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Surface Corrections to the Specific Heat of Ferromagnetic Films*

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The surface correction to the low-temperature form of the specific heat of ferromagnetic films is discussed. It is pointed out that the low-temperature form of the surface correction depends only on the curvature of the *bulk* spin-wave dispersion relation near $k=0$, provided the exchange interactions between the spins are short-ranged in a sense described in the text. Hence, the surface correction to the magnon specific heat is insensitive to changes in the exchange constants in the film surfaces. We carry out the discussion with a simple method that does not require the use of Green's functions.

I. INTRODUCTION

In the usual discussions of the thermodynamic properties of crystals, one computes the various quantities by taking the mathematical limit of allowing the volume of the crystal to become infinite. In this limit, the specific heat of the solid becomes proportional to the volume V of the crystal. For a crystal of finite size, the form of the specific heat obtained by allowing V to become infinite provides only a first approximation to the actual specific heat of the material. The first correction to the "infinite-volume" specific heat is proportional to the surface area of the crystal. One should be able to observe the surface corrections to the thermodynamic properties of crystals by performing experiments on collections of small particles, so the total surface-to-volume ratio of the sample is large.

Theoretical treatments of the surface correction to the phonon specific heat have been discussed by a number of authors.[1] More recently, the contribution to the surface specific heat from magnons in simple models of semi-infinite ferromagnets[2] and antiferromagnets[3] have appeared.

In the calculations just cited, specific models of semi-infinite crystal lattices have been employed. It is generally assumed that the layer of surface atoms is identical in structure to a similar layer of atoms in the bulk, and that the appropriate force constants are also the same in the surface layer as in the bulk. While it often does appear that the geometrical arrangement of the atoms in the surface layer is the same as in the appropriate bulk atomic planes, it is evidently true that there can be large changes in the interatomic coupling constants. Comparison between calculations of the mean-square displacement of atoms in the surface layer of crystals and low-energy electron-diffraction (LEED) measurements of the mean-square displacements indicate that the force constants in the surface layer are considerably smaller than the bulk values of the force constants.[4] Recently, the sublattice magnetization in the surface of the antiferromagnetic crystal NiO has been measured.[5] These measurements indicate that the exchange interactions between Ni spins in the surface layer are strongly reduced, compared to the bulk values.

From the preceding discussion, it is clear that the theoretical models employed so far in the study of surface corrections to thermodynamic properties of crystals are severe idealizations of the conditions realized in practice. One must explore the effect of changes in the interatomic coupling near the surface in order to obtain a complete description of the surface corrections.

The purpose of the present paper is to examine the surface specific heat of a ferromagnetic film, within the framework of a discussion that allows for changes in the exchange constants in the surface layer. In an earlier work,[2] the surface correction to the specific heat of a simple cubic ferromagnet with a (100) free surface and nearest- and next-nearest-neighbor exchange interactions was examined. It was found that the surface specific heat was proportional to the temperature T in the low-temperature region. This work confined its attention to a specific geometry and presumed the exchange constants in the surface layer assume their bulk values. Recent experimental measurements of the specific heat of small yttrium-iron-garnet (YIG) particles[6] in the liquid-helium temperature range show a contribution to the specific heat that is linear in the temperature. This portion of the specific heat has tentatively been attributed to the surface correction to the bulk specific heat. However, the magnitude of the apparent surface term is very large compared to the theoretical result of Ref. 2. One might expect that the surface specific heat could be enhanced by a softening of the exchange constants in the surface layer. However, the present work indicates that if the alteration of the exchange constants is confined to the surface layers only, then the leading term in the low-temperature sur-

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face specific heat is independent of these changes in the exchange constants. Indeed, the surface specific heat depends (in the low-temperature limit) only on the curvature of the bulk spin-wave dispersion relation near $\mathbf{k}=0$. The physical reason why the low-temperature form of the surface specific heat is insensitive to changes in the exchange interactions in the surface layer is that the spin waves that make the dominant contribution to the specific heat for $T \ll$ Curie temperature T_c have a long wavelength compared to the lattice constant. These waves are not strongly affected by the alteration of the properties of a single atomic layer of spins. Thus, it appears difficult to explain the data on the specific heat of small YIG particles in the liquid-He temperature range as a surface effect, so long as alterations in the exchange constants are confined to within a small number of atomic layers of the surface.

The spins in the surface layer of a ferromagnetic crystal may also be subjected to strong pinning fields. The presence of a pinning field inhibits the motion of spins in the surface layer, and, hence depresses the surface correction to the specific heat. The effect of a surface pinning field on the specific heat has been explored in another work.[7] We shall ignore the effect of surface anisotropy fields in the present paper.

In Sec. II we explore the nature of the spin waves in a ferromagnetic film that consists of N layers of spins. It is assumed that the range of the exchange interactions in the direction normal to one of the layers is sufficiently short so that a spin in a given layer is coupled only to spins within the same layer, and to spins within the layer just above and just below the layer in question. We discuss the surface modes, as well as the bulk waves, presuming that the exchange interactions within the surface layer may differ in value from the bulk exchange constants. In Sec. III we use the information contained in Sec. II to construct an expression for the surface specific heat. This may be done without making specific assumptions about the range of the intraplanar exchange interactions, or the geometrical arrangement of the spins within one of the N layers. Provided the exchange interactions differ from the bulk value only within the two surface layers, no detailed assumptions about the magnitude of the changes need be made. As remarked earlier, the low-temperature form of the surface specific heat (the term linear in T) may be expressed entirely in terms of the parameters appropriate to the bulk spin-wave dispersion relation for this case.

II. EFFECT OF FREE SURFACES ON SPIN-WAVE SPECTRUM OF THIN FILMS

In this section, we discuss the properties of spin waves in a ferromagnetic film constructed from N atomic layers of spins. We assume each layer lies parallel to the x-y plane, and we label the planes with the index $l_z=1, 2, \cdots, N$. We suppose the Hamiltonian has the usual Heisenberg form, with isotropic exchange interactions between ions with spin angular momentum S. Since the Hamiltonian is invariant under spin rotations, we may allow the saturation magnetization to be directed along any convenient axis. We choose to orient the saturation magnetization parallel to the z axis. Let $J_{l_z}(\delta_{\parallel},\delta_z)$ be the magnitude of the exchange interaction between a given spin located in the plane l_z, and its neighbor located at the position

$$\boldsymbol{\delta}=\boldsymbol{\delta}_{\parallel}+\hat{z}\delta_z$$

relative to the given spin, where the vector

$$\boldsymbol{\delta}_{\parallel}=\hat{x}\delta_x+\hat{y}\delta_y\,.$$

We shall assume that the exchange interactions in the film have the following properties:

(1) The range of the exchange interaction in the direction normal to the plane is one interplaner distance, i.e., the exchange constant $J_{l_z}(\boldsymbol{\delta}_{\parallel},\delta_z)=0$ unless $\delta_z=0$ or $\delta_z=\pm a$, where a is the distance between adjacent planes.

(2) The exchange interactions assume their bulk value everywhere except for the interactions between two spins within the surface layers $l_z=1$ and $l_z=N$. We denote the "bulk" values of the exchange interactions by $J(\boldsymbol{\delta}_{\parallel},\delta_z)$, and we write $J_1(\boldsymbol{\delta}_{\parallel},0)$ and $J_N(\boldsymbol{\delta}_{\parallel},0)$ in the form

$$J_1(\boldsymbol{\delta}_{\parallel},0)=J_N(\boldsymbol{\delta}_{\parallel},0)=J(\boldsymbol{\delta}_{\parallel},0)-\Delta J(\boldsymbol{\delta}_{\parallel},0)\,.$$

In this last expression, the quantity $-\Delta J(\boldsymbol{\delta}_{\parallel},0)$ is the change in the exchange interaction between two spins separated by $\boldsymbol{\delta}_{\parallel}$ within one of the surface layers. We choose the sign convention so that when $\Delta J>0$, the exchange interactions have been softened.

