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[14]It is easy to show that the logarithmic divergences cancel in the specific heat at constant field. This suggests that the energy fluctuations remain finite on the coexistence curve, and invites the exploration of nonlinear realizations in which $\sum_i^n s_i^2$ is kept constant, as suggested in Ref. 6 and studied extensively by S. Weinberg, Phys.

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Surface States of an Induced-Moment System and a Hydrogen-Bonded Ferroelectric*

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We have investigated the surface bound states and resonances that occur on a (001) surface of either a two-level induced-moment system or the tunneling model of a hydrogen-bonded ferroelectric. We have assumed (a) that there is a perfectly sharp surface and (b) that only parameters on the surface have values different from those in the bulk of the crystal, and we have used the random-phase approximation to solve the equations of motion for the thermodynamic Green's functions. Analytical expressions have been obtained for the complete Green's functions. Three phases can exist: (i) Both the surface and the bulk are disordered, (ii) the surface is ordered but the bulk is disordered, or (iii) both the surface and the bulk are ordered. In phases (i) and (ii) only one kind of localized mode can appear, while in phase (iii) two kinds, localized on the first and second layers, can exist. No resonances appear inside the bulk band when both surface and bulk are disordered, but resonances can appear in the other two phases. Some criteria for the appearance of bound states have been derived and numerical calculations have been carried out for the three phases at zero temperature. Some experiments are suggested.

I. INTRODUCTION

There has been considerable interest recently in the modes that are localized on and near the surface of magnetically ordered crystals which are described by the Heisenberg Hamiltonian with possibly anisotropic exchange interactions. We shall be concerned here with modes that occur upon one surface of an otherwise infinite or periodic crystal. Early work was done by Wallis *et al.*[1] and Mills and Maraduddin[2] on the Heisenberg ferromagnet and was concerned with the modes excited on a free surface (whereon the exchange interaction is the same as that in the bulk) and their effects on thermodynamic quantities. Other early works were those of Fillipov[3] (see also deWames and Wolfram[4]) and Mills,[5] who investigated the effect of changing the exchange interactions upon the surface and between the surface and second layer from that of the bulk. This problem was also treated by deWames and Wolfram[6] (see also Ilisca and Motchane[7]). These authors restricted themselves to isotropic interactions. More recently, the effects of exchange anisotropy has been considered by Osborne,[8] Ilisca and Motchane,[7] and Levy, Ilisca, and Motchane,[9] together with next-nearest-neighbor exchange coupling by Levy, Ilisca, and Motchane.[10] Recent work on the Heis-

enberg antiferromagnet has been done by Mills[11] on the surface spin-flop state and by Mills and Saslow[12] on surface effects in general, while Sparks[13] has considered both the ferro- and anti-ferromagnet.

There is, however, a large class of magnetically ordered systems for which the Hamiltonian may contain, in addition to the bilinear Heisenberg term, terms due to the effects of crystal fields. The magnetic behavior of such systems is of particular interest when the magnitude of the crystal field parameters is comparable to that of the exchange interaction, which is the situation that appears to exist in the light rare-earth metals. One of the best-studied examples is that of Pr^{3+} ions in various crystal field environments (see Rainford and Gylden Houmann[14] and other references therein). In a hexagonal crystal field, the lowest ionic states are a magnetic singlet, a higher-lying singlet, and a doublet. Because the z component of the total magnetic-moment operator $\vec{J}$ has a nonzero matrix element between the two singlets, a nonzero value of magnetization can occur if the ratio of the magnitude of the exchange interaction to that of the crystal field splitting between the two singlets is sufficiently large. Here we shall assume that the system with which we are concerned has two nondegenerate singlets as the

lowest crystal field eigenstates, with all other eigenstates lying ignorably higher.

One attractive feature of the effective Hamiltonian of this system is that it is mathematically equivalent to that which is used to describe the proton (deuteron) dynamics in the simplest tunneling model of the hydrogen-bonded ferroelectric KH_2PO_4 (KD_2PO_4), customarily called KDP (KDDP). In this case the singlet-singlet crystal field splitting becomes the particle (proton or deuteron) tunneling frequency along the hydrogen bond in the double-minimum potential well,[15] and the exchange interaction becomes the effective particle-particle interaction. In this model the motion of the $[KPO_4]$ complex is ignored, as is any motion of the particles perpendicular to the hydrogen bond.[16]

We shall investigate the surface modes that arise in these two systems. Since there is an energy gap in the bulk excitation band, surface modes can appear in the gap and their effect upon thermodynamic quantities may be more easily observed than in isotropic ferromagnets. In Sec. II the model will be outlined, and in Sec. III we shall calculate the relevant thermodynamic Green's functions. In Sec. IV some analytical results will be given, while in Sec. V the results of numerical calculations will be presented.

II. MODELS

We shall first describe the properties of the ions or hydrogen bonds that lie in the bulk, far from the surface. For the ith ion, located by vector $\vec{i}$, in the induced-moment system the eigenstates of the crystal field operator V_i^c are $|A_i\rangle$ and $|B_i\rangle$ belonging to eigenvalues 0 and Δ_i. All matrix elements of $\vec{J}$ in this two-dimensional space are zero except $\langle A_i|J_i^z|B_i\rangle = c_i$ (real). We assume that other crystal field states are sufficiently high so that they may be ignored. We shall take the Hamiltonian to be

$$\mathcal{H} = - \sum_{j\delta} K_{j\,j+\delta}\vec{J}_j\cdot\vec{J}_{j+\delta} + \sum_j V_j^c, \quad K_{j\,j+\delta} > 0 . \quad (1)$$

We have restricted ourselves to nearest-neighbor ferromagnetic interactions, though it should be noted that Pr metal appears to have an antiferromagnetic interaction between the ions located at hexagonal sites.[14] $\vec{\delta}$ is a vector between nearest neighbors. We map the operators in (1) onto a set of pseudo-spin-$\frac{1}{2}$ operators:

$$J_j^z = 2c_j S_j^z, \quad J_j^\pm = 0, \quad V_j^c = \Delta_j(\tfrac{1}{2} - S_j^x) , \quad (2)$$

so that we obtain a Hamiltonian of an Ising model in a perpendicular magnetic field,

$$\mathcal{H} = - \sum_{j\delta} J_{j\,j+\delta} S_j^z S_{j+\delta}^z - \sum_j \Delta_j S_j^x + \tfrac{1}{2}\sum_j \Delta_j ,$$
$$J_{jk} = 4 c_j c_k K_{jk} . \quad (3)$$

In the case of the hydrogen-bonded system the Hamiltonian for the tunneling model is[17]

$$\mathcal{H} = \sum_i H_1(\vec{r}_i) + \sum_{i>j} H_2(\vec{r}_i,\vec{r}_j) + \cdots , \quad (4)$$

where the successive terms describe one-, two-, ...particle interactions. This model does not include the vibrations of the $[KPO_4]$ complex,[18] so that it does not sufficiently clarify the mechanism of the transition from the ferroelectric to the paraelectric phase. It is sufficient, however, for getting a first idea of what kind of predominantly tunneling modes arise. The particle in the ith bond moves along the bond in a potential having two symmetric minima, labeled A_i and B_i. If a_i, $a_i^\dagger$, b_i, and $b_i^\dagger$ are the annihilation and creation operators for a particle located at A_i and B_i, then we can define pseudo-spin-$\frac{1}{2}$ operators

$$S_j^x = \tfrac{1}{2}(a_j^\dagger b_j + b_j^\dagger a_j), \quad iS_j^y = \tfrac{1}{2}(a_j^\dagger b_j - b_j^\dagger a_j) ,$$
$$S_j^z = \tfrac{1}{2}(a_j^\dagger a_j - b_j^\dagger b_j), \quad 1 = a_j^\dagger a_j + b_j^\dagger b_j . \quad (5)$$

The Hamiltonian becomes

$$\mathcal{H} = - \sum_{ij} [J_{ij} S_i^z S_j^z + L_{ij}(S_i^x S_j^z + S_i^z S_j^x) + R_{ij} S_i^x S_j^x]$$
$$- \sum_j \Delta_j S_j^x . \quad (6)$$

The term in Δ_j describes the tunneling of the jth particle between the two minima. In a first approximation the terms in L_{ij} and R_{ij} are omitted[17] and the particle-particle interactions J_{ij} are nonzero only if i and j are nearest neighbors. Thus (6) assumes the same form as (3).

