

On the Theory of Spin Waves in Ferromagnetic Media

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The theory of spin waves, leading to the Bloch $T^{\frac{3}{2}}$ law for the temperature variation of saturation magnetization, is discussed for ferromagnetic insulators and metals, with emphasis on its relation to the theory of the energy of the Bloch interdomain wall. The analysis indicates that spin-wave theory is of more general validity than the Heitler-London-Heisenberg model from which it was originally derived. Many properties of spin waves of long wavelength can be derived without specialized assumptions, by a field-theoretical treatment of the ferromagnetic material as a continuous medium in which the densities of the three components of spin are regarded as amplitudes of a quantized vector field. As applications, the effects of anisotropy energy and magnetic forces are calculated; and it is shown that the Holstein-Primakoff result

for the field dependence of the saturation magnetization can be derived in an elementary manner. An examination of the conditions for validity of the field theory indicates that it should be valid for insulators, and probably also for metals, independently of any simplifying assumptions. The connection with the itinerant electron model of a metal is discussed; it appears that this model is incomplete in that it omits certain spin wave states which can be proved to exist, and that when these are included, it will yield both a magnetization reversal proportional to $T^{\frac{3}{2}}$ and a specific heat proportional to T . Incidental results include some insight into the relation between the exchange and Ising models for a two-dimensional lattice, an upper limit to the effective exchange integral, and a treatment of spin waves in rhombic lattices.

I. INTRODUCTION

THE quantum-mechanical theory of ferromagnetism¹ is beset by so many difficulties and uncertainties that especial importance attaches to those few quantitative relationships between measurable quantities which it is capable of predicting with reasonable rigor. One such relationship, which is generally regarded as being valid whenever the basic assumptions of the Heitler-London-Heisenberg model are applicable, is Bloch's $T^{\frac{3}{2}}$ law of variation of saturation moment with temperature near the absolute zero, based on the theory of spin waves.² According to this model the decrease of saturation moment with increasing temperature is determined by the "stiffness" of the exchange coupling which tends to align the spins of all the atoms parallel. This same stiffness, in competition with anisotropy forces, determines the thickness and specific surface energy of the boundary region, known as the Bloch wall, which separates adjacent domains having different directions of magnetization.³ If the anisotropy constants are known, one can, according to this model, deduce the exchange stiffness and hence the temperature variation of magnetization from a knowledge of the Bloch wall energy, or vice versa. When this is done, the relation between these, in principle, measurable quantities [Eq. (5) below] turns out to involve only the saturation magnetization, and to be independent of such details of the model as the number of nearest neighbors. This suggests that the validity of this relation is more general than that of the Heitler-London-Heisenberg model from which it was derived. This surmise acquires added plausibility from the success of

some attempts to develop the theory of spin waves on a more or less phenomenological basis.⁴ The principal purposes of the present paper are to verify this surmise, to give a more soundly based phenomenological theory of spin waves, and to show that with the aid of this theory one can deduce quite simply all of the formulas governing a broad class of properties of a ferromagnetic substance in the region of low temperatures.

Since only rather simple reasoning is required for the exposition of the present approach to spin wave theory, and for the derivation of practical results from it, we shall present these topics first, in Secs. IIA and IIB, respectively. The applications include calculations of the effect of anisotropy and magnetic forces on spin waves and the $T^{\frac{3}{2}}$ law, and it will be shown that the results of Holstein and Primakoff⁵ on the field dependence of intrinsic magnetization can be derived easily by the present method. Appendix A gives a brief derivation of the principal equations of the theory for the special case in which the atomic model is assumed, and evaluates the coefficient in the $T^{\frac{3}{2}}$ law for a simple rhombic lattice. Section III is devoted to an analysis of the justification of the theory of spin waves and especially of the form of it presented in Sec. II, which enables all of the properties of spin waves to be derived from the Bloch wall coefficient, A , defined by Eq. (3) below. This analysis, though incomplete, seems to us to indicate strongly that the methods of Sec. II are justified, and that their justification is not contingent upon the choice of any particular approximate model for the ferromagnetic electrons. A corollary of this conclusion is that the criticisms which Wohlfarth⁶ has

¹ For a brief critical review of this field see, for example, J. H. Van Vleck, *Revs. Modern Phys.* **17**, 27 (1945).

² F. Bloch, *Z. Physik* **61**, 206 (1930); **74**, 295 (1932); C. Møller, *Z. Physik* **82**, 559 (1933); W. Opechowski, *Physica* **4**, 715 (1937).

³ F. Bloch, *Z. Physik* **74**, 295 (1932); L. Landau and E. Lifshitz, *Physik. Z. Sowjetunion* **8**, 153 (1935); E. Lifshitz, *J. Phys. (U.S.S.R.)* **8**, 337 (1944); L. Néel, *Cahiers phys.* **25**, 1 (1944). For a summary see C. Kittel, *Revs. Modern Phys.* **21**, 541 (1949).

⁴ G. Heller and H. A. Kramers, *Proc. Roy. Acad. Amsterdam* **37**, 378 (1934); E. Lifshitz, *J. Phys. (U.S.S.R.)* **8**, 337 (1944); W. Döring, *Z. Physik* **124**, 501 (1947). In Appendix A of the present paper we give a simple derivation of the phenomenological theory from the atomic model.

⁵ T. Holstein and H. Primakoff, *Phys. Rev.* **58**, 1098 (1940).

⁶ E. P. Wohlfarth, *Proc. Leeds Phil. Soc.* **5**, 213 (1949). E. C. Stoner, Report of the Grenoble Conference (1950).

recently leveled against the theory of spin waves and the $T^{\frac{1}{2}}$ law are not justified.

A brief recapitulation of the results yielded by the atomic model for the temperature variation of magnetization² and for the Bloch wall³ will serve to clarify our first objectives and to introduce some basic equations and definitions. If $M(T)$ is the saturation magnetization at temperature T , the $T^{\frac{1}{2}}$ law can be written as²

$$M(T)/M(0) = 1 - (T/\Theta)^{\frac{1}{2}} + O(T^2), \quad (1)$$

where for any crystal structure of high symmetry^{6a}

$$\theta^* = 2.21Z(R_n^3/\Omega_0)^{2/3}S_0^{5/3}(J/k), \quad (2)$$

Z being the number of nearest neighbors of any given atom, R_n their distance, Ω_0 the atomic volume, S_0 the spin quantum number of an individual atom, k Boltzmann's constant, and J the interatomic exchange integral, defined so that the effective interaction energy of two nearest neighbor atoms is a constant minus $2JS_{01} \cdot S_{02}$. The temperature dependence given by Eq. (1) constitutes a significant prediction even if J is regarded as an adjustable parameter; however, as we have pointed out above, the same model which leads to Eq. (1) also leads to a relation between J and the specific surface energy of the Bloch wall. This surface energy, and the thickness of the transition region as well, can be computed by a simple variational calculation based on the assumption that the energy per unit volume at any point in the transition region is a sum of two terms: a term arising from anisotropy and magnetostrictive effects, which depends on the local orientation of the magnetization vector, and a term

$$A|\nabla\mathbf{M}|^2/M^2 \quad (3)$$

proportional to the square of the rate at which the direction of the magnetization vector \mathbf{M} is changing with position.^{6b} The atomic model on which Eq. (2) is

^{6a} It is shown in Appendix A that for a simple rhombic lattice J has merely to be replaced by the geometric mean of the J 's going with the three rectangular directions.