We now write down the equations of motion of the spin deviation operator $S^+(\mathbf{l})$ associated with the spin at the lth lattice site. The equations will be linearized in the sense of spin-wave theory by replacing the combination $S^z(\mathbf{l})S^+(\mathbf{l}')$ by $SS^+(\mathbf{l}')$. We then consider eigensolutions for which the time dependence of S^+ is given by $\exp(-i\Omega t)$. Finally, we note that for the film, the translational symmetry of the Hamiltonian in the x and y directions is maintained. Thus, we seek solutions of the Bloch form in the x and y directions. We write

$$S^+(l)=\exp(i\mathbf{k}_{\parallel}\cdot\mathbf{l}_{\parallel}-i\Omega t)s(l_z)\,, \tag{2.1}$$

where

$$\mathbf{k}_{\parallel}=\hat{x}k_x+\hat{y}k_y\,.$$

By employing Eq. (2.1) and noting the earlier remarks about the range of the exchange interactions, one may easily derive a set of N equations from which the coefficients $s(l_z)$ may be determined. We write the results in the form

$$\Omega s(l_z)=[b_0(0)+2b_1(0)-b_0(\mathbf{k}_{\parallel})]s(l_z) -b_1(\mathbf{k}_{\parallel})[s(l_z+1)+s_z(l_z-1)] \qquad l_z\neq 1, N \tag{2.2a}$$

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[7] Leonard Dobrzynski and D. L. Mills, Phys. Rev. (to be published).

and for the surface layers,

$$\Omega s(1)=[b_0(0)+b_1(0)-b_0(\mathbf{k}_{\parallel})]s(1)-[\Delta b_0(0)-\Delta b_0(\mathbf{k}_{\parallel})]s(1)-b_1(\mathbf{k}_{\parallel})s(2)\,, \quad (2.2\text{b})$$

$$\Omega s(N)=[b_0(0)+b_1(0)-b_0(\mathbf{k}_{\parallel})]s(N)-[\Delta b_0(0)-\Delta b_0(\mathbf{k}_{\parallel})]s(N)-b_1(\mathbf{k}_{\parallel})s(N-1)\,. \quad (2.2\text{c})$$

We have defined the quantities

$$b_{l_z}(\mathbf{k}_{\parallel})=S\sum_{\delta_{\parallel}} J(\boldsymbol{\delta}_{\parallel},l_za)e^{i\mathbf{k}_{\parallel}\cdot\delta_{\parallel}} \quad (2.3\text{a})$$

and

$$\Delta b_0(\mathbf{k}_{\parallel})=S\sum_{\delta_{\parallel}} \Delta J(\boldsymbol{\delta}_{\parallel},0)e^{i\mathbf{k}_{\parallel}\cdot\delta_{\parallel}}\,. \quad (2.3\text{b})$$

One has $b_{l_z}(\mathbf{k}_{\parallel})=b_{-l_z}(\mathbf{k}_{\parallel})$, and for all geometries of interest in the present work, the b_{l_z}'s will be real. For later discussions, it will be convenient to write Eqs. (2.2) in a more compact form by introducing an $N\times N$ matrix $\mathbf{D}(\mathbf{k}_{\parallel})$ with matrix elements $D_{l_zl_z'}(\mathbf{k}_{\parallel})$ so that Eqs. (2.2) become

$$\Omega s_z(l_z)=\sum_{l_z'} D_{l_zl_z'}(\mathbf{k}_{\parallel})s_z(l_z')\,. \quad (2.4)$$

We now proceed to a discussion of the properties of the solutions to Eqs. (2.2).

There are two classes of solutions to the equations of motion of interest in the present paper. These are the bulk modes, in which the spin deviation extends throughout the slab, and surface modes for which the spin deviation is localized near the surfaces. Consider the surface modes first. Let us first examine surface modes in a sample semi-infinite in extent. We imagine that $N\to\infty$, while the plane $l_z=1$ remains in the x-y plane. Then consider a solution of Eqs. (2.2) of the form

$$s(l_z)=Ce^{-qal_z}. \quad (2.5)$$

Substitution of this form into Eq. (2.2a) requires the frequency Ω of the mode be given by

$$\Omega=b_0(0)+2b_1(0)-b_0(\mathbf{k}_{\parallel})-2b_1(\mathbf{k}_{\parallel})\cosh(qa)\,. \quad (2.6)$$

Upon inserting Eq. (2.5) into Eq. (2.2b), we obtain a second relation between Ω and the attenuation constant q. Elimination of the frequency then yields the result

$$e^{-qa}=\frac{b_1(\mathbf{k}_{\parallel})}{b_1(0)+[\Delta b_0(0)-\Delta b_0(\mathbf{k}_{\parallel})]}\equiv\gamma(\mathbf{k}_{\parallel})\,. \quad (2.7)$$

For surface spin waves to exist, the quantity γ must be less than unity in value. We shall give some brief examples of situations were this occurs in the discussions below. For the moment, we assume $\gamma<1$. The frequency of the surface mode is thus

$$\Omega_s(\mathbf{k}_{\parallel})=b_0(0)+2b_1(0)-b_0(\mathbf{k}_{\parallel})(\gamma^{-1}+\gamma)\,. \quad (2.8)$$

Note that in the present system the bulk spin-wave dispersion relation $\Omega_B(\mathbf{k}_{\parallel},k_z)$ may be written in the form

$$\Omega_B(\mathbf{k}_{\parallel},k_z)=b_0(0)+2b_1(0)-b_0(\mathbf{k}_{\parallel})-2b_1(\mathbf{k}_{\parallel})\cos(k_za)\,. \quad (2.9)$$

For a given value of $\mathbf{k}_{\parallel}$, the lowest bulk spin-wave frequency is obtained by setting $k_z=0$ in Eq. (2.9). The difference between the surface mode frequency and the frequency of the bottom of the bulk band associated with a given value of $\mathbf{k}_{\parallel}$ is thus

$$\Omega_B(\mathbf{k}_{\parallel},0)-\Omega_s(\mathbf{k}_{\parallel})=b_1(\mathbf{k}_{\parallel})(1-\gamma)^2/\gamma\,. \quad (2.10)$$

In the study of the low-temperature specific heat, we shall be interested in modes with long wavelength compared to the lattice constant. The quantity $\gamma\to1$ in the limit as $\mathbf{k}_{\parallel}\to0$. Thus, when $|\mathbf{k}_{\parallel}a|\ll1$, one can expand γ in a power series in $\mathbf{k}_{\parallel}$. The leading term will be quadratic in $\mathbf{k}_{\parallel}$:

$$\gamma(\mathbf{k}_{\parallel})=1-(k_{\parallel}a)^2f(\hat{k}_{\parallel})+\cdots,$$

where $f(\hat{k}_{\parallel})$ is a function only of the direction of $\mathbf{k}_{\parallel}$. Thus from Eq. (2.10), one sees quite generally that the frequency of the surface mode differs from $\Omega_B(\mathbf{k}_{\parallel},0)$ only by terms of order $(k_{\parallel}a)$.[4] This feature of the surface-magnon dispersion relation has been noted in earlier studies of specific geometries.[8,9] We shall find it useful in Sec. III to use the fact that to lowest order in $(k_{\parallel}a)$ one has

$$\Omega_s(\mathbf{k}_{\parallel})=\Omega_B(\mathbf{k}_{\parallel},0)\,.$$

Let us turn to brief discussions of specific geometries to illustrate the points made in the preceding discussion.

(i) The simple cubic ferromagnet with a (100) surface, nearest-neighbor exchange J_1, and next-nearest exchange J_2, with exchange constants equal to the bulk value everywhere: This is the case considered in Ref. 8. For this case, one has

$$\Delta b_0(\mathbf{k}_{\parallel})\equiv0\,,$$

$$b_1(\mathbf{k}_{\parallel})=J_1+2J_2(\cos k_xa+\cos k_ya)\,,$$

and

$$\gamma=b_1(\mathbf{k}_{\parallel})/b_1(0)\,.$$

Clearly, one has $\gamma<1$ for all k_x and k_y so one has a surface mode present, provided $J_2\neq0$. One finds (note that our definition of the exchange constants differs from that of Ref. 8 by a factor of 2)

$$\Omega_B(\mathbf{k}_{\parallel},0)-\Omega_S(\mathbf{k}_{\parallel})=16S[J_2^2/(J_1+4J_2)](\sin^2\tfrac{1}{2}k_xa+\sin^2\tfrac{1}{2}k_ya)^2\,.$$

(ii) The simple cubic ferromagnet with a (110) surface, nearest-neighbor exchange J_1 only, with no changes in the exchange constants: For this geometry, one "breaks" two bonds non-normal to the surface in form-

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[8] R. F. Wallis, A. A. Maradudin, I. P. Ipatova, and A. A. Klochikhin, Solid State Commun. **5**, 89 (1967).

[9] B. N. Filipov, Fiz. Tverd. Tela **7**, (1966) [English transl.: Soviet Phys.—Solid State **9**, 1098 (1967)].

ing the film surface. Then we find

$$\gamma(\mathbf{k}_{\parallel})=\cos(ak_x/\sqrt{2})$$

and

$$\Omega_B(\mathbf{k}_{\parallel},0)-\Omega_S(\mathbf{k}_{\parallel})=16S^2J_1{}^2\sin^4(k_xa/2\sqrt{2})\,.$$

The gap between the bulk manifold and the surface branch is highly anisotropic in this case.

