $(1-\overline{I})$, the inverse of the exchange enhancement factor, is allowed to approach zero, the static correlation length remains microscopic in the surface layer, while in the bulk it diverges as $(1-\overline{I})^{-1/2}$. The form of the static correlation function is more sensitive to the parameters that characterize the surface environment (in our case, the change in intra-atomic Coulomb interaction near the surface) than to the value of $\overline{I}$.

Recently, a theory of chemisorption has been advanced by Schrieffer and Gomer.[4] This theory relates the chemisorption energy to the local susceptibility of the metal at the surface. Our result suggests that the Schrieffer-Gomer expression for the chemisorption energy should be insensitive to the presence of bulk exchange enhancement. To the extent that one may replace the parameter $1-\overline{I}$ of the paramagnon theory by $(T-T_c)/T_c$, the results also suggest that the chemisorption energy should not exhibit an anomaly as the temperature of a ferromagnetic substrate passes through $T_c$. We also note that Suhl and co-workers[5] have presented a theory of spin-fluctuation-induced desorption in nearly ferromagnetic metals. A central approximation used in this work is that the dynamic wave-vector-dependent susceptibility near the surface is taken to be the same as that in the bulk. We cannot make direct contact with this work, because we have not obtained information about the frequency dependence of the susceptibility near the surface. However, we feel our results for the static susceptibility cast some doubts on the validity of the approximation used by Suhl *et al.*, since we find the local static susceptibility is insensitive to $\overline{I}$, as mentioned earlier.

## II. RPA EQUATIONS FOR THE SEMI-INFINITE MATERIAL

In this section we sketch the derivation of an equation for the dynamic susceptibility of a semi-infinite gas of interacting electrons. The model described in Sec. I will be employed, and the decoupling scheme we use is the random-phase approximation (RPA). Since the use of the RPA is by now a standard procedure, we only provide a brief sketch of the procedure. This section serves primarily to establish notation and define the model.

As we stated earlier, we consider a single band of electrons. We assume that the electrons move in an energy band that may be described by the tight-binding picture. Then the kinetic energy $T$ of the electrons may be written in second-quantized form:

$$T=\sum_{\vec{l}\vec{\delta}\vec{\sigma}} t(\vec{\delta})c^{\dagger}_{\vec{l}+\vec{\delta},\sigma}c_{\vec{l}\sigma}\ , \tag{1}$$

where $c_{\vec{l}\sigma}, c^{\dagger}_{\vec{l}\sigma}$ destroy or create electrons of spin $\sigma$ on the site $l$ of the lattice. The quantity $t(\vec{\delta})$ describes the hopping rate between site $\vec{l}$ and $\vec{l}+\vec{\delta}$. The sum over sites in Eq. (1) is presumed to extend only over a semi-infinite solid. An electron at a site in the surface layer thus can "hop" to fewer sites than an electron in the bulk. In general, one expects the transfer integrals $t(\vec{\delta})$ to assume values in the surface layer different from those appropriate to the bulk. Since little is known about these changes at the present time, we assume that the hopping integral between sites in and near the surface is the same as in the bulk. The form of the formal results of this section are not affected by this assumption, and the effects of changes in $t(\vec{\delta})$ near the surface are easily incorporated into the discussion of Sec. III, although the results presented there will then assume a more complicated algebraic form.

The electrons interact with each other by means of the intra-atomic Coulomb interaction in the model. We write the Coulomb term in the Hamiltonian in the form

$$V_C=\sum_{\vec{l}} U(l_z)n_{\vec{l}\uparrow}n_{\vec{l}\downarrow} \,. \tag{2}$$

The strength of the intra-atomic Coulomb integral is allowed to vary with the distance $l_z$ of site $\vec{l}$ from the surface. Particularly in nearly ferromagnetic metals, one expects that changes in the strength of the Coulomb interaction near the surface will play an important role in determining the magnetic response. The total Hamiltonian is thus

$$H=T+V_C \,. \tag{3}$$

We wish to study the correlation function

$$S(\vec{l}_1\vec{l}_2\vec{l}_3\vec{l}_4;\, t)=i\theta(t)\langle[c^\dagger_{\vec{l}_1\uparrow}(t)c_{\vec{l}_2\downarrow}(t),\, c^\dagger_{\vec{l}_3\downarrow}(0)c_{\vec{l}_4\uparrow}(0)]\rangle \,. \tag{4a}$$

Attention will be focused on the particular combination

$$\begin{aligned}\chi(\vec{l}\vec{l}\,';t)&=S(\vec{l},\vec{l},\vec{l}\,',\vec{l}\,';t)\\ &=i\theta(t)\langle[s^+_{\vec{l}}(t),s^-_{\vec{l}\,'}(0)]\rangle \,.\end{aligned} \tag{4b}$$

In Eq. (4b), $s^+_{\vec{l}}$ and $s^-_{\vec{l}\,'}$ are the spin raising the lowering operators for the site $\vec{l}$. If a transverse magnetic field of frequency $\omega$ is applied locally to site $\vec{l}\,'$ of the system, then the amplitude of the spin density induced at site $\vec{l}$ is proportional to

$$\chi(\vec{l}\vec{l}\,';\omega)=\int\frac{d\omega}{2\pi}\,e^{i\omega t}\chi(\vec{l}\vec{l}\,',t) \,. \tag{5}$$

To derive an equation satisfied by $\chi(\vec{l}\vec{l}\,',t)$, one begins by computing $i\,\partial S(\vec{l}_1\vec{l}_2\vec{l}_3\vec{l}_4,t)/\partial t$ in the standard manner. The resulting equation of motion contains terms that arise from the Coulomb interaction. These terms involve a more complicated correlation function of the form

$$\theta(t)\langle[c^\dagger_{\vec{l}_1\sigma_1}(t)c_{\vec{l}_2\sigma_2}(t)c^\dagger_{\vec{l}_5\sigma_5}(t)c_{\vec{l}_6\sigma_6}(t),\; c^\dagger_{l_3\downarrow}(0)c_{l_4\uparrow}(0)]\rangle \,.$$

The RPA consists of approximating the sequence of four operators at the time $t$ by the following form:

$$\begin{aligned}c^\dagger_i c_j c^\dagger_k c_l\rightarrow\langle c^\dagger_i c_j\rangle c^\dagger_k c_l-\langle c^\dagger_i c_l\rangle c^\dagger_k c_j\\ +\langle c^\dagger_k c_l\rangle c^\dagger_i c_j-\langle c^\dagger_k c_j\rangle c^\dagger_i c_l \,.\end{aligned}$$

From the truncated equation of motion, one may then derive a closed equation for the Fourier transform $\chi(\vec{l}\vec{l}\,',\omega)$ introduced above. The equation assumes the form

$$\begin{aligned}\chi(\vec{l}\vec{l}\,',\omega)&=\chi_0(\vec{l}\vec{l}\,';\omega)\\ &+\sum_{\vec{l}\,''}\chi_0(\vec{l},\vec{l}\,'',\omega)\,U(l''_z)\,\chi(\vec{l}\,''\vec{l}\,',\omega) \,.\end{aligned} \tag{6}$$