^{6b} As none of the references we have cited explains why Eq. (3) should be the most general allowable form for this term in a cubic crystal, a word of explanation is in order here. Since we are interested only in non-uniformities in spin direction which change very gradually with position, we wish an expression which is of the lowest order in the derivatives of \mathbf{M} which the symmetry of the problem permits; this requires that the expression be quadratic in the derivatives, but as there are three such quantities which have the symmetry required for an isotropic medium (*viz.* $|\nabla\mathbf{M}|^2$, $(\nabla \cdot \mathbf{M})^2$, and $|\nabla \times \mathbf{M}|^2$), and four which have the symmetry required for a cubic crystal, one might think that any linear combination of these would be a possible form for the required energy expression. The reason this is not so is that the energy expression in question is intended to represent only the energy increase which would result from the given variation of \mathbf{M} if there were no magnetic terms in the hamiltonian, the latter being taken into account by magnetic, anisotropy, and magnetostrictive terms in the macroscopic calculation (see Kittel, reference 3). When magnetic terms are omitted from the hamiltonian, the energy is invariant with respect to spin rotations, so the required expression must have the form $\sum_{\mu\nu\alpha} C_{\mu\nu}(\partial M_\alpha/\partial x_\mu)(\partial M_\alpha/\partial x_\nu)$, with $C_{\mu\nu}$ a tensor with the symmetry of the crystal. For cubic crystals Eq. (3) is, therefore, the most general allowable form, while for hexagonal and tetragonal classes two coefficients, A_{11} and A_{12} , would be required.

based gives for the coefficient A in Eq. (3)

$$A = ZS_0^2R_n^2J/6\Omega_0. \quad (4)$$

Since the other quantities entering into the surface energy of the Bloch wall are measurable, elimination of J between Eqs. (2) and (4) amounts to a prediction of a definite relationship between this surface energy and the variation of saturation magnetization with temperature, both measurable quantities.^{7,8} It is noteworthy that the relation obtained from Eqs. (2) and (4), *viz.*,

$$A = 0.0754(S_0/\Omega_0)^{\frac{1}{2}}k\theta^*, \quad (5)$$

involves only the magnetization per unit volume, and is independent of the atomic arrangement. We shall attempt to show in this paper that Eq. (5) is always valid, regardless of whether the atomic model used by Heisenberg and Bloch is a good approximation.

II. FIELD THEORY OF SPIN WAVES

A. Basic Equations

We shall begin by showing how the properties of spin waves of long wavelength can be derived formally by treating the ferromagnetic material as a continuous medium in which the densities of the three components of spin are regarded as amplitudes of a vector field which is quantized in the way demanded by the known commutation relations for spin components. Our approach will be merely a more sophisticated version of that used by Lifshitz⁴ who, following a suggestion of Landau, interpreted the energy (3) as implying the existence of a restoring torque tending to straighten out any distortion in the spin alignment and who used this torque to construct a quasi-classical time-dependent wave equation for the spin. This approach differs from that of Heller and Kramers⁴ and that of Döring⁴ in that it is not based explicitly on a model in which each electron is attached to a particular atom; and it differs from that of Bloch² and of Møller² both in this respect and in that the problem is formulated in terms of densities of spin moment, rather than in terms of probability amplitudes for the different states of spin.

Consider the vector operator defined by

$$\mathbf{s}^{(r)} = \sum_i \sigma^{(i)} \delta(\mathbf{r} - \mathbf{r}_i), \quad (6)$$

where $\sigma_x^{(i)}$, $\sigma_y^{(i)}$, $\sigma_z^{(i)}$ are the Pauli matrices for the i th electron, \mathbf{r}_i is its position vector, δ is the Dirac delta-function, and the summation is over all the electrons of a ferromagnetic crystal. The operator (6) represents the density of spin moment per unit volume at the point \mathbf{r} , in units of $\hbar/2$. Its Fourier components are the operators

$$\mathbf{s}^{(k)} = \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i) \sigma^{(i)}. \quad (7)$$

⁷ Careful measurements of M at low temperatures have been made for several ferromagnetic elements and alloys by M. Fallot, *Ann. physique* **6**, 305 (1936).

⁸ A rough measurement of the surface energy of Bloch wall in 3.85 percent SiFe has been obtained by Williams, Bozorth, and Shockley, *Phys. Rev.* **75**, 155 (1949); there is hope that more accurate measurements may be possible in the future.

From the commutation relations

$$\sigma_x^{(i)}\sigma_y^{(j)} - \sigma_y^{(j)}\sigma_x^{(i)} = 2i\delta_{ij}\sigma_z^{(i)},$$

etc., we find easily

$$s_x^{(r)}s_y^{(r')} - s_y^{(r')}s_x^{(r)} = 2is_z^{(r)}\delta(\mathbf{r}-\mathbf{r}') \quad (8)$$

$$s_x^{(k)}s_y^{(k')} - s_y^{(k')}s_x^{(k)} = 2is_z^{(k+k')}, \quad (9)$$

with corresponding equations resulting from cyclic permutation of x, y, z . If k and k' are small and if the specimen has an almost uniform spontaneous magnetization in the z -direction, the right of Eq. (9) will have very nearly the eigenvalue zero if $\mathbf{k}+\mathbf{k}'\neq 0$, and the eigenvalue $4iS$ if $\mathbf{k}+\mathbf{k}'=0$, where S is the total spin quantum number for the ferromagnetic ground state of the specimen, which we suppose to have very nearly the same energy and magnetic moment as the state in question. Since the hermitian adjoint of $\mathbf{s}^{(k)}$ is $\mathbf{s}^{(k)+} = \mathbf{s}^{(-k)}$, we can rewrite Eq. (9) for this case as

$$s_x^{(k)+}s_y^{(k)} - s_y^{(k)}s_x^{(k)+} \approx 4iS\delta_{kk'}. \quad (10)$$

We now make the assumption that, since the mean energy of any slightly non-uniform distribution of spin density is given by the volume integral of Eq. (3), this integral in operator form can be used as a hamiltonian to find the stationary states associated with the spin fluctuations. The legitimacy of this assumption will be discussed in Sec. III below; it is obviously applicable only to spin disturbances of long wavelength. For the present case, where \mathbf{M} is always oriented very nearly in the z -direction, this hamiltonian for a specimen of volume Ω takes the form

$$\begin{aligned} H' &= (A\Omega^2/4S^2) \int |\nabla\mathbf{s}^{(r)}|^2 d\tau = (A\Omega/4S^2) \sum_k k^2 \mathbf{s}^{(k)+} \cdot \mathbf{s}^{(k)} \\ &\approx (A\Omega/4S^2) \sum_k k^2 (s_x^{(k)+}s_x^{(k)} + s_y^{(k)+}s_y^{(k)}) \end{aligned} \quad (11)$$

if higher order terms in $s_x^{(k)}$ and $s_y^{(k)}$ are neglected. The general term of the summation in Eq. (11) can be thrown into harmonic oscillator form by expressing it in terms of the hermitian operators defined by

$$\begin{aligned} Q_+^{(k)} &= (8S)^{-\frac{1}{2}}(s_x^{(k)} + s_x^{(k)+}), \\ P_+^{(k)} &= (8S)^{-\frac{1}{2}}(s_y^{(k)} + s_y^{(k)+}), \\ Q_-^{(k)} &= i(8S)^{-\frac{1}{2}}(s_y^{(k)} - s_y^{(k)+}), \\ P_-^{(k)} &= i(8S)^{-\frac{1}{2}}(s_x^{(k)} - s_x^{(k)+}). \end{aligned} \quad (12)$$

It is easily verified that the first two and the last two lines of Eq. (12) each constitute a canonically conjugate pair. The hamiltonian (11) reduces to

$$\begin{aligned} H' &= (2A\Omega/S) \sum_{\text{half } k} \frac{1}{2}(P_+^{(k)2} + Q_+^{(k)2} \\ &\quad + P_-^{(k)2} + Q_-^{(k)2})k^2, \end{aligned} \quad (13)$$

where the summation is to be extended over only half of k -space, since the contributions of \mathbf{k} and $-\mathbf{k}$ to Eq. (11) are both included in the k th term of Eq. (13).

The hamiltonian (11) or (13) yields both the equations of motion of the spin system in time, and the

eigenvalues of the energy. The latter are of course sums of expressions of the form $(n_{\pm}^{(k)} + \frac{1}{2})(2A\Omega/S)k^2$, where $n_{\pm}^{(k)} = 0, 1, 2, \dots$. Since the ground state, whose energy we shall take to be E_0 , is the state for which all $n_{\pm}^{(k)} = 0$, the levels are

$$E(n_{\pm}^{(k)}s) = E_0 + \sum_{\text{half } k} (n_+^{(k)} + n_-^{(k)})(2A\Omega/S)k^2. \quad (14)$$

Thus, the energy of a spin wave of wave vector \mathbf{k} is $(2A\Omega/S)k^2$; this relation between A and the energy of the spin wave is the same as that yielded by the atomic-model theories of reference 2; and when the usual statistical treatment is employed to calculate the number of spin waves excited at temperature T , it gives a value for the θ^* of Eq. (1) agreeing with Eq. (5).