(iii) The simple cubic ferromagnet with a (100) surface, nearest-neighbor exchange only, with exchange constants in the surface layer reduced by the amount ΔJ: This geometry has been considered by Fillipov.[9] One finds for this case that

$$\gamma(\mathbf{k}_{\parallel})=\{1+2(\Delta J/J)[2-\cos k_xa-\cos k_ya]^{-1}\}\,.$$

Thus, for all k_x and k_y, one has $\gamma<1$, provided that the exchange interactions in the surface layer are softened ($\Delta J>0$). Also,

$$\Omega_B(\mathbf{k}_{\parallel},0)-\Omega_S(\mathbf{k}_{\parallel})$$
$$=16S\Delta J\frac{(\sin^2\tfrac{1}{2}k_xa+\sin^2\tfrac{1}{2}k_ya)^2}{1+4(\Delta J/J)(\sin^2\tfrac{1}{2}k_xa+\sin^2\tfrac{1}{2}k_ya)}\,.$$

From the above examples, one sees that the present formulation of the surface-mode problem allows one to easily determine the dispersion relation and attenuation length for a variety of geometries, provided the exchange constants differ from their bulk value only in the surface layer, and provided the range of the exchange interactions in the direction normal to the surfaces has a sufficiently short range. As we mentioned earlier, one sees from the examples that in the long-wavelength limit, the surface branch is depressed below the bulk value by an amount proportional to $(k_{\parallel}a)^4$. Also, for surface modes to split off below the bulk manifold associated with a given value of $\mathbf{k}_{\parallel}$, either one must "sever" bonds non-normal to the surface in forming the surface layer [examples (i) and (ii)] or one must soften the exchange interactions in the region of the surface [example (iii)].

Next we consider the bulk excitations of a film of finite thickness (i.e., spin-wave modes in which the spin deviation extends throughout the film). In addition to the surface solutions just discussed, the equations of motion admit bulk solutions in which

$$s(l_z)=\alpha e^{ik_zal_z}+\beta e^{-ik_zal_z} \tag{2.11}$$

for particular values of k_z. Insertion of this form into Eq. (2.2a) shows that the eigenfrequency $\Omega_B(\mathbf{k}_{\parallel},k_z)$ is that given in Eq. (2.9). One determines the allowed values of k_z, as well as the ratio α/β, by requiring the function $s(l_z)$ to satisfy the equations of motion for the spins in the surface layers ($l_z=1$ and $l_z=N$). Consider first Eq. (2.2b), which describes the motion of the spins in the lower surface layer at $l_z=1$. Upon employing the expression in Eq. (2.9) for the frequency $\Omega_B(\mathbf{k}_{\parallel},k_z)$ with Eq. (2.2a), one finds

$$[1-2\gamma(\mathbf{k}_{\parallel})\cos(k_za)]s(1)+\gamma(\mathbf{k}_{\parallel})s(2)=0\,, \tag{2.12}$$

where the quantity $\gamma(\mathbf{k}_{\parallel})$ has been introduced in Eq. (2.7). After insertion of Eq. (2.11) into Eq. (2.12), we find

$$\frac{\alpha}{\beta}=-\frac{\gamma(\mathbf{k}_{\parallel})-e^{-ik_za}}{\gamma(\mathbf{k}_{\parallel})-e^{+ik_za}}\,. \tag{2.13}$$

If Eq. (2.2c) is rearranged in the fashion just described, one obtains

$$[1-2\gamma(\mathbf{k}_{\parallel})\cos(k_za)]s(N)+\gamma(\mathbf{k}_{\parallel})s(N-1)=0\,.$$

This equation yields a second condition on the ratio of α to β:

$$\frac{\alpha}{\beta}=-e^{-i2Nk_za}\frac{1-\gamma(\mathbf{k}_{\parallel})e^{-ik_za}}{1-\gamma(\mathbf{k}_{\parallel})e^{+ik_za}}\,. \tag{2.14}$$

The values of k_z permitted by the boundary conditions for a given value of the wave may be obtained by equating the right-hand sides of Eqs. (2.13) and (2.14), and then solving the resulting equation for k_z. We find

$$e^{+i2Nk_za}=\frac{2\gamma(\mathbf{k}_{\parallel})-e^{ik_za}-\gamma^2(\mathbf{k}_{\parallel})e^{-ik_za}}{2\gamma(\mathbf{k}_{\parallel})-e^{-ik_za}-\gamma^2(\mathbf{k}_{\parallel})e^{ik_za}}\,. \tag{2.15}$$

We introduce a phase angle $\varphi(\mathbf{k}_{\parallel},k_z)$ as follows:

$$2\gamma(\mathbf{k}_{\parallel})-e^{ik_za}-\gamma^2(\mathbf{k}_{\parallel})e^{-ik_za}=r(\mathbf{k}_{\parallel},k_z)e^{-i\varphi_B(\mathbf{k}_{\parallel},k_z)}\,.$$

Explicitly, one has

$$\varphi_B(\mathbf{k}_{\parallel},k_z)$$
$$=\tan^{-1}\left(\frac{\sin(k_za)[1-\gamma^2(\mathbf{k}_{\parallel})]}{2\gamma(\mathbf{k}_{\parallel})-[1+\gamma^2(\mathbf{k}_{\parallel})]\cos(k_za)}\right)\,. \tag{2.16}$$

Equation (2.15) then becomes

$$e^{i2Nk_za}=e^{-i2\varphi_B(\mathbf{k}_{\parallel},k_z)}\,.$$

The allowed values of k_z, which we denote by $k_z(n)$, are then the solutions of the equation

$$ak_z(n)=(\pi/N)n-N^{-1}\varphi_B[\mathbf{k}_{\parallel},k_z(n)]\,,\qquad n=0,\,1,\,2,\,\cdots \tag{2.17}$$

where the angle φ_B is defined above.

We shall base our study of the surface specific heat presented in Sec. III on the properties of the surface modes discussed earlier in the section, and on the distribution of the allowed values of k_z determined by solving Eq. (2.17). Note one point before proceeding. Suppose we consider a solid of infinite extent, constructed by placing atomic planes parallel to each other. Let us then study the excitation spectrum of the solid by applying periodic boundary conditions in the z directions, i.e., we require

$$s(l_z)=s(l_z+N)\,.$$

Then the only solutions of the equations of motion are bulk solutions, with $k_za=n\pi/N$. The information about the effect of forming a real surface, with exchange constants altered in the surface layer, and spins in the surface coupled to fewer neighboring spins than spins in the bulk, is then contained in the surface spin-wave spectrum, and in the deviation in allowed k_z values for bulk waves away from the values $n\pi/N$ appropriate to periodic boundary conditions applied in the z direction. The latter information is thus contained in the angle $\varphi_B(\mathbf{k}_{\|},k_z)$ defined in Eq. (2.16),

III. SURFACE CORRECTIONS TO SPECIFIC HEAT OF FILM

In this section, we consider the magnon contribution to the specific heat of the film discussed in Sec. II. It has been pointed out[7] that when the thickness of the film is large compared to the wavelength of a spin wave with energy k_BT, then the specific heat may be written as a sum of two terms, one proportional to the volume and a correction term proportional to the surface area. Suppose that we consider a large crystal in which the spin-wave dispersion relation assumes the long-wavelength form

$$\Omega_B(\mathbf{k}_{\|},k_z)=D_xk_x^2+D_y^2k_y^2+D_zk_z^2. \qquad (3.1)$$

Then the low-temperature form of the volume specific heat is given by the well-known expression[10]

$$C_v(T)=V\frac{15\zeta(\frac{5}{2})}{32\pi^{3/2}}k_B\frac{(k_BT)^{3/2}}{(D_xD_yD_z)^{1/2}}. \qquad (3.2)$$

Now let us consider the form of the specific heat of a film with the properties described in Sec. II. We shall compute the specific heat by first calculating the low-temperature form of the magnon contribution to the internal energy of the film, and then differentiating this quantity with respect to temperature. If one considers a material with excitations that obey Bose-Einstein statistics, then the internal energy U of the material is given by the expression

$$U(T)=\hbar\sum_{\alpha}\Omega_\alpha n(\Omega_\alpha),$$

where the symbol α denotes the set of quantum numbers of the mode, and

$$n(\Omega)=[e^{\hbar\beta\Omega_\alpha}-1]^{-1} \quad\text{with}\quad \beta=(k_BT)^{-1}.$$