The sum over $\vec{l}\,''$ extends over the semi-infinite crystal. The function $\chi_0(\vec{l}\vec{l}\,';\omega)$ is the dynamic susceptibility of the medium, calculated from one-electron theory. This function is not the same as the dynamic susceptibility of the Bloch electrons for the infinitely extended crystal because of two effects that modify the single-particle wave functions. The wave functions of the crystal must be calculated in the presence of the Hartree potential, which is modified by the presence of the surface. An electron in the unit cell $\vec{l}$ with spin $\sigma$ sees the Hartree potential $U(l_z)\langle n_{\vec{l}-\sigma}\rangle$. For the model the Hartree potential is a constant in the bulk of the crystal, but it clearly varies near the surface, because $U$ may change there, and the surface will induce variations in the number density in its vicinity. The wave function of the electron is also changed by the fact that a site in the surface is coupled to fewer sites by $t(\vec{\delta})$ than a site in the bulk.

The function $\chi_0(\vec{l}\vec{l}\,',\omega)$ is well approximated by the bulk response when $\vec{l}$ and $\vec{l}\,'$ lie well within the crystal. However, from the preceding paragraph, when either $\vec{l}$ or $\vec{l}\,'$ lies in or close to the surface, we see that $\chi_0(\vec{l}\vec{l}\,',\omega)$ will differ from values appropriate to the bulk. Since $\chi_0(\vec{l}\vec{l}\,',\omega)$ is the response function appropriate to the one-electron problem in the semi-infinite medium, one does not expect large changes in $\chi_0$ unless $\vec{l}$ or $\vec{l}\,'$ lies in the surface layer or within a short microscopic distance the order of the Fermi wavelength from it.[6]

In the presence of a free surface, the crystal remains periodic in the two directions parallel to the surface.[7] This fact may be used to simplify Eq. (6). Let the surface layer be parallel to the $x$-$y$ plane, and denote vectors which lie in the $x$-$y$ plane by use of the subscript $\parallel$. Then $\chi(\vec{l}\vec{l}\,',\omega)$ and $\chi_0(\vec{l}\vec{l}\,',\omega)$ depend only on the difference $\vec{l}_\parallel-\vec{l}\,'_\parallel$, although they depend on $l_z$ and $l'_z$ separately. One may then make a partial Fourier transform and write

$$\chi(\vec{l}\vec{l}\,',\omega)=\frac{1}{N_s}\sum_{\mathcal{K}_\parallel}e^{i\mathcal{K}_\parallel\cdot(\vec{l}_\parallel-\vec{l}\,'_\parallel)}\chi(\vec{\mathcal{K}}_\parallel\omega;\,l_z,l'_z) \,, \tag{7}$$

with a similar transformation of $\chi_0(\vec{l}\vec{l}\,',\omega)$. In this expression $N_s$ is the number of unit cells in the surface layer. Upon insertion of Eq. (6) into Eq. (7), one obtains

$$\begin{aligned}\chi(\vec{\mathcal{K}}_\parallel\omega;l_zl'_z)&=\chi_0(\vec{\mathcal{K}}_\parallel\omega;l_zl'_z)\\ &+\sum_{l''_z}\chi_0(\vec{\mathcal{K}}_\parallel\omega;l_zl''_z)\,U(l''_z)\,\chi(\vec{\mathcal{K}}_\parallel\omega;l''_zl'_z) \,.\end{aligned} \tag{8}$$

The result in Eq. (8) will form the starting point for the approximate theory discussed in Sec. IV. First, in Sec. III, we turn to a study of the kernel $\chi_0(\vec{\mathcal{K}}_\parallel\omega;l_zl'_z)$.

## III. STUDY OF THE FUNCTION $\chi_0(\vec{\mathcal{K}}_\parallel\omega;l_zl'_z)$

In this section we obtain an expression for the kernel $\chi_0(\vec{\mathcal{K}}_\parallel\omega;l_zl'_z)$ that appears in Eq. (8). It is a difficult matter to do this for a general surface geometry even for a system described by the simple Hamiltonian of Eq. (3). We therefore restrict our attention to a particularly simple model, although the techniques described below may readily be adapted to a more realistic situation. The purpose of this section is to attempt to estimate the extent to which the response function $\chi_0(\vec{\mathcal{K}}_\parallel \omega, l_z l_z')$ deviates from its bulk character when $l_z$ and/or $l_z'$ lie near the surface. While the initial remarks in this section are quite general, we soon restrict attention to a simple cubic crystal with a (100) surface. We also neglect the effect of the change in the Hartree potential near the surface, so the modification we find in $\chi_0(\mathcal{K}_\parallel \omega; l_z l_z')$ comes about by the fact that an atom in the surface layer has one nearest neighbor less than an atom in the bulk. We also confine our attention to paramagnetic metals.

Suppose $\varphi_n(\vec{l})$ is the $n$th electronic eigenfunction appropriate to the semi-infinite solid, in the presence of the surface. Let $\mathcal{E}_n$ be its energy. For the moment, we need not imagine that the Hartree potential is ignored. Define a spectral-density function $\rho(\vec{l}\,\vec{l}', \Omega)$ as follows:

$$\rho(\vec{l}\,\vec{l}'; \Omega) = \textstyle\sum_n \varphi_n(\vec{l})\,\varphi_n^*(\vec{l}')\,\delta(\Omega - \mathcal{E}_n) . \tag{9}$$

It is a straightforward matter to show that

$$\chi_0(\vec{l}\,\vec{l}'; \omega) = \int \frac{d\Omega_1\, d\Omega_2 [\, f(\Omega_1) - f(\Omega_2)]}{\Omega_2 - \Omega_1 - \omega - i\eta} \times \rho(\vec{l}\,\vec{l}'; \Omega_1)\,\rho(\vec{l}'\,\vec{l}; \Omega_2) , \tag{10}$$

where $f(\Omega) = (e^{\beta\Omega} + 1)^{-1}$ is the Fermi-Dirac function.

The problem is thus to compute the spectral-density function. This may be done by introducing the Green's function

$$g(z) = 1/(z - H_1) ,$$

where $H_1$ is the Hamiltonian of the one-electron problem. Let $G(\vec{l}\,\vec{l}', z)$ denote the matrix element of the operator $g(z)$ between the Wannier states associated with sites $\vec{l}$ and $\vec{l}'$. We write

$$G(\vec{l}\,\vec{l}', z) = \langle \vec{l} | g(z) | \vec{l}' \rangle .$$

Then we have

$$\rho(\vec{l}'\,\vec{l}, \Omega) = (1/i\pi)\,\mathrm{Im}[G(\vec{l}\,\vec{l}', \Omega - i\eta)] .$$

We now compute the function $G(\vec{l}\,\vec{l}', z)$ by a technique that has proved of value in closely related problems.[2] It will be useful to specialize the discussion to the simple case mentioned above. We imagine we begin with a large macroscopic cube with sides of length $L$. The cube is assumed to be a perfect simple-cubic crystal, and we apply periodic boundary conditions to the large cube. Then form two free (100) surfaces normal to the $z$ axis by setting to zero in the Hamiltonian all of the hopping integrals that connect a site on the plane $l_z = 0$ with sites on the plane $l_z = 1$. In effect, this creates an extended planar defect in the otherwide perfect crystal. The form of the Green's function may be obtained by the methods of defect theory. If we were to consider a more realistic model, we could at this point add to the Hamiltonian the terms that describe the change in the Hartree potential near the surface.

