Green-function theory for an isolated magnetic impurity near the surface of a ferromagnet

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Localized states of an isolated magnetic impurity situated near or within the surface of a semi-infinite Heisenberg ferromagnet are studied. A Green-function approach is used to determine the localized "defect modes" and "resonance modes" associated with the impurity at energies outside and inside the regions of bulk spin waves and surface spin waves. The density of spin-wave states is also calculated for the case of low impurity concentrations. It is shown how the proximity of the defect to the surface leads to modifications in the defect-associated modes.

I. INTRODUCTION

It is well known from earlier work that localized spin waves may occur associated with an isolated magnetic impurity, or a low concentration of random impurities, in *bulk* ferromagnets and antiferromagnets. The relevant Green-function theories have been described by several authors[1–5] in the context of the Heisenberg model. This has led to the prediction of "defect modes" occurring outside the band of bulk spin waves and "resonance modes" within the spin-wave band. Related experimental investigations have included the use of Raman scattering and inelastic neutron scattering (e.g., see Refs. 6 and 7 for reviews), as discussed further in Sec. V.

In this paper we derive a theory for the spin-wave states associated with an isolated magnetic defect at or near the surface of a *semi-infinite* Heisenberg ferromagnet. In this geometry there may be surface spin waves as well as the usual bulk spin waves.[8,9] We find that both types of spin waves influence the defect modes, giving rise to a shift and (in some cases) a splitting of the infinite-crystal defect modes. These effects occur because the spin-spin correlations (as expressed through the spin-dependent Green functions) are modified in the vicinity of a surface and also because there are missing exchange interactions due to the surface. We note that the presence of an *isolated* defect breaks the translational symmetry parallel to the surface, so this problem is quite distinct from theoretical studies for a layer of impurities embedded in a semi-infinite magnetic medium,[10,11] where a two-dimensional wave vector can be introduced for a description of the energy spectrum of the impure system.

In Sec. II we present a Green-function formalism for an isolated impurity spin embedded in a semi-infinite Heisenberg ferromagnet at an arbitrary distance from the surface. A simple-cubic ferromagnetic structure is assumed, but the results may be generalized to other lattice structures. The energies of the impurity modes are deduced in Sec. III and the spin-wave density of states is discussed in Sec. IV.

II. THE GREEN-FUNCTION FORMALISM

The system under study is a semi-infinite ferromagnet with a (001) surface and a simple-cubic structure (lattice constant a). An isolated single magnetic impurity is taken to be embedded in the medium at distance $(N-1)a$ from the surface (where integer $N \geq 1$). The Heisenberg Hamiltonian used to describe the system is

$$\mathcal{H} = -\frac{1}{2}\sum_{\mathbf{r},\mathbf{r}'} J(\mathbf{r},\mathbf{r}')\mathbf{S}_{\mathbf{r}}\cdot\mathbf{S}_{\mathbf{r}'} - \sum_{\mathbf{r}} h(\mathbf{r})S_{\mathbf{r}}^{z} , \tag{1}$$

where $\mathbf{S}_{\mathbf{r}}$ is the spin operator at site $\mathbf{r}$, having spin quantum number S everywhere except at the impurity site (labeled by $\mathbf{c}$) where the spin quantum number is denoted by S'. We assume that the exchange $J(\mathbf{r},\mathbf{r}')$ couples only the nearest neighbors, having values in the pure medium equal to J_s if both spins are in the surface layer and J otherwise. The exchange interaction between the impurity and its neighbors is denoted by J', with the exception that when $N=1$ the exchange between the impurity and its neighbors in the surface layer is J_s'. The final term in Eq. (1) describes an external magnetic field B_0 applied to the system in the z direction: $h(\mathbf{r})=g\mu_B B_0 \equiv h$ except at the impurity site where $h(\mathbf{r}=\mathbf{c})=g'\mu_B B_0 \equiv h'$, allowing for a modified g value there.

Using the Holstein-Primakoff transformation, the spin operators are expressed in terms of boson operators $b_{\mathbf{r}}$ and $b_{\mathbf{r}}^{\dagger}$. At low enough temperatures ($k_B T \ll JS$), the linearized spin-wave approximation can be used to give

$$\begin{aligned} S_{\mathbf{r}}^{+} &= (2S - b_{\mathbf{r}}^{\dagger}b_{\mathbf{r}})^{1/2}b_{\mathbf{r}} \simeq (2S)^{1/2}b_{\mathbf{r}} , \\ S_{\mathbf{r}}^{-} &= b_{\mathbf{r}}^{\dagger}(2S - b_{\mathbf{r}}^{\dagger}b_{\mathbf{r}})^{1/2} \simeq (2S)^{1/2}b_{\mathbf{r}}^{\dagger} , \\ S_{\mathbf{r}}^{z} &= S - b_{\mathbf{r}}^{\dagger}b_{\mathbf{r}} . \end{aligned} \tag{2}$$