We shall consider a crystal having one surface, extending to infinity in a direction perpendicular to that surface, and having periodic boundary conditions in the two directions parallel to the surface. A perfectly sharp surface will be taken as a first approximation to what probably exists in real cases.[19] For simplicity we shall consider a simple cubic crystal having a surface in the a-b plane [a (001) surface]. Planes parallel to the surface are labeled 1,2,..., beginning with the surface, and primitive lattice vectors parallel to and perpendicular to the surface are $\vec{\rho}$ and $\vec{\tau}$. Thus Δ_j and $J_{j\,j+\delta}$ can be replaced by Δ_n and $J_{n\,n+\delta}$, with $n=1,2,...$ labeling the layers. Since we are considering a (001) surface, hydrogen bonds, in the ferroelectric case, are parallel to the surface. Thus, the potential should retain its symmetric double-minimum property on the surface, though Δ_n and $J_{n\,n+\delta}$ may change. In the induced-moment case, the reduction of symmetry at the surface will mean that the lowest eigenstates of the crystal field may not be two magnetic singlets. In this event, however, additional parameters will enter the problem. In order to retain a minimum number of parameters, we shall assume that the surface

ionic states are the two bulk singlets, though their splitting and the exchange interaction may change. Thus (3) is valid for the entire crystal and we shall assume that only on the surface layer are the splitting and coupling constant changed from their values deep in the bulk:

$$\Delta_n = \Delta \text{ unless } n = 1, \quad J_{1\,1+\rho} = \mathcal{J}_1, \quad J_{n\,n+\delta} = \mathcal{J} \text{ otherwise.}$$

III. FORMAL SOLUTIONS

It is convenient to make use of the transformation

$$S_j^z = \sigma_j^z \sin 2\phi_j - \sigma_j^x \cos 2\phi_j,$$
$$S_j^x = \sigma_j^z \cos 2\phi_j + \sigma_j^x \sin 2\phi_j, \quad \phi_j \text{ real} \tag{7}$$

where the σ_j^α are a new set of pseudo-spin-$\frac{1}{2}$ operators and ϕ_j will be chosen so that $\langle \sigma_j^x \rangle = 0$ (stability condition). We shall obtain expressions for the thermodynamic Green's functions[20]

$$G_{jk}^{\alpha\zeta}(E) = \pi(\sigma_j \sigma_k)^{-1/2} \langle P_j | Q_k \rangle_E, \tag{8}$$

where $P_j = \sigma_j^+$ or σ_j^- if $\alpha = 1$ or 2, and $Q_k = \sigma_k^-$ or σ_k^+ if $\zeta = 1$ or 2 and $\sigma_j = \langle \sigma_j^z \rangle$. The label E will be omitted unless required. The Green's functions can be written as $G_{nm}^{\alpha\zeta}(k_{\parallel} - j_{\parallel})$, where the vectors $\vec{j}$ and $\vec{k}$ have been written in terms of their layer components (n, m) and their components parallel to the surface $(j_{\parallel}, k_{\parallel})$. We then perform a two-dimensional Fourier transform to obtain Green's functions $G_{nm}^{\alpha\zeta}(\lambda)$ depending upon a wave vector $\vec{\lambda}$ parallel to the surface. After performing a random-phase-approximation (RPA) decoupling,[21] the equations of motion contain the Green's function $\langle \sigma_j^x | Q_k \rangle$. The requirement that $\langle \sigma_j^x \rangle = 0$ necessitates that $\langle \sigma_j^x | Q_k \rangle = 0$, which in turn gives the stability condition

$$2 \cos 2\phi_n \sum_{\tau} J_{n\,n+\tau} \sigma_{n+\tau} \sin 2\phi_{n+\tau}$$
$$+ 2J_n(0) \cos 2\phi_n \sin 2\phi_n - \Delta_n \sin 2\phi_n = 0,$$
$$J_n(\lambda) = \sum_{\rho} J_{n\,n+\rho} e^{i\vec{\lambda}\cdot\vec{\rho}}, \quad n = 1, 2, \dots. \tag{9}$$

The equations of motion can be written as a matrix equation, the components of which are

$$E G_{nm}^{\alpha\zeta}(\lambda) = (-1)^{\alpha+1} \delta_{\zeta\alpha} \delta_{mn} + \sum_{l\beta} A_{nl}^{\alpha\beta}(\lambda) G_{lm}^{\beta\zeta}(\lambda), \tag{10}$$
$$\alpha, \beta, \zeta = 1, 2, \quad n, l, m = 1, 2, \dots$$

with

$$A_{nn}^{11}(\lambda) = \Delta_n \cos 2\phi_n + 2 \sin 2\phi_n \Big(\sum_{\tau} J_{n\,n+\tau} \sigma_{n+\tau} \sin 2\phi_{n+\tau}$$
$$+ \sigma_n J_n(0) \sin 2\phi_n \Big) - \sigma_n J_n(\lambda) \cos^2 2\phi_n$$
$$= -A_{nn}^{22}(\lambda),$$

$$A_{nn}^{12}(\lambda) = -\sigma_n J_n(\lambda) \cos^2 2\phi_n = -A_{nn}^{21}(\lambda), \tag{11}$$

$$A_{n\,n+\tau}^{1\zeta}(\lambda) = -J_{n\,n+\tau}(\sigma_n \sigma_{n+\tau})^{1/2} \cos 2\phi_n \cos 2\phi_{n+\tau}$$
$$= -A_{n\,n+\tau}^{2\zeta}(\lambda),$$

$$A_{nl}^{\alpha\beta}(\lambda) = 0 \text{ otherwise.}$$

If we denote by ϕ and σ the values of ϕ_n and σ_n deep in the bulk, then (9) shows that there are three kinds of solution.

(i) $\phi_1 = \phi = 0$. In this phase both the surface and the bulk are disordered.

(ii) $\phi_1 > 0$, $\phi = 0$. Here the bulk is disordered but the surface is ordered.

(iii) ϕ_1, $\phi > 0$. Both the bulk and the surface are ordered.

We shall make the approximation $\sigma_n = \sigma$, which is adequate because σ_n is not the magnetization of the nth layer, which is $\langle J_n^z \rangle = \sigma_n \sin 2\phi_n$, and the quantity sensitive to change is ϕ_n. We shall also assume that $\phi_n = \phi$ unless $n = 1$. This is rigorously correct when both surface and bulk are disordered.

Accordingly, the set (10) can be written in the form

$$\omega_\alpha(1) X_{1m}^f - q(1) X_{1m}^g - p(X_{2m}^f + X_{2m}^g) = -\delta_{m1}(1 - \delta_{f2}), \tag{12}$$

$$\omega_\alpha(2) X_{2m}^f - q X_{2m}^g - p(X_{1m}^f + X_{1m}^g) - (X_{3m}^f + X_{3m}^g)$$
$$= -\delta_{m2}(1 - \delta_{f2}), \tag{13}$$

$$\omega_\alpha X_{nm}^f - q X_{nm}^g - (X_{n-1\,m}^f + X_{n+1\,m}^f + X_{n-1\,m}^g + X_{n+1\,m}^g)$$
$$= -\delta_{mn}(1 - \delta_{f2}), \quad n > 2 \tag{14}$$

where f, $g = 1, 2$, $g \neq f$, $\alpha = 1, 2$, and

$$\omega_\alpha(1) = \frac{A_{11}^{11}(\lambda) + (-1)^\alpha E}{\sigma \mathcal{J} \cos^2 2\phi}, \quad \omega_\alpha(2) = \frac{A_{22}^{11}(\lambda) + (-1)^\alpha E}{\sigma \mathcal{J} \cos^2 2\phi},$$