In Sec. II, we noticed that there are two classes of excitations in the film: the surface magnons and bulk modes in which the spin deviation extends throughout the slab. First consider the contribution to the specific heat from the surface modes. For a given value of the wave vector $\mathbf{k}_{\|}$ parallel to the surface, one has two surface modes. In the limit of large film thickness, one mode is associated with each surface, and the modes are degenerate. We suppose the film is sufficiently thick so that the modes may be presumed to be degenerate. Indeed, it is easy to see that the specific heat may be decomposed into a bulk and a surface term only in this limit. The contribution of the surface magnons to the internal energy is thus given by the quantity $U_s(T)$, where

$$U_s(T)=2\hbar\sum_{k_xk_y}\Omega_s(\mathbf{k}_{\|})n[\Omega_s(\mathbf{k}_{\|})], \qquad (3.3)$$

where the sum over k_x and k_y ranges over the appropriate two-dimensional Brillouin zone. To compute the low-temperature limiting form of $U_s(T)$, one may replace $\Omega_s(\mathbf{k}_{\|})$ by its long-wavelength limit, then convert the sums over k_x and k_y to integrals and extend the upper limits of integration to infinity. In Sec. II, we noticed quite generally that in the long-wavelength limit

$$\Omega_s(\mathbf{k}_{\|})=\Omega_B(\mathbf{k}_{\|},0)+\text{terms of order }(k_{\|}a)^4.$$

Thus, in Eq. (3.3), we replace $\Omega_s(\mathbf{k}_{\|})$ by $\Omega_B(\mathbf{k}_{\|},0)$. We assume the the surface is normal to the z axis, and use the long-wavelength form of $\Omega_B(\mathbf{k}_{\|},0)$ given in Eq. (3.1). If the total surface area of the film is S, one then obtains

$$U_S(T)=\frac{S}{4\pi}\zeta(2)\frac{(k_BT)^2}{\hbar(D_xD_y)^{1/2}} \qquad (3.4)$$

for the low-temperature form of the surface spin-wave contribution to the internal energy. The surface magnon contribution to the specific heat is thus

$$C_S(T)=\frac{S}{2\pi}\zeta(2)k_B\frac{k_BT}{\hbar(D_xD_y)^{1/2}}. \qquad (3.5)$$

We turn next to the contribution to the specific heat from the bulk modes. For the model films considered, the dispersion relation of the bulk modes is given in Eq. (2.9), where, as we have seen, only certain discreet values of k_z are allowed by the boundary conditions. We denote the allowed values of the frequency by $\Omega_B[\mathbf{k}_{\|},k_z(n)]$, where the integer n labels the allowed values of k_z. The bulk-mode contribution to the specific heat is thus

$$U_B(T)=\hbar\sum_{k_xk_y}\sum_{n}\Omega_B[\mathbf{k}_{\|},k_z(n)]n\{\Omega_B[\mathbf{k}_{\|},k_z(n)]\}.$$

When the film is sufficiently thick, the sum over n may be replaced by an integration, to a very good approximation:

$$\begin{aligned}U_B(T)&\\ &\cong\hbar\sum_{k_xk_y}\int_0^\infty dn\,\Omega_B[\mathbf{k}_{\|},k_z(n)]n[\Omega_B(\mathbf{k}_{\|},k_z)]\\ &=\hbar\sum_{k_xk_y}\int_0^\infty dk_z\left(\frac{dn}{dk_z}\right)\Omega_B(\mathbf{k}_{\|},k_z)n[\Omega_B(\mathbf{k}_{\|},k_z)]. \qquad (3.6)\end{aligned}$$

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[10] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 55.

In this last step, we have converted the integral over n to an integral over k_z. Note that the quantity dn/dk_z is a function of $\mathbf{k}_{\parallel}$. It will be useful to introduce a quantity $\rho_B(\mathbf{k}_{\parallel},\Omega)$ defined by

$$\rho_B(\mathbf{k}_{\parallel},\Omega)=\int_0^{\infty} dk_z\left(\frac{dn}{dk_z}\right)\delta[\Omega-\Omega_B(\mathbf{k}_{\parallel},k_z)]. \tag{3.7}$$

Equation (3.6) then becomes

$$U_B(T)=\sum_{k_xk_y}\hbar\int_0^{\infty} d\Omega\;\Omega n(\Omega)\rho_B(\mathbf{k}_{\parallel},\Omega). \tag{3.8}$$

From Eq. (3.8), it is apparent that the quantity $\rho_B(\mathbf{k}_{\parallel},\Omega)d\Omega$ may be interpreted as the number of bulk excitations in the film with wave vector $\mathbf{k}_{\parallel}$ parallel to the surface and with frequency between Ω and $\Omega+d\Omega$. This will prove to be a useful quantity in the discussion that follows.

A convenient expression for dk_z/dn may be obtained from Eq. (2.17). Differentiation of each side of this equation gives

$$\begin{aligned} a\frac{dk_z}{dn}&=\frac{\pi}{N}-\frac{1}{N}\frac{\partial\varphi_B}{\partial n}(\mathbf{k}_{\parallel},k_z(n))\\ &=\frac{\pi}{N}-\frac{1}{N}\frac{\partial\varphi_B}{\partial k_z}(\mathbf{k}_{\parallel},k_z)\frac{dk_z}{dn}. \end{aligned}$$

Thus, if we let $L=Na$ denote the thickness of the film

$$\frac{dn}{dk_z}=\frac{L}{\pi}+\frac{1}{\pi}\frac{\partial\varphi_B}{\partial k_z}(\mathbf{k}_{\parallel},k_z),$$

then for the density of states $\rho_B(\mathbf{k}_{\parallel},\Omega)$ we have

$$\begin{aligned} \rho_B(\mathbf{k}_{\parallel},\Omega)&=\frac{L}{\pi}\left(\frac{\partial\Omega}{\partial k_z}\right)^{-1}+\frac{1}{\pi}\int_0^{\infty} dk_z\frac{\partial\varphi_B}{\partial k_z}\delta[\Omega-\Omega(\mathbf{k}_{\parallel},k_z)]\\ &=\frac{L}{\pi}\left(\frac{\partial\Omega}{\partial k_z}\right)^{-1}+\frac{1}{\pi}\left(\frac{\partial k_z}{\partial\Omega}\right)\frac{\partial\varphi_B}{dk_z}\\ &=\rho_B{}^{(0)}(\mathbf{k}_{\parallel},\Omega)+\Delta\rho_B(\mathbf{k}_{\parallel},\Omega). \end{aligned}$$

In this last expression, we define

$$\rho_B{}^{(0)}(\mathbf{k}_{\parallel},\Omega)=\frac{L}{\pi}\left(\frac{\partial\Omega}{\partial k_z}\right)^{-1} \tag{3.9a}$$

and

$$\Delta\rho_B(\mathbf{k}_{\parallel},\Omega)=\frac{1}{\pi}\left(\frac{\partial k_z}{\partial\Omega}\right)\frac{\partial\varphi_B}{\partial k_z} \tag{3.9b}$$

$$\equiv\frac{1}{\pi}\frac{\partial\varphi_B}{\partial\Omega}, \tag{3.9c}$$

where in the last step we note that φ may be expressed as a function of Ω by eliminating k_z through Eq. (2.9).

The contribution $\rho_B{}^{(0)}$ to the density of states defined in Eq. (3.9a) is just the density of states of a solid of N atomic layers, with periodic boundary conditions imposed in the z direction. The second term $\Delta\rho_B$ contains the information concerning the change in density of states resulting from the fact that the exchange constants in the layer may differ from their bulk values, and that spins in the surface are coupled to fewer neighbors than spins in the bulk. To verify the first statement, one may insert $\rho_B{}^{(0)}(\mathbf{k}_{\parallel},\Omega)$ into Eq. (3.8):

$$\begin{aligned} U_B{}^{(0)}(T)&=\frac{\hbar L}{\pi}\sum_{k_xk_y}\int_0^{\infty} d\Omega\;\Omega n(\Omega)\left(\frac{\partial\Omega}{\partial k_z}\right)^{-1}\\ &\equiv\frac{\hbar L}{\pi}\sum_{k_xk_y}\int_0^{\pi/a} dk_z\;\Omega_B(\mathbf{k}_{\parallel},k_z)n[\Omega_B(\mathbf{k}_{\parallel},k_z)]\\ &=\frac{\hbar L}{2\pi}\sum_{k_xk_y}\int_{-\pi/a}^{+\pi/a} dk_z\;\Omega_B(\mathbf{k}_{\parallel},k_z)n[\Omega_B(\mathbf{k}_{\parallel},k_z)]. \end{aligned}$$

To make the significance of the last statement clear, we can convert the integral over k_z back to a sum using the rule

$$\frac{L}{2\pi}\int_{-\pi la}^{+\pi/a} dk_z\rightarrow\sum_{k_z}.$$

Thus,

$$U_B{}^{(0)}(T)=\hbar\sum_{k_xk_yk_z}\Omega_B(\mathbf{k}_{\parallel},k_z)n[\Omega_B(\mathbf{k}_{\parallel},k_z)].$$

It is clear that $U_B{}^{(0)}(T)$ represents the contribution to the internal energy proportional to the volume that one encounters in the standard discussions of spin-wave theory. If the low-temperature form of $U_B{}^{(0)}(T)$ is computed, and the specific heat is obtained from its temperature derivative, the well-known result of Eq. (3.2) results.