At impurity site $\mathbf{c}$ the spin quantum number S above becomes replaced by the corresponding value S'. Substituting Eq. (2) into (1), we may write the linearized Hamiltonian as $\mathcal{H}=\mathcal{H}_0+\mathcal{H}'$, where $\mathcal{H}_0$ is just the Hamiltonian for the pure semi-infinite ferromagnet:

$$\mathcal{H}_0=S\sum_{\mathbf{r}}\left[\sum_{\mathbf{r}'}J(\mathbf{r},\mathbf{r}')+h\right]b_{\mathbf{r}}^{\dagger}b_{\mathbf{r}}-S\sum_{\mathbf{r},\mathbf{r}'}J(\mathbf{r},\mathbf{r}')b_{\mathbf{r}}^{\dagger}b_{\mathbf{r}'}\ , \tag{3}$$

and $\mathcal{H}'$ is the perturbation due to the impurity. When $N>1$ we have

$$\mathcal{H}'=-JS\sum_{\mathbf{d}}(\gamma b_{\mathbf{c}}b_{\mathbf{d}}+\gamma b_{\mathbf{c}}^{\dagger}b_{\mathbf{d}}-\epsilon b_{\mathbf{c}}^{\dagger}b_{\mathbf{c}}-\rho b_{\mathbf{d}}^{\dagger}b_{\mathbf{d}})-(h'-h)b_{\mathbf{c}}^{\dagger}b_{\mathbf{c}}\ , \tag{4}$$

where $\mathbf{d}$ runs over the six nearest neighbors of the impurity at site $\mathbf{c}$. Also we have defined the following quantities,

$$\gamma=\frac{J'}{J}\left[\frac{S'}{S}\right]^{1/2}-1,\quad \rho=\frac{J'S'}{JS}-1,\quad \epsilon=\frac{J'}{J}-1\ . \tag{5}$$

In the special case of $N=1$ the impurity spin is in the surface layer, where it has only *five* nearest neighbors and the exchange interactions with the impurity spin may be different from those in the bulk. The corresponding perturbation Hamiltonian for $N=1$ is then

$$\mathcal{H}'=-JS(\gamma b_{\mathbf{c}}b_{\mathbf{d}''}+\gamma b_{\mathbf{c}}^{\dagger}b_{\mathbf{d}''}-\epsilon b_{\mathbf{c}}^{\dagger}b_{\mathbf{c}}-\rho b_{\mathbf{d}''}b_{\mathbf{d}''})-(h'-h)b_{\mathbf{c}}^{\dagger}b_{\mathbf{c}}-JS\sum_{\mathbf{d}'}(\gamma_s b_{\mathbf{c}}b_{\mathbf{d}'}^{\dagger}+\gamma_s b_{\mathbf{c}}^{\dagger}b_{\mathbf{d}'}-\epsilon_s b_{\mathbf{c}}^{\dagger}b_{\mathbf{c}}-\rho_s b_{\mathbf{d}'}^{\dagger}b_{\mathbf{d}'})\ . \tag{6}$$

Here $\mathbf{d}''$ denotes the site on layer $N=2$ immediately below the impurity at $\mathbf{c}$, and $\mathbf{d}'$ runs over the four nearest neighbors in the surface layer ($N=1$). Also γ_s, ϵ_s, and ρ_s are obtained, respectively, from γ, ϵ, and ρ in Eq. (5) by replacing J' with J_s' and adding a term $(1-J_s/J)$.

We now introduce the retarded commutator Green function $G(\mathbf{r},\mathbf{r}';t)=\langle\langle b_{\mathbf{r}}(t);b_{\mathbf{r}'}^{\dagger}(0)\rangle\rangle$ for the impure system. Its Fourier component, defined as

$$G(\mathbf{r},\mathbf{r}';E)\equiv\langle\langle b_{\mathbf{r}};b_{\mathbf{r}'}^{\dagger}\rangle\rangle_E=\frac{1}{2\pi}\int_{-\infty}^{\infty}G(\mathbf{r},\mathbf{r}';t)\exp(iEt)dt\ , \tag{7}$$

satisfies the standard equation of motion[12]

$$E\langle\langle b_{\mathbf{r}};b_{\mathbf{r}'}^{\dagger}\rangle\rangle_E=\frac{1}{2\pi}\langle[b_{\mathbf{r}},b_{\mathbf{r}'}^{\dagger}]\rangle+\langle\langle[b_{\mathbf{r}},\mathcal{H}];b_{\mathbf{r}'}^{\dagger}\rangle\rangle_E\ . \tag{8}$$