The time derivative of the spin density at the point \mathbf{r} can be obtained from the integral expression for the hamiltonian in Eq. (11): using the usual square bracket abbreviation for the commutator of two operators and the summation convention for repeated suffixes, we have

$$\begin{aligned} -i\hbar\dot{s}_{\alpha}^{(r)} &= [H', s_{\alpha}^{(r)}] \\ &= (A\Omega^2/4S^2) \int \left[\frac{\partial s_{\beta}^{(r')}}{\partial x_{\gamma}'} \frac{\partial s_{\beta}^{(r')}}{\partial x_{\gamma}'} , s_{\alpha}^{(r)} \right] d\tau' \\ &= (A\Omega^2/4S^2) \int \left\{ \frac{\partial s_{\beta}^{(r')}}{\partial x_{\gamma}'} \frac{\partial}{\partial x_{\gamma}'} [s_{\beta}^{(r')}, s_{\alpha}^{(r)}] \right. \\ &\quad \left. + \frac{\partial}{\partial x_{\gamma}'} [s_{\beta}^{(r')}, s_{\alpha}^{(r)}] \frac{\partial s_{\beta}^{(r')}}{\partial x_{\gamma}'} \right\} d\tau' \\ &= 2i(A\Omega^2/4S^2) \epsilon_{\alpha\beta\mu} (\nabla^2 s_{\beta}^{(r')} s_{\mu}^{(r)} + s_{\mu}^{(r)} \nabla^2 s_{\beta}^{(r')}) \end{aligned} \quad (15)$$

by Eq. (8), where $\epsilon_{\alpha\beta\mu} = 1$ if $\alpha\beta\mu$ is an even permutation of xyz , -1 if an odd permutation, and 0 otherwise. If we set $\mathbf{M} = -(e\hbar/2mc)\mathbf{s}^{(r)}$ in Eq. (15) and ignore the noncommutativity of the different components, we get the equation of motion derived phenomenologically by Landau and Lifshitz³ and by Döring:⁴

$$d\mathbf{M}/dt = -2(e/mc)(A/M^2)\mathbf{M} \times \nabla^2 \mathbf{M}. \quad (16)$$

Note that this is the same as Eq. (A4) of Appendix A. As can be seen from this or from the classical approximation to the motion of one of the oscillators of Eq. (13), a spin wave of large amplitude is a disturbance in which the direction of \mathbf{M} at each point of space moves in time around a narrow cone, the amplitude of the motion being a sinusoidal function of position. From this physical picture of the motion it is obvious that the first two terms of Eq. (1) will give a good approximation to the saturation moment as long as the temperature is low enough so that the only disturbances of the spin system which are appreciably excited are ones of sufficiently long wavelength for Eq. (3) to apply to them, i.e., of a wavelength much greater than the lattice constant.

B. Effect of Magnetic Fields, Anisotropy, etc., on Spin Waves

So far we have considered only the energy levels of an assembly of electrons uninfluenced by any purely magnetic forces. In actual materials there will be a spin-orbit interaction giving rise to anisotropy effects, a long-range magnetic interaction of the spins which will increase the energy of states for which the magnetization has a divergence, and, of course, a magnetic interaction of the electrons with any external field which may be applied. The last-named interaction is modified by the spin-orbit interaction in such a manner as to give an effective g -factor differing slightly from 2; higher order effects of this sort will for simplicity be neglected in the present treatment, though they might be treated by methods similar to those used here. To this approximation, at least, the magnetic effects which we have named can all be taken into account by adding appropriate terms to the hamiltonian (11) or (13). If one is not interested in zero-point energy, the effect of these additional terms on the energy levels can be calculated even more simply by merely adding appropriate terms to the phenomenological equation of motion (16) and calculating the frequencies of the normal modes classically. Such calculations amount to a simplified version of the theory of Holstein and Primakoff,⁵ with the advantage of not being based on any particular atomic model. In this section we shall carry these calculations far enough to show that anisotropy and spin-spin interactions do not modify the $T^{\frac{1}{2}}$ law (1) appreciably, and shall give expressions which need only be integrated by the methods of Sec. IV of reference 5 in order to give the formulas of Holstein and Primakoff for the dependence of intrinsic magnetization on field.

Our starting point is Eq. (16) which gives the contribution of the spatial variation of the magnetization \mathbf{M} to the time derivative $d\mathbf{M}/dt$; we must add to this the contributions of the various magnetic interactions. A magnetic field \mathbf{H} , whether externally imposed or due to the spins themselves, contributes a term $-(e/mc)\mathbf{M}\times\mathbf{H}$ to $d\mathbf{M}/dt$. The effect of anisotropy forces on $d\mathbf{M}/dt$ is similar to the effect of a field, and can be written $-(e/mc)\mathbf{M}\times\mathbf{H}_{\text{eff}}$ when \mathbf{M} deviates only slightly from a direction of easy magnetization. For example, for a cubic crystal with the (001) direction an easy direction of magnetization the anisotropy energy per unit volume is given, for small values of the angle θ between \mathbf{M} and (001), by $f_K \cong K\theta^2$, where K is the first-order anisotropy constant. Comparison with the expression $-\mathbf{H}\cdot\mathbf{M}$ for the magnetic energy gives, therefore, for this case

$$H_{\text{eff}} = 2K/M. \quad (17)$$

Gathering together the terms enumerated, we have as the equation of motion for \mathbf{M} ,

$$d\mathbf{M}/dt = -(e/mc)[2(A/M^2)\mathbf{M}\times\nabla^2\mathbf{M} + \mathbf{M}\times(\mathbf{H}_{\text{ext}} + \mathbf{H}_{\text{eff}} + \mathbf{H}_s)], \quad (18)$$

where \mathbf{H}_{ext} is the externally applied field and \mathbf{H}_s is the field due to the spins themselves. The only complicating feature in the problem of determining the normal frequencies is the fact that \mathbf{H} , depends on the distribution of \mathbf{M} . Explicitly, it is determined by

$$\nabla\cdot\mathbf{H}_s = -4\pi\nabla\cdot\mathbf{M}, \quad \nabla\times\mathbf{H}_s = 0. \quad (19)$$

If we try to get a solution of the form

$$\mathbf{M} = \mathbf{M}_s + \Delta\mathbf{M}_0 \exp[i(\omega t + \mathbf{k}\cdot\mathbf{r})] \quad (20)$$

$$\mathbf{H}_s = \mathbf{H}_0 \exp[i(\omega t + \mathbf{k}\cdot\mathbf{r})], \quad (21)$$

we find from Eq. (19)

$$\mathbf{H}_0 = -4\pi\mathbf{k}\cdot\Delta\mathbf{M}_0\mathbf{k}/k^2.$$

Inserting this into Eq. (18), taking \mathbf{M}_s in the z -direction, and neglecting second-order terms, we get the pair of equations

$$i\omega\Delta M_{0x} = -\xi(k_x k_y/k^2)\Delta M_{0x} - [\eta k^2 + \zeta + \xi(k_y^2/k^2)]\Delta M_{0y} \quad (22)$$

$$i\omega\Delta M_{0y} = [\eta k^2 + \zeta + \xi(k_x^2/k^2)]\Delta M_{0x} + \xi(k_x k_y/k^2)\Delta M_{0y},$$

where $\xi = 4\pi M_s(e/mc)$, $\eta = 2(A/M_s)(e/mc)$, $\zeta = (H_{\text{ext}} + H_{\text{eff}})(e/mc)$. These give a secular equation for ω , whose solution is

$$\omega^2 = \eta^2 k^4 + (2\eta\zeta + \xi\eta \sin^2\theta_k)k^2 + \zeta^2 + \xi\zeta \sin^2\theta_k, \quad (23)$$

where θ_k is the angle between \mathbf{k} and the z -direction, i.e., \mathbf{M}_s .

The first term on the right of Eq. (23) represents the square of the frequency of a spin wave in the absence of magnetic interactions and coincides with the value used in the preceding section. For large k the difference between this and the correct frequency is given by

$$\hbar\omega - \hbar\eta k^2 \sim \hbar[\zeta + (\xi/2)\sin^2\theta_k] = 2(H_{\text{ext}} + H_{\text{eff}})\beta + 4\pi M_s \beta \sin^2\theta_k, \quad (24)$$

where β is the Bohr magneton, $e\hbar/2mc$. As $k \rightarrow 0$,

$$\hbar\omega \rightarrow \hbar[\zeta^2 + \xi\zeta \sin^2\theta_k]^{\frac{1}{2}} = [(H_{\text{ext}} + H_{\text{eff}}) \times (H_{\text{ext}} + H_{\text{eff}} + 4\pi M_s \sin^2\theta_k)]^{\frac{1}{2}} \beta, \quad (25)$$

a quantity which is always less than Eq. (24). Equation (25) is related to the expression $(BH)^{\frac{1}{2}}$, which occurs in the theory of ferromagnetic resonance. From Eqs. (24) and (25) one can infer the behavior shown schematically in Fig. 1 for $\hbar\omega$ as a function of k . It is easily verified that the difference $(\hbar\omega - \hbar\eta k^2)$ is always less than the right of Eq. (24), so if this quantity is $\ll kT$ over the range of temperatures normally used in comparing the $T^{\frac{1}{2}}$ law with experiment, the conventional treatment which assumes $\omega = \eta k^2$ can legitimately be used for the calculation of θ^* in Eq. (1). If $(H_{\text{ext}} + H_{\text{eff}}) \ll 4\pi M_s$, the condition is $T \gg 4\pi M_s/k = 1.7^\circ$ if $M_s = 2 \times 10^3$ gauss; it is thus fairly well satisfied for the common ferromagnetic substances over the experimentally significant part of the low temperature range. However, for paramagnetic salts (if such exist) with high anisotropy

energy and low Curie points the anisotropy corrections could be very important and could change the character of the temperature dependence of the saturation magnetization.

