PHYSICAL REVIEW B VOLUME 25, NUMBER 10 15 MAY 1982

Some simple, exactly soluble models for surfaces and interfaces

Mark Mostoller and A. K. Rajagopal*
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
(Received 17 November 1981)

Exact analytical results are given for several simple models of elementary excitations at surfaces or interfaces, based on one- or two-band Hamiltonians with interactions between atoms in the zeroth to first or second neighboring planes. Illustrative applications are made to the fcc (110) face of a Heisenberg ferromagnet and to electrons at the (001) surface of diamond or zinc-blende crystals; surface states appear in both cases. An extension of the general theory is presented in an appendix.

I. INTRODUCTION

A number of three-dimensional problems can be mapped, by appropriate transformations, onto a linear chain. One example of such a mapping is the real-space recursion method,[1] which has been very useful for calculating approximate local densities of states for a variety of systems[2]: perfect crystal surfaces,[3-5] bulk alloys,[6,7] random networks,[8] and dislocations,[9] to name a few. A second class of examples is provided by surfaces or interfaces in ordered crystals with interactions of finite range—electrons described by tight-binding Hamiltonians, phonons in the Born–von Kármán or related bond-angle models, and magnons in the Heisenberg model. Here, taking the two-dimensional transform with respect to the surface or interfacial wave vector $\vec{q}_s$ yields an effective linear-chain Hamiltonian whose elements represent $\vec{q}_s$-dependent interplanar interactions. In a recent paper, Mostoller and Kaplan[10] (referred to as MK hereafter) outlined an exact formal solution of this problem, using a matrix continued fraction approach to determine the desired blocks of the Green's function. Subsequent work by Dy and coworkers[11,12] provides valuable further elaboration of the theory, and the transfer matrix method of Falicov and Yndurain[13,14] describes somewhat related techniques.

Most applications of linear-chain mappings have involved reductions to linear chains with first-nearest-neighbor (1NN) interactions only because analytic solutions are available for this case. Real-space recursion calculations generally fall into this category. Kalkstein and Soven[15] illustrated their pioneering work on elementary excitations at surfaces with examples of this kind, the (100) and (111) faces of what is sometimes called cubium—*s* electrons in a simple cubic crystal with 1NN interactions. Models that reduce to linear chains with 1NN interactions have been used more recently to study a variety of interesting phenomena such as chemisorption on metals,[16] spin waves at stepped surfaces,[17] and surface instabilities and superstructures.[18,19]

In this paper, we present exact analytic solutions for two other simple linear-chain-like models that in their most general form yield two bands of unequal width. Depending on the model parameters, they correspond to one- or two-band Hamiltonians with interactions between atoms in the same to first or second neighboring planes. Two physical applications are given, to electrons at the (001) surface of diamond or zinc-blende crystals and to spin waves at the fcc (110) face of a Heisenberg ferromagnet. We believe that our exact results are of intrinsic interest, as has proven to be the case for the very simplest linear-chain-like model, and the analytic solutions may also allow numerical checks of more elaborate calculations.

In Sec. II the model Hamiltonians are defined and expressions for the Green's function in the surface region are derived. Results for certain electron bands at the diamond or zinc-blende (001) surface are given in Sec. III. The fcc (110) face of a Heisenberg ferromagnet is discussed in Sec. IV and a few concluding remarks are made in Sec. V. A more general theoretical extension is outlined in Appendix C.

II. MODEL SURFACE HAMILTONIANS AND THEIR SOLUTION

We follow the notation of MK (Ref. 10), and refer the reader to that paper for details of how the problem is set up and solved. The two-dimensional transform of the Hamiltonian with respect to the surface wave vector $\vec{q}_s$ is assumed to have the block tridiagonal form

$$\mathscr{H}(\vec{q}_s)=\begin{bmatrix} \underline{A}_1 & \underline{B}_1 & \underline{0} & \underline{0} & \\ \underline{B}_1^\dagger & \underline{A}_2 & \underline{B}_2 & \underline{0} & \\ \underline{0} & \underline{B}_2^\dagger & \underline{A}_3 & \underline{B}_3 & \\ \underline{0} & 0 & \underline{B}_3^\dagger & \underline{A}_4 & \\ & & & & \ddots \end{bmatrix}, \tag{1}$$

in which the elements $\underline{A}_i(\vec{q}_s)$,$\underline{B}_i(\vec{q}_s)$ are $(n-1)\times(n-1)$ square blocks whose elements in turn are interplanar transform matrices $\underline{H}(L,L';\vec{q}_s)$. Here n specifies the range of the interplanar interactions, so that atoms in plane $L=1$ interact with atoms in planes $L'=1$ to $L'=n$, those in plane 2 with atoms in planes 1 to $n+1$, and from $L=n$ on down, atoms in plane L interact with atoms in planes $L-n+1$ to $L+n-1$. The dimension of the interplanar Hamiltonian transforms $\underline{H}(L,L';\vec{q}_s)$ is the size of the basis: three for phonons, for example, or four for an *s-p* tight-binding model for electrons in semiconductors. This blocking is important; as we shall see later, the work of Dy and co-workers[11,12] is flawed by incorrect blocking that in their method of solution leads to calls to invert singular matrices, although the method itself is sound.

The Hamiltonian in Eq. (1) is the same as that for a semi-infinite linear chain. For a basis of one state, for example, it corresponds to a linear chain with first to $(n-1)$st-neighbor interactions.