$$\omega_\alpha = \frac{A_{nn}^{11}(\lambda) + (-1)^\alpha E}{\sigma \mathcal{J} \cos^2 2\phi} \quad (n > 2), \quad q(1) = \frac{J_1(\lambda) \cos^2 2\phi_1}{\mathcal{J} \cos^2 2\phi}, \tag{15}$$

$$q = J(\lambda)/\mathcal{J}, \quad p = \cos 2\phi_1 / \cos 2\phi, \quad J_1(\lambda) = \mathcal{J}_1 z_{\parallel} \Lambda_\lambda,$$
$$J(\lambda) = \mathcal{J} z_{\parallel} \Lambda_\lambda, \quad \Lambda_\lambda = z_{\parallel}^{-1} \sum_\rho e^{i\vec{\lambda}\cdot\vec{\rho}},$$

where $z_{\parallel}$ represents the number of nearest neighbors in the (001) plane. The solutions to Eqs. (12)–(14) are functions of the sets $\{\omega_\alpha(1), \omega_\alpha(2), \omega_\alpha\}$ and we shall denote them by $X_{nm}^f(\alpha, \beta)$, α, $\beta = 1, 2$, $\beta \neq \alpha$. The relations between the Green's functions and these solutions are

$$\sigma \mathcal{J} \cos^2 2\phi \, G_{nm}^{\alpha\alpha} = X_{nm}^1(\alpha, \beta), \quad \sigma \mathcal{J} \cos^2 2\phi \, G_{nm}^{\alpha\beta} = X_{nm}^2(\alpha, \beta),$$
$$\alpha, \beta = 1, 2, \quad \beta \neq \alpha. \tag{16}$$

Equations (12)–(14) can be solved by the standard method of generating functions (see the Appendix), and the solutions are

$$X_{lm}^1(\alpha, \beta) = \frac{2\cosh\theta - \omega_\beta}{2\Omega \sinh\theta} \Big(e^{-|l-m|\theta}$$
$$- \frac{\mathcal{D}(\alpha, \beta, -\theta)}{\mathcal{D}(\alpha, \beta, \theta)} e^{-(l+m)\theta} \Big) - \frac{\delta_{ml}}{\Omega}, \quad (l, m > 2)$$

$$X_{1m}^1(\alpha, \beta) = \frac{\nu_2(\alpha, \beta) e^{-m\theta}}{\Omega \mathcal{D}(\alpha, \beta, \theta)} (2\cosh\theta - \omega_\beta),$$

$$X_{2m}^1(\alpha, \beta) = \frac{\gamma_1(\alpha, \beta)}{\nu_2(\alpha, \beta)} X_{1m}^1(\alpha, \beta), \quad (m > 2)$$

$$X_{l\zeta}^1(\alpha, \beta) = \left(N_\zeta(\alpha, \beta, -\theta) e^{-(l-1)\theta} - N_\zeta(\alpha, \beta, \theta) \right.$$

$$\left. \times \frac{\mathfrak{D}(\alpha, \beta, -\theta)}{\mathfrak{D}(\alpha, \beta, \theta)} e^{-(l+1)\theta} \right) \Big/ 2\nu_2(\alpha, \beta)\Omega \sinh\theta,$$

$$(l > 2) \tag{17}$$

$$X_{1\zeta}^1(\alpha, \beta) = N_\zeta(\alpha, \beta, \theta) e^{-\theta}/\Omega \mathfrak{D}(\alpha, \beta, \theta) ,$$

$$X_{2\zeta}^1(\alpha, \beta, \theta) = \frac{\gamma_1(\alpha, \beta)}{\nu_2(\alpha, \beta)} X_{1\zeta}^1(\alpha, \beta) - (-1)^\zeta \frac{f_\zeta(\alpha, \beta)}{\nu_2(\alpha, \beta)\Omega} ,$$

$$X_{\zeta m}^2(\alpha, \beta) = \frac{\Omega_\alpha(\zeta)}{\Omega_\beta(\zeta)} X_{\zeta m}^1(\alpha, \beta) + \frac{\delta_{m\zeta}}{\Omega_\beta(\zeta)} ,$$

$$X_{lm}^2(\alpha, \beta) = \frac{\Omega_\alpha}{\Omega_\beta} X_{lm}^1(\alpha, \beta) + \frac{\delta_{ml}}{\Omega_\beta} , \quad (l > 2), \quad \zeta = 1, 2$$

where

$$\Omega_\alpha(1) = \omega_\alpha(1) + q(1), \quad \Omega_\alpha(2) = \omega_\alpha(2) + q, \quad \Omega_\alpha = \omega_\alpha + q,$$

$$\Omega(\zeta) = \Omega_1(\zeta) + \Omega_2(\zeta), \quad \Omega = \Omega_1 + \Omega_2 ,$$

$$K_\alpha(\zeta) = \frac{\Omega_\alpha(\zeta)}{\Omega(\zeta)} , \quad K_\alpha = \frac{\Omega_\alpha}{\Omega} , \quad \zeta = 1, 2$$

$$\nu_3(\alpha, \beta) = \frac{K_\beta}{K_\beta(2)} , \quad \nu_2(\alpha, \beta) = p\nu_3(\alpha, \beta),$$

$$\nu_1(\alpha, \beta) = p\frac{K_\beta}{K_\beta(1)} , \quad f_3(\alpha, \beta) = \frac{\omega_\beta(1)\Omega_\beta}{\Omega_\beta(1)} ,$$

$$f_5(\alpha, \beta) = \frac{\Omega_\beta}{\Omega_\beta(2)}, \quad f_2(\alpha, \beta) = pf_5(\alpha, \beta) , \tag{18}$$

$$f_4(\alpha, \beta) = \omega_\beta(2)f_5(\alpha, \beta), \quad f_3(\alpha, \beta) = \frac{p}{\omega_\beta(1)} f_1(\alpha, \beta) ,$$

$$\gamma_1(\alpha, \beta) = \frac{\omega_1(1)\omega_2(1) - q(1)^2}{\Omega_\beta(1)} \frac{\Omega_\beta}{\Omega} ,$$

$$\gamma_2(\alpha, \beta) = \frac{\omega_1(2)\omega_2(2) - q^2}{\Omega_\beta(2)} \frac{\Omega_\beta}{\Omega} ,$$

$$\gamma = \frac{\omega_1\omega_2 - q^2}{\Omega} = 2\cosh\theta ,$$

$$\mathfrak{D}(\alpha, \beta, \theta) = e^{-2\theta} [\gamma_1(\alpha, \beta)\gamma_2(\alpha, \beta) - \nu_1(\alpha, \beta)\nu_2(\alpha, \beta)$$
$$- \gamma_1(\alpha, \beta)\nu_3(\alpha, \beta) e^{-\theta}] ,$$

$$N_1(\alpha, \beta, \theta) = e^{-\theta} [f_3(\alpha, \beta)\nu_2(\alpha, \beta) - f_1(\alpha, \beta)\gamma_2(\alpha, \beta)$$
$$+ f_1(\alpha, \beta)\nu_3(\alpha, \beta) e^{-\theta}] ,$$

$$N_2(\alpha, \beta, \theta) = e^{-\theta}\{f_2(\alpha, \beta)\gamma_2(\alpha, \beta) - f_4(\alpha, \beta)\nu_2(\alpha, \beta)$$
$$+ [f_5(\alpha, \beta)\nu_2(\alpha, \beta) - f_2(\alpha, \beta)\nu_3(\alpha, \beta)]e^{-\theta}\} .$$

The bulk excitation band lies between the limits $-1 < \cosh\theta < 1$, where $\theta = i\psi$. As the energy increases and the excitation band is approached from below, θ is real and $\theta \to 0$. Inside the band, ψ increases from 0 to π as the energy increases. Above the band, $\theta = \theta' + i\pi$, where θ' is real and increases from 0 as the energy increases from the top of the band. These results are consistent with the requirement that the Green's functions inside the bulk excitation band are functions of $E - i\eta$,

where $\eta \to 0^+$. For energies outside the bulk band, localized surface modes will be determined by the zeros of $\mathfrak{D}(\alpha, \beta, \theta)$, since these give poles of the Green's functions.