The complete expression for the magnetization M at any low temperature T can be deduced as a function of H_{ext} by evaluating the integral

$$\int_0^\infty \frac{k^2 dk}{\exp(\hbar\omega/kT) - 1}, \quad (26)$$

which is proportional to $M(0) - M(T)$. Since ω is given by Eq. (23), approximations must be used to evaluate the integral; as this problem has been fully discussed by Holstein and Primakoff in Sec. IV of their paper,⁵ we shall give merely the correspondence between our notation and theirs, which enables the treatment we have just given to be substituted for the first three sections of their paper. They express $\hbar\omega$ as $(A_k^2 - |B_k|^2)^{1/2}$, where, as comparison of their expressions with Eq. (23) shows, we must take

$$A_k = (4A/M_s)\beta k^2 + 2(H_{\text{ext}} + H_{\text{eff}})\beta + 4\pi M_s \beta \sin^2\theta_k \quad (27)$$

$$|B_k| = 4\pi M_s \beta \sin^2\theta_k. \quad (28)$$

Holstein and Primakoff⁵ have pointed out that even at the absolute zero the magnetization is slightly dependent on the field, and that, strictly speaking, this variation should be added to that of $M(T) - M(0)$ to get the total variation of $M(T)$ with H_{ext} . This variation of $M(0)$ with H_{ext} , which arises from the field dependence of the zero-point energy of the spin waves, is negligible for most practical purposes; however, it is interesting to examine how it comes about physically. Consider a spin wave whose wave vector \mathbf{k} is in the x -direction, \mathbf{M}_s being, as always, in the z -direction. From Eq. (22) we find for the ratio of axes of the elliptical cone which the spin vector describes

$$\Delta M_{0x}/\Delta M_{0y} = i[(\eta k^2 + \zeta)/(\eta k^2 + \zeta + \xi)]^{1/2}. \quad (29)$$

A straightforward calculation of the magnetic, anisotropy, and exchange energy associated with this spin wave gives

$$\text{total energy} = [\Omega/4(e/mc)M_s][(\eta k^2 + \zeta + \xi)|\Delta M_{0x}|^2 + (\eta k^2 + \zeta)|\Delta M_{0y}|^2], \quad (30)$$

where Ω is the volume of the specimen. Setting this equal to $\hbar\omega/2$ and using Eq. (29), we can calculate the zero-point amplitudes ΔM_{0x} and ΔM_{0y} . In particular, we find

$$|\Delta M_{0x}|^2 |\Delta M_{0y}|^2 = (4\beta M_s/\Omega)^2. \quad (31)$$

Thus the geometric mean of $|\Delta M_{0x}|^2$ and $|\Delta M_{0y}|^2$ is always the same as in the simple theory which neglects magnetic effects. Their algebraic mean, which determines the magnetization reversal associated with the spin wave, is always greater than the geometric mean, by an amount which increases as their ratio departs

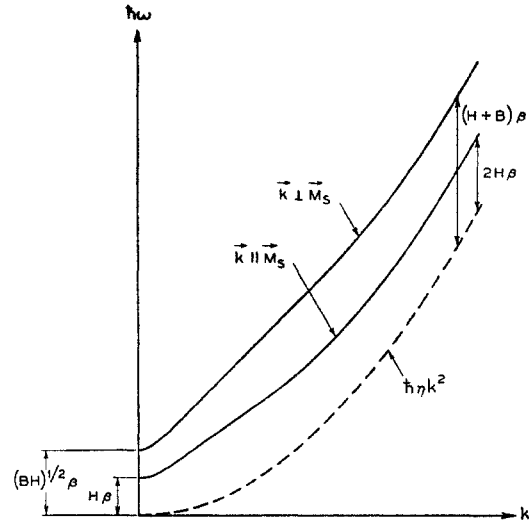


FIG. 1. Schematic variation of the frequency ω of a spin wave with its wave vector \mathbf{k} , in the presence of external and anisotropy fields, for $\mathbf{k} \parallel \mathbf{M}_s$ ($\theta=0$) and $\mathbf{k} \perp \mathbf{M}_s$ ($\theta=\pi/2$). The dashed line is the parabola given by the simple theory, ignoring magnetic and anisotropy terms. Distances above it are expressed in terms of $H = H_{\text{ext}} + H_{\text{eff}}$ and $B = H + 4\pi M_s$. When H becomes $\ll 4\pi M_s$, the $\theta=0$ curve approaches the dashed parabola, while for small k the curve for $\theta=\pi/2$ approaches a straight line passing through the origin.

increasingly from unity. If $(H_{\text{ext}} + H_{\text{eff}}) \ll 4\pi M_s$, the absolute value of the right of Eq. (29) will be $\ll 1$ for spin waves of small k , so that these spin waves will give a greater magnetization reversal than the simple theory predicts, and in particular, a nonvanishing zero-point reversal.

It is interesting to note that for a two-dimensional lattice the integral corresponding to Eq. (26), which has k instead of k^2 in the numerator, diverges if ω is taken proportional to k^2 , as in the simple theory, but converges if ω is modified by an anisotropy field according to Eq. (23). The divergence given by the simple theory signifies that in the absence of anisotropy a two-dimensional lattice cannot be ferromagnetic;^{8a} the convergence in the presence of anisotropy suggests that in layer lattices with exchange interaction the anisotropy energy may be able to induce a type of ferromagnetic behavior.

^{8a} This was first pointed out by F. Bloch, *Z. Physik* **61**, 206 (1930). The transition in thin films between three dimensions and two dimensions has recently been studied theoretically by M. J. Klein and R. S. Smith, *Phys. Rev.* **81**, 378 (1951). However, L. Onsager, *Phys. Rev.* **65**, 117 (1944), finds that if one uses the Ising model interaction $\sum S_i^z S_j^z$, two-dimensional lattices are ferromagnetic. The different types of behavior can be understood physically in terms of the energy required to reach a state of zero magnetic moment, starting from a saturated ground state. For a plane array N atoms on a side the energy required on the Ising model is $\approx NJ$, while on the correct exchange model it is $\approx J$. The latter result is readily demonstrated: the exchange energy between two spins making an angle φ with each other is $\approx J\varphi^2$, where we wish φ to be of the order of $1/N$ for a state of zero net moment. The number of pairs of spins involved is of the order of N^2 , so that the energy is $\approx J(1/N)^2 N^2 = J$.

III. CRITIQUE OF THE FIELD THEORY

A. Survey of Evidence on the Validity of the Spin Wave Picture

We turn now to the question of the validity of the theory of spin waves as applied to the calculation of the properties of ferromagnetics at moderately low temperatures, and in particular to the validity of the formulation which we have given in the preceding sections, according to which the properties of long-wavelength spin waves are derivable from the value of the Bloch wall coefficient A of Eq. (3). Although it would be difficult to construct a completely rigorous theory of spin waves, and especially so if one wished to avoid assuming any specialized model for the ferromagnetic crystal, there are a number of arguments which seem to us to indicate fairly convincingly that the theory of spin waves, in the form used in this paper, is fairly accurately valid for any ferromagnetic substance, i.e., that equations such as Eqs. (1), (5), etc., are correct over an experimentally significant range of temperatures, and that this validity is not dependent on the choice of any particular theoretical model. Since Wohlfarth⁶ and Stoner⁶ have recently argued the contrary, we shall undertake to summarize the evidence from the literature and to add some new arguments.