The corresponding unperturbed Green function can be obtained by solving the above equation with $\mathcal{H}$ replaced by $\mathcal{H}_0$. The solution, which represents the case of a pure semi-infinite ferromagnet, is well known and given by[13]

$$G^{(0)}(\mathbf{r},\mathbf{r}';E)=\frac{1}{M}\sum_{\mathbf{q}_{\parallel}}\exp[i\mathbf{q}_{\parallel}\cdot(\mathbf{r}_{\parallel}-\mathbf{r}_{\parallel}')]\frac{1}{2\pi JS(x-x^{-1})}\times\left[x^{|n-n'|}-\left[\frac{1+\Delta x^{-1}}{1+\Delta x}\right]x^{n+n'}\right] \tag{9}$$

where $\mathbf{q}_{\parallel}=(q_x,q_y)$ and M is the number of sites in any layer parallel to the surface. Also $\mathbf{r}_{\parallel}$ and $\mathbf{r}_{\parallel}'$ are two-dimensional vectors representing the projection of $\mathbf{r}$ and $\mathbf{r}'$ in the xy plane, and n and n' are the layer numbers for the sites $\mathbf{r}$ and $\mathbf{r}'$, respectively (with $n=1$ being the surface layer, etc.). The complex quantity x (satisfying the condition $|x|\le 1$) is defined by

$$x+x^{-1}=(h-E)/(JS)+2[3-\cos(q_x a)-\cos(q_y a)]\ , \tag{10}$$

and Δ depends on $\mathbf{q}_{\parallel}$ and the exchange parameters:

$$\Delta=2(J_s/J-1)[2-\cos(q_x a)-\cos(q_y a)]-1\ . \tag{11}$$

The bulk spin waves of the pure semi-infinite ferromagnet correspond to $|x|=1$. Setting $x=\exp(iq_z a)$ for this case, we obtain $E=E_B(\mathbf{q})$ from Eq. (10) where

$$E_B(\mathbf{q})=h+2JS[3-\cos(q_x a)-\cos(q_y a)-\cos(q_z a)] \tag{12}$$

is the dispersion relation for bulk spin waves of wave vector $\mathbf{q}=(q_x,q_y,q_z)$. Also there are surface spin waves at values of E corresponding to $x=-1/\Delta$, provided the existence condition $|\Delta|>1$ is satisfied (e.g., see Ref. 13). From Eq. (10) we obtain the surface spin-wave dispersion relation as

$$E_S(\mathbf{q})=h+2JS[2-\cos(q_x a)-\cos(q_y a)]-JS(\Delta+1/\Delta)\ . \tag{13}$$

If $J_s/J<1$ there may be *acoustic* spin waves, having energies below the bulk band, whereas if $J_s/J>1.25$ there may be *optic* surface spin waves above the bulk band.

The Green-function equation of motion for the semi-infinite ferromagnet with an impurity can be constructed from Eq. (8) using the full form of the Hamiltonian $\mathcal{H}$. The result can eventually be expressed in the form of a Dyson equation relating $G(\mathbf{r},\mathbf{r}';E)$ to the unperturbed Green function $G^0(\mathbf{r},\mathbf{r}';E)$:

$$\sum_{\mathbf{s}'}\left[1-\sum_{\mathbf{s}}G^0(\mathbf{r},\mathbf{s};E)V(\mathbf{s},\mathbf{s}')\right]G(\mathbf{s}',\mathbf{r}';E)=G^0(\mathbf{r},\mathbf{r}';E)\ . \tag{14}$$

Here V is an effective potential related to the perturbation produced by the presence of the impurity. It is given, for $N>1$, by

$$V(\mathbf{s},\mathbf{s}')=2\pi JS\sum_{\mathbf{d}}(\rho\delta_{\mathbf{s},\mathbf{d}}\delta_{\mathbf{d},\mathbf{s}'}-\gamma\delta_{\mathbf{s},\mathbf{d}}\delta_{\mathbf{c},\mathbf{s}'}-\gamma\delta_{\mathbf{s},\mathbf{c}}\delta_{\mathbf{d},\mathbf{s}'})+2\pi JS[6\epsilon-(h'-h)/(JS)]\delta_{\mathbf{s},\mathbf{c}}\delta_{\mathbf{c},\mathbf{s}'} \tag{15}$$

and, for $N=1$, by

$$V(s,s')=2\pi JS\sum_{d'}(\rho_s\delta_{s,d'}\delta_{d',s'}-\gamma_s\delta_{s,d'}\delta_{c,s'}-\gamma_s\delta_{s,c}\delta_{d',s'})$$
$$+2\pi JS(\rho\delta_{s,d''}\delta_{d'',s'}-\gamma\delta_{s,d''}\delta_{c,s'}-\gamma\delta_{s,c}\delta_{d'',s'})$$
$$+2\pi JS[4\epsilon_s+\epsilon-(h'-h)/(JS)]\delta_{s,c}\delta_{c,s'}\ . \quad (16)$$

We note that in the presence of an *isolated* impurity, the translational symmetry does not exist in any of the three dimensions. It is no longer possible to introduce a two-dimensional wave vector as in the cases of a pure semi-infinite medium or a layered system, and we have to work in terms of the real space to solve the above Eqs. (14)–(16).