The Green's function or resolvent matrix, blocked in the same way as the total Hamiltonian, has the form

$$\underline{G}(\vec{q}_s,z)=[z\underline{I}-\underline{\mathscr{H}}(\vec{q}_s)]^{-1}$$

$$=\begin{bmatrix} \underline{G}_{11} & \underline{G}_{12} & \underline{G}_{13} & \\ \underline{G}_{21} & \underline{G}_{22} & \underline{G}_{23} & \\ \underline{G}_{31} & \underline{G}_{32} & \underline{G}_{33} & \\ & & & \ddots \end{bmatrix}. \tag{2}$$

We redefine the upper left, surface block of $\underline{G}$ as $\underline{g}_1$, that is,

$$\underline{g}_1(\vec{q}_s,z)=\underline{G}_{11}(\vec{q}_s,z)\ , \tag{3}$$

and find that $\underline{g}_1$ is the solution of a recursive sequence of equations,

$$\underline{g}_1=(z\underline{1}-\underline{A}_1-\underline{B}_1\cdot\underline{g}_2\cdot\underline{B}_1^\dagger)^{-1}\ , \tag{4a}$$

$$\underline{g}_2=(z\underline{1}-\underline{A}_2-\underline{B}_2\cdot\underline{g}_3\cdot\underline{B}_2^\dagger)^{-1}\ , \tag{4b}$$

$$\cdots$$

At some depth in the crystal, say for $i\geq m$, the Hamiltonian blocks $\underline{A}_i$ and $\underline{B}_i$ settle down to their bulk values $\underline{A}_b$ and $\underline{B}_b$. Then starting at level m, the equations in the sequence (4) repeat, and can be solved exactly for what we will call the terminated bulk Green's function $\underline{g}_b=\underline{g}_{m+j}$, $j\geq 0$,

$$\underline{g}_b=(z\underline{1}-\underline{A}_b-\underline{B}_b\cdot\underline{g}_b\cdot\underline{B}_b^\dagger)^{-1}\ . \tag{5}$$

Once $\underline{g}_b$ has been determined from Eq. (5), the surface Green's function $\underline{g}_1$ can be found by working back up the sequence in Eq. (4), allowing variations in interactions in the surface region if desired.

The simplest possible case that can occur is when the matrices $\underline{A}_i$,$\underline{B}_i$ in Eqs. (1), (4), and (5) are scalars. The problem then reduces to that of a monatomic linear chain with 1NN interactions, and the solution for the terminated bulk Green's function is

$$g_b=\frac{1}{2\,|\,B_b\,|^2}\{\,z-A_b-[\,(z-A_b)^2-4\,|\,B_b\,|^2]^{1/2}\,\}\ , \tag{6}$$

where the branch to be chosen is that for which $g_b\rightarrow 1/E$ for $z=E\rightarrow\pm\infty$ and $\mathrm{Im}g_b(z=E+i0+)\leq 0$. This describes a single continuous band of excitations on the interval

$$z=(A_b-2\,|\,B_b\,|\,,A_b+2\,|\,B_b\,|\,)\ ,$$

and is the conventional termination for real-space recursion calculations.[1,2] We will now show how two other simple models that allow two bands of unequal width and interactions out to second neighbors can be treated exactly. We begin by defining the Hamiltonians for the two models.

Model A:

$$\underline{A}_b=\begin{bmatrix} e_A & t_{AB} \\ t_{AB} & e_B \end{bmatrix}, \tag{7a}$$

$$\underline{B}_b=\begin{bmatrix} t_{AA} & 0 \\ t'_{AB} & t_{BB} \end{bmatrix}. \tag{7b}$$

This model describes a system with one state per atom, and interactions between atoms in the same-, first-, and second-neighboring planes. It should occur rather frequently along high-symmetry directions in the surface Brillouin zones (SBZ's) for low-Miller-index faces of cubic crystals. Depending on the values of the parameters, model A may give one or two bands. This will be illustrated by our two applications, both of which correspond to this model.

Model B:

$$\underline{A}_b=\begin{bmatrix} e_A & t_1 \\ t_1 & e_B \end{bmatrix}, \tag{8a}$$

$$\underline{B}_b=\begin{bmatrix} t_{AA} & t_2 \\ t_2 & t_{BB} \end{bmatrix}. \tag{8b}$$

This model describes a system with two states per atom, interacting with the same states on neighbors in the same- and first-neighbor planes. It would be appropriate, for example, for the (001) surface of a bcc crystal with two bands and 1NN interactions.

We will show how to solve for the terminated bulk and bulk Green's functions by working out case A. The solution for the second case is given in Appendix A.

Let the elements of $\underline{g}_b$ and its determinant be defined by

$$\underline{g}_b=\begin{bmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{bmatrix}, \tag{9}$$

$$D=\det \underline{g}_b=g_{11}g_{22}-g_{12}g_{21}, \tag{10a}$$

$$d=Dt_{AA}t_{BB}. \tag{10b}$$

From the matrix inverse of Eq. (5), it follows that

$$g_{11}=D[z-e_B-(t_{AB}'^2g_{11}+t_{BB}^2g_{22}+2t_{AB}'t_{BB}g_{12})], \tag{11a}$$

$$g_{22}=d(z-e_A-t_{AA}^2g_{11}), \tag{11b}$$

$$g_{12}=g_{21}=\frac{D}{1-d}(t_{AB}+t_{AB}'t_{AA}g_{11}). \tag{11c}$$

With some straightforward algebra, g_{11} and hence g_{ij} can be expressed in terms of D and d,

$$g_{11}=F\{(1-d)[z-e_B-Dt_{BB}^2(z-e_A)]-2Dt_{BB}t_{AB}t_{AB}'\}, \tag{12}$$

$$F=\frac{D}{(1+d)[(1-d)^2+Dt_{AB}'^2]}. \tag{13}$$

It remains to find D. This is done by substituting Eqs. (11)–(13) into Eq. (10). The result, after elimination of some common factors, is

$$\begin{aligned}0=d^4+1-[(z-e_A)(z-e_B)-(t_{AB}^2+t_{AB}'^2)]D(d^2+1)+[t_{BB}(z-e_A)+t_{AA}(z-e_B)+t_{AB}t_{AB}']^2D^2\\ -2[(z-e_A)(z-e_B)-(t_{AB}^2+t_{AB}'^2)]Dd-2d^2.\end{aligned} \tag{14}$$

For $t_{AA}t_{BB}=0$, and hence $d=Dt_{AA}t_{BB}=0$, this reduces to a quadratic for D. For the more general case that $t_{AA}t_{BB}\neq 0$, Eq. (14) can be rewritten as a biquadratic for d. From the structure of this biquadratic, if d is a solution, then so is $1/d$. This suggests the transformation

$$\delta=d+\frac{1}{d}, \tag{15a}$$

$$d=\tfrac{1}{2}[\delta-(\delta^2-4)^{1/2}]. \tag{15b}$$

This yields a quadratic for δ, whose solution is as follows:

$$\delta=\tfrac{1}{2}[E_AE_B-(c^2+c'^2)+\sigma], \tag{16}$$

$$\sigma=\{[(E_A-2)(E_B-2)-(c+c')^2]\times[(E_A+2)(E_B+2)-(c-c')^2]\}^{1/2}, \tag{17}$$

$$E_A=(z-e_A)/t_{AA}, \tag{18a}$$

$$E_B=(z-e_B)/t_{BB}, \tag{18b}$$

$$c^2=t_{AB}^2/t_{AA}t_{BB}, \tag{19a}$$

$$c'^2=t_{AB}'^2/t_{AA}t_{BB}. \tag{19b}$$

Some care must be taken with the square roots in Eqs. (15b) and (17). The rule is to choose the physical branch, for which $g_{ii}\to 1/E$ for $z=E\to\pm\infty$ along the real axis.