We now turn to the contribution to $\Delta\rho_B(\mathbf{k}_{\parallel},\Omega)$ exhibited in Eq. (3.9c). It is now clear that the change in density of states coming from $\Delta\rho_B$ is associated with alteration of the frequency distribution of bulk modes that results from the change in environment felt by spins in the surfaces.

From Eq. (3.9c), we see that the change in density of states inside the bulk continuum is given by

$$\Delta\rho_B(\mathbf{k}_{\parallel},\Omega)=\frac{1}{\pi}\frac{\partial\varphi_B}{\partial\Omega}, \tag{3.10}$$

where we recall from Sec. II that

$$\begin{aligned} &\varphi_B(\mathbf{k}_{\parallel},k_z)\\ &\quad=\tan^{-1}\left(\frac{\sin(k_za)\;[1-\gamma^2(\mathbf{k}_{\parallel})]}{2\gamma(\mathbf{k}_{\parallel})-[1+\gamma^2(\mathbf{k}_{\parallel})]\cos(k_za)}\right). \end{aligned} \tag{3.11}$$

It will be convenient to write the frequencies of the bulk modes in the form

$$\Omega(\mathbf{k}_{\parallel},k_z)=A(\mathbf{k}_{\parallel})-B(\mathbf{k}_{\parallel})\cos(k_z a)\,, \tag{3.12}$$

where the coefficients A and B defined in Eq. (3.12) may be obtained from Eq. (2.9).

We have demonstrated that Eq. (3.10) is valid inside the bulk frequencies, i.e., for $\Omega_m(\mathbf{k}_{\parallel})<\Omega<\Omega_M(\mathbf{k}_{\parallel})$, where $\Omega_m(\mathbf{k}_{\parallel})=A(\mathbf{k}_{\parallel})-B(\mathbf{k}_{\parallel})$ is the minimum bulk spin-wave frequency associated with a given value of $\mathbf{k}_{\parallel}$, and $\Omega_M(\mathbf{k}_{\parallel})=A(\mathbf{k}_{\parallel})+B(\mathbf{k}_{\parallel})$ is the maximum bulk frequency for a given $\mathbf{k}_{\parallel}$. We now extend the definition of the phase angle φ_B outside the open interval $[\Omega_m,\Omega_M]$ by writing $\Delta\rho_B(\mathbf{k}_{\parallel},\Omega)$ in the form of Eq. (3.10) for all frequencies from zero to infinity. This may be done by noting that the phase angle φ must be a constant [and hence $\partial\varphi/\partial\Omega=0$] in regions where the density of states is zero. Furthermore, we see that φ must have the following two properties:

(i) There must be a jump of 2π in φ at the surface spin-wave frequency $\Omega_s(\mathbf{k}_{\parallel})$. This means the change in density of states will have a δ-function singularity, with a weight corresponding to two states.

(ii) In the open interval $[\Omega_m,\Omega_M]$, φ must exhibit the frequency dependence of that deduced from the right-hand side of Eq. (3.11).

We shall choose φ so that $\varphi\equiv 0$ in the interval from $\Omega=0$ to $\Omega_s(\mathbf{k}_{\parallel})$, where $\Delta\rho$ must vanish. Then the most general form possible for the phase angle that enters the formula for the density of states is the following:

$$\begin{aligned}\varphi(\mathbf{k}_{\parallel},\Omega)&=0, \quad 0<\Omega\leq\Omega_s(\mathbf{k}_{\parallel})\\ &=2\pi, \quad \Omega_s(\mathbf{k}_{\parallel})<\Omega\leq\Omega_m(\mathbf{k}_{\parallel})\\ &=\varphi_1+\varphi_B(\mathbf{k}_{\parallel},\Omega), \quad \Omega_m(\mathbf{k}_{\parallel})<\Omega\leq\Omega_M(\mathbf{k}_{\parallel})\\ &=\varphi_2, \quad \Omega_M(\mathbf{k}_{\parallel})<\Omega<\infty\,.\end{aligned} \tag{3.13}$$

We have introduced two arbitrary constants φ_1 and φ_2 in Eq. (3.13), and $\varphi_B(\mathbf{k}_{\parallel},\Omega)$ is the phase angle defined in Eq. (3.11), with k_z eliminated in favor of Ω by using Eq. (3.12). Until this point, the expression in Eq. (3.13) with the two arbitrary constants φ_1 and φ_2 is consistent with the existing constants that have been placed on the density of states. In a moment, we shall consider additional constraints placed on φ by two sum rules. These sum rules will allow φ_1 and φ_2 to be uniquely determined.

To appreciate the importance of the precise value of φ_1 and φ_2, let us consider the variation of φ_B in the region $[\Omega_m,\Omega_M]$. At the bottom of the bulk band ($k_z=0$), the argument of the $\tan^{-1}$ on the right-hand side of Eq. (3.11) vanishes. This quantity also vanishes at the top of the band ($k_z a=\pi$). Furthermore, the numerator is positive everywhere. The denominator has a single zero when $k_z=k_z^0$, where

$$\cos k_z^0 a=(2\gamma)^{-1}(1+\gamma^2)<1\,.$$

For $k_z<k_z^0$, the denominator is negative, while it is positive for $k_z>k_z^0$. For definiteness, we choose the branch of the $\tan^{-1}$ function so that $\varphi_B(\mathbf{k}_{\parallel},\,k_z=0)=0$. Then as k_z increases from 0 to π/a, the angle φ_B becomes negative, passing through $-\frac{1}{2}\pi$ when $k_z=k_z^{(c)}$, and becoming equal to $-\pi$ when $k_z=\pi/a$. With this information in hand, one may see that for general values of φ_1 and φ_2, $\varphi(\mathbf{k}_{\parallel},\Omega)$ may have jump discontinuities at Ω_m and Ω_M. These jump discontinuities contribute δ functions to the change in density of states. Since the strength of the δ functions at Ω_m and Ω_M depend on φ_1 and φ_2, we must pin down the value of these quantities in an unambiguous fashion.

Let us consider the eigenvalue equation studied in Sec. II. Equation (2.4) will be a convenient form for our present purposes. These equations form a set of $N\times N$ linear eigenvalue equations. For a given value of $\mathbf{k}_{\parallel}$, one thus must have precisely N eigenvalues. Thus, if $\rho(\mathbf{k}_{\parallel},\Omega)$ is the density of normal modes associated with a given value of $\mathbf{k}_{\parallel}$, we must have

$$N=\int_0^\infty d\Omega\,\rho(\mathbf{k}_{\parallel},\Omega)$$

for all $\mathbf{k}_{\parallel}$. We write

$$\rho(\mathbf{k}_{\parallel},\Omega)=\rho_B^{(0)}(\mathbf{k}_{\parallel},\Omega)+\frac{1}{\pi}\frac{\partial\varphi}{\partial\Omega}(\mathbf{k}_{\parallel},\Omega)\,,$$

where $\rho_B^0(\mathbf{k}_{\parallel},\Omega)$ is given by Eq. (3.9a), and is nonzero only in the interval from Ω_m to Ω_M. Noting that $L=Na$, we have

$$\begin{aligned}N&=\frac{Na}{\pi}\int_{\Omega_m}^{\Omega_M}d\Omega\left(\frac{\partial k_z}{\partial\Omega}\right)+\frac{1}{\pi}\int_0^\infty d\Omega\frac{\partial\varphi}{\partial\Omega}\\ &=\frac{Na}{\pi}\int_0^{\pi/a}dk_z+\frac{1}{\pi}[\varphi(\mathbf{k}_{\parallel},\,\Omega=\infty)-\varphi(\mathbf{k}_{\parallel},\,\Omega=0)]\\ &=N+(1/\pi)\varphi_2\,,\end{aligned}$$

where φ_2 has been introduced in Eq. (3.13). Hence, we need

$$\varphi_2\equiv 0$$

for this last result to be an identity.