III. IMPURITY MODES

In this section we solve for the energy spectrum of the modes associated with the impurity. In the site representation, we label the impurity site c in layer N by index 1, its four neighbors in the same layer by 2–5, and its neighbors in layers $N-1$ and $N+1$ by 6 and 7, respectively. Clearly neighbor 6 is absent when $N=1$. The Dyson's equation (14) can be rewritten in a matrix form,

$$[\underline{I}-\underline{G}^0(E)\underline{V}]\underline{G}(E)=\underline{G}^0(E)\ . \quad (17)$$

As in the corresponding calculations for an impurity in an *infinite* ferromagnet,[1–3,14] the only nonvanishing part of the potential matrix $\underline{V}$ is a 7×7 submatrix corresponding to the impurity spin and its six (five in the case of $N=1$) neighbors.

It then follows from Eq. (17) that the excitation energies associated with the impurity spin are give by the condition

$$\det[\underline{I}-\underline{G}^0(E)\underline{V}]=0\ . \quad (18)$$

On substituting Eq. (15) or (16) into the above equation, we find that the determinant can be factorized as

$$\det[\underline{I}-\underline{G}^0(E)\underline{V}]=D_A(E)D_B(E)^2D_C(E)\ , \quad (19)$$

with

$$D_A(E)=\rho_N[G^0(2,3)-G^0(1,1)]+1/(2\pi JS)\ , \quad (20)$$

$$D_B(E)=\rho_N[2G^0(2,4)-G^0(1,1)-G^0(2,3)]+1/(2\pi JS) \quad (21)$$

$$D_C(E)=\det\underline{D}(E)\ . \quad (22)$$

For convenience we have omitted the E labeling in the site-dependent Green functions G^0, and the elements of the 4×4 matrix $\underline{D}(E)$ in Eq. (22) are defined by

$$\begin{aligned}
D_{1,1}&=-\xi_NG^0(1,1)+4\gamma_NG^0(1,2)\\
&\quad+\gamma G^0(1,7)+1/(2\pi JS)\ ,\\
D_{2,1}&=-\xi_NG^0(1,2)+\gamma_N[G^0(1,1)+G^0(2,3)\\
&\quad+2G^0(2,4)]+\gamma G^0(2,7)\ ,\\
D_{3,1}&=-\xi_NG^0(1,6)\\
&\quad+\gamma_N[4G^0(2,6)+G^0(6,6)+G^0(6,7)]\ ,\\
D_{4,1}&=-\xi_NG^0(1,7)+4\gamma_NG^0(2,7)+\gamma G^0(7,7)\ ,\\
D_{1,2}&=4[\gamma_NG^0(1,1)-\rho_NG^0(1,2)]\ ,\\
D_{2,2}&=4\gamma_NG^0(1,2)-\rho_N[G^0(1,1)+G^0(2,3)\\
&\quad+2G^0(2,4)]+1/(2\pi JS)\ ,\\
D_{3,2}&=4[\gamma_NG^0(1,6)-\rho_NG^0(2,6)]\ ,\\
D_{4,2}&=4[\gamma_NG^0(1,7)-\rho_NG^0(2,7)]\ ,\\
D_{1,3}&=\gamma G^0(1,1)-\rho G^0(1,6)\ ,\\
D_{2,3}&=\gamma G^0(1,2)-\rho G^0(2,6)\ ,\\
D_{3,3}&=\gamma G^0(1,6)-\rho G^0(6,6)+1/(2\pi JS)\ ,\\
D_{4,3}&=\gamma G^0(1,7)-\rho G^0(6,7)\ ,\\
D_{1,4}&=\gamma G^0(1,1)-\rho G^0(1,7)\ ,\\
D_{2,4}&=\gamma G^0(1,2)-\rho G^0(2,7)\ ,\\
D_{3,4}&=\gamma G^0(1,6)-\rho G^0(6,7)\ ,\\
D_{4,4}&=\gamma G^0(1,7)-\rho G^0(7,7)+1/(2\pi JS)\ .
\end{aligned} \quad (23)$$

Here we have denoted $\rho_N=\rho_s$, $\gamma_N=\gamma_s$, and $\xi_N=4\epsilon_s+\epsilon-(h'-h)/(JS)$ when $N=1$; and $\rho_N=\rho$, $\gamma_N=\gamma$, and $\xi_N=6\epsilon-(h'-h)/(JS)$ when $N\geq2$. Note also that for the case of $N=1$, all Green functions associated with site 6 are defined to be zero.

The impurity-associated modes in the semi-infinite ferromagnet may now be obtained from Eqs. (20)–(23) by finding the E values for which $D_A(E)$ $D_B(E)$ or $D_C(E)$ vanishes. It is useful to distinguish between "defect modes," which are nonresonant with any of the bulk or surface spin waves of the pure semi-infinite ferromagnet, and "resonance modes," which occur for E within the bands of bulk or surface spin waves. In either case the first step is the evaluation of the position-dependent Green functions G^0 appearing in Eqs. (20)–(23). In any specific application these may be found using Eq. (9) and carrying out the summation over the two-dimensional wave vector $\mathbf{q}_\parallel$ numerically. For the case of defect modes these Green functions are all real quantities, whereas for resonance modes the Green functions will generally be complex.