IV. SOME ANALYTICAL RESULTS

A. Surface Phase Transition

It is possible to obtain poles of the Green's functions due to the vanishing of $\mathfrak{D}(\alpha, \beta, \theta)$ apparently yielding localized modes with energy $E(\lambda)$ which goes to zero for $\lambda > 0$. In order to show that such modes are spurious since they violate the stability condition, we first calculate $\mathfrak{D}(\alpha, \beta, \theta) = 0$ for $E = 0$ and find that the critical value of $J_1' = \mathfrak{J}_1/\mathfrak{J}$ at which the surface mode becomes soft in the disordered region is

$$J_1' = \frac{z\Delta_1'}{\sigma z_{\parallel}} - \frac{e^{-\theta}}{z_{\parallel}}, \quad \Delta_1' = \frac{\Delta_1}{2\mathfrak{J}z} . \tag{19}$$

In order to show that this is given by the stability condition as the surface makes the transition from the ordered to the disordered phase, we assume that the bulk is disordered so that all $\phi_n > \phi_{n+1}$ and $\phi_n \approx 0$, so that $\cos 2\phi_n \approx 1$ and $\hat{R}_n = \sin 2\phi_{n+1}/\sin 2\phi_n$ = finite. From Eq. (9) for $n = 1$ we have

$$J_1' = \frac{z\Delta_1'}{\sigma z_{\parallel}} - \frac{1}{z_{\parallel}} \frac{\sin 2\phi_2}{\sin 2\phi_1} . \tag{20}$$

If we divide Eq. (9) for $n = n + 1$ by $\sin 2\phi_n$, we have

$$1 + \hat{R}_n \hat{R}_{n+1} - 2\cosh\theta \hat{R}_n = 0, \quad 2\cosh\theta = z\Delta'/\sigma - z_{\parallel},$$
$$\Delta' = \Delta/2\mathfrak{J}z . \tag{21}$$

In the limit that all $\phi_n \to 0$ we can take $\hat{R}_{n+1} = \hat{R}_n$, whence the solution that satisfies the relevant boundary conditions is $\hat{R}_n = e^{-\theta}$.

B. Conditions for Existence of Bound States

The equation for the existence of bound states can be solved for $e^{-\theta}$. For bound states below the band $0 \leq e^{-\theta} \leq 1$, while for those above the band $-1 \leq e^{-\theta} \leq 0$, so that we obtain inequalities which must be satisfied for the existence of bound states:

$$\gamma_1(\alpha, \beta)\gamma_2(\alpha, \beta) - \nu_1(\alpha, \beta)\nu_2(\alpha, \beta)$$

$$\leq \gamma_1(\alpha, \beta)\nu_3(\alpha, \beta) \quad \text{below band}$$

$$\geq -\gamma_1(\alpha, \beta)\nu_3(\alpha, \beta) \quad \text{above band.} \tag{22}$$

(i) *Disordered phase.* The equation for the bottom of the bulk band is

$$E_B^2 = \Delta'^2 - \frac{2\Delta'\sigma}{z} - \frac{\Delta'\sigma}{z} z_{\parallel}\Lambda_\lambda . \tag{23}$$

The first inequality in (22) can be rearranged and combined with (23) to give bounds on the energy $E_b(\Lambda)$ of a localized mode:

$$E_L(\Lambda)^2 = \Delta_1'^2 - \frac{\sigma\Delta_1'}{z} - \frac{\sigma\Delta_1'}{z} J_1' z_{\shortparallel} \Lambda_\lambda \leq E_b(\Lambda)^2 \leq E_B(\Lambda)^2 .$$

(24)

The curves defined by $E_L(\Lambda)$ and $E_B(\Lambda)$ may intersect outside the physical range $1 \geq \Lambda_\lambda \geq -1$. Inside the physical range their point of intersection tells where a localized mode enters or leaves the band. The equalities in (24) give the value of Λ_λ, $\Lambda_\lambda(b)$, at which a mode appears at the band edge:

$$\Lambda_\lambda(b) = \frac{\Delta'^2 - \Delta_1'^2 - (\sigma/z)(2\Delta' - \Delta_1')}{(\sigma z_{\shortparallel}/z)(\Delta' - \Delta_1' J_1')} \quad \text{if } \Delta' \neq \Delta_1' J_1' .$$

(25)

To see whether the mode is entering or leaving the band as Λ_λ decreases, we calculate

$$\left(\frac{\partial E_L}{\partial \Lambda}\right)_{\Lambda=\Lambda(b)} \Big/ \left(\frac{\partial E_B}{\partial \Lambda}\right)_{\Lambda=\Lambda(b)} = R_{\text{D-D}}(b) ,$$

where D-D (O-D) means that the surface is disordered (ordered) with the bulk disordered, and find the simple result that

$$R_{\text{D-D}}(b) = \Delta_1' J_1'/\Delta' .$$

(26)

By using the second inequality in (22) a similar analysis can be performed for the existence of bound states above the band. The value of Λ_λ, $\Lambda_\lambda(b)$, at which a localized mode appears at the top of the band is

$$\Lambda_\lambda(b) = \frac{\Delta'^2 - \Delta_1'^2 + (\sigma/z)(2\Delta' - \Delta_1')}{(\sigma z_{\shortparallel}/z)(\Delta' - \Delta_1' J_1')} \quad \text{if } \Delta' \neq \Delta_1' J_1' .$$

(27)

A calculation of the ratio of slopes to discover whether the mode is leaving or entering yields (26) again. Thus, as a function of decreasing Λ_λ: For modes below the band, $R_{\text{D-D}} > 1$ (<1) indicates that a mode is entering (leaving) the band, while for modes above the band, $R_{\text{D-D}} > 1$ (<1) indicates that a mode is leaving (entering) the band.

(ii) Surface-ordered, bulk-disordered phase. By repeating the analysis above we find that the inequalities for the existence of a bound state of energy $E_b(\Lambda)$ are

$$\left(\frac{\sigma J_1'}{z} z_{\shortparallel}\right)^2 - \frac{\Delta_1'^2}{z_{\shortparallel} J_1'} - \Delta_1'^2 \Lambda_\lambda \leq E_b(\Lambda)^2$$

$$\leq \Delta'^2 - \frac{2\Delta'\sigma}{z} - \frac{\sigma\Delta'}{z} z_{\shortparallel}\Lambda_\lambda$$

$$= E_B(\Lambda)^2 \text{ below band,} \quad (28)$$

$$E_T(\Lambda)^2 = \Delta'^2 + \frac{2\Delta'\sigma}{z} - \frac{\sigma\Delta'}{z} z_{\shortparallel}\Lambda_\lambda \leq E_b(\Lambda)^2$$

$$\leq \left(\frac{\sigma J_1'}{z} z_{\shortparallel}\right)^2 + \frac{\Delta_1'^2}{z_{\shortparallel} J_1'} - \Delta_1'^2 \Lambda_\lambda \text{ above band,}$$

where $E_B(\Lambda)$ and $E_T(\Lambda)$ represent the bottom and top of the band, respectively. The values of Λ_λ, $\Lambda_\lambda(b)$, at which modes appear below or above the bulk band are

$$\Lambda_\lambda(b) = \frac{\Delta'^2 \mp 2\Delta'\sigma/z \pm \Delta_1'^2/z_{\shortparallel} J_1' - [(\sigma J_1'/z)z_{\shortparallel}]^2}{(\sigma\Delta'/z)z_{\shortparallel} - \Delta_1'^2} ,$$

if $\sigma\Delta' z_{\shortparallel}/z \neq \Delta_1'^2 .$

(29)

Again, a calculation of the ratio of the slopes as done above gives

$$R_{\text{O-D}} = \Delta_1'^2 z/\sigma\Delta' z_{\shortparallel} .$$

(30)

As a function of decreasing Λ_λ: For modes below the band, $R_{\text{O-D}} > 1$ (<1) indicates that a mode is entering (leaving) the band, while for modes above the band, $R_{\text{O-D}} > 1$ (<1) indicates that a mode is leaving (entering) the band.

