electrons collectively interacting via their magnetic dipole moments would then be transferred to the lattice at the rate $2T_{1e}^{-1}$. Although it was originally our intent, we do not present for LMN: 5-at.% $Nd^{3+}$ a quantitative attempted fit to models involving proton relaxation via the electron dipolar reservoir,[9] since complications arising from the hyperfine structure of $^{143}Nd$ and $^{145}Nd$, effects of the more rapidly relaxing trace $Ce^{3+}$, and the rather long $T_{1p}$ obtained at low temperatures for crystals with small $Nd^{3+}$ concentrations make any such quantitative conclusions difficult and ambiguous. However, the results of this work, taken together with that in Ref. 1, indicate that any correct interpretation of proton relaxation in LMN must include strong collective electron effects for Nd concentrations of approximately 1 at.% and more.

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[1]O. S. Leifson and Eric Vogel, Phys. Rev. B **2**, 4626 (1970).

[2]We abbreviate $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$ as LMN.

[3]O. S. Leifson and Robert L. Paulson, Bull. Am. Phys. Soc. **17**, 148 (1972); Bull. Am. Phys. Soc. **17**, 681 (1972).

[4]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, U.P., London, 1961); M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Oxford U.P., London, 1970); C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience, New York, 1963).

[5]P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

[6]For a general discussion of nuclear relaxation in weakly paramagnetic solids see, for example, Ref. 4.

[7]Extensive studies of proton relaxation in LMN: $Ce^{3+}$, portions of which have been previously reported in Ref. 2, are to be submitted for publication.

[8]P. Brady (private communication).

[9]Experimental results obtained by rf saturation techniques and a discussion of electron dipolar reservoir effects for LMN: $Nd^{3+}$ appear also in G. M. van den Heuvel, T. J. B. Swanenburg, and N. J. Poulis, Physica (Utr.) **56**, 365 (1971).

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# Surface Susceptibility of Exchange-Enhanced Paramagnets

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The effects of a surface on the static spin susceptibility of an exchange-enhanced paramagnet are calculated in the random-phase approximation, where effects due to reflection of electrons from the surface are included in the effective interaction. It is found that the enhancement of the susceptibility close to the surface may be greater than that in the bulk for what appear to be reasonable choices of the parameters characterizing the surface reflection terms in the effective interaction.

The recent work of Schrieffer and Gomer[1] and Suhl *et al.*[2] on chemisorption on strongly paramagnetic metals has depended on the spin susceptibility at the surface of such a metal having the same enhancement and time and space dependence as the bulk susceptibility. In a previous paper[3] (hereafter referred to as MBW), we have shown in an approximation to the random-phase approximation (RPA) in an exchange-enhanced paramagnet that the surface susceptibility does not display the enhancement found in the bulk. The approximation used was to replace the noninteracting or bare spin susceptibility in the presence of the surface, which consists of the bare susceptibility of the bulk material plus terms due to the reflection of electrons and/or holes from the surface, by the bare bulk susceptibility alone. The reduction of the surface susceptibility in this approximation is thus due to the application of boundary conditions appropriate to a semi-infinite medium. A further approximation in MBW was to use a phenomenological expression for the bare bulk susceptibility.

In this paper we include the effects of the reflection terms in the bare susceptibility. A phenomenological expression for them is obtained by requiring consistency between the exact expression for the bare susceptibility in terms of an energy-band model, the phenomenological bulk susceptibility of MBW, and our expression for the reflection terms. The bare susceptibility in the presence of the surface [ Eq. (22) of MBW] can be written

$$\chi_0(l_z, l_z') = g(l_z - l_z', l_z - l_z') + g(l_z + l_z', l_z + l_z') - g(l_z - l_z', l_z + l_z') - g(l_z + l_z', l_z - l_z'), \quad (1)$$

$$g(l, l') = \frac{1}{NL^2} \sum_{\vec{k}_\parallel, k, k'} e^{-ikl + ik'l'} \frac{f(E(\vec{k}_\parallel, k)) - f(E(\vec{k}_\parallel, k'))}{E(\vec{k}_\parallel, k') - E(\vec{k}_\parallel, k)}, \quad (2)$$

where we have set $\vec{k}_\parallel = \omega = 0$ for convenience and have taken the $z$ direction to be perpendicular to the surface. In MBW we kept only the first term of Eq. (1), which can readily be recognized as the bare bulk susceptibility

$$g(l, l) = \chi_0^{\text{bulk}}(l) .$$

Using the small-wave-number approximation for the Fourier transform

$$\chi_0^{\text{bulk}}(q) \simeq \chi_0(1 - \sigma^2 q^2) \simeq \chi_0/(1 + \sigma^2 q^2) , \quad (3)$$