We first discuss the results for defect modes, since this case is more straightforward. In Fig. 1 we show some numerical examples in which the defect-mode energies are plotted against J'/J for the cases of $N=1$ (solid lines) and $N=10$ (dashed lines). In the latter case N is sufficiently large that the curves are essentially the same as calculated from previous theories for infinite ferromag-

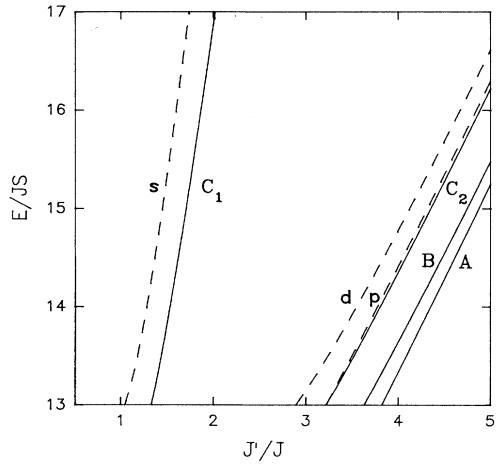

FIG. 1. Defect energies associated with an isolated magnetic impurity in the surface layer ($N=1$) of a semiinfinite ferromagnet (solid curves) compared with those for $N=10$ (dashed curves). The results are plotted against J'/J and the parameter values used are given in the text.

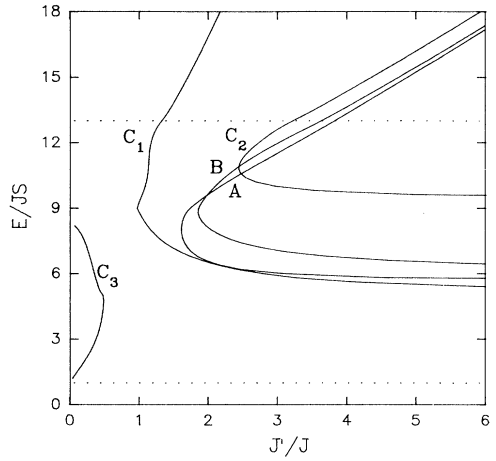

FIG. 2. Modes associated with an impurity spin in the surface layer ($N=1$) plotted for a wider range of the energy E and showing both the defect and resonance modes. The upper and lower edges of the bulk band are indicated by the two dotted horizontal lines at $E/JS=13$ and 1, respectively, in this example (see text).

nets,[1,3] where the modes are conventionally labeled as s, p, and d. This symmetry labeling is no longer applicable when the impurity is close to the surface, but the curve C_1 for $N=1$ corresponds to a mode that is mainly localized on the impurity (like the s mode at large N), whereas the curves C_2, A, and B correspond to modes that are mainly associated with neighbors of the impurity (like the p and d modes). These neighbors do not all have the same symmetry with respect to the surface, and this produces a splitting of some modes. The parameters assumed in this example are $J_s/J=1$, $h=h'=SJ$, $S=1$, and $S'=2$: in this case the top of the bulk spin-wave band corresponds to $E/SJ=13$ and there are no surface spin waves of the semi-infinite ferromagnet. In Fig. 2 we show the impurity-associated modes for a wider range of energies, taking the above $N=1$ case with the same parameters. In this case there are no defect modes below the bottom of the bulk continuum, which corresponds to $E/JS=1$. However, within the bulk spin-wave band ($13\geq E/JS\geq 1$) there may be resonance modes associated with the impurity, depending on the value of J'/J. It is interesting to note that the "kinks" evident in some of the curves at points where $E/JS=5$ and 9 correspond to the top of the bulk continuum at $\mathbf{q}_\parallel=(0,0)$ and the bottom of the continuum at $\mathbf{q}_\parallel=(\pi/a,\pi/a)$, respectively, where the density of states of the pure system changes abruptly.