It should be noted that since the inequalities (24) and (28) are linear in $E_b(\Lambda)^2$, then only one kind of localized surface mode can appear (predominantly on the surface layer) when the system is either wholly disordered or when only the surface is ordered. This should be contrasted with the third case below.

(iii) Ordered phase. Here, our results will depend upon the assumption that $\cos 2\phi_n = \cos 2\phi$ except when $n = 1$. We now have to solve the stability equation for $\cos 2\phi_1$. Because of the complicated form that the inequalities (22) now assume, we shall define some new quantities so that they look somewhat similar to those in the disordered case. If we define

$$\tilde{\Delta}_1' = \frac{\Delta_1' \cos 2\phi_1 + (\sigma/z)\sin 2\phi_1 (J_1' z_{\shortparallel} \sin 2\phi_1 + \sin 2\phi)}{\cos^2 2\phi} ,$$

$$\tilde{\Delta}_2' = \frac{\Delta' \cos 2\phi + (\sigma/z)\sin 2\phi [(z_{\shortparallel} + 1)\sin 2\phi + \sin 2\phi_1]}{\cos^2 2\phi} ,$$

(31)

$$\tilde{J}_1' = J_1' \frac{\cos^2 2\phi_1}{\cos^2 2\phi} , \quad \tilde{E} = \frac{E}{\cos^2 2\phi} , \quad \cos 2\phi = \frac{\Delta'}{\sigma} ,$$

$$\tilde{\Delta}' = (\Delta' \cos 2\phi + 2\sigma \sin^2 2\phi)/\cos^2 2\phi ,$$

then the inequalities take on the following forms for the energies of localized states below (+) and above (−) the band:

$$\pm\left[\left(\tilde{\Delta}_1'^2 - \tilde{E}_b^2 - \frac{\sigma\tilde{\Delta}_1'}{z} \tilde{J}_1' z_{\shortparallel} \Lambda_\lambda\right)\left(\tilde{\Delta}_2'^2 - \tilde{E}_b^2 - \frac{\sigma\tilde{\Delta}_2'}{z} z_{\shortparallel} \Lambda_\lambda\right)\right.$$

$$\left. - \frac{\sigma^2}{z^2} \tilde{\Delta}_1' \tilde{\Delta}_2' \frac{\cos^2 2\phi_1}{\cos^2 2\phi}\right]$$

$$\leq \frac{\sigma\tilde{\Delta}_2'}{z}\left(\tilde{\Delta}_1'^2 - \tilde{E}_b^2 - \frac{\sigma\tilde{\Delta}_1'}{z} \tilde{J}_1' z_{\shortparallel} \Lambda_\lambda\right) . \quad (32)$$

That this is quadratic in $\tilde{E}_b^2$ indicates that there is a possibility of two kinds of bound states, localized predominantly on the first and second layers. The equations for the bottom (−) and top (+) of the bulk band are

$$\tilde{E}_{B,T}(\Lambda)^2 = \frac{\sigma^2 \mp 2\Delta'^2/z - (\Delta'^2/z)z_{\shortparallel}\Lambda_\lambda}{\cos^4 2\phi} .$$

(33)

It is now a simple matter to find the values of $\Lambda_\lambda(b)$ at which bound states appear, as we did above, by putting $\tilde{E}_b(\Lambda(b)) = \tilde{E}_B$ or $\tilde{E}_T$ evaluated at

$\Lambda(b)$, and to find out whether they are entering or leaving the band.

C. Surface Resonances

In investigating resonances we shall first make use of a spin-wave–like approximation in (3). By putting

$$\sigma_j^z = \tfrac{1}{2} - a_j^\dagger a_j , \quad \sigma_j^x \approx \tfrac{1}{2}(a_j + a_j^\dagger), \quad [a_j, a_{j'}^\dagger] = \delta_{j'j} , \tag{34}$$

writing the site label j as (n (for layers), k (for layer sites)), performing a two-dimensional Fourier transform on k, and then, via a Bogoliubov transformation, diagonalizing terms that do not involve a coupling between layers, we obtain

$$\mathcal{H} = \sum_{n\lambda} \Bigg(E_{n\lambda} \alpha_{n\lambda}^\dagger \alpha_{n\lambda}$$
$$- \tfrac{1}{4} \sum_\tau J_{n\,n+\tau} \cos 2\phi_n \cos 2\phi_{n+\tau} (p_{n\lambda} - q_{n\lambda})$$
$$\times (p_{n+\tau\,\lambda} - q_{n+\tau\,\lambda})(\alpha_{n+\tau\,\lambda}^\dagger \alpha_{n\lambda} + \alpha_{n\lambda}^\dagger \alpha_{n+\tau\,\lambda}$$
$$+ \alpha_{n\lambda}\alpha_{n+\tau\,-\lambda} + \alpha_{n\lambda}^\dagger \alpha_{n+\tau\,-\lambda}^\dagger) \Bigg) , \tag{35}$$

$[\alpha_{n\lambda}, \alpha_{n'\lambda'}^\dagger] = \delta_{n'n}\delta_{\lambda'\lambda}$, $p_{n\lambda}^2 - q_{n\lambda}^2 = 1$, $E_{n\lambda} = (A_{n\lambda}^2 - B_{n\lambda}^2)^{1/2}$,

$p_{n\lambda} = B_{n\lambda}/[2E_{n\lambda}(A_{n\lambda} - E_{n\lambda})]^{1/2}$, $B_{n\lambda} = -\tfrac{1}{2}J_n(\lambda)\cos^2 2\phi_n$,

$A_{n\lambda} = \Delta_n \cos^2 2\phi_n + J_n(0)\sin^2 2\phi_n$

$$+ \sum_\tau J_{n\,n+\tau} \sin 2\phi_n \sin 2\phi_{n+\tau} + B_{n\lambda} .$$

The second term in $\mathcal{H}$ describes the interaction between excitations propagating on different layers, and its magnitude gives an indication of whether surface resonances are to be expected. It can be seen that its magnitude depends upon $\cos 2\phi_n$, so that it will be large in the disordered phase and smaller as the system becomes more ordered. We shall discuss this in Sec. V. In order to study the resonances, however, we shall not use Green's functions like $\langle \alpha_{n\lambda} | \alpha_{n\lambda}^\dagger \rangle$ because, in the case that the crystal is surfaceless and periodic, the $\alpha_{n\lambda}^\dagger$ are not the Fourier transform of $b_{\mu\lambda}^\dagger$ which creates one-particle eigenstates [labeled by wave vectors $\vec{\lambda}$ and μ parallel and perpendicular to the (001) plane] of $\mathcal{H}$ from its approximate ground state. Only if the terms in $\alpha_{n\lambda}\alpha_{n+\tau\,-\lambda}$ and $\alpha_{n\lambda}^\dagger \alpha_{n+\tau\,-\lambda}^\dagger$ were absent would $\langle \alpha_{n\lambda} | \alpha_{n\lambda}^\dagger \rangle$ be suitable.