In our case, if $t$ is the nearest-neighbor hopping integral, the Hamiltonian $H_1$ may be written

$$H_1 = H_0 + V , \tag{11}$$

where $H_0$ is the Hamiltonian of the perfect macroscopic cube,

$$H_0 = t \sum_{\vec{l},\vec{\delta}} c^\dagger(\vec{l} + \vec{\delta})\, c(\vec{l}) , \tag{12}$$

and $V$ subtracts from $H_0$ the contribution from the bonds that connect the surface at $l_z = 0$ and $l_z = 1$:

$$V = -t \sum_{\vec{l}_\parallel} [c^\dagger(\vec{l}_\parallel, 0)\, c(\vec{l}_\parallel, 1) + c^\dagger(\vec{l}_\parallel, 1)\, c(\vec{l}_\parallel, 0)] , \tag{13}$$

where we use a more explicit notation $c(\vec{l}_\parallel l_z)$ to denote the destruction operator appropriate to the site $\vec{l} = \vec{l}_\parallel + \hat{z} l_z$. We use units where the lattice constant is taken to be unity, and omit explicit reference to spin. Define the Green's function $G_0(\vec{l}\,\vec{l}', z)$ of the infinitely extended crystal:

$$G_0(\vec{l}\,\vec{l}', z) = \langle \vec{l} | (z - H_0)^{-1} | \vec{l}' \rangle .$$

Then the full Green's function of the cut crystal satisfies

$$G(\vec{l}\,\vec{l}', z) = G_0(\vec{l}\,\vec{l}', z) + \sum_{\vec{l}''\vec{l}'''} G_0(\vec{l}\,\vec{l}'', z) \langle \vec{l}'' | V | \vec{l}''' \rangle\, G(\vec{l}''', z) . \tag{14}$$

We now introduce Fourier transforms with respect to the two spatial variables parallel to the surface, as we did earlier. Let

$$G(\vec{l}\,\vec{l}', z) = (1/N_s) \sum_{\vec{k}_\parallel} g(\vec{k}_\parallel z; l_z l_z')\, e^{i\vec{k}_\parallel \cdot (\vec{l}_\parallel - \vec{l}_\parallel')} .$$

For the present simple model Eq. (14) then becomes

$$g(\vec{k}_\parallel z; l_z l_z') = g_0(\vec{k}_\parallel z; l_z - l_z') - t g_0(\vec{k}_\parallel z; l_z)\, g(\vec{k}_\parallel z; 1, l_z') - t g_0(\vec{k}_\parallel z; l_z - 1)\, g(\vec{k}_\parallel z; 0, l_z') . \tag{15}$$

Equation (15) is readily solved in closed form. To exhibit the form of the solution, we omit the common factor $\vec{k}_\parallel z$ that appears in each of the quantities in Eq. (15). Define

$$g_0(\pm) = g_0(1) \pm g_0(0) ,$$

where $g_0(1) = g_0(\vec{k}_\parallel z; l_z)|_{l_z} = 1$. Then the solution to Eq. (15) is

$$g(l_z l'_z) = g_0(l_z - l'_z) + \frac{t}{2}\,\frac{[g_0(l_z) - g_0(l_z - 1)][g_0(l'_z) - g_0(l'_z - 1)]}{1 + t g_0(-)} - \frac{t}{2}\,\frac{[g_0(l_z) + g_0(l_z - 1)][g_0(l'_z) + g_0(l'_z - 1)]}{1 + t g_0(+)} \ . \tag{16}$$

The solution in Eq. (16) may be simplified using some relations from earlier work.[8] We wish to know the Green's function near the real axis, for $z = \Omega - i\epsilon$. We choose units in which the lattice constant is unity, and define a variable

$$\zeta = \frac{\Omega - 2t(\cos k_x + \cos k_y)}{2t}$$

and let

$$\eta = \begin{cases} \zeta - (\zeta^2 - 1)^{1/2}, & \zeta < 1 \\ \zeta + i(1 - \zeta^2)^{1/2}, & -1 < \zeta < 1 \\ \zeta + (\zeta^2 - 1)^{1/2}, & \zeta < -1 \ . \end{cases}$$

Then $g_0(l_z)$ may be written in the form

$$g_0(l_z) = \frac{1}{t}\,\frac{\eta^{1+|l_z|}}{1 - \eta^2} \ . \tag{17}$$

We are interested in the form of $g(l_z, l'_z)$ for the case where $l_z$, $l'_z$ lie on the same side of the one surface. Let $l_z$ and $l'_z$ lie above the surface at $l_z = 1$. For this case, Eq. (16) reduces to the remarkably simple form

$$g(l_z, l'_z) = g_0(l_z - l'_z) - g_0(l_z + l'_z), \quad l_z, l'_z > 1 \ . \tag{18}$$

We now return to the computation of the spectral density. We Fourier transform the spectral density, as we have other quantities that have entered the theory:

$$\rho(\vec{l}\,\vec{l}\,', \Omega) = \frac{1}{N_s} \sum_{\vec{k}_\parallel} \rho(\vec{k}_\parallel \Omega; l_z l'_z)\, e^{i\vec{k}_\parallel \cdot (\vec{l}_\parallel - \vec{l}'_\parallel)} \ . \tag{19}$$

From Eq. (18) we see that

$$\rho(\vec{k}_\parallel \Omega; l_z l'_z) = \rho_0(\vec{k}_\parallel \Omega; l_z - l'_z) - \rho_0(\vec{k}_\parallel \Omega; l_z + l'_z) \ . \tag{20}$$

If we define

$$E(\vec{k}) = 2t(\cos k_x + \cos k_y + \cos k_z) \ ,$$

the energy of a Bloch electron of wave vector $\vec{k}$ in the perfect crystal, then one easily finds

$$\rho_0(\vec{k}_\parallel \Omega; l_z l'_z) = \frac{1}{L} \sum_{k_z} e^{ik_z(l_z - l'_z)}\, \delta(\Omega - E(\vec{k}_\parallel k_z)) \ ,$$

so that the explicit form of $\rho(\vec{k}_\parallel \Omega; l_z l'_z)$ becomes

$$\rho(\vec{k}_\parallel \Omega; l_z l'_z) = \frac{1}{L} \times \sum_{k_z} e^{ik_z(l_z - l'_z)} (1 - e^{i2k_z l'_z})\, \delta(\Omega - E(\vec{k}_\parallel k_z)) \ . \tag{21}$$