Evidence from the past literature consists of a number of indications that the theory of spin waves is valid for the atomic model. These include:

(i) Bethe's⁹ rigorous calculation of the energy levels of a linear chain of one-electron atoms, based on the hamiltonian $-J\sum S_i \cdot S_j$. This shows that the distribution of states in energy for this model is at low energies asymptotically the same as that given by Bloch's² theory of spin waves, and does not deviate significantly from the latter until energies are reached for which the mean number of reversed spins is a perceptible fraction of the total.

(ii) Opechowski's² calculation of the partition function for a three-dimensional array of atoms, with the hamiltonian $-J\sum S_i \cdot S_j$. This calculation, though not rigorous in the mathematical sense, is significant in that it uses an approach totally different from that of the spin wave theory, yet arrives at an identical result; moreover, by evaluating the T^2 term in Eq. (1), it indicates that the T^3 law is a good approximation until several percent of the spins have been reversed. It is interesting to note that the statistical treatment of Kramers,¹⁰ on which Opechowski based his work, assumes at the outset the physically obvious fact that the crystal is homogeneous; i.e., that the logarithm of the partition function is asymptotically proportional to the number N of atoms in the crystal. This fact can be seen, in an intuitive way, to be the reason that the criterion for validity of Bloch's theory should be the smallness of the mean fraction r/N of the spins which are reversed, rather than the smallness of the ratio r^2/N , whose exponential $\exp(r^2/N)$ gives the factor by which Bloch's theory overestimates the number of states with r reversed spins.

(iii) The analysis of Holstein and Primakoff,⁵ who have made a rough estimate of the errors involved in Bloch's spin wave

⁹ H. A. Bethe, *Z. Physik* **71**, 205 (1931); *Handbuch der Physik* **XXIV** 2, p. 604. Some, for our purposes, minor corrections have been given by L. Hulthén, *Astron. Fysik* **26A**, No. 11 (1938).

¹⁰ H. A. Kramers, *Communs. Kamerlingh Onnes Lab. Univ. Leiden*, Suppl. No. 83 (1936).

treatment and have concluded that they are probably small in the range of temperatures where the proportion of reversed spins is not over one or two percent.

From this evidence one might conclude merely that the theory of spin waves and the T^3 law are valid for the atomic model, but that they might fail for metals, where the occurrence of nonintegral magneton numbers shows the atomic model in its simple form to be inapplicable. However, it will be shown in a forthcoming paper by one of us¹¹ that spin waves also have a place in the so-called "itinerant electron" model of a ferromagnetic metal, and that, at least as far as the calculations have been carried, the whole theory of Sec. IIA seems to be as valid for this as for the atomic model.

Forgetting specific models for the moment, one can argue quite generally that for any ferromagnetic there must exist many low lying energy states which differ from the ground state principally in having the direction of the magnetization vector \mathbf{M} fluctuate from point to point; moreover, if by linear combinations of these we form a state in which \mathbf{M} approximates to a classical vector field of varying direction, the change of \mathbf{M} with time must be given by Eq. (16). This can be seen from the fact that application of a magnetic field $-2(A/M^2)\nabla^2\mathbf{M}$ would make the given distribution of \mathbf{M} an equilibrium distribution; the time change of \mathbf{M} in the absence of any such field will therefore be essentially the same as that which would be produced by the reverse field, and the latter is known from ferromagnetic resonance experiments to be a gyroscopic response to the type (16). It therefore seems fairly certain that the k th Fourier component of the temperature fluctuations in \mathbf{M} will have the amplitude given by the equipartition principle whenever this amplitude is large enough for this component of the motion to be treated classically. This seems to justify the spin wave theory for the calculation of the temperature variation of magnetization, as far as the contributions of very small wave vectors \mathbf{k} are concerned. If we can justify the theory for values of \mathbf{k} for which the quantum energy is of the order of kT , therefore, it will probably be safe to accept the theory completely.

The following two sections will be devoted for the most part to the problem just mentioned, or more specifically, to the problem of the existence of excited states of the crystal which have the properties of spin waves with single-quantum excitation, and the energies of these states. This problem is much simpler for a ferromagnetic insulator than for a metal, for reasons which are illustrated in Fig. 2. Here the energies of the various stationary states are depicted for various values of the quantum numbers commonly used to classify the states. These quantum numbers are S , the total spin, S_z , the z -component of spin, and \mathbf{k} , the total wave vector, defined by the condition that $\exp(-i\mathbf{k}\cdot\mathbf{t})$ be the eigenvalue of the operation of translating the whole

¹¹ C. Herring, *Energy of a Bloch Wall on the Band Picture, II. Perturbation Approach* (to be published).

wave function by a lattice vector \mathbf{t} . In general there will be an infinite number of eigenfunctions associated with each set of values of these quantum numbers. As is shown graphically in Fig. 2, the corresponding energy values have a continuous distribution if we are dealing with a metal; but for the case of a ferromagnetic insulator the lower lying states are discrete, at least for the ground-state value of S and the next smaller value.¹² This difference between insulators and metals makes the case of an insulator much easier to discuss. We shall, therefore, attack insulators first, in the section to follow, where without assuming any specific model it will be shown that the energy of a spin wave of wave vector \mathbf{k} is asymptotically $(2A\Omega/S)k^2$ when k is small, provided the Slater picture of Fig. 2 is qualitatively correct and provided two further physical assumptions, both almost certainly correct, are fulfilled. By showing the kind of physical assumptions which one must make to establish this result, this proof will clarify the problem of justifying the field theory for the case of a ferromagnetic metal, which we shall discuss in Sec. III C.

B. Relation of the Wall and Spin Wave Problems for an Insulator

Referring to Fig. 2, let us consider a ferromagnetic insulator whose ground state has energy E_0 and quantum numbers $S, k=0$, and let Ψ_0 be that one of the degenerate set of ground-state wave functions which has $S_z=S$. For an insulator we may define a spin wave state in general to be any eigenstate Ψ_k of spin $(S-1)$ and wave vector $\mathbf{k} \neq 0$; we shall be concerned almost exclusively with spin wave states of the lowest band, defined as those whose energies join on continuously to E_0 as \mathbf{k} is decreased to zero.

Let us assume the spin wave states and their energies to be known, and calculate the coefficient A in Eq. (3) by a perturbation method. If we assume a small torque $\sigma_y R \sin kx$ to act on each electron, the hamiltonian will contain a term which by Eq. (7) may be written

$$(R/2i)(s_y^{(k)} - s_y^{(-k)}). \tag{32}$$

The perturbation of the energy of Ψ_0 by this operator can be calculated and compared with what we would expect phenomenologically from Eq. (3). For the perturbed state we may set

$$M_y = M_y^0 \sin kx. \tag{33}$$

The change in energy density, relative to the unperturbed state, consists of a positive term of the form (3)

¹² These qualitative facts relating to the existence and spectrum of spin waves for an insulator have been elegantly demonstrated by J. C. Slater, Phys. Rev. 52, 198 (1937). Slater's picture is based on a solution of the quantum-mechanical problem which is only approximate, but which is sufficiently good to leave no doubt that the qualitative features of the spectrum would be unchanged by any further refinements, provided that the ground state of the insulator can be at least roughly described as having a filled band of majority spin electrons.

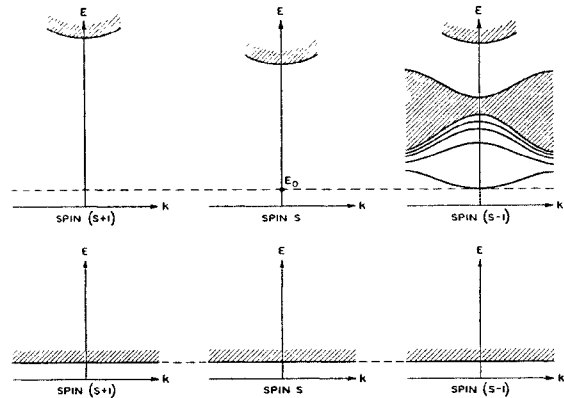


Fig. 2. Portions of typical energy spectra for a ferromagnetic insulator (top row) and a ferromagnetic metal (bottom row). The ground state is taken to have spin S , wave vector $k=0$, and energy E_0 . For an insulator the lowest excited states with spin S correspond essentially to excitation of one of the ferromagnetic electrons to a higher band without change of spin; the lowest states for spin $(S+1)$ correspond to excitation of an electron of minority spin to a higher band, with reversal of spin. For spin $< S$, on the other hand, there are spin wave states whose energies get almost as low as E_0 , and, at somewhat higher energies, a continuum corresponding to reversal of spins of electrons in the ferromagnetic band. The form shown for these levels is essentially that given by Slater (reference 12). For a metal with partially filled bands of both spins, on the other hand, there is an energy continuum whose bottom for $k \neq 0$ or for spin $\neq S$ is only infinitesimally above E_0 ; a metal with only completely filled bands of minority spin would differ from the case shown in having no low-lying states of spin $(S+1)$.