To discover the appropriate Green's function, let $s_{\mu\lambda}^\pm$ satisfy the equations ($\mathcal{H}$ is for a surfaceless system) in the RPA,

$$[s_{\mu\lambda}^+, s_{\mu'\lambda'}^-] \approx \delta_{\mu'-\mu}\delta_{\lambda'-\lambda}, \quad [s_{\mu\lambda}^-, \mathcal{H}] = -E_{\mu\lambda}s_{\mu\lambda}^- , \tag{36}$$

where $E_{\mu\lambda}$ is the excitation spectrum for the periodic surfaceless system. Then

$$s_{n\lambda}^- = (1/\sqrt{N_\perp}) \sum_\mu e^{i\mu n} s_{\mu\lambda}^- \tag{37}$$

creates an excitation of wave vector $\vec{\lambda}$ located on the nth layer, and $N_\perp$ is the number of layers. If we represent $\langle s_{n\lambda}^+ | s_{m\,-\lambda}^- \rangle_E$ by $\mathcal{G}_{nm}(\lambda, E)$, then at zero

temperature the thermal average becomes an average over the ground state, $|0\rangle$, so that if we assume that $\langle 0 | s_{n\,-\lambda}^+(t) s_{n\lambda}^-(0) | 0 \rangle$ is of the form $A_{n\lambda} \exp(i\psi_{n\lambda}) \exp[i(\epsilon_{n\lambda} + \tfrac{1}{2}i\Gamma_{n\lambda})t]$, where $s_{n\lambda}^+(t)$ is $s_{n\lambda}^+$ in Heisenberg's picture, then

$$\left(\mathrm{Im}\lim_{\eta \to 0^+} \mathcal{G}_{nn}(\lambda, E - i\eta) \right)^2 + \left(\mathrm{Re}\lim_{\eta \to 0^+} \mathcal{G}_{nn}(\lambda, E - i\eta) \right)^2$$
$$= \frac{A_{n\lambda}^2}{16\sigma_n^2[(E - \epsilon_{n\lambda})^2 + (\tfrac{1}{2}\Gamma_{n\lambda})^2]} = R_n . \tag{38}$$

For a surfaceless system a Bogoliubov transformation connects the s and σ operators,[22]

$$s_{\mu\lambda}^+ = c_{\mu\lambda}\sigma_{\mu\lambda}^+ + s_{\mu\lambda}\sigma_{\mu\lambda}^- , \quad c_{\mu\lambda}^2 - s_{\mu\lambda}^2 = 1 . \tag{39}$$

Thus,

$$\mathcal{G}_{nn}(\lambda, E) = \sum_{l,m} (c_{l-n\,\lambda}c_{m-n\,\lambda}\langle \sigma_{l\lambda}^+ | \sigma_{m-\lambda}^- \rangle$$
$$+ s_{l-n\,\lambda}c_{m-n\,\lambda}\langle \sigma_{l\lambda}^- | \sigma_{m-\lambda}^- \rangle + c_{l-n\,\lambda}s_{m-n\,\lambda}\langle \sigma_{l\lambda}^+ | \sigma_{m-\lambda}^+ \rangle$$
$$+ s_{l-n\,\lambda}s_{m-n\,\lambda}\langle \sigma_{l\lambda}^- | \sigma_{m-\lambda}^+ \rangle) ,$$
$$c_{m-n\,\lambda} = (1/N_\perp) \sum_\mu e^{i\mu(m-n)} c_{\mu\lambda} . \tag{40}$$

In order to calculate the effect of surfaces we shall replace the Green's functions on the right-hand side by $X_{lm}^1(1, 2)$, $X_{lm}^2(1, 2)$, $X_{lm}^2(2, 1)$, and $X_{lm}^1(2, 1)$, respectively, and divide by $\pi \cos^2 2\phi$. The results of calculations shall be presented in Sec. V.

Finally, it should be noted that the angle $\psi = -i\theta$ inside the band is the relative phase angle of precessing pseudospins as one goes from one layer to another. This can be seen by considering the Fourier transforms, perpendicular to the surface, of the Green's functions and comparing them with those for a surfaceless periodic crystal.

V. NUMERICAL RESULTS

All calculations were done for zero temperature and we took $\sigma = \tfrac{1}{2}$. We shall refer to the interaction between the nth and $(n+1)$st layer, shown in the second term of $\mathcal{H}$ in (35), as $I_{n\,n+1}$.

(i) *Disordered phase.* Figure 1 shows some bound states that occur when both the bulk and surface are disordered, with $\Delta' = 0.7$ and Δ_1' and J_1' as given for each mode which is localized predominantly on the first layer. As one would expect, by considering the inequalities (24) as well as those for above the band, the energy gap of the localized modes is determined by Δ_1' (for fixed J_1'), while the slope as a function of Λ_λ is determined by J_1' (for fixed Δ_1'). A free surface will not support bound states. This can be seen by showing that $\mathcal{D}(\alpha, \beta, \theta) = 0$ if and only if $\Delta' = 0$. This is a contradictory result because the bulk becomes ordered if $\Delta' < 0.5$. The magnitude of I_{12} was calculated as a function of Λ_λ for the modes with Δ_1', J_1' values of 0.6, 0.7; 0.6, 1.4; and 0.8, 1.4. It was found that this interaction was of the approximate magnitude of I_{23} and that both range from ~ 1.5 to ~ 0.8,
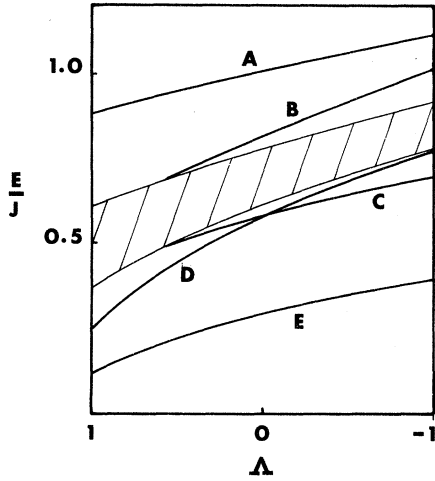
FIG. 1. Surface and bulk disordered. $\Delta' = 0.7$. A: $\Delta_1' = 1.0$, $J_1' = 0.7$. B: $\Delta_1' = 0.8$, $J_1' = 1.4$. C: $\Delta_1' = 0.6$, $J_1' = 0.7$. D: $\Delta_1' = 0.6$, $J_1' = 1.4$. E: $\Delta_1' = 0.3$, $J_1' = 0.7$. All modes localized predominantly on layer 1.

in units of $\mathcal{J}$, as Λ_λ ranges from 1 to -1. A calculation of R_n for $n = 1, 2, 3$ showed that no resonances appeared inside the band, though for $n = 1$ it became greatly distorted towards where the mode joined the band (Fig. 2). This was true even when a bound state appeared to sweep across the band as a function of $\Lambda_\lambda (\Delta' = 1.0$, $\Delta_1' = 1.1$, $J_1' = 2.5)$, the bound state being below the band for $1 \geqslant \Lambda_\lambda \geqslant 0.05$ and above the band for $-0.2 \geqslant \Lambda_\lambda \geqslant -1$ [compare (iii) below].

(ii) *Surface-ordered, bulk-disordered phase.* In Fig. 3 some localized modes, again all predominantly on the first layer, are shown for $\Delta' = 0.7$. Now, since the surface is ordered, the energy gap is determined by J_1' and the slope by Δ_1'. Because Δ_1' may not be too large compared to J_1' in order that the surface be ordered, the slopes of localized modes in this phase will be smaller in general than those in the disordered phase. A free surface has no meaning in this phase. For $\Delta_1' = 0.2$, $J_1' = 1.4$ a
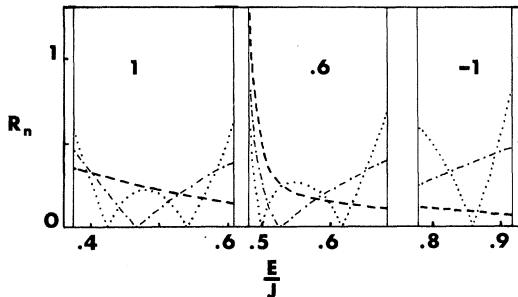

FIG. 2. Surface and bulk disordered. $\Delta' = 0.7$, $\Delta_1' = 0.6$, $J_1' = 0.7$. R_1 (heavy dash), R_2 (dot-dash), R_3 (dot), and values of Λ as indicated between band limits.
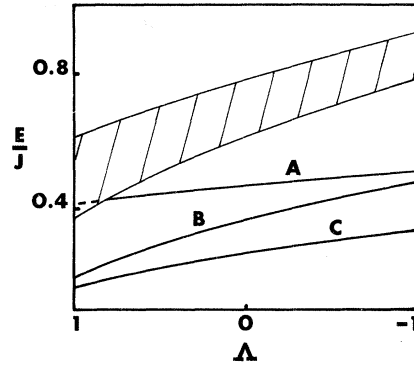

FIG. 3. Surface ordered, bulk disordered. $\Delta' = 0.7$. A: $\Delta_1' = 0.2$, $J_1' = 1.4$. B: $\Delta_1' = 0.3$, $J_1' = 1.0$. C: $\Delta_1' = 0.2$, $J_1' = 0.8$. All modes localized predominantly on layer 1.

calculation of $I_{n\,n+1}$ showed that, although those for $n = 2, 3, \ldots$ range from ~ 1.4 to ~ 0.8, I_{12} ranges from ~ 0.5 to ~ 0.4. When R_n was calculated for $n = 1, 2, 3$, it was found that a resonance appeared near the bottom of the bulk band as shown by the dashed line in Fig. 3 which represents the locus of the peak. This resonance is nearly wholly located on layer 1, a small part ($\sim 10\%$) being located on layer 2. In addition, there is a distortion of R_3. We have not plotted this since it is similar to results of the ordered phase.