Dy, Wu, and Spratlin[11] (DWS) have outlined a method for solving the general problem posed by Eq. (5) for $\underline{g}_b$ by transforming it into a λ-matrix problem.[20] Let $\underline{Y}=\underline{g}_b\cdot\underline{B}_b^\dagger$, or $\underline{g}_b=\underline{Y}\cdot(\underline{B}_b^\dagger)^{-1}$ (our $\underline{g}_b$ is the same as DWS's $\underline{\Delta}$). Then Eq. (15) can be rewritten as

$$0=\underline{B}_b\cdot\underline{Y}\cdot\underline{Y}-(z\underline{1}-\underline{A}_b)\cdot\underline{Y}+\underline{B}_b^\dagger. \tag{20}$$

A transformation $\underline{Q}$ is introduced to diagonalize $\underline{Y}$,

$$\underline{Y}=\underline{Q}\cdot\underline{y}\cdot\underline{Q}^{-1},\quad y_{ij}=y_i\delta_{ij}, \tag{21}$$

and the columns of $\underline{Q}$ are denoted as vectors $\vec{q}(i)$, i.e., $q_k(i)=Q_{ki}$. It follows from Eqs. (20) and (21) that

$$0=[y_i^2\underline{B}_b-y_i(z\underline{1}-\underline{A}_b)+\underline{B}_b^\dagger]\cdot\vec{q}(i), \tag{22}$$

which requires that the determinant vanish,

$$0=\det[y^2\underline{B}_b-y(z\underline{1}-\underline{A}_b)+\underline{B}_b^\dagger]. \tag{23}$$

The method of DWS can be used to determine the terminated bulk Green's functions for our two models. This is shown explicitly for model A in Appendix B. For problems in which the Hamiltonian matrices $\underline{A}_i,\underline{B}_i$ are larger than 2×2's, the method appears to be very promising. Regarding such applications, a comment on blocking is in order. Equations (20)–(23) above and the development they summarize from DWS follow from the definition $g_b=\underline{Y}\cdot(\underline{B}_b^\dagger)^{-1}$. For our two models [cf. Eqs. (7b) and (8b)], $\underline{B}_b^\dagger$ is upper triangular or full, and nonsingular except in special cases. In contrast, both in DWS and in a subsequent paper by Brasher and Dy,[12] $B_b^\dagger$ ($C^\dagger$ in their notation) is defined as a singular matrix with zero elements everywhere below and on the diagonal. Since $(\underline{B}_b^\dagger)^{-1}$ does not exist, only some combinations of the elements of g_b, rather than all elements, can be found from $\underline{Y}=g_b\cdot\underline{B}_b^\dagger$.[21]

The source of the problem with blocking in Refs. 11 and 12 lies in the structure of the Hamiltonians assumed there. In both cases, the Hamiltonians block like diatomic rather than monatomic chains, settling down to an alternating sequence $(\underline{A}_{b1},\underline{B}_{b1})$, $(\underline{A}_{b2},\underline{B}_{b2})$, $(\underline{A}_{b1},\underline{B}_{b1}),\ldots$ in the bulk instead of a single pair $(\underline{A}_b,\underline{B}_b)$. The generalization of the theory of MK and DWS to this important class of problems is given in Appendix C.

III. DIAMOND OR ZINC BLENDE (001)

In calculations of bulk electronic energy bands or vibrational spectra, it is conventional to use symmetry arguments to block-diagonalize the Hamiltonian along high-symmetry directions in the three-dimensional Brillouin zone. The same can be done for surface or interfacial problems at certain points or along symmetry directions in the two-dimensional surface Brillouin zone (SBZ). Our first example falls into this category.

Chadi and Cohen[22] have shown that an orthogonal tight-binding approach including s and p states, with general first-neighbor interactions and one particular second-neighbor coupling, can give an accurate picture of the valence bands of the group-IV and III-VI semiconductors. Along two high-symmetry directions in the SBZ for the (001) surface of these semiconductors, the Chadi-Cohen model yields surface-wave-vector transform Hamiltonians that contain decoupled 2×2 blocks corresponding to our model A.

The surface wave vector for the (001) face of any fcc-based crystal is

$$\vec{q}_s=(2\pi/a)(\zeta_1+\zeta_2,-\zeta_1+\zeta_2,0)\ , \tag{24}$$

where $-\frac{1}{2}<\zeta_1,\zeta_2<\frac{1}{2}$ in the first SBZ. A diamond or zinc-blende crystal has two sublattices, one (labeled 1) with first neighbors at (1,1,1), (1,−1,−1,), (−1,1,−1), (−1,−1,1) in units of $a/4$, the other (labeled 2) with first neighbors at (−1,−1,−1), (−1,1,1), (1,−1,1), (1,1,−1). Along the direction $\zeta_2=0$, that is, for $\vec{q}_s=(2\pi/a)(\zeta,-\zeta,0)$, and for a sublattice-1 termination of the crystal, the states that transform like $(x+y)$ split off from the s, z, and $(x-y)$ states to give a model A Hamiltonian as follows [cf. Eqs. (7a) and (7b)]:

$$e_A=E(1x,1x;000)\ , \tag{25a}$$

$$e_B=E(2x,2x;000)\ , \tag{25b}$$

$$t_{AB}=2[E(1x,2x;111)-E(1x,2y;111)]\cos\pi\zeta_1\ , \tag{25c}$$

$$t'_{AB}=2[E(1x,2x;111)+E(1x,2y;111)]\ , \tag{25d}$$

$$t_{AA}=2E(1x,1x;022)\cos\pi\zeta_1\ , \tag{25e}$$

$$t_{BB}=2E(2x,2x;0\overline{2}\overline{2})\cos\pi\zeta_1\ . \tag{25f}$$

The notation above corresponds to that in Slater and Koster,[23] with sublattice designations added. For a sublattice-2 termination of the crystal, we exchange $e_A\leftrightarrow e_B$, $t_{AB}\leftrightarrow t'_{AB}$, $t_{AA}\leftrightarrow t_{BB}$.