and a negative term proportional to the amount of yielding to the applied force; if Ω is the volume of the crystal the change in energy is therefore, to the second order in R ,

$$\Delta E = (\Omega A M_y^0 k^2 / 2M^2) - (\Omega R M_y^0 / 2).$$

The value of M_y^0 must be so chosen as to make this a minimum; this gives

$$M_y^0 = RM^2 / 2k^2 A, \tag{34}$$

and

$$\Delta E = -\Omega R^2 M^2 / 8k^2 A, \tag{35}$$

or

$$A = -\Omega R^2 M^2 / 8k^2 \Delta E. \tag{36}$$

Thus, A can be calculated from the second-order energy perturbation by Eq. (36) or from the first-order perturbation of \mathbf{M} by Eq. (34). If the perturbations are calculated by applying the Rayleigh-Schrödinger method with the perturbation operator (32), this method of calculating A involves an assumption which we shall label (a) to facilitate reference to it later:

(a) It is assumed that the value of A associated with very small perturbations—i.e., those for which $M_y^0 <$ the zero-point fluctuation in the corresponding Fourier component of M_y —is the same as that going with the larger perturbations to which Eq. (3) is intended to apply. It seems physically obvious that this will be the case here, because the energy depends only on local conditions,

whose change in a relatively large perturbation is qualitatively the same as that in a small one.¹³

Let us therefore consider Eq. (32). It connects the unperturbed state Ψ_0 only with states of wave vector $\pm\mathbf{k}$, and since it is the y component of a vector operator, it can connect Ψ_0 only with states of spin S or $S\pm 1$, $S_z = S\pm 1$. All of the states satisfying these requirements lie above E_0 by an amount which remains finite as $k\rightarrow 0$, except for states of the lowest spin wave band (Fig. 2). Thus, only the latter states can give a contribution of order $1/k^2$ to the energy perturbation; and so by Eq. (36) only these states need be considered in the calculation of A . The energy perturbation ΔE accordingly consists of two equal terms, the contributions from the spin wave states Ψ_k and Ψ_{-k} of the lowest band. Explicitly,

$$\Delta E = -R^2 |[\Psi_k, s_y^{(k)}\Psi_0]|^2 / 2(E_k - E_0). \quad (37)$$

Now, it is not hard to see that, as $k\rightarrow 0$, the numerator of Eq. (37) must approach a limit independent of the detailed nature of the wave functions. A simple way of proving this is to calculate the energy of the state $s_y^{(k)}\Psi_0$. For small k this state is everywhere very similar to Ψ_0 as far as local properties of the wave function are concerned, and its energy is easily shown to differ from E_0 by an amount of order k^2 , being, as is shown in Appendix B,

$$(s_y^{(k)}\Psi_0, Hs_y^{(k)}\Psi_0) / (s_y^{(k)}\Psi_0, s_y^{(k)}\Psi_0) = E_0 + (N/2S)k^2 \quad (38)$$

rydberg units if k is in a_H^{-1} , where N is the total number of electrons in the specimen. Since $s_y^{(k)}\Psi_0$ has wave vector \mathbf{k} , it must be a linear combination of Ψ_k and states of the higher spin wave bands. Since the latter have energies which remain above E_0 by a finite amount as $k\rightarrow 0$, their coefficients must be $0(k)$, so we must have

$$|(\Psi_k, s_y^{(k)}\Psi_0)|^2 = (s_y^{(k)}\Psi_0, s_y^{(k)}\Psi_0) + 0(k^2). \quad (39)$$

In Appendix B it is shown that the first term on the right of Eq. (39) has asymptotically the value $2S$ when the specimen is very large and k very small.

Combining this value of Eq. (39) with Eqs. (37) and (36) we get for the value of the coefficient A in Eq. (3)

$$A = \frac{S}{2\Omega} \lim_{k\rightarrow 0} \left(\frac{E_k - E_0}{k^2} \right) \quad (40)$$

in agreement with Eq. (14). This relation should be rigorously valid for any ferromagnetic insulator. Besides (a), we have used two further assumptions in its derivation:

(b) It has been assumed that the only states with which $s_y^{(k)}$ connects Ψ_0 are the spin wave state Ψ_k of the lowest band and

¹³ The correctness of this assumption can be confirmed for a special case in the Slater-Fock approximation of determinantal wave functions, since calculations with and without this assumption agree. These will be reported in two papers to be published by C. Herring.

other states whose energies remain above E_0 by a finite amount as $k\rightarrow 0$.

(c) Appendix B has made use of the assumption that when the system is in the state Ψ_0 , there is no long-range correlation between the values of the x - and y -components of the spins of electrons found in elements of volume which are a moderately large distance apart.

The former of these, especially, is not obviously true for a metal, since, as Fig. 2 shows, there is a continuum of states with which $s_y^{(k)}$ might conceivably connect Ψ_0 . However, we shall cite evidence in the next section that something very similar to this assumption is probably true for metals.

We have thus shown that for an insulator the correctness of the energies predicted by the field theory of Sec. IIA for states of single-quantum excitation is equivalent to the correctness of assumptions (a), (b), and (c). This complements the classical argument, given at the end of the preceding section, to the effect that the theory should be correct for motions with many-quantum excitation.

C. Spin Waves in a Metal

As a background for a discussion of spin waves in a metal it will be helpful to recall some of the properties which the itinerant electron model predicts for the energy spectrum of a metal. In the familiar form of the theory using this model the various energy levels must be classified merely according to the z -component of spin, since the determinantal wave functions which the theory uses are in general not eigenfunctions of S^2 . When overlapping bands are present, the minimum of the total energy occurs in general for a state corresponding to partially filled bands of both spins; this is of course the way in which nonintegral magneton numbers are explained by this model. This fact implies that there will in general be low-lying excited states of the metal with both higher and lower values of S_z than the ground state. It is commonly assumed that for a more exact model the same property would be possessed by the total spin S . If this is the case, a decrease of magnetization with temperature can result only from there being more states per unit energy in the low energy range for values of S smaller than the ground state value than for values the same amount larger. The usual form of the itinerant electron model does in fact predict an asymmetry of this sort in the distributions for different values of S_z , and this asymmetry has been shown by Stoner¹⁴ to lead to a temperature variation of magnetization of the form

$$M(T)/M(0) \sim 1 - CT^2. \quad (41)$$

¹⁴ E. C. Stoner, Proc. Roy. Soc. (London) **A165**, 372 (1938). Stoner's derivation assumes a parabolic band form but is easily generalized to bands of arbitrary form, no specializing assumption being necessary except that the exchange terms in the energy be approximated in such way as to yield an electronic specific heat linear in T at low temperatures. However, whereas C in Eq. (41) is always positive if the band form is parabolic, it may be of either sign with more general band forms.

When in the ground state one of the two directions of spin has only completely filled or completely empty bands of electrons, there is a minimum energy below which excited states of higher or lower spin do not exist, the lowest such states being ones of lower spin; for this case (41) is replaced by an exponential approach to saturation.

The success of the itinerant electron model in accounting for such phenomena as electronic specific heat suggests that the true energy states of a ferromagnetic metal correspond to a considerable degree with those given by the picture just described. However, it is easy to show that the correspondence is incomplete in one important respect: there exist low-lying states of the metal which are orthogonal to all the low-lying states of the usual itinerant electron model; and, as far as we have been able to deduce their properties, these states are of the nature of spin waves. To show that these states exist, consider the state Ψ_w of the metal which is derived from the ground state Ψ_0 by applying a sinusoidal perturbing torque of amplitude R and long wavelength $2\pi/k$ to the spin system, i.e., by adding a term of the form (32) to the hamiltonian. The derivative $\partial\Psi_w/\partial R$ will be a linear combination of those states of the metal with which the perturbation operator connects Ψ_0 , and in order that the energy of Ψ_w contain a term of order R^2/k^2 as $k\rightarrow 0$ [see Eq. (35)], at least some of these states must have energies which are infinitesimal of order k^2 . Now, if the stationary states of the metal are assumed to be of the determinantal form occurring in the itinerant electron theory, the only states with which the perturbation operator (32) will connect Ψ_0 will be states with an electron removed from some state \mathbf{k}_e and placed in a state $(\mathbf{k}_e+\mathbf{k})$ of opposite spin. When k is small, these states all have energies which lie above that of the ground state by amounts of the order of the exchange energy J of an electron; none of the energies is infinitesimal. Thus, the assumption that all the low-lying excited levels are the ones given by the usual itinerant electron theory leads to a contradiction with the existence of a term of the form (3) in the energy. It will be shown later by one of us¹¹ that when Ψ_w is approximated by a determinant, $\partial\Psi_w/\partial R$ is, in fact, independent of all the low-lying excited states which appear in the usual itinerant electron theory and has a mean energy E_k which is related to A by Eq. (40).