We next consider cases where the impurity is in the surface layer ($N=1$) and the value of J_s/J is such that surface spin-wave modes are present in the spectrum of the pure ferromagnet. In Fig. 3(a), we show a numerical example for the case of $J_s<J$ when an acoustic surface mode is present (split off below the lower edge of the bulk continuum). Compared with Fig. 2, all curves are shifted to the right with the A and B modes most strongly affected. This result can be easily understood as follows: When the exchange among the spins on the surface is reduced, so is the coupling of the impurity spin to its neighbors near the surface and hence to the rest of the system. It is then easier to excite any mode associated with the impurity compared with the case when it is strongly coupled to the whole system. For the same reason, the relatively extended A and B modes are more strongly affected than the relatively localized C_1 and C_2 modes. On the other hand, when $J_s>1.25J$ there is an optical surface mode that branches out from the top of the bulk spin-wave energy continuum band in the energy spectrum of the pure material. The maximum energy of this optical branch is at the zone boundary wave-vector $\mathbf{q}_\parallel=(\pi/a,\pi/2)$, and is given by

$$E_m^{\rm op}/JS=h+1+8J_s/J+[8(J_s/J)-9]^{-1}\ . \qquad (24)$$

In Fig. 3(b) we show an example with $J_s/J=1.5$; this corresponds to $E_m^{\rm op}/JS=14.33$, whereas the energy E_m^b of the top of the bulk band occurs at $E_m^b/JS=13$. It is seen that all the impurity modes are dramatically disturbed by the presence of the surface optical mode. First, all the curves are shifted to the left compared with the situation in the absence of surface optical spin waves (e.g., see Fig. 2). Second, "kinks" are produced in some of the curves near the maximum energy $E_m^{\rm op}$ of the optical mode. At this energy the density of states of the surface optical mode becomes rather large, which allows a very strong mixing between the surface optical mode and any impurity mode that is close in energy.

Figure 4 is included, together with Fig. 3(b), to show how the impurity modes change with the depth of the impurity embedded underneath the surface (N dependence). When the impurity is no longer in the surface layer ($N=1$) but is in the next layer down ($N=2$), significant changes in impurity modes are expected for the following

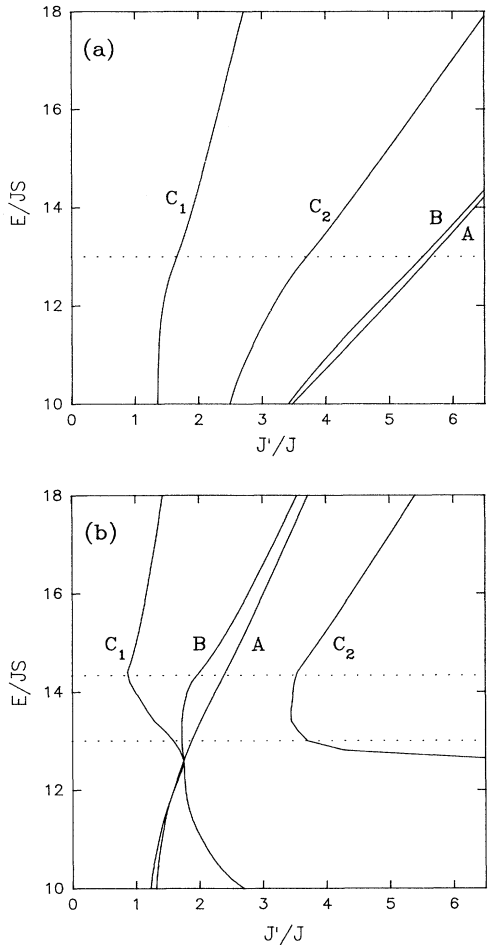

FIG. 3. Impurity modes shown near the top of the bulk spin-wave band and above in the presence of (a) an acoustic surface mode (taking $J_s/J=0.75$) and (b) an optical surface mode (taking $J_s/J=1.5$), assuming the impurity to be in the surface layer ($N=1$) in both cases. Other parameters are as for Fig. 1. In b the dotted line at $E/JS=14.3$ indicates the maximum energy of the optical surface mode.

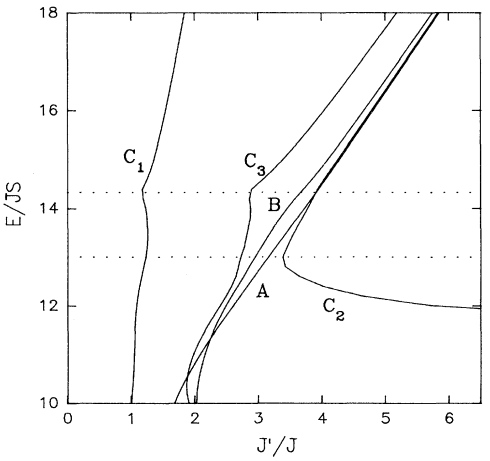

FIG. 4. As for Fig. 3(b), but taking the case of $N=2$ with other parameters unchanged.

reasons. First, the impurity spin now will have six nearest neighbors (instead of five), and hence one more mode appears as indicated by C_3 in Fig. 4. Second, apart from the difference in the number of neighbors, the exchange integrals between the impurity spin and its neighbors are also quite different for the cases of $N=2$ and $N=1$, especially when J_s is not too close to J.