It follows that

$$\chi_0(\vec{\mathcal{K}}_\parallel \omega, l_z l'_z) = \frac{1}{NL} \times \sum_{\vec{\kappa}_\parallel \kappa_z \kappa'_z} e^{-i(\kappa_z - \kappa'_z)(l_z - l'_z)} [1 - e^{i2\kappa_z l_z}][1 - e^{i2\kappa'_z l'_z}] \times \frac{f(E(\vec{\kappa}_\parallel + \vec{\mathcal{K}}_\parallel, \kappa_z)) - f(E(\vec{\kappa}_\parallel, \kappa'_z))}{E(\vec{\kappa}_\parallel \vec{\kappa}'_z) - E(\vec{\kappa}_\parallel + \vec{\mathcal{K}}_\parallel, \kappa_z) - \Omega + i\epsilon} \ . \tag{22}$$

The result in Eq. (22) is the principal result of the present section. The surface effects in the response function are contained in the factors $e^{i2\kappa_z l_z}$ and $e^{i2\kappa'_z l'_z}$ inside the square brackets. If these factors in Eq. (22) are ignored, then the expression reduces to the usual formula for the dynamical susceptibility in the bulk. One can see that the effect of the surface on the response is localized to a distance the order of the Fermi wavelength from the surface. When $k_F l_z \gg 1$, the exponential factors oscillate rapidly as $\kappa_z$ and $\kappa'_z$ are summed over, so the contributions from the correction terms are small. At large distances from the surfaces these corrections will oscillate like $(\cos 2k_F l_z)/l_z$ in the manner appropriate to Rudermann-Kittel oscillations in one dimension.[9]

To obtain a feeling for the nature of the corrections to the bulk response contained in Eq. (22), suppose a static spatially varying magnetic field as applied to the system. Let the field that acts on site $\vec{l}$ be given by

$$h(\vec{l}) = h \cos(\vec{q} \cdot \vec{l} + \phi) \ ,$$

where $h$ and the phase angle $\phi$ are real.

The moment $m(\vec{l})$ induced at the site $\vec{l}$ is given by

$$m(\vec{l}) = h \sum_{\vec{l}'} \chi_0(\vec{l}\vec{l}', 0) \cos(\vec{q} \cdot \vec{l}' + \phi) \ . \tag{23}$$

The sum over $\vec{l}'$ in Eq. (23) is confined to the half-space $l_z \geq 1$, of course. Upon replacing the sum $\sum_{l_z \geq 1} \exp(ikl_z)$ by $\frac{1}{2}\delta_{k,0} L$ in the limit as $L \to \infty$, we find for $l_z \geq 1$

$$m(\vec{l}) = \frac{h}{2V} [\cos(\vec{q} \cdot \vec{l} + \phi) + \cos(\vec{q}_r \cdot \vec{l} + \phi)] \times \sum_{\vec{\kappa}} (1 - \cos 2\kappa_z l_z)\, \theta(\vec{\kappa}, \vec{\kappa} + \vec{q}) + \frac{h}{2V} [\sin(\vec{q} \cdot \vec{l} + \phi) + \sin(\vec{q}_r \cdot \vec{l} + \phi)] \times \sum_{\vec{\kappa}} \sin(2\kappa_z l_z)\, \theta(\vec{\kappa}, \vec{\kappa} + \vec{q}) \ . \tag{24}$$

In this expression $V = L^3$ is the volume of the original cube,[10] $\vec{q}_r = \vec{q}_\parallel - \hat{z} q_z$, and

$$\theta(\vec{\kappa}, \vec{\kappa} + \vec{q}) = \frac{f(E(\vec{\kappa})) - f(E(\vec{\kappa} + \vec{q}))}{E(\vec{\kappa} + \vec{q}) - E(\vec{\kappa})} \ . \tag{24a}$$

The method we have employed to derive the susceptibility gives a form applicable to a slab of thickness $L$. The first line of Eq. (24) indicates that the exciting field, chosen to be a plane wave of vector $\vec{q}$, excites first of all a standing wave inside the slab. The factor of $\cos(2\kappa_z l_z)$ shows that the amplitude of the standing wave varies near the surface. On the second line a set of terms appears that arises specifically from the presence of the surface. The terms of the second line describe a standing-wave response 90° out of phase with the driving wave. The amplitude of this wave is zero except near the surface, since the factor of $\sin(2\kappa_z l_z)$ will cause the amplitude of the wave to decay rapidly as one moves into the crystal.

Now we take the limit of Eq. (24) as the wave vector $\vec{q} \to 0$. This will give us an expression for the spatial variation near the surface of the moment induced by a static external field that is uniform in space. The terms proportional to $\sin\phi$ drop out, since $\lim_{\vec{q}\to 0}\theta(\vec{\kappa}, \vec{\kappa}+\vec{q})$ is an even function of $\kappa_z$. In the $\lim \vec{q} \to 0$, $m(\vec{1})$ also depends on $l_z$. Then

$$m(l_z) = h\cos\phi \,\frac{1}{V}\sum_{\vec{\kappa}} (1-\cos 2\kappa_z l_z) \lim_{q\to 0}\theta(\vec{\kappa}, \vec{\kappa}+\vec{q})$$

$$= \frac{h\cos\phi}{V}\sum_{\vec{\kappa}} (1-\cos 2\kappa_z l_z)\delta(E_F - E_{\vec{\kappa}}) \;.$$

Define the functions

$$\chi_\infty = \frac{1}{N}\sum_{\vec{\kappa}} \delta(E_F - E_{\vec{\kappa}}) \;,$$

$$\chi(l_z) = \frac{1}{N}\sum_{\vec{\kappa}} (1-\cos 2\kappa_z l_z)\delta(E_F - E_{\vec{\kappa}}) \;.$$

Then the ratio

$$r(l_z) = \chi(l_z)/\chi_\infty$$

provides a measure of the importance of surface effects in the response of the medium to a static spatially uniform magnetic field. This ratio is the ratio of the magnetic moment induced in layer $l_z$ to that induced in the bulk by a static spatially uniform field.

This ratio may be expressed in terms of tabulated functions. Define

$$G_{\vec{1}}(E) = \frac{1}{N}\sum_{\vec{k}} \frac{e^{i\vec{k}\cdot\vec{1}}}{E - E_{\vec{k}} - i\epsilon} \;.$$

Numerical values of some of these functions have been tabulated in a number of papers.[11] The ratio $r(l_z)$ then assumes the form

$$r(l_z) = 1 - \frac{\mathrm{Im}[G_{2l_z}(E_F)]}{\mathrm{Im}[G_0(E_F)]} \;. \tag{25}$$

Recall that our convention places the surface at $l_z = 1$.

There is only one parameter other than $l_z$ in Eq. (25), and that is the position of the Fermi level relative to the bottom of the band. If $W$ is the bandwidth, let $P = E_F/W$. Then as the band proceeds from full to empty, $P$ varies from 1 to 0. It is straightforward to show that Eq. (25) is symmetric about $P = \frac{1}{2}$.