We need one more constraint to fix the value of φ_1. A second sum rule on the perturbed density of states may be obtained from Eqs. (2.4). Let $\Omega_\alpha(\mathbf{k}_{\parallel})$ denote one of the N eigenvalues of Eq. (2.4). Then

$$\sum_\alpha \Omega_\alpha(\mathbf{k}_{\parallel})=\int_0^\infty d\Omega\,\Omega\rho(\mathbf{k}_{\parallel},\Omega)=\mathrm{Tr}\mathbf{D}(\mathbf{k}_{\parallel})=\sum_{l_z=1}^{N}D_{l_z l_z}(\mathbf{k}_{\parallel})\,.$$

The trace of the matrix $\mathbf{D}(\mathbf{k}_{\parallel})$ may be computed explicitly by making use of Eqs. (2.2). One has

$$\begin{aligned}\mathrm{Tr}\mathbf{D}(\mathbf{k}_{\parallel})&=N[b_0(0)+2b_1(0)-b_0(\mathbf{k}_{\parallel})]\\ &\qquad-2[b_1(0)+\Delta b_0(0)-\Delta b_0(k_{\parallel})]\\ &\equiv NA(\mathbf{k}_{\parallel})-B(\mathbf{k}_{\parallel})/\gamma(\mathbf{k}_{\parallel})\,.\end{aligned}$$

We have employed the definitions of the quantities $A(\mathbf{k}_{\parallel})$ and $B(\mathbf{k}_{\parallel})$ introduced in Eq. (3.12), and the quantity $\gamma(\mathbf{k}_{\parallel})$ defined in Eq. (2.7). A short calculation shows that

$$\int_{\Omega_m}^{\Omega_M} d\Omega\,\Omega\rho_B{}^0(\mathbf{k}_{\parallel},\Omega)=NA(\mathbf{k}_{\parallel})\,.$$

We thus obtain a second constraint on the angle φ:

$$\frac{1}{\pi}\int_0^{\infty} d\Omega\,\Omega\frac{\partial\varphi}{\partial\Omega}(\mathbf{k}_{\parallel},\Omega)=-\frac{B(\mathbf{k}_{\parallel})}{\gamma(\mathbf{k}_{\parallel})}\,. \tag{3.14}$$

The integral on the left-hand side of Eq. (3.14) may be evaluated explicitly. This calculation is presented in the Appendix. From Eq. (A3) of the Appendix, one has

$$\int_0^{\infty}\frac{d\Omega}{\pi}\Omega\frac{\partial\varphi}{\partial\Omega}(\mathbf{k}_{\parallel},\Omega)=-\frac{B(\mathbf{k}_{\parallel})}{\gamma(\mathbf{k}_{\parallel})}\left[1+\frac{2\gamma(\mathbf{k}_{\parallel})}{\pi}\left(\varphi_1-\frac{3\pi}{2}\right)\right]. \tag{3.15}$$

Upon equating the right-hand sides of Eqs. (3.14) and (3.15), we have

$$\varphi_1=\tfrac{3}{2}\pi.$$

We have thus determined the frequency variation of the phase angle $\varphi(\mathbf{k}_{\parallel},\Omega)$, including the magnitude of the jump at the maximum and minimum frequencies of the bulk continuum. The angle $\varphi(\mathbf{k}_{\parallel},\Omega)$ has a jump of magnitude $-\frac{1}{2}\pi$ at $\Omega=\Omega_m(\mathbf{k}_{\parallel})$ and $\Omega=\Omega_M(\mathbf{k}_{\parallel})$. We may now proceed with the calculation of the change in specific heat that results from the redistribution of the bulk eigenvalues.

The change in internal energy from redistribution in frequency of the bulk modes is thus

$$\Delta U_B(T)=\hbar\sum_{k_xk_y}\int_{\Omega_S(k_{\parallel})+}^{\Omega_M(\mathbf{k}_{\parallel})}\frac{d\Omega}{\pi}\frac{\partial\varphi}{\partial\Omega}(\mathbf{k}_{\parallel},\Omega)\Omega n(\Omega)\,. \tag{3.16}$$

There are two contributions to Eq. (3.16). One comes from the jump discontinuity of $\varphi(\mathbf{k}_{\parallel},\Omega)$ at $\Omega=\Omega_m(\mathbf{k}_{\parallel})$, and the second has its origin in the frequency variation of $\varphi(\mathbf{k}_{\parallel},\Omega)$ in the bulk continuum from $\Omega_m(\mathbf{k}_{\parallel})$ to $\Omega_M(\mathbf{k}_{\parallel})$. Upon noticing that $\varphi(\mathbf{k}_{\parallel},\Omega)$ has a jump discontinuity of $-\frac{1}{2}\pi$ at $\Omega_m(\mathbf{k}_{\parallel})$, the quantity $\partial\varphi(k_{\parallel},\Omega)/\partial\Omega$ contains the term $-\frac{1}{2}\pi\delta[\Omega-\Omega_m(\mathbf{k}_{\parallel})]$. Thus, the first contribution to $\Delta U_B(T)$ is

$$\Delta U_B{}^{(1)}(T)=-\frac{\hbar}{2}\sum_{k_xk_y}\Omega_m(\mathbf{k}_{\parallel})n[\Omega_m(\mathbf{k}_{\parallel})]. \tag{3.17}$$

If one compares this expression with Eq. (3.3), one sees that in the low-temperature limit, where one may replace $\Omega_s(\mathbf{k}_{\parallel})$ by $\Omega_m(\mathbf{k}_{\parallel})$, the contribution in Eq. (3.17) just cancels 25% of the surface-wave contribution to the specific heat. Thus,

$$U_s(T)+\Delta U_B{}^{(1)}(T)=\frac{3S}{16\pi}\zeta(2)\frac{(k_BT)^2}{\hbar(D_xD_y)^{1/2}}$$

and

$$C_s(T)+\Delta C_B{}^{(1)}(T)=\frac{3S}{8\pi}\zeta(2)k_B\frac{k_BT}{\hbar(D_xD_y)^{1/2}}\,. \tag{3.18}$$

Finally, we consider the contribution from inside the bulk spin-wave continuum. Denoting this contribution by $\Delta U_B{}^{(2)}(T)$,

$$\Delta U_B{}^{(2)}=\hbar\sum_{k_xk_y}\int_{\Omega_m(k_{\parallel})}^{\Omega_M(k_{\parallel})}\frac{d\Omega}{\pi}\frac{\partial\varphi_B}{\partial\Omega}(k_{\parallel},\Omega)\Omega n(\Omega)\,, \tag{3.19}$$

where $\varphi_B(\mathbf{k}_{\parallel},\Omega)$ is defined in Eq. (3.11). In what follows, we shall only consider the low-temperature form of $\Delta U_B{}^{(2)}(T)$. Consequently, the upper limit of the integral in Eq. (3.19) eventually will be replaced by infinity. We first convert the integral in Eq. (3.19) from an integral over frequency to an integral over the variable $\theta_z=k_za$. We recall Eq. (3.12) and write

$$\Delta U_B{}^{(2)}=\frac{\hbar}{\pi}\sum_{k_xk_y}\int_0^{\pi} d\theta_z\frac{\partial\varphi_B}{\partial\theta_z}(\mathbf{k}_{\parallel},\theta_z)$$
$$\times[A(\mathbf{k}_{\parallel})-B(\mathbf{k}_{\parallel})\cos\theta_z]n[A(\mathbf{k}_{\parallel})-B(\mathbf{k}_{\parallel})\cos\theta_z].$$

In the discussion below, we shall omit reference to $\mathbf{k}_{\parallel}$ in the various quantities, for compactness. After computing the derivative $\partial\varphi_B/\partial\theta_z$, one has

$$\Delta U_B{}^{(2)}=-\frac{\hbar}{\pi}\sum_{k_xk_y}(1-\gamma^2)\int_0^{\pi}d\theta_z\frac{A-B\cos\theta_z}{(1+\gamma^2)-2\gamma\cos\theta_z}\times n(A-B\cos\theta_z)$$
$$\equiv-\frac{\hbar}{2\pi}\sum_{k_xk_y}(1-\gamma^2)\times\int_{-\pi}^{+\pi}d\theta\frac{(A-B)+B(1-\cos\theta_z)}{(1-\gamma)^2+2\gamma(1-\cos\theta_z)}\times n[(A-B)+B(1-\cos\theta_z)].$$