where $\chi_0$ is the unenhanced single-electron static susceptibility in the bulk, equal to the density of states at the Fermi level, and $\sigma$ is a microscopic length on the order of the Fermi wavelength, we have

$$\chi_0^{\text{bulk}}(l) = (\chi_0/2\sigma)\, e^{-|l|/\sigma} . \quad (4)$$

This gives a phenomenological expression for the first two terms in $\chi_0(l, l')$. The last two terms are more difficult to deal with. We have taken the point of view that, having used a phenomenological expression for $\chi_0^{\text{bulk}}$, we do not wish to carry out a complicated exact calculation of these reflection terms. Instead we shall require that $g(l, l')$ be consistent with our choice for $\chi_0^{\text{bulk}}$ and that it satisfy various conditions based on the inversion symmetry of the underlying band,

$$g(l, l') = g(l', l) = g(|l|, |l'|) .$$

The form we have used is

$$g(l, l') = \frac{\chi_0}{2\sigma} e^{-(|l| + |l'|)/2\sigma} \cos\left(\frac{\pi(|l| - |l'|)}{2\sigma'}\right) . \quad (5)$$

We have chosen to include oscillatory behavior in $g(l,l')$ to simulate the oscillatory behavior of the ratio $m_0(l)/m_0$ (bulk),

$$m_0(l) = \sum_{l'=1}^{\infty} \chi_0(l, l') ,$$

plotted as Fig. 1 in MBW. In a continuum approximation, i.e., replacing the sum above by an integral from 0 to $\infty$, we obtain from Eq. (5) a bare surface magnetization of zero (which is expected from the surface boundary conditions); however, doing the sum explicitly, we have

$$\frac{m_0(l = 1)}{m_0(l \gg 1)} = \frac{1 - 2e^{-1/\sigma}\cos(\pi/\sigma') + e^{-2/\sigma}}{1 + e^{-1/\sigma}} , \quad (6)$$

which enables the surface-to-bulk-magnetization ratio to oscillate about 1 as a function of $\sigma'$. Furthermore, these oscillations can be expected to include some of the effects of the oscillatory behavior of the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction, which is the Fourier trans-

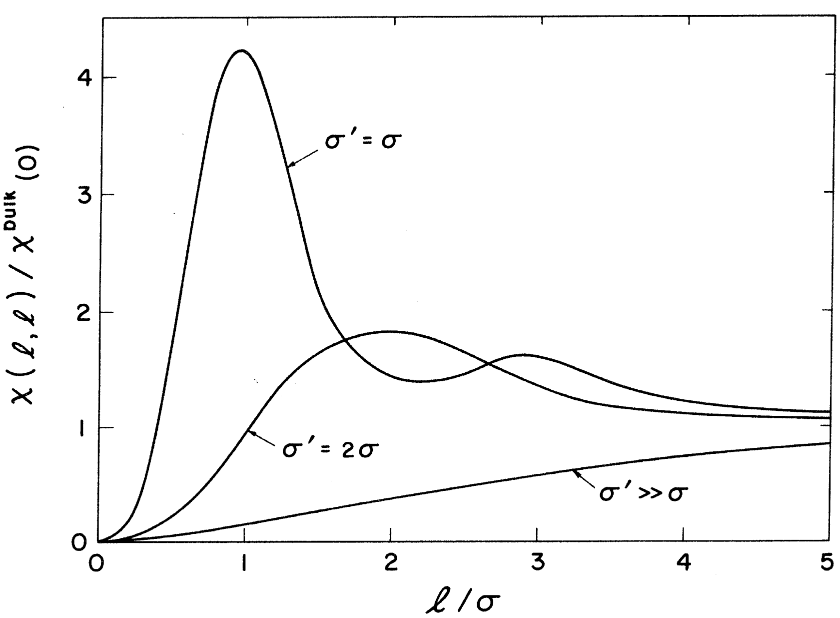


FIG. 1. Local susceptibility $\chi(l, l)$ for various values of $\sigma'$. In all cases, the plotted ratio $\chi(l, l)/\chi^{\text{bulk}}(0) \to 1$ as $l/\sigma \to \infty$.

form of the exact $\chi_0(q)$. We therefore expect that a reasonable value for $\sigma'$ will be on the order of a lattice spacing, i.e., of the same order of magnitude as the range $\sigma$.