(iii) *Ordered phase.* Figure 4 shows two cases. As in (ii), the energy gap of the localized mode is determined by J_1', while the slope is determined by Δ_1'. In the ordered phase a free surface will support a bound state because $\phi_1 \neq \phi$ (the pseudospins on the surface are canted with respect to those in the bulk). In Fig. 4(a), $\Delta' = 0.45$, and for a variety of choices of Δ_1' and J_1' only one bound state appears which is localized predominantly on the surface. The magnitude of $I_{n\,n+1}$ for $n = 2, 3, \ldots$ ranges from ~ 1.1 to ~ 0.7 as Λ_λ ranges from 1 to -1, while I_{12} ranges from ~ 0.5 to ~ 0.35. Thus we would expect a resonance at least on the first layer. This was found and the positions of the surface resonance peaks are shown as dashed lines. The plots, in Fig. 5, of R_n when $\Delta_1' = 0.2$, $J_1' = 1.20$ show that a bound state localized on the second layer may be nearly formed at the top of the band. Here we see R_1 sharpen and disappear as the mode becomes localized, and the distortion of R_2 and R_3 near the top of the band as $\Lambda_\lambda \to -1$. In Fig. 4(b) examples of bound states localized on both the first and second layers are shown. Here $\Delta' = 0.20$ and the mixing of the two surface modes is seen in the region $0.2 > \Lambda_\lambda > -0.4$. As expected from the narrowness of the band, $I_{n\,n+1}$ is small: $I_{n\,n+1} \approx 0.15$ for $n = 2, 3, \ldots$ and I_{12} ranges from ~ 0.45 to ~ 0.33. Again, then, we expect to find first layer reso-

nances and a calculation of R_n bears this out. In Fig. 4(b) the gradual disappearance of the resonance when $\Delta_1' = 0.3$, $J_1' = 1.20$ is shown. At this point it is equally distributed between the first and second layers as shown in Fig. 6. That the third layer behaves like a free surface when there are two localized modes can be seen here from the shape of R_3. This is reasonable since the bulk and the two surface layers do not exchange energy to any extent.

VI. CONCLUSIONS

We have investigated the surface bound states and resonances that occur in a two-level induced-moment system or a tunneling model of a hydrogen-bonded ferroelectric. We used the random-phase approximation and adopted a simple model of a surface by assuming (a) a perfectively sharp surface and (b) that only parameters on the surface have values different to those deep in the bulk. We made simplifying assumptions about the averages $\langle \sigma_n^z \rangle$ and "molecular-field" angles ϕ_n, and obtained explicit analytical expressions for the complete Green's functions. We found that three phases could exist:
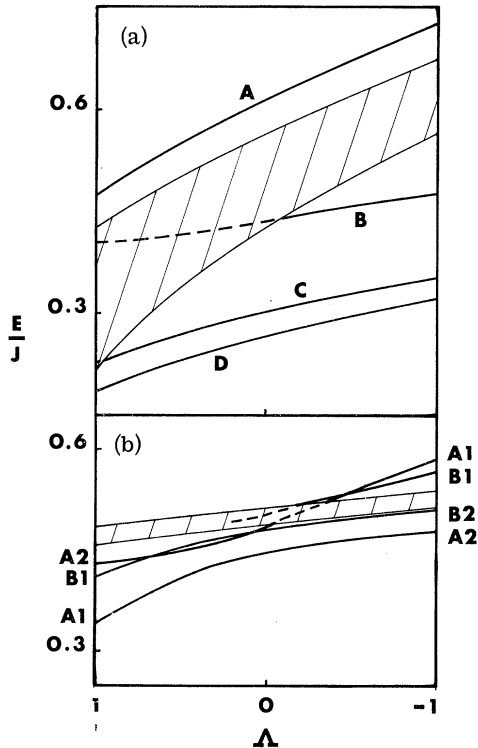
FIG. 4. Surface and bulk ordered. (a) $\Delta' = 0.45$. A: $\Delta_1' = 0.6$, $J_1' = 0.77$. B: $\Delta_1' = 0.2$, $J_1' = 1.2$. C: $\Delta_1' = 0.2$, $J_1' = 0.77$. D: $\Delta_1' = 0.2$, $J_1' = 0.65$. All modes localized predominantly on layer 1. (b) $\Delta' = 0.2$. An ($n = 1$, 2); $\Delta_1' = 0.45$, $J_1' = 0.77$. Bn ($n = 1$, 2): $\Delta_1' = 0.3$, $J_1' = 1.2$. These are localized predominantly on layer n.
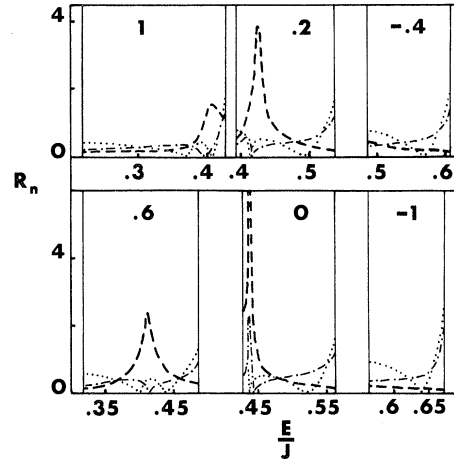
FIG. 5. Surface and bulk ordered. $\Delta' = 0.45$, $\Delta_1' = 0.2$, $J_1' = 1.2$. R_1 (heavy dash), R_2 (dot-dash), R_3 (dot), and values of Λ as indicated between band limits.

(i) Both the surface and the bulk are disordered, (ii) the surface is ordered but the bulk is disordered, or (iii) both the surface and the bulk are ordered. The transition between phases (i) and (ii) is triggered by a soft mode, and we showed that "modes" in phase (i) having energy $E(\lambda)$ with $E(\lambda) \to 0$ for $\lambda > 0$ were unphysical. The Green's functions all contain a factor $e^{-m\theta}$, (m is a positive integer). For energies outside the bulk band, θ is positive real (below band) or θ is positive real $+ i\pi$ (above band), showing that the effects of the surface decay with the distance into the crystal. Inside the band $\theta = i\psi$ ($0 \le \psi \le \pi$), and ψ is the relative phase angle between precessing pseudospins on adjacent layers.

In both phases (i) and (ii) we showed that only one kind of localized mode could exist (localized predominantly on the surface) and that in phase (i) a free surface would not support bound states. In phase (iii), however, two kinds of localized modes could appear (on the first and second layers predominantly) and a free surface could support bound states.