Along the direction $\zeta_1=0$, or for $\vec{q}_s=(2\pi/a)(\zeta,\zeta,0)$, it is the states that transform like $(x-y)$ that split off. For this case, with sublattice-1 atoms in the top layer, Eqs. (25a)–(25f) apply if we let $\zeta_1\rightarrow\zeta_2$, $t_{AB}\leftrightarrow t'_{AB}$.

Surface states may occur at isolated poles of the terminated bulk Green's functions given by Eqs. (11)–(13), that is, at zeros of the denominator of the function F in Eq. (13). It turns out that there is no singularity in g_{ij} for $0=1+d$, so the potential surface-state energies are determined by $0=(1-d)^2+Dt'^2_{AB}$. These energies are

$$E_{s\pm}=\{\,2[(t_{AA}-t_{BB})^2+t'^2_{AB}]\,\}^{-1}\times\{\,[t'^2_{AB}(e_A+e_B)-2(t_{AA}-t_{BB})(t_{BB}e_A-t_{AA}e_b)-2t_{AB}t'_{AB}(t_{AA}+t_{BB})]\pm t'_{AB}(t'^2_{AB}-4t_{AA}t_{BB})^{1/2}(e_A-e_B)\,\}\ . \tag{26}$$

There are surface states if the residues of g_{ij} at these energies are nonzero. These residues may be found analytically, but it is extremely tedious to do so. Instead, we determine them numerically by calculating $(z-E_{s\pm})g_{ij}$ for $z-E_{s\pm}=2\epsilon$ and ϵ, where ϵ is small, and requiring that the values for 2ϵ and ϵ be the same within prescribed limits. A good check on the calculations is provided by the requirement that the residues of g_{ii} at $E_{s\pm}$ and the integral of the band-state spectral density, $-(1/\pi)\mathrm{Im}g_{ii}$, sum to unity. It should be noted that even when surface states appear to be allowed, that is, when the energies $E_{s\pm}$ lie outside the band-state spectra, zero residues can signal the absence of surface states. This occurs for the Ge(001) surface discussed below; along the $(\zeta,-\zeta,0)$ direction, the nominal $(x+y)$ surface states have nonzero residues for a sublattice-1 termination of the crystal, but the residues are zero if the outermost plane belongs to sublattice 2. The situation is reversed along the $(\zeta,\zeta,0)$ direction.

Figure 1 shows spectral densities for the $(x+y)$ states of terminated bulk Ge(001), with a sublattice-1 termination of the crystal, at four wave vectors along the $(\zeta,-\zeta,0)$ direction in the SBZ. Parameters for the calculation are taken from Table 1 of Chadi and Cohen,[22] with E_s in that table shifted down to -5.79 eV to make the top of the valence band fall at $E=0$. The surface state in the gap is shown as a vertical line with a height equal to the residue for plane 1. The surface-wave-vector transform of the bulk Green's function in the top panel was found by the methods outlined in Appendix B of MK. As ζ increases from the SBZ center to $\zeta=\frac{1}{2}$, the band states narrow and the strength of the surface state for plane 1 increases, until at the zone boundary, all of the spectral density for plane 1 is in the surface state, and the band states for plane 2 are δ functions of strength $\frac{1}{2}$ at $E=-1.60$ and 6.84 eV.

The energy bands for the $(x+y)$ states along the $(\zeta,-\zeta,0)$ direction are shown in Fig. 2, where the narrowing of the band states and the small dispersion of the surface state can be seen more explicitly.

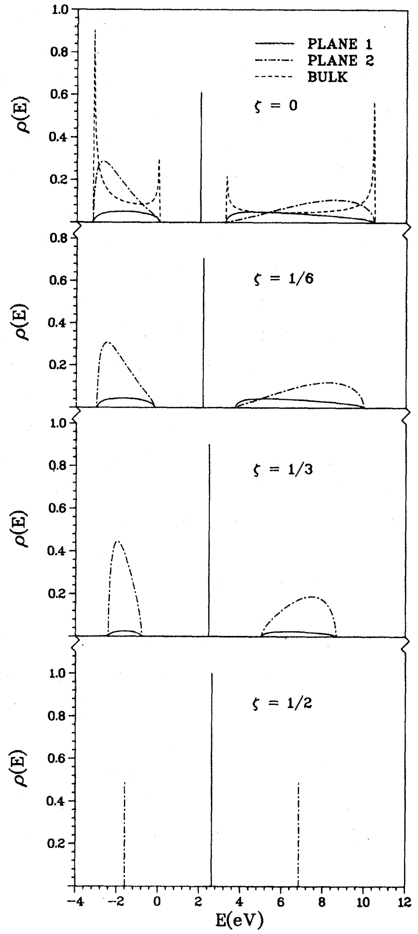

FIG. 1. Spectral densities for the $(x+y)$ states at the Ge(001) surface along the $(\zeta,-\zeta,0)$ direction in the SBZ. The surface plane belongs to sublattice 1.

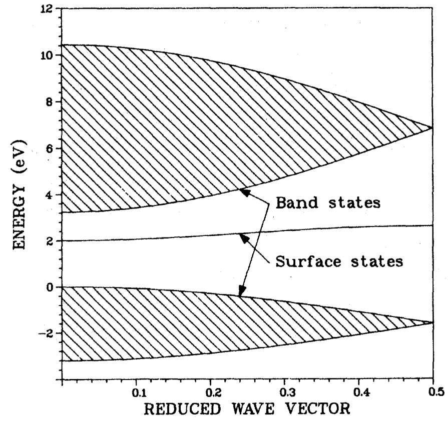

FIG. 2. Energy bands for the $(x+y)$ states of Ge(001) along the $(\zeta,-\zeta,0)$ direction.