We now convert the sum over k_x and k_y to an integral. Let S be the total surface area of the sample (recall that there are two surfaces), and let $\theta_x=k_xa$, $\theta_y=k_ya$, where a is the spacing between adjacent atomic planes, measured in the direction normal to the surface. Thus,

$$\Delta U_B{}^{(2)}(T)=-\frac{S\hbar}{2(2\pi)^3a^2}\int_{-\pi}^{+\pi}\frac{d^3\theta(1-\gamma^2)[(A-B)+B(1-\cos\theta_z)]n[(A-B)+B(1-\cos\theta_z)]}{(1-\gamma^2)+2\gamma(1-\cos\theta_z)}.$$

Now, we are interested only in the low-temperature form of $\Delta U_B{}^{(2)}(T)$. We thus may extend the limits on all integrals to infinity. Furthermore, only values of θ_x, θ_y, and $\theta_z \ll 1$ will be important because of the Bose-Einstein factor. Hence, we replace $\cos\theta_z$ by $1-\frac{1}{2}\theta_z{}^2$. Furthermore, the combination $A(\mathbf{k}_{\shortparallel})-B(\mathbf{k}_{\shortparallel})$ is the frequency of a bulk spin wave of wave vector $\mathbf{k}_{\shortparallel}$ propagating parallel to the surface. When k_x and k_y are small, and the x and y directions suitably chosen, we have seen that one has

$$A(\mathbf{k}_{\shortparallel})-B(\mathbf{k}_{\shortparallel})=D_xk_x{}^2+D_yk_y{}^2=\beta_x\theta_x{}^2+\beta_y\theta_y{}^2\,,$$

where

$$\beta_x=D_xa^2,\quad \beta_y=D_ya^2$$

and

$$\theta_x=k_xa,\quad \theta_y=k_ya\,.$$

Further, define

$$\beta_z=\tfrac{1}{2}B(\mathbf{k}_{\shortparallel})\,.$$

One then has

$$\Delta U_B{}^{(2)}(T)=-\frac{S\hbar}{2(2\pi)^3a^2}\int d^3\theta\,\frac{(1-\gamma^2)(\beta_x\theta_x{}^2+\beta_y\theta_y{}^2+\beta_z\theta_z{}^2)}{(1-\gamma)^2+\gamma\theta_z{}^2}\times n(\sum_i\beta_i\theta_i{}^2)\,.\quad(3.20)$$

Now let

$$K_i=\beta_i{}^{1/2}\theta_i,\quad i=x,y,z\,.$$

Then, after a bit of rearranging,

$$\Delta U_B{}^{(2)}(T)=-\frac{S\hbar}{2(2\pi)^3a^2}(\beta_x\beta_y\beta_z)^{-1/2}\times\int d^3K\,K^2\frac{1-\gamma^2}{(1-\gamma)^2+\gamma\beta_z{}^{-1}K_z{}^2}n(K^2)\,.\quad(3.21)$$

Next, consider the form of γ. Recall that γ is a function of the wave-vector components $\mathbf{k}_{\shortparallel}=\hat{x}k_x+\hat{y}k_y$. Thus, in our present notation, γ depends only on K_x and K_y. Furthermore, when the spins in the surface layer are coupled to fewer neighbors than spins in the bulk, with the possibility of softened exchange constants in the surface layer, we have seen that $\gamma(\mathbf{k}_{\shortparallel})<1$. We insert an expansion for γ valid for small K_x and K_y into Eq. (3.21), since these are the only values important in the low-temperature limit. By orienting the K_x and K_y axes properly, this expansion can be placed in the form

$$\gamma=1-\sigma_xK_x{}^2-\sigma_yK_y{}^2+\cdots.$$

We then decompose the integral over $|\mathbf{K}|$ and an integral over the direction of $\mathbf{K}$:

$$\Delta U_B{}^{(2)}(T)=-\frac{S\hbar}{(2\pi)^3a^2}\left(\frac{\beta_z}{\beta_x\beta_y}\right)^{1/2}\int_0^\infty dK\,K^4n(K^2)\int_0^{2\pi}d\varphi\int_0^\pi d\theta\times\frac{\sin^3\theta(\sigma_x\cos^2\varphi+\sigma_y\sin^2\varphi)}{\cos^2\theta+\beta_zK^2\sin^2\theta(\sigma_x\cos^2\varphi+\sigma_y\sin^2\varphi)^2}\,.\quad(3.22)$$

Next, consider the integration over the angle θ. When $K\ll 1$, the quantities $\beta_zK^2\sigma_{x,y}{}^2$ are very small compared to unity. In this limit, the integrand is sharply peaked about the midpoint $\theta\simeq\frac{1}{2}\pi$. This means physically that the dominant contribution to $\Delta U_B{}^{(2)}$ comes from the bulk waves that propagate nearly parallel to the surface. The values of k_z that are most important are values of $k_z\leq ak_{\shortparallel}{}^2$, where $k_{\shortparallel}{}^2=k_x{}^2+k_y{}^2$. In the limit $K\ll 1$, an approximate value of the integral may be obtained by replacing $\cos\theta$ by $(\frac{1}{2}\pi-\theta)$, its value near $\frac{1}{2}\pi$, and $\sin\theta$ by unity. Then

$$\int_0^\pi\frac{d\theta\,\sin^3\theta}{\cos^2\theta+[\beta_z{}^{1/2}K(\sigma_x\cos^2\varphi+\sigma_y\sin^2\varphi)]^2}\cong\int_{-\infty}^{+\infty}\frac{d\eta}{\eta^2+[\beta_z{}^{1/2}K(\cdots)]^2}=\pi/\beta_z{}^{1/2}K(\sigma_x\cos^2\varphi+\sigma_y\sin^2\varphi)\,.$$

Then

$$\Delta U_B{}^{(2)}(T)\cong-\frac{S\hbar(\beta_x\beta_y)^{-1/2}}{2(2\pi)^2a^2}\int_0^\infty dK\,K^3n(K^2)\int_0^{2\pi}d\varphi=-\frac{S\hbar(\beta_x\beta_y)^{-1/2}}{2(2\pi)^2a^2}\int_{-\infty}^{+\infty}dK_xdK_y\times(K_x{}^2+K_y{}^2)n(K_x{}^2+K_y{}^2)\,.\quad(3.23)$$

Let us now transform the integral to an integral over k_x and k_y, using the relations

$$K_x=\beta_x{}^{1/2}ak_x\quad\text{and}\quad K_y=\beta_y{}^{1/2}ak_y\,.$$

Then

$$\Delta U_B{}^{(2)}(T)=-\hbar\frac{S}{2(2\pi)^2}\int_{-\infty}^{+\infty}dk_xdk_y\times(D_xk_x{}^2+D_yk_y{}^2)n(D_xk_x{}^2+D_yk_y{}^2)\,.\quad(3.24)$$

We now notice that in the long-wavelength limit

$$\Omega_m(\mathbf{k}_{\shortparallel})=D_xk_x{}^2+D_y{}^2k_y{}^2\,,$$

and S is the total surface area of the film (i.e., twice the area of one of the surfaces). Equation (3.24) may then be rewritten in the form

$$\Delta U_B^{(2)}(T)=-\hbar\sum_{k_xk_y}\Omega_m(\mathbf{k}_{\parallel})n[\Omega_m(\mathbf{k}_{\parallel})].$$

Thus, the total change in internal energy from the presence of the free surfaces is the sum of three terms:

$$\Delta U_s^{(\mathrm{TOT})}=\Delta U_s+\Delta U_B^{(1)}+\Delta U_B^{(2)}\equiv\tfrac{1}{4}\Delta U_s(T).$$

The frequency shifts of the bulk waves cancels out precisely $\frac{3}{4}$ of the contribution from the surface magnons. The total low-temperature surface specific heat is thus 75% of the amount contributed by the surface waves alone:

$$C_s^{(\mathrm{TOT})}(T)=\tfrac{1}{4}C_s(T)=\frac{S}{8\pi}\zeta(2)\frac{k_BT}{\hbar(D_xD_y)^{1/2}}. \quad (3.25)$$

The result in Eq. (3.25) has been obtained by Green's-functions methods in earlier treatments.[11] As we remarked earlier, the previous work has ignored changes in the exchange constants in the surface layer, and has also confined its attention to very specific geometries.