It is helpful to interpret some of the above results qualitatively by using an Ising model cluster approximation for the impurity modes (in a similar fashion to that described by Cowley and Buyers[6] for impurities in *bulk* antiferromagnets). This involves replacing the $\mathbf{S}_r\cdot\mathbf{S}_{r'}$ interaction in Eq. (1) by its longitudinal (or Ising) part $S_r^z S_{r'}^z$ and ignoring the transverse part of the interaction. Consider first a spin of the bulk of a *pure* ferromagnet: the exchange energy associated with the coupling of that spin to its six neighbors is $\omega_B \equiv 6JS$ in the Ising approximation. Now, for the case of a defect spin situated in a layer with $N \geq 3$, it is easy to show that we have exchange energies ω_d and ω_n associated with the defect and any one of its neighbors, respectively, where

$$\omega_d=\omega_B(1+\epsilon), \quad \omega_n=\omega_B[1+(\rho/6)] \tag{25}$$

and the parameters ϵ and ρ are defined in Eq. (5). When $N=2$ the results for ω_d and for ω_n corresponding to five of the neighbors are unchanged, but the energy for the remaining neighbor (the one in the surface layer) is given by

$$\omega_n'=\omega_B[1+(\rho/6)+\tfrac{1}{6}(4J_s/J-5)] \; . \tag{26}$$

Finally, when $N=1$, the exchange energy of the defect is

$$\omega_d''=\omega_B[1+\tfrac{1}{6}(4J_s'/J+J'/J-6)] \tag{27}$$

and the neighbor in layer 2 is associated with energy ω_n as given in Eq. (25) while the four neighbors in layer 1 have energy given by

$$\omega_n''=\omega_B[1+\tfrac{1}{6}(J_s'S'/JS+3J_s/J-5)] \; . \tag{28}$$

In an infinite ferromagnet the ω_d mode of the Ising cluster approximation becomes the s mode and the ω_n Ising mode splits to give the p and d modes, when the full form of the Hamiltonian is taken into account. For $N \geq 3$ in the semi-infinite ferromagnet, the same qualitative behavior is obtained but the mode energies are perturbed (and split in some cases) because the Green functions are modified. For $N=2$ and $N=1$, the mode energies are shifted more dramatically in accordance with Eqs. (26)–(28).

IV. DENSITY OF STATES

We next employ the Green-function results of Sec. II to calculate the density of spin-wave states of the impure semi-infinite system. It is well known (e.g., see Ref. 1) that the density of states of the system $d(E)$ can be expressed quite generally in terms of the retarded Green function as

$$d(E)=-\frac{2}{\Omega}\mathrm{Im}\sum_{\mathbf{r}} G(\mathbf{r},\mathbf{r};E)$$
$$=-\frac{2}{\Omega}\mathrm{Im}\frac{d}{dE}\ln\det\underline{G}^{-1}(E)\ , \tag{29}$$

where Ω is the total number of sites in the system. Because the density-of-states contribution from a *single* impurity (or even from a number of isolated impurities embedded in one of the layers) will be negligibly small compared with $d(E)$ for a semi-infinite ferromagnet (due to factors of order $1/\Omega$), we adopt the following procedure used in some previous calculations for surface problems. We consider a low concentration $C(N)$ of uncorrelated impurities randomly distributed on a single layer, taken to be at a distance $(N-1)a$ from the surface, and we introduce a depth-dependent *integrated* density of states defined as[15]

$$d(E,N_0)=-\frac{2}{N_0 M}\mathrm{Im}\sum_{\mathbf{r}}{}' G(\mathbf{r},\mathbf{r};E)\ , \tag{30}$$

where the prime indicates that the three-dimensional summation over $\mathbf{r}$ is here restricted to the first N_0 layers from the surface. The total number of sites in that region is $N_0 M$, where M denotes the number of sites in any one layer. Using Eqs. (17) and (19), the above Eq. (30) gives

$$d(E,N_0)=d_0(E,N_0)-\frac{2C(N)}{N_0}\mathrm{Im}\frac{d}{dE}\ln\det[\underline{I}-\underline{G}^0(E)\underline{V}]$$
$$=d_0(E,N_0)$$
$$-\frac{2C(N)}{N_0}\mathrm{Im}\left[\frac{D_A'(E)}{D_A(E)}+2\frac{D_B'(E)}{D_B(E)}+\frac{D_C'(E)}{D_C(E)}\right]. \tag{31}$$

Here $d_0(E,N_0)$ is the corresponding *integrated* density of states of the *pure* semi-infinite ferromagnet and the prime indicates differentiation with respect to E. Using Eqs. (20)–(23), as well as the Green function of the pure system to obtain $d_0(E)$, numerical calculations of $d(E,N_0)$ can be carried out for any given values of J'/J, the impurity concentration $C(N)$, and N_0. The arbitrary cutoff N_0 for the summation in the z direction is essentially like a normalization parameter; usually we would choose $N_0 > N$.