IV. SURFACE SPIN WAVES IN fcc FERROMAGNETS

For a semi-infinite Heisenberg system at $T=0$ in the random-phase approximation (RPA), the surface-wave-vector transform of the spin-wave Green's function satisfies the equation

$$2\langle\langle S_z(L)\rangle\rangle\delta(L,L') = \sum_{L_1}\{[z-J_0(L)]\delta(L,L_1)+J(L,L_1;\vec{q}_s)\} \times\mathscr{G}(L_1,L';\vec{q}_s,z)\ , \tag{27}$$

$$\langle\langle S_z(L)\rangle\rangle=\frac{1}{N_s}\sum_{l}\langle S_z(L,l)\rangle\ , \tag{28}$$

$$J(L,L';\vec{q}_s)=\frac{1}{N_s}\sum_{l,l'}e^{i\vec{q}_s\cdot[\vec{R}(L,l)-\vec{R}(L',l')]} \times\langle S_z(L,l)\rangle\mathscr{J}(L,l;L',l')\ , \tag{29a}$$

$$J_0(L)=\frac{1}{N_s}\sum_{l,L_1,l_1}\mathscr{J}(L,l;L_1,l_1)\langle S_z(L_1,l_1)\rangle\ . \tag{29b}$$

In the above, $\mathscr{J}(L,l;L',l')$ is the exchange interaction between atom l in plane L and atom l' in plane L', and the notation otherwise is taken from MK.

Demangeat and co-workers[24] have investigated complex spin arrangements at the (001) surface of an fcc crystal by searching for soft surface spin waves. Weling[25] has considered the (001) surface magnetization of a simple cubic crystal described by a one-band Hubbard model Hamiltonian that, in the bulk, maps onto a monatomic linear chain with 1NN interactions. Salzberg and Falicov[17] have studied spin waves at a stepped surface of an fcc ferromagnet, modeling the surface in a way that also allows the algebra of the linear chain with 1NN interactions to be used. Here, we will discuss the physically simpler problem of spin waves at the (001) and (110) surfaces of fcc crystals, restricting calculations to the latter. The spins are assumed to be aligned ferromagnetically and they and the exchange interactions are assumed to be the same in the surface region as in the bulk. These simplifying assumptions can of course be relaxed (particularly the second) to treat more general cases.

With these assumptions, the Green's functions can be renormalized by defining $G=\mathscr{G}/2\langle S_z\rangle$, and the exchange interactions in real space by $J(L,l;L',l')=\langle S_z\rangle\mathscr{J}(L,l;L',l')$. Equations (27)–(29) then reduce to

$$\delta(L,L')=\sum_{L_1}\{[z-J_0(L)]\delta(L,L_1) +J_0(L,L_1;\vec{q}_s)\}G(L_1,L';\vec{q}_s,z)\ , \tag{30}$$

$$J(L,L';\vec{q}_s)=\sum_{l'}e^{i\vec{q}_s\cdot[\vec{R}(L,0)-\vec{R}(L',l')]}J(L,0;L',l')\ , \tag{31a}$$

$$J_0(L)=\sum_{L_1l_1}J(L,l;L_1,l_1)\ . \tag{31b}$$

For both the fcc (001) and (110) surfaces with 1NN and 2NN interactions J_1 and J_2, Eqs. (30) and (31) correspond to model A Hamiltonians with $e=e_A=e_B$, $t_1=t_{AB}=t'_{AB}$, $t_2=t_{AA}=t_{BB}$. For the (001) face, $\vec{q}_s$ is given by Eq. (24), and

$$e=2J_1[6-(\cos2\pi\zeta_1+\cos2\pi\zeta_2)] +2J_2(3-2\cos2\pi\zeta_1\cos2\pi\zeta_2)\ , \tag{32}$$

$$t_1=-4J_1\cos\pi\zeta_1\cos\pi\zeta_2\ , \tag{33}$$

$$t_2=-J_2\ . \tag{34}$$

For the (110) face, the surface wave vector is

$$\vec{q}_s=(2\pi/a)(\zeta_2,-\zeta_2,\zeta_1)\ , \tag{35}$$

and the elements of the Hamiltonian are

$$e=2J_1(6-\cos2\pi\zeta_2)+2J_2(3-\cos2\pi\zeta_1)\ , \tag{36}$$

$$t_1=-4J_1\cos\pi\zeta_1\cos\pi\zeta_2\ , \tag{37}$$

$$t_2=-J_1-2J_2\cos2\pi\zeta_2\ . \tag{38}$$

As was discussed for phonons in MK, the terminated bulk Green's function for spin waves is not a proper Green's function for a cleaved crystal. The Goldstone rule is violated at the terminated bulk surface, since $e+t_1+t_2\neq0$ for $\zeta=0$; instead, the bulk sum rule is obeyed, $e+2t_1+2t_2=0$ for $\zeta=0$, which is why we use the terminology "terminated bulk." Even without changes in the exchange interactions, the diagonal elements of the Hamiltonian change in the surface region to satisfy the Goldstone rule [cf. Eq. (31b)]. For the (001) surface, the change is given by

$$\underline{A}_1-\underline{A}_b=-\begin{bmatrix}4J_1+J_2 & 0\\ 0 & J_2\end{bmatrix}\ , \tag{39}$$

while for the (110) surface, it is

$$\underline{A}_1-\underline{A}_b=-\begin{bmatrix}5J_1+2J_2 & 0\\ 0 & J_1+2J_2\end{bmatrix}\ . \tag{40}$$

For the (110) surface, second-neighbor exchange does not extend the range of the interplanar interactions in Eqs. (36)–(38), but modifies the results obtained with first-neighbor exchange only. As shown by Demangeat and Mills[24] for the (001) face, the modifications can be quite significant, producing soft surface spin waves and magnetic reconstruction for J_2 antiferromagnetic ($J_2 < 0$) and greater in magnitude than some critical value. In going from Eqs. (27)–(29) to Eqs. (30) and (31), however, we have made simplifying assumptions inconsistent with a study here of surface magnetic reconstruction. For convenience, we therefore further simplify by neglecting second-neighbor exchange and set $J_2 = 0$, $J_1 = J$.