We derived criteria for the appearance of bound states in any of the three phases which enable us to decide whether a mode is above or below the bulk band and whether it is entering or leaving the band as a function of decreasing Λ_λ. We investigated the magnitude of the coupling between excitations on two adjacent layers parallel to the surface and showed when a resonance might be expected (if the interaction is of magnitude ~ 1, in suitable units, a resonance appears unlikely, while if it is of magnitude $\lesssim 0.7$, a resonance might appear). We presented some numerical calculations of bound states and resonances for zero temperature and all three phases.
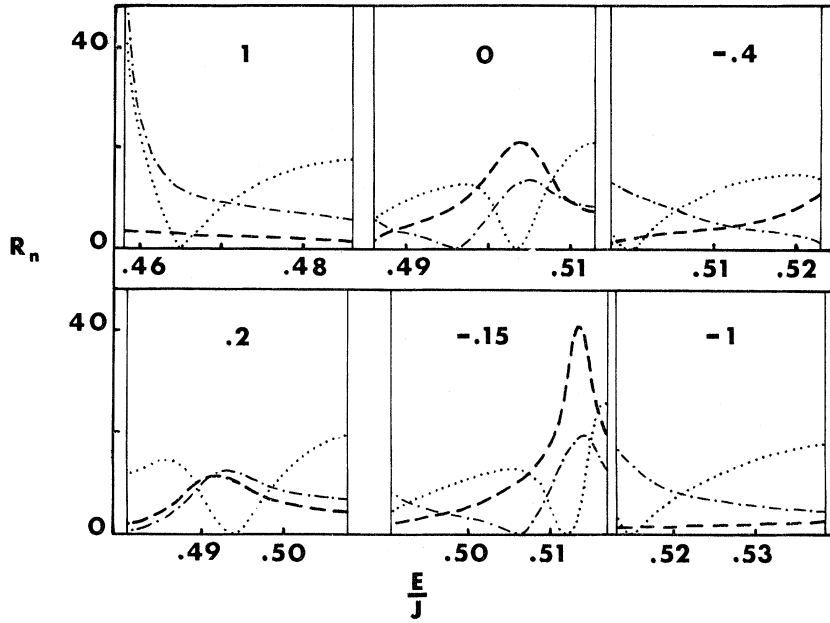
FIG. 6. Surface and bulk ordered. $\Delta' = 0.2$, $\Delta_1' = 0.3$, J_1' $= 1.2$. R_1 (heavy dash), R_2 (dot-dash), R_3 (dot), and values of Λ as indicated between band limits.

Finally, it would be of interest to measure the surface absorption of infrared radiation on the part of KDP or KDDP for a surface cut perpendicularly to the polarization axis. In this case the hydrogen bonds lie in the plane of the surface and may retain their symmetric double-minimum potential. If such a measurement yielded useful information, a similar measurement with a surface cut at an angle to the axis of polarization would possibly give information regarding how surface hydrogen bonds, which are not in the plane of the surface, are distorted. This case is not covered here because it is felt that the feasibility of testing these calculations should be established before more complicated situations are considered.

ACKNOWLEDGMENTS

APPENDIX

If we subtract Eq. (12) for $\alpha = 2$ from (12) for $\alpha = 1$, Eq. (13) for $\alpha = 2$ from (13) for $\alpha = 1$, and Eq. (14) for $\alpha = 2$ from (14) for $\alpha = 1$, we find that

$$X^2_{1m}(\alpha, \beta) = [\Omega_\alpha(1)X^1_{1m}(\alpha, \beta) + \delta_{m1}]/\Omega_\beta(1) , \quad (A1)$$

$$X^2_{2m}(\alpha, \beta) = [\Omega_\alpha(2)X^1_{2m}(\alpha, \beta) + \delta_{m2}]/\Omega_\beta(2) , \quad (A2)$$

$$X^2_{nm}(\alpha, \beta) = [\Omega_\alpha X^1_{nm}(\alpha, \beta) + \delta_{mn}]/\Omega_\beta , \quad (A3)$$

which, when substituted back into (12)–(14), give

$$\gamma_1(\alpha, \beta)X^1_{1m}(\alpha, \beta) - \nu_2(\alpha, \beta)X^1_{2m}(\alpha, \beta)$$
$$= [-f_1(\alpha, \beta)\delta_{m1} + f_2(\alpha, \beta)\delta_{m2}]/\Omega , \quad (A4)$$

$$\gamma_2(\alpha, \beta)X^1_{2m}(\alpha, \beta) - \nu_1(\alpha, \beta)X^1_{1m}(\alpha, \beta) - X^1_{3m}(\alpha, \beta)$$
$$= [-f_4(\alpha, \beta)\delta_{m2} + f_3(\alpha, \beta)\delta_{m1} + \delta_{m3}]/\Omega , \quad (A5)$$

$$\gamma X^1_{3m}(\alpha, \beta) - \nu_3(\alpha, \beta)X^1_{2m}(\alpha, \beta) - X^1_{4m}(\alpha, \beta)$$
$$= [-\omega_\beta\delta_{m3} + f_5(\alpha, \beta)\delta_{m2} + \delta_{m4}]/\Omega , \quad (A6)$$

$$\gamma X^1_{nm}(\alpha, \beta) - X^1_{n-1\,m}(\alpha, \beta) - X^1_{n+1\,m}(\alpha, \beta)$$
$$= (-\omega_\beta\delta_{mn} + \delta_{m\,n-1} + \delta_{m\,n+1})/\Omega , \quad n > 3. \quad (A7)$$

We then multiply (A4), (A5), (A6), and (A7) by z, z^2, z^3, and z^n $(n > 3)$, respectively, and add them to obtain

$$\Xi(z) = \sum_{l=1}^{\infty} X^1_{lm}(\alpha, \beta)z^l$$

$$= \frac{1}{\sinh\theta} (\{[1 - \nu_1(\alpha, \beta)]z^3 + [\gamma_1(\alpha, \beta) - \gamma]z^2 + z\}X^1_{1m}(\alpha, \beta) + \{[1 - \nu_3(\alpha, \beta)]z^4 + [\gamma_2(\alpha, \beta) - \gamma]z^3 + [1 - \nu_2(\alpha, \beta)]z^2\}$$

$$X^1_{2m}(\alpha, \beta) + (1/\Omega)\{[f_1(\alpha, \beta)z^2 - f_3(\alpha, \beta)z^3]\delta_{m1} + [f_4(\alpha, \beta)z^3 - f_5(\alpha, \beta)z^4 - f_2(\alpha, \beta)z^2]\delta_{m2}$$

$$+ (\omega_\beta z^{m+1} - z^{m+2} - z^m)(1 - \delta_{m1})(1 - \delta_{m2})\}) \sum_{l=1}^{\infty} \sinh l\theta\, z^{l-1} . \quad (A8)$$

Here we have made use of the expansion

$$z^2 - \gamma z + 1 = (\sinh\theta)^{-1} \sum_{l=1}^{\infty} \sinh l\theta \, z^{l-1} \, .$$

The second boundary condition is that, since for a

surfaceless periodic lattice the Green's functions have the property $\lim G_{lm}^{\alpha\xi}(\lambda) = 0$ as $|l - m| \to \infty$, then we shall require that $\lim X_{lm}^{f}(\alpha, \beta) = 0$ as $|l - m| \to \infty$. The solutions in (17) follow.

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Logarithmic Corrections to the Molecular-Field Behavior of Critical and Tricritical Systems

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The asymptotic critical form of thermodynamic functions is analyzed by means of renormalization-group techniques. If certain exponent relations are satisfied, then the critical behavior is not described by a simple power law, but a power law multiplied by a fractional power of a logarithm. The approach is applied to two special systems whose critical exponents are molecular-field-like. (i) For ordinary critical transitions in four dimensions we find the same logarithmic factors previously computed by Larkin and Khmel'nitskii. (ii) For tricritical transitions in three dimensions we compute the logarithmic corrections to the molecular-field tricritical behavior discussed in an earlier publication.

I. INTRODUCTION

Renormalization-group techniques yield power laws for the expectation values of different operators and susceptibilities near criticality,[1,2] which can be characterized by sets of critical exponents. If these exponents satisfy certain relations, then the power laws are modified by logarithmic *factors*.[3] If in particular an operator has a vanishing scaling index y (for a definition of y see Sec. II of the present paper and Ref. 3), then this gives rise

to factors of fractional powers of logarithms. In terms of the renormalization-group procedure this is due to the very slow decay of the field of this operator. Examples where this situation occurs are (i) the critical behavior of four-dimensional systems[2] and (ii) the tricritical behavior of three-dimensional systems.[4] For both cases[5] the Gaussian fixed point of the renormalization-group equations leads to respective sets of molecular-field values for the critical exponents.[2,4,6] In this paper we show that the molecular-field results for the two sys-