In Fig. 1 we plot the ratio of the moment induced in the surface layer to the value in the bulk [the quantity $r(1)$] as a function of $P$. If the band is nearly empty or nearly full, the moment induced in the surface is very much smaller than that in the bulk. When $0.2 < P < 0.8$, the effect of the surface on the response is a 10 or 15% effect; i.e., it is a rather small effect. This lends support to the procedure employed in Sec. IV, where the function $\chi_0(\vec{1}\,\vec{1}', \omega)$ in Eq. (6) is replaced by that appropriate to the bulk.

## IV. EFFECT OF ELECTRON-ELECTRON INTERACTIONS ON RESPONSE; NEARLY FERROMAGNETIC LIMIT

In this section we discuss the effect of host exchange enhancement on the response of the semi-infinite medium.

In Sec. III we studied the function $\chi_0(\vec{1}\,\vec{1}', \omega)$ for a very specific and simple model of a semi-infinite paramagnetic metal. Even for this simple model, the form of $\chi_0(\vec{1}\,\vec{1}', \omega)$ is not easy to deal with. Thus there seems to be little hope that one can solve Eq. (8) for a realistic model without an extensive program of numerical studies. In this paper we begin with Eq. (8) and then make a series of modifications until we reach a form that may be solved analytically. While we make important and serious approximations to Eq. (8) to do this, we feel that the essential features remain, in the limit that the exchange enhancement in the bulk becomes very large.

In fact, we only consider the case where the exchange enhancement of the bulk becomes very large. This means, in the conventional notation, that $(1-\bar{I}) \ll 1$, where $\bar{I} = U_0 N(0)$. The parameter $U_0$ is the Coulomb interaction strength in the bulk and $N(0)$ is the bulk density of states at the Fermi level. An essential feature of the limit $(1-\bar{I}) \ll 1$ is that the static correlation length $\xi$ becomes very large, since $\xi \sim (1-\bar{I})^{-1/2}$ in the RPA. If the crystal is subjected to a static perturbation, then the magnetization produced will vary slowly in space, and appreciable variations in the magnetization can result only in the length $\xi$. Thus we expect the variation produced by the surface in the response function $\chi(\vec{\mathcal{K}}_\parallel \omega; l_z l_z')$ of Eq. (8) to extend into the crystal a distance $\xi$, in the limit of small $\omega$ and small $\vec{\mathcal{K}}_\parallel$. For fixed $l_z$ and $l_z'$, the sum over $l_z''$ thus will include a set of planes that extends over the distance $\xi$, in this limit. We have seen in the preceding section that $\chi_0(\vec{\mathcal{K}}_\parallel \omega, l_z l_z')$ differs from the bulk value only when $l_z$ or $l_z'$ lies within

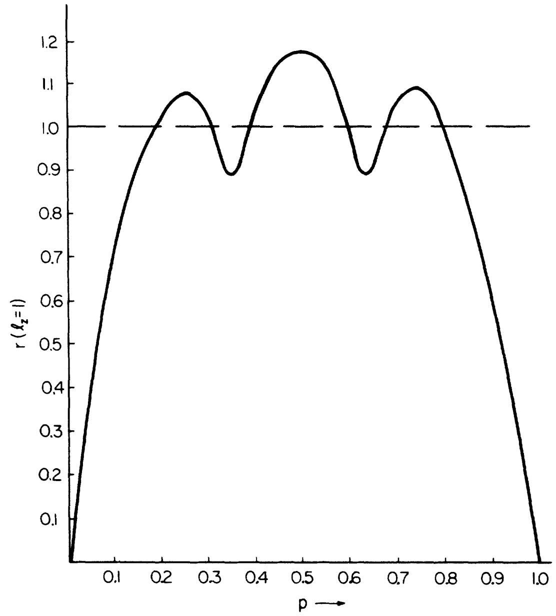

FIG. 1. Ratio $r(1)$ as a function of the reduced Fermi energy $P$ for the model discussed in Sec. III of the text.

one or two atomic layers of the surface, since the Fermi wavelength is the order of the lattice constant. Thus, when $\xi$ is very large compared to the lattice constant, we should not make a serious error by replacing $\chi_0(\vec{\mathcal{K}}_\parallel\omega; l_z l'_z)$ by the infinite-medium response, which we denote by the symbol $\chi_0^{(\infty)}(\vec{\mathcal{K}}_\parallel\omega; l_z - l'_z)$. Thus our first step is to replace Eq. (8) by the approximate form

$$\chi(\vec{\mathcal{K}}_\parallel\omega, l_z l'_z) = \chi_0^{(\infty)}(\vec{\mathcal{K}}_\parallel\omega; l_z - l'_z) + \sum_{l''_z} \chi_0^{(\infty)}(\vec{\mathcal{K}}_\parallel\omega; l_z - l''_z) \times U(l''_z)\, \chi(\vec{\mathcal{K}}_\parallel\omega; l''_z\, l'_z) \; . \tag{26}$$

We allow $U$ to vary near the surface. Variations in $U$ may become particularly important when the bulk is nearly ferromagnetic. At the same time, one expects one can mimic effects of the variation in $\chi_0(\vec{\mathcal{K}}_\parallel\omega, l_z l'_z)$ near the surface by varying $U(l''_z)$. An increase (or decrease) in $U$ near the surface enhances (or suppresses) the response of the surface region over the value appropriate to the case where $U$ assumes the bulk value near the surface. This effect is quite similar to that produced by an enhancement (or decrease) in the one-electron response function $\chi_0(\vec{\mathcal{K}}_\parallel\omega; l_z l'_z)$, at least in a qualitative sense.

Equation (26) still cannot be solved in general, without a specific form for $\chi_0^{(\infty)}$. We write

$$\chi_0^{(\infty)}(\vec{\mathcal{K}}_\parallel\omega; l_z - l'_z) = \sum_{\vec{1}_\parallel} e^{-i\vec{\mathcal{K}}_\parallel\cdot(\vec{1}_\parallel - \vec{1}'_\parallel)} \chi_0^{(\infty)}(\vec{1} - \vec{1}'; \omega) \; , \tag{27a}$$

where

$$\chi_0^{(\infty)}(\vec{1} - \vec{1}'; \omega) = \frac{1}{N} \sum_{\vec{k}} \chi_0^{(\infty)}(\vec{k}, \omega)\, e^{i\vec{k}\cdot(\vec{1}-\vec{1}')} \; . \tag{27b}$$

Our procedure will be to assume a model form for $\chi_0^{(\infty)}(\vec{k}, \omega)$ in Eq. (27b), then obtain an analytic formula for $\chi_0^{(\infty)}(\vec{\mathcal{K}}_\parallel\omega; l_z - l'_z)$ in Eq. (27a).