With all of the simplifying assumptions we have made, the terminated bulk Green's function g_b has no surface states, but the proper cleaved crystal Green's function, for which the Goldstone rule is satisfied, does. With the intraplanar interactions at the surface changed according to Eq. (40), the cleaved surface Green's function is determined from Eqs. (4a), (5), (9), (10a), and (10b) by

$$\begin{aligned} \underline{g}_1 &= \underline{g}_b \cdot [\underline{1} - (\underline{A}_1 - \underline{A}_b) \cdot \underline{g}_b]^{-1} \\ &= \frac{1}{1 + 5Jg_{11} + Jg_{22} + 5d} \\ &\quad \times \begin{bmatrix} g_{11} + JD & g_{12} \\ g_{21} & g_{22} + 5JD \end{bmatrix} . \end{aligned} \tag{41}$$

The surface-state energy $z = E_s$ is found by setting the denominator in Eq. (41) equal to zero, which leads to a biquadratic equation for E_s; we solve for E_s and the residues numerically.

Figure 3 is a plot of the band and surface-state energy bands along the $(\zeta, -\zeta, \zeta)$ direction in the SBZ. At the zone boundary, $\zeta = 0.5$, where the band states are shown to extend from $E = 12J$ to $E = 16J$, the spectral density in plane 1 is actually all in the surface-state δ function at $E = 8.8J$. Figure 4 compares bulk, terminated bulk, surface band state and surface-state densities of states. For plane 1, 64% of the spin-wave spectral density lies in the surface states, while for plane 2, a very substantial majority fraction of 90% is in the band states. The surface states compelled by the Goldstone rule are therefore strongly localized at the surface.

V. CONCLUSIONS

The models we have considered are quite simple ones, with the advantage that they can be solved analytically. Applications to spin waves at surfaces and interfaces are immediate; we have given

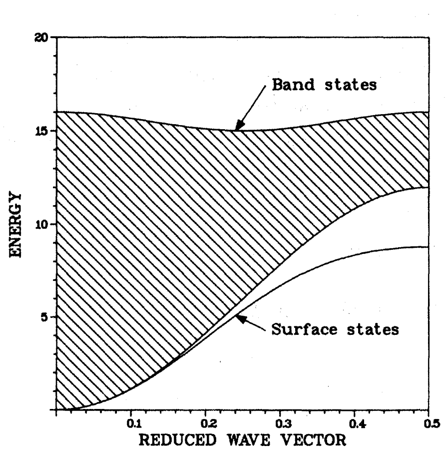

FIG. 3. Spin-wave energy bands along the $(\zeta, -\zeta, \zeta)$ direction in the SBZ of the fcc (110) face of a Heisenberg ferromagnet. The energy is in units of J.

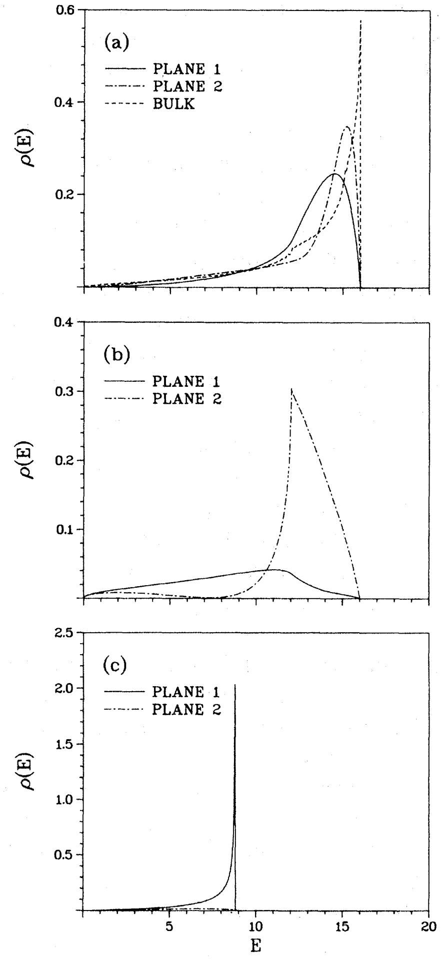

FIG. 4. fcc (110) densities of states for a Heisenberg ferromagnet: (a) terminated bulk and bulk, (b) surface band states, and (c) surface states. The energy is in units of J.

one example here. For electronic and vibrational states, the utility of the models for most problems will lie at symmetry points or lines in the SBZ, where the Hamiltonian contains decoupled 2×2 blocks. This offers the additional value of allowing numerical checks of calculations for more complicated Hamiltonians that reduce to our models in special cases.

We have not shown examples for clean interfaces or for surfaces and interfaces containing impurities. However, once the terminated bulk Green's function has been calculated, the properties of clean surfaces or interfaces can be investigated [cf. Eqs. (4a), (4b),. . .)] as the Hamiltonian parameters are allowed to vary near the interface. The states of isolated impurities or periodic arrays of them at interfaces, which can be important for problems like grain boundary segregation and embrittlement,[26] can also be studied.

Finally, both models can give two bands of different widths. They might therefore be useful for real-space recursion calculations where this situation occurs.

ACKNOWLEDGMENTS

The authors are grateful to J. F. Cooke, H. L, Davis, and R. F. Wood for helpful discussions, and to T. Kaplan for critically reading the manuscript. One of us (A.K.R.) would also like to thank the Solid State Division at the Oak Ridge National Laboratory for its hospitality during his visits, and A. K. Vasudevan at the Alcoa Aluminum Company of America for pointing out the paper of Losch (Ref. 26) and the importance of investigating the electronic structure of grain boundaries. This research was sponsored by the Division of Materials Sciences, U. S. Department of Energy under Contract No. W-7405-eng-26 with Union Carbide Corporation.