One is thus led to surmise that the low-lying stationary states of a ferromagnetic metal are of two types: first, states which may be described as having "no spin waves excited" and which have a distribution in energy and in S_z which is qualitatively similar to the distribution in energy and S_z which the itinerant electron model predicts; second, states derivable from these by excitation of spin waves. Each state of the former type may, we surmise, be the ancestor of many successive generations of the second type, of successively lower values of S . These progeny will cause a marked asymmetry

in the densities of states for spins higher and lower than that of the ground state, and will lead to the $T^{\frac{1}{2}}$ law (1); however, they will contribute only a $T^{\frac{1}{2}}$ term to the specific heat,¹⁵ which as $T\rightarrow 0$ will be swamped by the T term contributed by the parent states. If, as this picture suggests, the T^2 effect of Eq. (41) and the $T^{\frac{1}{2}}$ effect of Eq. (1) are simultaneously present, it will provide a natural explanation for the apparent mild contradiction between the experiments of Fallo⁴ and the theoretical finding of Opechowski² that on the atomic model the coefficient of the small T^2 term in Eq. (1) should have a positive sign.

Although this hypothesis is still very much in the realm of speculation, the evidence already discussed in support of it can be reinforced by a few additional fragments of reasoning. To begin with, we may inquire what meaning can be given to the conception of a "state with no spin waves excited." The reasoning of the preceding section and of Appendix B suggests that the states to which this designation can most conveniently be applied are those states with $S_z=S$ which satisfy assumption (c), i.e., which have no long-range correlation between the x - and y -components of the spins of electrons in different parts of the crystal, if stationary states with this property exist. It is shown in Appendix B that any operator of the form $[s_x^{(k)}+is_y^{(k)}]$, k small, takes any state of the type just mentioned into a state whose normalization integral is very small. Since this operator is essentially the destruction operator for a spin wave of wave vector \mathbf{k} in the field theory, this suggests describing the states in question as having "no spin waves excited," at least as far as long wavelength spin waves are concerned. Moreover, any linear combination of a small number of such states will have approximately the same property. Finally, it is physically plausible that when the hamiltonian operates on a wave function without long-range spin correlations, the result will nearly always be a wave function with the same property. It is, therefore, reasonable to expect that stationary states will exist which possess, or almost possess, this property.

A second point concerns the interpretation of the result, quoted above, that when the eigenfunction Ψ_w in a sinusoidal perturbing field is approximated by a determinant of one-electron functions, the mean energy of $\partial\Psi_w/\partial R$ is given by Eq. (40). Now for an insulator $\partial\Psi_w/\partial R$ is an eigenfunction with energy E_k , plus terms of order k as $k\rightarrow 0$; for a metal, on the other hand, we have to consider the possibility that $\partial\Psi_w/\partial R$ may be a linear combination of a number of low energy eigenfunctions with appreciably different energies. One might at first think that mere knowledge of the mean energy of $\partial\Psi_w/\partial R$ would give almost no information on the energies of the latter states, since some might lie above and some below the mean. However, it is shown in

¹⁵ See, for example, N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, 1936), p. 237.

Appendix C by a comparison of this mean energy with the perturbed energy of Ψ_w and an application of the Schwarz inequality one can deduce the relation

$$\bar{E} - E_0 \leq (2\Omega/S)Ak^2 + O(k^4), \quad (42)$$

where \bar{E} is the mean energy of $\partial\Psi_w/\partial R$, E_0 is the ground state energy, and k is the wave vector of the perturbation (32). The equality, i.e., Eq. (40), can hold only if the expansion coefficients c_i and energies E_i of the eigenfunctions contained in $\partial\Psi_w/\partial R$ satisfy the condition

$$c_i(E_i - E_0) = c_i\delta E + O(k), \quad (43)$$

where δE is independent of i . For this case the energies E_i of these states for which c_i is of order k^{-2} or larger must lie in a very narrow range centered at the point $(E_0 + \delta E)$. Thus, if the equality which has been proved to hold in Eq. (42) in the determinantal approximation holds true in general, $\partial\Psi_w/\partial R$ will be very nearly an eigenfunction of a single energy, which may be called a spin wave. Moreover, it is shown in Appendix C that in this case $\partial\Psi_w/\partial R$ will differ only infinitesimally from a multiple of $(P_-^{(k)} + iQ_-^{(k)})\Psi_0$, where the operator in parentheses is just the creation operator for the "minus" type of spin wave in the theory of Sec. IIA.

D. Miscellaneous Comments

It is worth pointing out that there are more familiar problems which involve an approximation similar to that involved in the substitution of the H' of Eq. (11), a quadratic expression in the spin densities, for the true hamiltonian H . This substitution is *not* analogous to the substitution of $-2\sum J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ for the true hamiltonian in an exchange degeneracy problem: in the latter case a certain subspace of Hilbert space, known at the outset, is taken into itself by the approximate hamiltonian, whose matrix in this subspace coincides with that of the true hamiltonian; in our case no such subspace is known. This leads to the paradox that, although the eigenfunction of Eq. (11) having a $n_+^{(k)} = 1$, other $n'_s = 0$, is proportional to $(P_+^{(k)} + iQ_+^{(k)})\Psi_0$, where Ψ_0 is the ground-state wave function, nevertheless, as can be seen from the analysis of Sec. IIIB, the energy of the state $(P_+^{(k)} + iQ_+^{(k)})\Psi_0$ as calculated with the true hamiltonian is in general significantly higher than the correct energy as given by Eq. (14).

The use of Eq. (11) is more nearly analogous to the use of the adiabatic approximation to calculate the low-lying vibrational levels of a molecule, a procedure which leads to a paradox of the same form as that just mentioned. If R is the internuclear distance in a diatomic molecule, p_R the conjugate momentum, μ the reduced mass, and ω the angular frequency of the vibration in R , the reader can easily verify that the wave function obtained by operating on the ground state eigenfunction with $p_R + i\mu\omega(R - R_0)$ has a mean energy, computed with the true hamiltonian for electrons and nuclei, which differs from that of the first

excited state by an amount of the same order as the energy of excitation itself. Another example, which resembles our magnetic problem more closely, is the problem of computing the quantized energies of the low-lying acoustical modes of vibration of a crystal whose unit cell contains atoms which do not occupy symmetry positions. It is well known that the energies of these acoustical vibrational levels can be computed from a knowledge of the elastic constants of the crystal; i.e., of the minimum energy consistent with a given long-wavelength variation of the mean displacement of the atoms in a unit cell. In general, however, any elastic distortion will change the relative positions of the atoms in a unit cell,¹⁶ and the eigenstates of a phenomenological hamiltonian constructed in the way we have been discussing will not manifest this change; they will therefore have the wrong energy when the energy is computed with the correct hamiltonian. Since the relative displacements are of the order of the amplitude, a , of the wave times its wave vector, k , the energy discrepancy per unit volume will be of order a^2k^2 , which is of the same order as the vibrational energy itself. In spite of this the phenomenological hamiltonian gives the correct energies.

Another point worth noting is that Eq. (38), which was derived primarily as a tool for the proof of Eq. (40), gives as a by-product an upper limit to E_k , and correspondingly an upper limit to A . In atomic units

$$A < N/4\Omega. \quad (44)$$

If this is applied to a case in which the Heitler-London-Heisenberg model is valid and in which it is legitimate to treat the ferromagnetic electrons as a system independent of the other electrons, so that $N/\Omega = 2S_0/\Omega_0$, we have from Eq. (4)

$$J < 3/ZS_0R_n^2. \quad (45)$$

Although this limit is some tens of times larger than the J 's usually assumed for ferromagnetic substances, it is interesting that a relation of this kind should exist, since the definition of J would lead one to expect merely an upper limit going as R_n^{-1} and, of course, independent of Z .

We wish to thank Professor J. M. Luttinger for some illuminating discussions of field theory.