We confine our attention only to the static ($\omega = 0$) response, and for $\chi_0^{(\infty)}(\vec{k}, 0)$ we choose the simple model form

$$\chi_0^{(\infty)}(k, 0) = \frac{\chi_0}{1 + \sigma^2 k^2} \; . \tag{28}$$

In Eq. (28), $\chi_0$ is the unenhanced (one-electron) static susceptibility of the bulk and $\sigma$ is a microscopic length, presumably the order of the Fermi wavelength.

This form for $\chi_0^{(\infty)}(\vec{k}, 0)$ provides only a crude representation of the bulk response function, since it is characterized only by the two parameters $\chi_0$ and the range parameter $\sigma$. The wave-vector dependence of $\chi_0^{(\infty)}(\vec{k}, 0)$ in a real material is much more complex than this. In particular, the form in Eq. (28) does not reproduce the Ruderman-Kittel-Kasuya-Yosida (RKKY) oscillations in real space, since the singularity in the slope at $k = 2k_F$ is not present in this simple form. We choose this form because it does crudely represent the principal over-all features of the bulk response, and we can proceed with the remainder of our discussion by the use of analytic methods. It is then straightforward to show that

$$\chi_0^{(\infty)}(\vec{\mathcal{K}}_\parallel 0; l_z - l'_z) = \frac{\chi_0}{2\sigma^2 \lambda(\vec{\mathcal{K}}_\parallel)}\, e^{-\lambda(\vec{\mathcal{K}}_\parallel)|l_z - l'_z|} \; , \tag{29}$$

where $\lambda(\vec{\mathcal{K}}_\parallel) = \sigma^{-1}(1 + \sigma^2 \mathcal{K}_\parallel^2)^{1/2}$.

If we insert the form in Eq. (29) into Eq. (26), and assume that the Coulomb interaction in the surface assumes a value $U_s$ different from the bulk value $U_0$, then we need to solve

$$\chi(\vec{\mathcal{K}}_\parallel 0; l_z l'_z) = \frac{\chi_0}{2\sigma^2 \lambda(\vec{\mathcal{K}}_\parallel)}\, e^{-\lambda(\vec{\mathcal{K}}_\parallel)|l_z - l'_z|} + \frac{\bar{I}}{2\sigma^2 \lambda(\vec{\mathcal{K}}_\parallel)} \sum_{l''_z} e^{-\lambda(\vec{\mathcal{K}}_\parallel)|\vec{1}_z - \vec{1}''_z|}\, \chi(\vec{\mathcal{K}}_\parallel 0; l''_z, l'_z) + \frac{\Delta\bar{I}}{2\sigma^2 \lambda(\vec{\mathcal{K}}_\parallel)}\, e^{-\lambda(\vec{\mathcal{K}}_\parallel) l_z}\, \chi(\vec{\mathcal{K}}_\parallel 0; 0 l'_z) \; , \tag{30}$$

where $\bar{I} = U_0 \chi_0$ and $\Delta I = (U_s - U_0)\chi_0$.

We now make one final approximation which is closely related to the approximation we already made for $\chi_0^{(\infty)}(\vec{\mathcal{K}}_\parallel 0, l_z l'_z)$. The sum over $l''_z$ in the right-hand side of Eq. (30) will be replaced by an integral. Since we have already washed out the details of the bulk response function at short wavelengths by the approximation in Eq. (28), to retain the sum in Eq. (30) would add little to the validity of the theory presented here, without at the same time improving Eq. (28).

Thus, we finally arrive at the approximate integral equation that will form the basis of the remainder of this section. We suppress repeated reference to the fact that $\omega = 0$, and write

$$\chi(\vec{\mathcal{K}}_\parallel; ll') = \frac{\chi_0}{2\sigma^2\lambda(\vec{\mathcal{K}}_\parallel)}\, e^{-\lambda(\vec{\mathcal{K}}_\parallel)|l-l'|} + \frac{\bar{I}}{2\sigma^2\lambda(\vec{\mathcal{K}}_\parallel)} \int_0^\infty dl''\, e^{-\lambda(\vec{\mathcal{K}}_\parallel)|l-l''|}\, \chi(\vec{\mathcal{K}}_\parallel; l''l') + \frac{\Delta\bar{I}}{2\sigma^2\lambda(\vec{\mathcal{K}}_\parallel)}\, e^{-\lambda(\vec{\mathcal{K}}_\parallel)|l|}\, \chi(\vec{\mathcal{K}}_\parallel; 0l') \,. \tag{31}$$

Recall that the lattice constant has been chosen to be unity.

The virtue of Eq. (31) is that it may be solved exactly by a variety of methods. We proceed by noting the following identity:

$$\frac{\partial^2}{\partial l^2}\, e^{-\lambda|l-l'|} = -2\lambda\delta(l-l') + \lambda^2 e^{-\lambda|l-l'|} \,. \tag{32}$$

We then consider Eq. (31) for $l > 0$, and operate on each side with $\partial^2/\partial l^2$. After employing Eq. (32) and rearranging the equation a bit, one obtains an inhomogeneous differential equation satisfied by $\chi(\vec{\mathcal{K}}_\parallel; ll')$:

$$\left(-\frac{\partial^2}{\partial l^2} + \xi^2(\vec{\mathcal{K}}_\parallel)\right)\chi(\vec{\mathcal{K}}_\parallel, ll') = \frac{\chi_0}{\sigma^2}\, \delta(l-l') \,, \tag{33}$$

where the quantity $\xi(\mathcal{K}_\parallel)$ is defined by

$$\xi(\mathcal{K}_\parallel) = \frac{1}{\sigma}\,[(1-\bar{I}) + \sigma^2\mathcal{K}_\parallel^2]^{1/2} \,. \tag{34}$$

When $\vec{\mathcal{K}}_\parallel = 0$, then $\xi(0) = 1/\sigma(1-\bar{I})^{1/2}$. This is just the inverse of the bulk correlation length mentioned earlier in the section. The general solution of Eq. (33) has the form

$$\chi(\mathcal{K}_\parallel; l, l') = \frac{\chi_0}{2\sigma^2\xi(\mathcal{K}_\parallel)} \times \{\theta(l'-l)\,[e^{+\xi(\vec{\mathcal{K}}_\parallel)(l-l')} + \beta(\mathcal{K}_\parallel, l')\, e^{-\xi(\vec{\mathcal{K}}_\parallel)(l-l')}] + \theta(l-l')\,[1 + \beta(\mathcal{K}_\parallel, l')]\, e^{-\xi(\mathcal{K}_\parallel)(l-l')}\} \,, \tag{35}$$

where

$$\theta(x) = 1 \quad \text{if } x > 0$$
$$= 0 \quad \text{if } x < 0 \,.$$

The function $\beta(\mathcal{K}_\parallel, l')$ may be determined by requiring Eq. (35) to be a solution of the original integral equation, (31). Define a parameter

$$p = \Delta U/U_0 \,,$$

the fractional change in the intra-atomic Coulomb interaction near the surface. Then define a quantity

$$\gamma(\mathcal{K}_\parallel) = 1 - \frac{2\xi(\mathcal{K}_\parallel)}{[\lambda(\mathcal{K}_\parallel) + \xi(\mathcal{K}_\parallel)]\{1 - p[\lambda(\mathcal{K}_\parallel) - \xi(\mathcal{K}_\parallel)]\}} \,. \tag{36}$$

One finds

$$\beta(\mathcal{K}_\parallel, l') = -\gamma(\mathcal{K}_\parallel)\, e^{-2\xi(\mathcal{K}_\parallel)l'} \,. \tag{37}$$

The static correlation function is thus given by

$$\chi(\vec{\mathcal{K}}_\parallel; ll') = \frac{\chi_0}{2\sigma^2\xi(\mathcal{K}_\parallel)}\, [e^{-\xi(\mathcal{K}_\parallel)|l-l'|} - \gamma(\mathcal{K}_\parallel)\, e^{-\xi(\mathcal{K}_\parallel)(l+l')}] \,. \tag{38}$$

The result in Eq. (38) is the principal feature of the present section. We conclude the section with a discussion of a number of features of Eq. (38).