IV. DISCUSSION

The purpose of this paper has been to point out that the expression for the surface specific heat derived in earlier work may be applied to a rather wide variety of geometries, provided the alterations in exchange interactions are confined to the surface layer. One must replace the single exchange constant D relevant to cubic crystals by the quantity $(D_xD_y)^{1/2}$, where D_x and D_y are the exchange constants appropriate to propagation of bulk waves along the two principal directions parallel to the surface.

As we remarked earlier, recent measurements of the specific heat of small YIG particles indicate the presence of a term linear in the temperature. However, the magnitude of the observed linear term is roughly 30 times larger than the prediction of Eq. (3.26). It thus appears difficult to account for the size of the observed term by assuming it is a surface effect, and using a model which assumes that alterations in the exchange constants are confined to only the surface layer.

Recently, measurements of the longitudinal nuclear relaxation time of the Fe^{57} nucleus in small YIG particles have appeared.[12] At 4.2°K, in zero magnetic field, it is found that in particles with a diameter of 5 μ, T_1 is smaller by roughly two orders of magnitude than the value of T_1 in the bulk crystal, at the same field and temperature. In an earlier work,[2] the variation of the mean spin deviation with distance from the surface was computed for a model which ignores changes in exchange constants near the surface. It was found that within a distance of roughly $(T_c/T)^{1/2}$ lattice constants of the surface, the mean spin deviation is roughly twice the bulk value. The result of the present work suggests that the behavior of the mean spin deviation may not be sensitive to changes in the exchange constants of the surface layer. While we have not attempted to compute the effective value of T_1 for an ensemble of spins in a small ferromagnetic particle, it appears difficult to see how the very large decrease in the observed T_1 could be accounted for in the framework of the theoretical model just described.

If the increase in specific heat and T_1^{-1} observed in small YIG particles are indeed associated with an increase in the mean spin deviation near the surface of the material, then we feel the current theoretical models may represent a considerable oversimplification of the effect of the surface on the properties of small magnetic particles. It would be extremely useful to perform a measurement of the magnetization of the spins in the surface layer of a ferromagnetic crystal, perhaps by LEED techniques of the type used recently in the study of antiferromagnetic NiO.[5]

APPENDIX

We shall evaluate the integral that appears on the right-hand side of Eq. (3.14). We consider

$$\mathcal{J}=\frac{1}{\pi}\int_0^\infty d\Omega\,\Omega\frac{\partial\varphi}{\partial\Omega}(\mathbf{k}_{\parallel})=-\frac{1}{\pi}\int_0^{\Omega_M}d\Omega\,\varphi(\mathbf{k}_{\parallel},\Omega). \quad (\mathrm{A1})$$

The last equality in Eq. (A1) follows after a partial integration, noting from Eq. (3.13) that $\varphi(\mathbf{k}_{\parallel},0)\equiv0$ and $\varphi(\mathbf{k}_{\parallel},\Omega)=0$ for $\Omega>\Omega_M$, since we have seen $\varphi_2=0$. In the discussion below, we suppress the explicit reference to $\mathbf{k}_{\parallel}$ in the quantities that appear, in order to make the equations more compact. Then from Eqs. (3.13) and (A1),

$$\begin{aligned}\mathcal{J}&=-2(\Omega_m-\Omega_s)-\frac{\varphi_1}{\pi}(\Omega_M-\Omega_m)-\int_{\Omega_m}^{\Omega_M}\frac{d\Omega}{\pi}\varphi_B(\Omega)\\&=-\frac{B(1-\gamma)^2}{\gamma}-\frac{2B}{\pi}\varphi_1-\int_0^\pi\frac{d\theta}{\pi}\frac{\partial\Omega}{\partial\theta}\varphi_B(\theta)\\&=-B\frac{(1-\gamma)^2}{\gamma}-\frac{2}{\pi}B\varphi_1-\frac{B}{\pi}\int_0^\pi d\theta\,\sin\theta\,\varphi_B(\theta),\end{aligned} \quad (\mathrm{A2})$$

where $\theta=k_za$.

To obtain Eq. (A2), we have expressed Ω_m, Ω_s, and Ω_M in terms of A, B, and γ, and we have converted the integral from an integral over frequency to one over the

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[11] The coefficient of the surface specific heat exhibit in Ref. 2 is in error by a factor of 2. See the discussion in Ref. 7, and A. A. Maradudin and D. L. Mills, J. Phys. Chem. Solids **30**, 784(E) (1969).

[12] S. M. Meyers, H. Meyer, and J. P. Remeika (unpublished).

variable $\theta = k_z a$. Let

$$I = \frac{1}{\pi}\int_0^\pi d\theta\, \sin\theta\, \varphi_B(\theta) = -\frac{1}{\pi}\int_0^\pi d\theta\, \frac{\partial}{\partial\theta}(\cos\theta)\,\varphi_B(\theta)$$

$$= -\frac{1}{\pi}\cos\theta\,\varphi_B(\theta)\Big|_0^\pi + \frac{1}{\pi}\int_0^\pi d\theta\, \cos\theta \frac{\partial\varphi_B}{\partial\theta}$$

$$1 + \int_0^\pi \frac{d\theta}{\pi}\, \frac{\cos\theta(1-\gamma^2)}{2\gamma\cos\theta - (1+\gamma^2)}$$

$$= -1 + \frac{1-\gamma^2}{2\gamma} - \frac{1-\gamma^4}{2\pi\gamma}\int_0^\pi \frac{d\theta}{(1+\gamma^2) - 2\gamma\cos\theta}\,.$$

The remaining integral may be obtained from standard integral tables:

$$\int_0^\pi \frac{d\theta}{1+\gamma^2 - 2\gamma\cos\theta} = \frac{\pi}{1-\gamma^2}\,.$$

Hence

$$\frac{1}{\pi}\int_0^\pi d\theta\, \sin\theta\, \varphi_B(\theta) = -(1+\gamma)\,,$$

and we obtain

$$\mathcal{J} = -(B/\gamma)[1 + (2\gamma/\pi)(\varphi_1 - \tfrac{3}{2}\pi)]. \qquad \text{(A3)}$$

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Properties of the Ni-Ir Alloy System

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Measurements of the lattice parameter, electronic specific heat, magnetic susceptibility, and Debye temperature are presented in the Ni-Ir alloy system from 0 to 100 at.% Ir. This system forms an uninterrupted series of solid solutions over the entire concentration range. No ordering nor decomposition could be observed after annealing for several days at temperatures between 500 and 1100°C. The system develops a sharp peak in the electronic specific heat versus concentration at 85 at.% Ni, a concentration slightly higher than the critical concentration determined magnetically (81 at.% Ni). A weak anomaly was found also in the T^3 term of the low-temperature specific heat around the same concentration. Generally, no low-temperature anomaly, such as was predicted by the early paramagnon theories, was detected down to 1.5°K. The susceptibility was measured on the paramagnetic side only up to 79 at.% Ni, where a spontaneous moment develops at low temperature.

I. INTRODUCTION

AMONG the transition-metal binary alloys the Ni-Ir system is one of the few cases which has not yet been explored. Nevertheless, this system presents some interesting aspects related to the questions of paramagnons.[1,2] In this respect, its behavior differs remarkably from the isoelectronic system Ni-Rh which we investigated earlier.[3] We shall discuss this difference briefly after presenting structural and electronic data of the Ni-Ir system.

II. RESULTS

A. Lattice Parameters

Prior to our investigation of the electronic properties, the phase diagram of the Ni-Ir system had to be established. Using powder x-ray diffraction, we found that the system exhibits complete solid solubility over the entire range of concentration. Figure 1 shows the lattice parameter a of the fcc lattice and the molar volume V_M as a function of the Ir concentration, both showing a positive deviation from linearity. This behavior is identical with Ni-Rh,[4] except that the difference in lattice constants between the end members is even larger in Ni-Ir. The formation of complete solid solutions is not self-evident. This can be demonstrated by considering the corresponding Rh alloy systems. While Rh forms complete solid solutions with Ni,[4] Pd,[5,6] and Cu,[4,7] at least at high temperatures, Ir shows decomposition in alloying with Pd [6] and partial immiscibility with Cu [8] in the solid state. Special attention was therefore paid to the possible occurrence of ordered phases or decomposition, but no indication of either

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[1] N. F. Berk and J. R. Schrieffer, Phys. Rev. Letters **17**, 433 (1966).

[2] S. Doniach and S. Engelsberg, Phys. Rev. Letters **17**, 750 (1966).

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[7] See Ref. 6 in Ref. 8.

[8] E. Raub and E. Röschel, Z. Metallk. **60**, 142 (1969).