APPENDIX A: SOLUTION FOR MODEL B

The solution for model B follows the same lines used for model A. With $\underline{A}_b$, $\underline{B}_b$, g_b, and D defined by Eqs. (8a)−(10a), the following expressions for g_{ij} emerge from Eq. (5) after some manipulation:

$$g_{11}=\widetilde{F}[\,-Dt_{BB}^2(z-e_A)+(1-Dt_2^2)(z-e_B)-2Dt_{BB}t_1t_2]\,, \tag{A1a}$$

$$g_{22}=\widetilde{F}[\,(1-Dt_2^2)(z-e_A)-Dt_{AA}^2(z-e_B)-2Dt_{AA}t_1t_2]\,, \tag{A1b}$$

$$\begin{aligned} g_{12}&=g_{21}\\ &=\widetilde{F}\{\,1+D(t_{AA}t_{BB}+t_2^2)]t_1+Dt_2[\,t_{BB}(z-e_A)+t_{AA}(z-e_B)]\,\}\,, \end{aligned} \tag{A1c}$$

$$\widetilde{F}=\frac{D}{1-\widetilde{d}^2}\,, \tag{A2}$$

$$\widetilde{d}=D(t_{AA}t_{BB}-t_2^2)\,. \tag{A3}$$

When the above expressions for g_{ij} are substituted back into the definition $D=g_{11}g_{22}-g_{12}g_{21}$, the resulting equation for D is

$$\begin{aligned} 0=\widetilde{d}^4+1&-[(z-e_A)(z-e_B)-t_1^2]D(\widetilde{d}^2+1)\\ &+[t_{BB}(z-e_A)+t_{AA}(z-e_B)+2t_1t_2]^2D^2\\ &-2[(z-e_A)(z-e_B)-t_1^2]D\widetilde{d}-2\widetilde{d}^2\,. \end{aligned} \tag{A4}$$

This has the same structure as Eq. (14) for model A, and the rest of the solution proceeds in the same way as for that case.

APPENDIX B: THE λ-MATRIX METHOD FOR MODEL A

In this appendix we sketch how to find the elements of g_b for model A using the method of DWS. Substituting the definitions of $\underline{A}_b$ and $\underline{B}_b$ given by Eqs. (7a) and (7b) into Eq. (22), we obtain relations between the elements of $\vec{q}$ (or $\underline{Q}$),

$$q_1(i)=-\frac{1}{\mu}\frac{cy_i+c'}{y_i^2-E_Ay_i+1}q_2(i) \tag{B1a}$$

$$=-\frac{1}{\mu}\frac{y_i^2-E_By_i+1}{(c'y_i+c)y_i}q_2(i)\,, \tag{B1b}$$

where $\mu=(t_{AA}/t_{BB})^{1/2}$, and E_A,E_B,c,c' are defined in Eqs. (18) and (19). From the condition (23) that the determinant vanish, or equivalently, from the equations for $q_k(i)$ above, the y_i's are roots of the biquadratic

$$\begin{aligned} 0=(y^2+1)^2&-(E_A+E_B+cc')y(y^2+1)\\ &+[E_AE_B-(c^2+c'^2)]y^2\,, \end{aligned} \tag{B2}$$

which factors easily to a pair of quadratics,

$$
\begin{aligned}
0= y^2+1 &\\
-\tfrac{1}{2}((E_A+E_B+cc') &\\
\pm\{ (E_A+E_B+cc')^2 &\\
-4[E_AE_B-(c^2+c'^2)]\}^{1/2})y\ . &\qquad \text{(B3)}
\end{aligned}
$$

According to DWS, the two roots y_1, y_2 to choose from the four allowed by Eq. (B3) are those that lie inside the unit circle.

To demonstrate the equivalence of the results obtained by the λ-matrix method and those found by the direct approach described in the main text, consider Eq. (B2). By inspection, if y_i is a solution of that equation, then so is $1/y_i$, and the four roots are $y_1, y_2, 1/y_1, 1/y_2$. From the coefficients of the linear and quadratic terms in Eq. (B2), it follows[27] that

$$y_1+y_2+1/y_1+1/y_2=E_A+E_B+cc'\ , \qquad \text{(B4)}$$

$$
\begin{aligned}
y_1y_2+1/y_1y_2+y_1/y_2+y_2/y_1 &\\
=E_AE_B-(c^2+c'^2)\ . &\qquad \text{(B5)}
\end{aligned}
$$

Now the determinant of g_b, scaled by $t_{AA}t_{BB}$, is $d=y_1y_2$ [cf. Eq. (10b)], so Eqs. (B4)–(B5) can be rewritten as

$$y_1+y_2=\frac{d}{1+d}(E_A+E_B+cc')\ , \qquad \text{(B6)}$$

$$y_1^2+y_2^2=-d^2+[E_AE_B-(c^2+c'^2)]d-1\ . \qquad \text{(B7)}$$

Solving Eq. (B6) for y_1 and $y_2=d/y_1$ in terms of d, then substituting in Eq. (B7), we obtain

$$
\begin{aligned}
0=d^4+1-[E_AE_B-(c^2+c'^2)]d(d^2+1) &\\
+\{ (E_A+E_B+cc')^2 &\\
-2[E_AE_B-(c^2+c'^2)]-2\}d^2\ , &\qquad \text{(B8)}
\end{aligned}
$$

which is equivalent to Eq. (14).

On working back through the transformation in Eqs. (20)–(24) to the λ-matrix problem to obtain expressions for g_{ij} in terms of y_1 and y_2, an interesting feature emerges. The results for the off-diagonal elements are

$$
\begin{aligned}
(t_{AA}t_{BB})^{1/2}g_{12}=\frac{1}{P_{1A}-P_{2A}}[P_{1A}(P_{2A}-c')y_1 &\\
-P_{2A}(P_{1A}-c')y_2]\ , &\qquad \text{(B9a)}
\end{aligned}
$$

$$(t_{AA}t_{BB})^{1/2}g_{21}=-\frac{1}{P_{1A}-P_{2A}}(y_1-y_2)\ , \qquad \text{(B9b)}$$

$$P_{iA}=\frac{cy_i+c'}{y_i^2-E_Ay_i+1}\ . \qquad \text{(B10)}$$

From general arguments and from Eq. (11c), we know that $g_{12}=g_{21}$, but this is not made explicit in Eqs. (B9a) and (B9b). The equality can of course be demonstrated, but only with some further algebraic manipulation.