First of all, suppose $\vec{l}$ and $\vec{l}\,'$ lie deep in the bulk of the crystal, much deeper than the correlation length $\xi^{-1}(\mathcal{K}_\parallel)$. The second term in Eq. (38) may then be ignored, and $\chi(\mathcal{K}_\parallel; ll')$ thus depends on $l - l'$. Then we can deduce the value of $\chi(\vec{k})$ predicted for the bulk by the theory from Eq. (27a) and Eq. (27b). One finds

$$\chi(\vec{k}) = \frac{\chi_0}{(1-\bar{I}) + \sigma^2 k^2} \,. \tag{39}$$

For $\bar{I}$ close to unity, this is the usual expression for the wave-vector-dependent static susceptibility of a material with strong exchange enhancement. In particular, it is clear that the static correlation length is $\sigma/(1-\bar{I})^{1/2}$. Thus, so long as $\vec{l}$ and $\vec{l}\,'$ lie a distance $\xi(0)^{-1}$ away from the surface, the static correlation function is unaffected by the surface.

Next suppose that $\vec{l}$ and $\vec{l}\,'$ lie in the surface layer. The static correlations within the surface layer are drastically different from the correlations in the bulk, within the framework of the present discussion. One may see this by letting $l$ and $l'$ approach zero in Eq. (38). Define $\chi_s(\mathcal{K}_\parallel) = \chi(\mathcal{K}_\parallel; 00)$. Then we have

$$\chi_s(\mathcal{K}_\parallel) = \frac{\chi_0}{\sigma^2}\, \frac{1}{[\lambda(\mathcal{K}_\parallel) + \xi(\mathcal{K}_\parallel)]\{1 - p[\lambda(\mathcal{K}_\parallel) - \xi(\mathcal{K}_\parallel)]\}} \,. \tag{40}$$

Recall that

$$\lambda(\mathcal{K}_\parallel) = (1/\sigma)[1 + (\sigma\mathcal{K}_\parallel)^2]^{1/2}$$

and

$$\xi(\mathcal{K}_\parallel) = (1/\sigma)\,[(1-\bar{I}) + (\sigma\mathcal{K}_\parallel)^2]^{1/2} \,.$$

Also note that $\chi_s(\vec{\mathcal{K}}_\parallel)$ measures the static correlations between two sites within the surface layer:

$$\langle s^+(l_\parallel, 0)\, s^-(l'_\parallel, 0)\rangle = \frac{1}{N_s} \sum_{\vec{\kappa}_\parallel} \chi_s(\vec{\mathcal{K}}_\parallel)\, e^{i\vec{\mathcal{K}}_\parallel\cdot(\vec{l}_\parallel - \vec{l}\,'_\parallel)} \,.$$

The basic difference between the static correlations within the surface and the bulk may be appreciated by noting two features of the form in Eq. (39): (i) $\chi(0) \to \infty$ as $\bar{I} \to 1$. The response of the bulk spins to a static spatially uniform magnetic field becomes infinitely large as $\bar{I} \to 1$. (ii) As $\bar{I} \to 1$, $\chi(\vec{k})$ peaks more and more sharply around $k = 0$. The range in $k$ space of $\chi(k)$ shrinks down to zero. Of course, this is just another way of saying that the static correlation length becomes very large in the bulk. Neither of these features is present in $\chi_s(\mathcal{K}_{\parallel})$. Even when $\bar{I} \equiv 1$, $\chi_s(0)$ is finite. In particular,

$$\chi_s(0) = \frac{\chi_0}{[1 + (1 - \bar{I})^{1/2}]\{\sigma - p[1 - (1 - \bar{I})^{1/2}]\}}, \tag{41}$$

and this function is perfectly finite at $\bar{I} = 1$. Furthermore, there is no tendency for $\chi_s(\mathcal{K}_{\parallel})$ to acquire a peak near $\mathcal{K}_{\parallel} = 0$ as $\bar{I} \to 1$. This means that within the surface layer the correlation length remains microscopic, always the order of $\sigma$.

It is useful at this point to make an analogy with earlier work[3] on a molecular-field-theory description of the behavior of the surface region of the Heisenberg ferromagnet and antiferromagnet near the ordering temperature. Equations (38) and (37) are virtually identical to the result for the static correlation function obtained for the Heisenberg model, provided one replaces $(1 - \bar{I})$ by $(T - T_c)/T_c$ and $p$ by the fractional change in the exchange interaction in the surface. Thus the static correlation length in the Heisenberg model also remains finite in the surface. In the earlier work it was also possible to solve for the temperature dependence of the spontaneous magnetization in the surface below $T_c$. In fact, as one expects, the surface magnetization vanishes at the bulk ordering temperature, although it is smaller than the bulk magnetization by one power of $(T_c - T)^{1/2}/T_c^{1/2}$. The physical picture that emerges from this work is that at $T_c$ the surface spins order only because they see an effective molecular field generated by the bulk spins. The static correlation length in the surface thus remains microscopic at $T_c$. While we have not studied the ferromagnetic phase of the metal in this paper, the results we obtain for the static correlation function suggest that the same physical picture obtains for the metal.

There is one unreasonable feature of the response function we obtain. If $p$ is large and positive, then $\chi_s(0)$ can become negative. One can see this from Eq. (41). This means that if the Coulomb interaction in the surface is larger than in the bulk, then the surface spins may order even though $\bar{I} < 1$. One would then have a long-range ferromagnetic order within the surface region of an otherwise paramagnetic metal. This is equivalent to the presence of long-range order in a two-dimensional system, since, unless $p$ is very near the critical value, the ordered region will have a thickness the order of the microscopic distance $\sigma$. Since long-range ferromagnetic order in two dimensions is not expected for very general reasons, the appearance of this singularity in $\chi_s(0)$ is a feature of our approximate theory. We ascribe the presence of the singularity to the use of the RPA description of the response, rather than the model form of the equations that leads to Eq. (38), since the RPA is a form of molecular-field theory. The presence of this singularity, which also occurred in the earlier work on the Heisenberg model,[3] suggests that if $U_s > U_0$, there may be long-range correlations between the spins; an investigation of this question would require a more sophisticated theory, however.