Using Eq. (5) for $g(l, l')$, the solution of the RPA can be directly obtained in the continuum limit. The RPA equation in the presence of the surface is then

$$\chi(l, l') = \chi_0(l, l') + U\int_0^\infty dl''\, \chi_0(l, l'')\chi(l'', l'), \qquad (7)$$

where $U$ is the intra-atomic Coulomb integral. Introducing

$$\psi(l, l') = \theta(l)\theta(l')\chi(l, l')\ , \qquad (8a)$$

$$\psi_0(l, l') = \theta(l)\theta(l')\chi_0(l, l')\ , \qquad (8b)$$

and their Fourier transforms

$$\psi(k, k') = \int_{-\infty}^{\infty} dl \int_{-\infty}^{\infty} dl'\ e^{ikl}\, e^{-ik'l'}\,\psi(l, l')\ , \qquad (9a)$$

$$\psi_0(k, k') = \int_{-\infty}^{\infty} dl \int_{-\infty}^{\infty} dl'\ e^{ikl}\, e^{-ik'l'}\,\psi_0(l, l')\ , \qquad (9b)$$

we have

$$\psi(k, k') = \psi_0(k, k') + U\int_{-\infty}^{\infty} \frac{d\bar{k}}{2\pi}\,\psi_0(k, \bar{k})\,\psi(\bar{k}, k')\ . \qquad (10)$$

The solution of Eq. (10) is simplified by noting that the $\theta$ functions in Eq. (8) require $k$ to lie in the upper half-plane and $k'$ to lie in the lower half-plane, at least infinitesimally, for the Fourier transforms to exist. Furthermore, if the Fourier transform of $\psi(k, k')$ is to reproduce the $\theta(l)\theta(l')$ factors in Eq. (8a) $\psi(k, k')$ must be analytic in the upper half $k$ plane and lower half $k'$ plane. Naturally, $\psi_0(k, k')$ has these analyticity properties. Using them, the $\bar{k}$ integral in Eq. (10) can be done by closing in the upper half-plane, picking up only the contributions from the poles of $\psi_0(k, \bar{k})$ at $\bar{k} = k$, $i$ and $k + i \pm \pi/\sigma'$. This reduces the integral equation to a difference equation relating $\psi(k, k')$ to $\psi(i, k')$ and $\psi(k + i \pm \pi/\sigma', k')$. By iterating the equation, we can eliminate the dependence on $\psi(k + i \pm \pi/\sigma', k')$, obtaining

$$\psi(k, k') = g_1(k, k') - \bar{I}g_2(k)\,\psi(i, k')\ , \qquad (11)$$

in which $g_1$ and $g_2$ are both analytic in the upper half $k$ plane except for a simple pole at $k = i(1-\bar{I})^{1/2}$. This pole is removed by requiring it to have zero residue, which serves to determine the unknown function $\psi(i, k')$.

The final result is an infinite series for $\psi(k, k')$, each term of which contains simple poles in the lower half $k$ plane and upper half $k'$ plane. Inversion of the Fourier transform yields a local susceptibility $\chi(l, l)$, which is plotted in Fig. 1 for $\bar{I} = 0.9$ and various values of $\sigma'$. When $\sigma'$ is large, i.e., when there are no oscillations in the surface terms, the results of MBW are obtained: There is no enhancement of the surface susceptibility. However, for $\sigma'$ on the order of $\sigma$, we find that the bulk enhancement near the surface is restored and, in fact, the surface susceptibility can be considerably larger than the bulk susceptibility. It is only right at the surface, where the boundary conditions require $\chi(0, 0) = 0$, that an unenhanced susceptibility is found. Since for $\sigma' \simeq \sigma$ the oscillations in $\chi(l, l)$ have a wavelength on the order of a lattice spacing, we have compared these continuum results with those obtained in an equivalent lattice calculation, and have found that the continuum approximation has little effect on the results.

The physical source of this additional enhancement near the surface is clear from the $\sigma'$ dependence of these results. The oscillations in the surface reflection terms $g(l \pm l', l \mp l')$ in $\chi_0(l, l')$ introduce an additional short-range attraction between the electron and hole near the surface, which tends to increase the effect of $U$ in enhancing the susceptibility. Unfortunately, this additional attraction also tends to cause a divergent susceptibility for $\bar{I} \lesssim 1$ as a function of $\sigma'$. In this case the additional attraction has pushed the RPA calculation of the surface susceptibility to a surface-phase transition before the bulk-phase transition. A similar surface-phase transition was found in MBW when the intra-atomic Coulomb integral was allowed to be larger at the surface than in the bulk and has been found in exact solutions of the RPA equations for the free-electron[4] and tight-binding[5] bands. While the surface-phase transition is clearly an artifact of our use of the RPA, and would not appear in a more complete theory which took into account the effects of fluctuations near the phase transition, the result that the oscillations in the surface reflection terms can produce an over-all attractive effect, and, hence, a greater enhancement of the susceptibility near the surface is probably real for $\bar{I}$ not too close to 1 (in our case, $\bar{I} \leq 0.98$). So long as the attractive effect is not too large and, hence, does not come too close to forcing a surface-phase transition, our use of a molecular-field theory should not prevent our results from having a qualitative significance.