APPENDIX C: THE ANALOG OF THE DIATOMIC LINEAR CHAIN

Equation (5) for the terminated bulk Green's function $\underline{g}_b$ is based on the assumption that the Hamiltonian blocks $\underline{A}_i$ and $\underline{B}_i$ in Eq. (1) settle down to a single pair of bulk matrices $\underline{A}_b$ and $\underline{B}_b$. Suppose that this is not the case, and instead, $(\underline{A}_i,\underline{B}_i)$ alternate between $(\underline{A}_{b1},\underline{B}_{b1})$ and $(\underline{A}_{b2},\underline{B}_{b2})$ in the bulk. Correspondingly, Eq. (5) is replaced by a pair of recursion equations.

$$\underline{g}_{b1}=(z\underline{1}-\underline{A}_{b1}-\underline{B}_{b1}\cdot\underline{g}_{b2}\cdot\underline{B}_{b1}^{\dagger})^{-1}\ , \qquad \text{(C1a)}$$

$$\underline{g}_{b2}=(z\underline{1}-\underline{A}_{b2}-\underline{B}_{b2}\cdot\underline{g}_{b1}\cdot\underline{B}_{b2}^{\dagger})^{-1}\ . \qquad \text{(C1b)}$$

If the matrices above are scalars, the solution is straightforward, and yields two bands of equal width. Otherwise, Eqs. (C1a) and (C1b) can be transformed to a λ-matrix problem.

For brevity, we omit the b subscript hereafter, and also the underlining and product (·) notation for the matrices, although the order of factors in matrix products will of course be maintained. If $X_1=g_1B_2^{\dagger}$ and $X_2=g_2B_1^{\dagger}$, then Eqs. (C1a) and (C1b) can be written as

$$0=B_1X_2X_1-(z-A_1)X_1+B_2^{\dagger}\ , \qquad \text{(C2a)}$$

$$0=B_2X_1X_2-(z-A_2)X_2+B_1^{\dagger}\ . \qquad \text{(C2b)}$$

Equation (C2b) is solved for X_2 in terms of X_1, and the result is substituted in Eq. (C2a). With the definition

$$
\begin{aligned}
Y&=B_1^{-1}[(z-A_1)X_1-B_2^{\dagger}]\\
&=B_1^{-1}[(z-A_1)g_1-1]B_2^{\dagger}\ , \qquad \text{(C3)}
\end{aligned}
$$

we obtain the following after some algebra:

$$0=\alpha YY+\beta Y+\gamma\ , \qquad \text{(C4)}$$

$$\alpha=B_2(z-A_1)^{-1}B_1\ , \qquad \text{(C5a)}$$

$$
\begin{aligned}
\beta=-[(z-A_2)-B_2(z-A_1)^{-1}B_2^{\dagger} &\\
-B_1^{\dagger}(z-A_1)^{-1}B_1]\ , &\qquad \text{(C5b)}
\end{aligned}
$$

$$\gamma = B_1^\dagger (z - A_1)^{-1} B_2^\dagger \ . \tag{C5c}$$

The transformation to the λ-matrix problem is completed by following Eqs. (20)–(23). The dimension of the problem is the same as that of A_1, B_1, A_2, and B_2, rather than twice that dimension as in Refs. 11 and 12. Furthermore, there is no call to invert singular matrices.

---

[*] Permanent address: Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803.

[1] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C 5, 2845 (1972); 8, 2591 (1975).

[2] M. J. Kelly, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 295.

[3] M. Mostoller and U. Landman, Phys. Rev. B 20, 1755 (1979).

[4] J. E. Black, B. Laks, and D. L. Mills, Phys. Rev. B 22, 1818 (1980).

[5] R. Haydock and M. J. Kelly, Surf. Sci. 38, 139 (1973).

[6] G. Cubiotti and B. Ginatempo, J. Phys. F 8, 601 (1978).

[7] M. Mostoller and T. Kaplan, Phys. Rev. B 19, 3938 (1979).

[8] M. J. Kelly and D. W. Bullett, Solid State Commun. 18, 593 (1976); Philos. Mag. B 38, 423 (1978).

[9] R. Jones, Philos. Mag. 35, 57 (1977).

[10] M. Mostoller and T. Kaplan, Phys. Rev. B 19, 552 (1979).

[11] K. S. Dy, Shi-Yu Wu, and T. Spratlin, Phys. Rev. B 20, 4237 (1979).

[12] J. D. Brasher and K. S. Dy, Phys. Rev. B 22, 4868 (1980).

[13] L. M. Falicov and F. Yndurain, J. Phys. C 8, 147 (1975).

[14] F. Yndurain and L. M. Falicov, J. Phys. C 8, 1571 (1975).

[15] D. Kalkstein and P. Soven, Surf. Sci. 26, 85 (1971).

[16] T. L. Einstein, Phys. Rev. B 12, 1262 (1975); T. L. Einstein and J. R. Schrieffer, *ibid.* 7, 3629 (1973).

[17] J. B. Salzberg and L. M. Falicov, Phys. Rev. B 15, 5320 (1977).

[18] D. Castiel, L. Dobrzynski, and D. Spanjaard, Surf. Sci. 63, 21 (1977); A. Blandin, D. Castiel, and L. Dobrzynski, Solid State Commun. 13, 1175 (1973).

[19] P. Masri, J. Phys. C 14, L385 (1981).

[20] H. W. Turnbull and A. C. Aitken, *An Introduction to the Theory of Canonical Matrices* (Blackie, Glasgow, 1945), p. 21.

[21] Brasher and Dy (Ref. 12) treat an asymmetric, tridiagonal Hamiltonian for which their Δ_R, Δ_L can be found directly from their Eqs. (7a) and (7b) without really going through the method of DWS. The latter yields two equations for the 11 and 21 elements of Δ_R or Δ_L, but is silent concerning the 12 and 22 elements, because the off-diagonal blocks C_R, C_L (B_b in our notation) have only a nonzero 21 element.

[22] D. J. Chadi and M. L. Cohen, Phys. Status Solidi B 68, 405 (1975).

[23] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[24] C. Demangeat and D. L. Mills, Phys. Rev. B 14, 4997 (1976); C. Demangeat, D. L. Mills, and S. E. Trullinger, Phys. Rev. B 16, 522 (1977).

[25] F. Weling, J. Phys. F 10, 1975 (1980).

[26] W. Losch, Acta Metall. 27, 1885 (1979).

[27] *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. A. Stegun (U.S. GPO, Washington, D. C., 1968), pp. 17 and 18.