The principal conclusions of our discussion are the following: The static correlation length in the surface remains finite as $\bar{I} \to 1$. In fact, the functional form of $\chi_s(\mathcal{K}_{\parallel})$ is remarkably insensitive to the value of $\bar{I}$. We illustrate this point in Fig. 2, where for $p = 0$ and $\sigma = 1$, we plot $\chi_s(\mathcal{K}_{\parallel})$ for $\bar{I} \equiv 1$ and $\bar{I} = 0.9$. The qualitative shape of the function is very similar in both cases, except for a small difference for $\mathcal{K}_{\parallel}\sigma < 0.5$. On the other hand, the form of $\chi_s(\mathcal{K}_{\parallel})$ is quite sensitive to the details of the surface environment. We illustrate this in

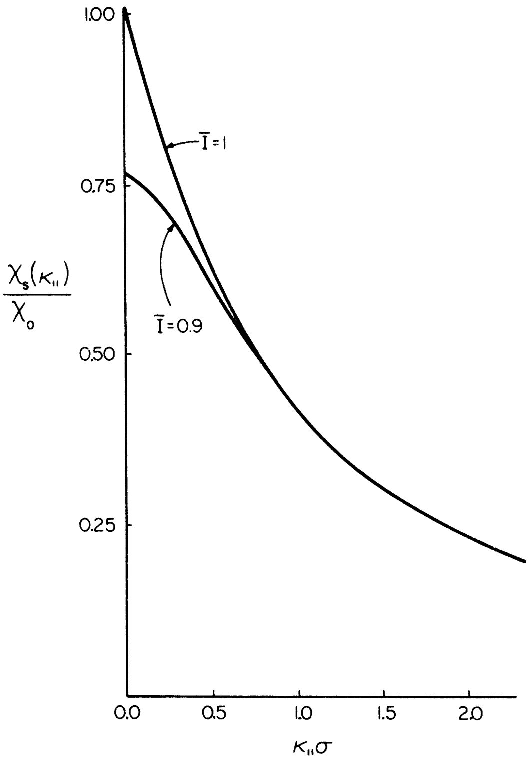

FIG. 2. Plot of $\chi_s(\mathcal{K}_{\parallel})$ for two values of $\bar{I}$ for the case where the Coulomb interaction in the surface is the same as in the bulk. The host range parameter $\sigma$ has been chosen equal to unity.

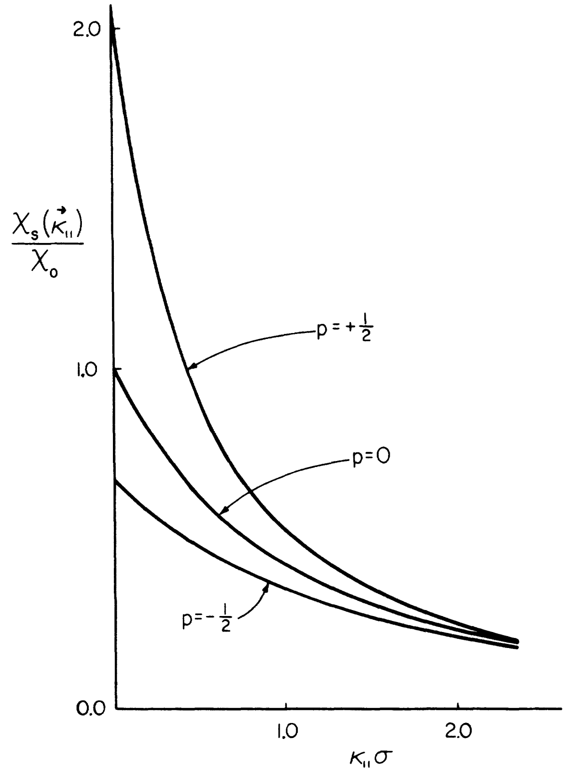

FIG. 3. Plot of $\chi_s(\mathcal{K}_{\parallel})$ for $\bar{I}=0$, for various values of the Coulomb interaction $U_s$ between electrons within the surface layer. The parameter $P=(U_s-U_0)/U_0$ and the range parameter has been chosen equal to unity.

Fig. 3, where for $\bar{I}=1$ and $\sigma=1$, we plot $\chi_s(\mathcal{K}_{\parallel})$ for $p=0$, $+\frac{1}{2}$, and $-\frac{1}{2}$. The static correlations are clearly more sensitive to the value of $p$ than whether or not the bulk material is near the ferromagnetic instability.

We have not been able to successfully study the frequency dependence of $\chi(\vec{\mathcal{K}}_{\parallel}\omega;00)$ in our model, although in principle one may do this in a straightforward manner. This problem is still under investigation. However, since $\chi_s(\mathcal{K}_{\parallel})$ is nonsingular at $\mathcal{K}_{\parallel}=0$ as $\bar{I}\rightarrow 1$, and since the correlation length remains microscopic in this limit, we feel that in the surface layer the characteristic frequency associated with spin fluctuations should be comparable to that of a noninteracting electron gas, rather than the much lower frequency associated with bulk paramagnons.

We conclude this section by computing the magnetization induced by a spatially uniform magnetic field. If $m(l)$ is the magnetization induced in layer $l$, then to within an over-all constant of proportionality we have

$$m(l)=h\int_0^{\infty}\chi(00;ll')\,dl' = \frac{\chi_0 h}{1-\bar{I}}\left[1-\frac{1}{2}[1+\gamma(0)]\exp\left(-\frac{\sigma l}{(1-\bar{I})^{1/2}}\right)\right]. \tag{42}$$

Far into the bulk, where $\sigma l/(1-\bar{I})^{1/2}\gg 1$, we have the usual expression for the magnetization in an exchange-enhanced metal:

$$m(l)=\chi_0 h/(1-\bar{I}). \tag{43}$$

However, in the surface we have

$$m(0)=\frac{1}{2}\,\frac{\chi_0 h}{1-\bar{I}}\,[1-\gamma(0)].$$

For $\bar{I}$ close to unity, this becomes

$$m(0)=\frac{\chi_0 h}{(1-\bar{I})^{1/2}}\,\frac{1}{(1-p/\sigma)}. \tag{44}$$

The magnetization in the surface layer is much smaller than that in the bulk, by the factor $(1-\bar{I})^{1/2}$. This result is also very similar to that obtained for the Heisenberg paramagnet,[3] within the framework of molecular-field theory.

Within the framework of the present model, the results of this section show that the local susceptibility, static correlations, and magnetic response of spins in the surface of a nearly ferromagnetic metal differ qualitatively from the bulk behavior. We feel this casts doubt on the ability of the Schrieffer-Gomer[4] theory to relate trends in the chemisorption energy to bulk magnetic properties of the material, and on the theory of Suhl and coworkers[5] on spin-fluctuation-induced desorption.

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