In Fig. 5 we give a numerical example of $D(E,N_0)$ corresponding to the case described in Fig. 3(a), taking $J'/J=4$ and $N_0=15$. The two-dimensional impurity concentration in layer $N=1$ is chosen to be $C(N)=0.03$, low enough to neglect correlations among the impurities. Due to the presence of the surface, the integrated density of states for the pure system (see dashed curve) is no longer symmetric about the midpoint of the continuum band (at $E/JS=7$ in this example), even in the absence of any surface mode. It increases slightly for the lower energy modes and decreases for the higher ones, similar to the phonon cases.[16] The peak in $d(E,N_0)$ (see the solid curve) at around $E/JS=13.2$ is associated with the factor $D_C(E)$ and is therefore labeled by C. The width of this peak is rather narrow (strictly it is a δ function) because it is a "defect" mode, not "in resonance" with either the bulk or surface modes for a pure semi-infinite ferromagnet. On the other hand, the resonant feature near $E/JS=10.8$ is in fact composed of two nearby peaks A and C, associated with factors $D_A(E)$ and $D_C(E)$, respectively. Since they are within the bulk continuum ($E/JS<13$), the widths of these peaks are much bigger than that of peak C and therefore they have shorter lifetimes. Antiresonance modes[14] or "holes"[9] in the bulk region of the density of states are also obtained, corresponding to those negative peaks near $E/JS=4.5$ and 7.8. If the isolated impurities are taken to be far below the surface layer (the case of large N, when the surface effects on the impurities can be neglected) we find that our density-of-states calculations are consistent with the results obtained by Izyumov and Medvedev[14] for the cases of impurities in an *infinite* system.

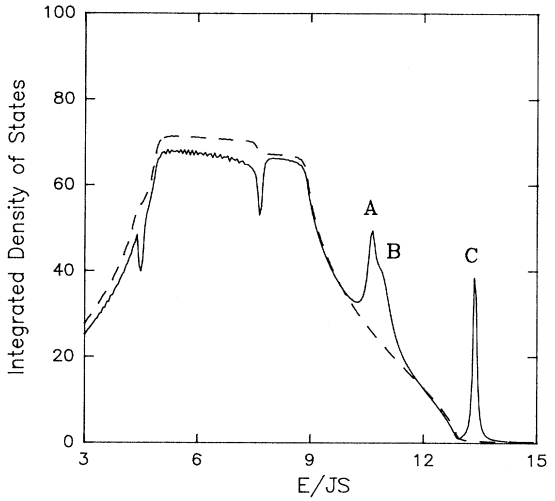

FIG. 5. The integrated density of states, plotted as a function of E/JS, for the impure system (solid curve) and the corresponding pure system (dashed curve), taking $N=1$ and $N_0=15$. The labeling of curves is explained in the text.

V. CONCLUSIONS

In this paper we have studied the effects of an isolated magnetic impurity embedded near the (001) surface of a simple-cubic Heisenberg ferromagnet. Within the random-phase approximation at low temperatures $T \ll T_c$, we have employed Green-function methods to calculate the spin-wave energies associated with the impurity spin for different values of J'/J, assumed to be greater than or equal to zero. We find that both "defect" and "resonance" modes are strongly affected by the surface acoustic or optic modes, especially when the impurity is in layer $N=1$ or 2. If N becomes very large we recover the previous results for infinite ferromagnets, as expected. We have also deduced results for the spin-wave density of states for the case of a low impurity concentration. Here defect peaks are found outside the bulk and/or surface mode region and resonance and antireso-

nance peaks are found inside the bulk and/or surface mode region, generalizing previous conclusions for infinite bulk systems.

Some straightforward generalizations of the present calculations would be to other crystal structures (such as fcc and bcc) and to other orientations of surface. This would allow applications to materials such as EuO and EuS using, for example, Brillouin light scattering. Both materials are good light scatterers and are optically relatively opaque, making them suitable for surface studies (e.g., see Ref. 7). It would be of interest to have Brillouin scattering data for EuO or EuS samples with a low concentration of substitutional magnetic impurities. Another extension of the theory is to the case of $J'/J < 0$ (antiferromagnetic impurity spin), which has already been studied in infinite ferromagnets.[17]

A more interesting extension, however, is to the case of an impurity near the surface of an antiferromagnet, since impurity effects have already been extensively studied in bulk antiferromagnets by experimental techniques such as light scattering and neutron scattering, as mentioned in Sec. I. For example, detailed Raman light scattering studies have been reported[18] for the impurity modes observed in bulk FeF_2 with Mn impurities and bulk MnF_2 with Fe impurities. Some theoretical results for impurities in semiinfinite rutile-structure antiferromagnets will be reported elsewhere.[19]

We finally note that the type of Green-function formalism employed here could, in principle, also be extended to localized phonon states, assuming a model with short-range force constants. An impurity atom near a surface would, in general, perturb the force constants in its vicinity and have a different mass from the other atoms. Some calculations for the impurity-mode frequencies for special cases, using methods different from that of the present paper, have been given (see Ref. 16 and references therein), including mention of a splitting due to the proximity of the surface.

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