Hence, the conclusion of MBW that the surface susceptibility of an exchange-enhanced paramagnet is not enhanced is considerably modified by the inclusion of the surface reflection terms. It is only in the unphysical limit of $\sigma'$ much greater than the lattice spacing that we find a small surface susceptibility. While we have introduced the oscillations in $g(l, l')$ in order to be able to match the surface-to-bulk-magnetization ratio of MBW, we expect that similar oscillatory terms must appear in the exact $\chi_0(l, l')$ since they appear in the RKKY interaction. Since the RKKY oscillations have a wavelength of $\frac{1}{2}\lambda_F$, where $\lambda_F$ is the Fermi wavelength, a value of $\sigma'$ on the order of the lattice spacing—roughly the same value as the range $\sigma$—is appropriate. Under these conditions the surface susceptibility is enhanced as much or somewhat more than the bulk susceptibility. Similar conclusions have also been reached in a continuum calculation using the exact $\chi_0(l, l')$ obtained from free-electron bands[4] and a lattice calculation using the exact $\chi_0(l, l')$ obtained from the tight-binding band.[5] Taken together, these results strongly suggest that there will be an exchange-enhanced surface magnetization in these materials. Unfortunately, all these calculations have been limited to the case $\vec{k}_{\parallel} = \omega = 0$. As it is the frequency-dependent $\vec{R}_{\parallel} = 0$ susceptibility, i.e., the site-site susceptibility on the surface, which is relevant for the application of these results to the induced-covalent-bond theory of chemisorption,[1,2] much more work is needed on the properties of these surface paramagnons.

[1]J. R. Schrieffer and R. Gomer, Surface Sci. 25, 315 (1971).
[2]H. Suhl, J. H. Smith, and Pradeep Kumar, Phys. Rev. Letters 25, 1442 (1970).
[3]D. L. Mills, M. T. Béal-Monod, and R. A. Weiner, Phys. Rev. B5, 4637 (1972).
[4]M. T. Béal-Monod, Pradeep Kumar, and H. Suhl, Solid State Commun. 11, 855 (1972).
[5]R. A. Weiner (unpublished).

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# Microwave Residual Surface Resistance of Superconductors*

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Two distinct models account for the microwave residual surface resistance of superconducting cavities with equally good agreement with the measured temperature and frequency dependence. In presenting his phonon-generation model. Passow claimed that Rabinowitz's fluxoid power-loss model of residual resistance does not fit the experimental data, whereas his does. In fact, the two models have essentially the same temperature and frequency dependence. Furthermore, Passow's phonon-generation model cannot explain the observed sensitivity to details of sample preparation and history while the fluxoid model can.

An analysis presented by Passow[1] showed that phonons generated in a superconductor by incident electromagnetic radiation result in a residual power loss with an equivalent surface resistance which agrees well with experimental measurements of temperature and frequency dependence. His expression for surface resistance is

$$R = \frac{4\pi}{c^2}\omega^2\Lambda\left(\rho + \frac{\beta v_s \Lambda^3}{(1+\omega^2\Lambda^2/v_s^2)^2}\right) . \tag{1}$$

The first term represents the superconducting surface resistance derived from the BCS theory.[2,3] The second term is related to the power loss as electromagnetic energy is transformed into acoustical energy. Passow claims that this latter term becomes dominant in superconductors at low temperatures, and that it "can account for the whole of the low-temperature surface resistance measured in the purest currently available materials." He goes on further to say, "Rabinowitz has tried to explain the residual surface rf resistance in terms of frozen-in magnetic flux.[4] However, experiments with cavities in high magnetic fields are reported to show a different frequency dependence from that predicted by his treatment."[5,6]

The oscillating-fluxoid power loss occurs in addition to the well-known BCS superconducting loss[2,3] and dominates over it at low temperature. The superconducting loss decreases rapidly with decreasing temperature at low temperature, whereas the fluxoid loss has a negligible temperature dependence at low temperature in agreement with experimental observations. The effective resistivity of an oscillating fluxoid is[4,7]

$$\rho = \{\omega^2\phi^2 H H_0 \mu^2/[\rho_n^2(\omega^2 M - p)^2 + \omega^2\phi^2 H_0^2\mu^2]\}\rho_n , \tag{2}$$

and the equivalent surface resistance is $R_f = \rho/2\lambda$.

$\rho$ has a different meaning here than in Eq. (1), but since we are only interested in comparing the frequency dependence of Eq. (2) with that of the second term in Eq. (1), it is sufficient to retain only the common symbol $\omega$ for the angular frequency. Hence we may write the second term of