APPENDIX A. SEMICLASSICAL THEORY OF SPIN WAVES ON THE ATOMIC MODEL, WITH APPLICATION TO RHOMBIC LATTICES

We give first a semiclassical derivation of spin-wave theory on the atomic model. The derivation is rather simpler and more concise than previous derivations in the literature.

The hamiltonian of the system is

$$H' = -2J\sum_{i>j}\mathbf{S}_i \cdot \mathbf{S}_j, \quad (A1)$$

where \mathbf{S}_i is the spin operator in units of \hbar for the i th atom. Each atom has $2S_0$ resultant electron spins. The quantum equation of

¹⁶ See, for example, M. Born and M. Goepfert-Mayer, *Handbuch der Physik* XXIV 2, p. 630.

motion for \mathbf{S}_m is

$$\begin{aligned} i\hbar d\mathbf{S}_m/dt &= [\mathbf{S}_m, H'] \\ &= 2J[(\sum \mathbf{S}_i \cdot \mathbf{S}_j)\mathbf{S}_m - \mathbf{S}_m(\sum \mathbf{S}_i \cdot \mathbf{S}_j)] \\ &= 2J\sum_j [(\mathbf{S}_m \cdot \mathbf{S}_j)\mathbf{S}_m - \mathbf{S}_m(\mathbf{S}_m \cdot \mathbf{S}_j)] \\ &= -2J\sum_j \mathbf{S}_j \times [\mathbf{S}_m \times \mathbf{S}_m], \end{aligned}$$

which becomes, using the commutation relation $\mathbf{S} \times \mathbf{S} = i\mathbf{S}$,

$$\hbar d\mathbf{S}_m/dt = 2J\mathbf{S}_m \times \sum \mathbf{S}_j. \quad (\text{A2})$$

For a simple cubic lattice with lattice constant a we have by series expansion

$$\sum_j \mathbf{S}_j = 6\mathbf{S}_m + a^2 \nabla^2 \mathbf{S} + \dots, \quad (\text{A3})$$

where the \mathbf{S} 's are now considered as classical vectors, and not as quantum operators. For small distortions we neglect higher order terms in the series expansion, and thus we have the equation of motion

$$\hbar d\mathbf{S}/dt = 2J a^2 [\mathbf{S} \times \nabla^2 \mathbf{S}]$$

for the spin considered as a classical quantity. One can easily verify, by replacing (A3) by an expression involving $\frac{1}{2}\sum R_\mu R_\nu \partial^2 \mathbf{S}_m / \partial x_\mu \partial x_\nu$, that for any lattice of cubic symmetry with Z nearest neighbors to each lattice site,

$$\hbar d\mathbf{S}/dt = (ZR_n^2 J/3)\mathbf{S} \times \nabla^2 \mathbf{S}, \quad (\text{A4})$$

where R_n is the separation of nearest neighbors. Let

$$\mathbf{S} = \mathbf{S}_0 + \boldsymbol{\epsilon} \quad (\text{A5})$$

where \mathbf{S}_0 is the unperturbed spin vector, and $\boldsymbol{\epsilon}$ represents a spin wave of small amplitude. With this substitution Eq. (A4) reduces to

$$d^2 \boldsymbol{\epsilon}_x / dt^2 = -(ZR_n^2 J S_0 / 3 \hbar)^2 \nabla^2 \boldsymbol{\epsilon}_x, \quad (\text{A6})$$

where we have supposed that $\epsilon/S_0 \ll 1$, thereby determining the range of validity of the theory. Equation (A6) is essentially a wave equation, and it has solutions of the form

$$\boldsymbol{\epsilon}_x = \boldsymbol{\epsilon}_0 \exp[i(\omega t + \mathbf{k} \cdot \mathbf{r})],$$

where

$$\hbar \omega = (ZR_n^2 J S_0 / 3) k^2. \quad (\text{A7})$$

This is the fundamental relation between frequency and wave number of a spin wave. The wave is quantized in the usual way, setting $E = n\hbar\omega$, where n is readily shown to be the number of reversed spins in the system.

We go on to consider spin wave theory for a simple rhombic lattice with exchange integrals J_a, J_b, J_c connecting neighbors along the three mutually perpendicular axes a, b, c . The equation of motion becomes

$$\hbar d\mathbf{S}/dt = 2\mathbf{S} \times \left(a^2 J_a \frac{\partial^2 \mathbf{S}}{\partial x^2} + b^2 J_b \frac{\partial^2 \mathbf{S}}{\partial y^2} + c^2 J_c \frac{\partial^2 \mathbf{S}}{\partial z^2} \right), \quad (\text{A8})$$

which leads to the relation

$$\hbar \omega = 2S_0(a^2 J_a k_x^2 + b^2 J_b k_y^2 + c^2 J_c k_z^2). \quad (\text{A9})$$

The reversed magnetization is proportional to

$$\int dk_x dk_y dk_z / [\exp(\hbar\omega/kT) - 1];$$

on substituting

$$\begin{aligned} x^2 &= 2S_0 a^2 J_a k_x^2 / kT; & z^2 &= 2S_0 c^2 J_c k_z^2 / kT; \\ y^2 &= 2S_0 b^2 J_b k_y^2 / kT; & r^2 &= x^2 + y^2 + z^2; \end{aligned}$$

the integral becomes

$$\frac{N(kT/2S_0)^{3/2}}{J_a^{1/2} J_b^{1/2} J_c^{1/2}} \int \frac{4\pi r^2 dr}{\exp(r^2) - 1}$$

where $N = 1/abc$ is the number of atoms per unit volume. This expression goes over into the usual expression for a simple cubic crystal on letting $a = b = c, J_a = J_b = J_c$. For the rhombic case we have

$$M_s = M_0 [1 - 0.117(kT/2S_0)^{3/2} / J_a^{1/2} J_b^{1/2} J_c^{1/2}]. \quad (\text{A10})$$

APPENDIX B. SOME PROPERTIES OF STATES OF THE FORM $s_y^{(k)}\Psi_0$, ETC.

Let Ψ_0 be a state with total spin S and z -component of spin $S_z = S$, and consider the state $s_y^{(k)}\Psi_0$, where $s_y^{(k)}$ is the k th Fourier component of the y -component of spin density, as defined by Eq. (7). The normalization integral of this state is the mean value, in the state Ψ_0 , of the operator

$$s_y^{(k)+} s_y^{(k)} = N + \sum_{i \neq j} \sigma_y^{(i)} \sigma_y^{(j)} \cos[\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)], \quad (\text{B1})$$

where N is the total number of electrons present. The mean value of the second term of (B1) in the state Ψ_0 is

$$\begin{aligned} \langle \Psi_0, \sum_{i \neq j} \sigma_y^{(i)} \sigma_y^{(j)} \cos[\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \Psi_0 \rangle \\ = \int \int \Delta P(\mathbf{r}_1, \mathbf{r}_2) \cos[\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] d\tau_1 d\tau_2, \quad (\text{B2}) \end{aligned}$$

where $\Delta P(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2$ is the probability that, when the system is in the state Ψ_0 , an electron will be found in $d\tau_1$ at \mathbf{r}_1 , another in $d\tau_2$ at \mathbf{r}_2 , these two having parallel y -components of spin, minus the corresponding probability for antiparallel y -components. Now, since Ψ_0 is an eigenfunction of S_z , the mean value of the y -component of spin of an electron found at any given point of space vanishes; if we may assume the physical nature of the problem to require that the spin distributions in $d\tau_1$ and $d\tau_2$ approach statistical independence as $|\mathbf{r}_1 - \mathbf{r}_2|$ becomes large, we must have

$$\Delta P(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 0 \quad \text{as} \quad |\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty.$$

This requirement, though undoubtedly fulfilled by the ground state of an insulator, is, as we shall see below, not necessarily fulfilled by other states, e.g., by spin wave states. Actually, it is to be expected that ΔP will differ significantly from zero only when $|\mathbf{r}_1 - \mathbf{r}_2|$ is less than a few lattice spacings. Since we are interested only in infinitesimal values of k , we may therefore set $\cos[\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] = 1$ in Eq. (B2):

$$\begin{aligned} (\text{B2}) &= \int \int \Delta P(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2 + O(k^2) \\ &= \langle \Psi_0, \sum_{i \neq j} \sigma_y^{(i)} \sigma_y^{(j)} \Psi_0 \rangle + O(k^2). \quad (\text{B3}) \end{aligned}$$

The scalar product in Eq. (B3) is easily expressed in terms of the spin quantum numbers. For

$$\mathbf{S}^2 = (3N/4) + \left(\frac{1}{4}\right) \sum_{i \neq j} \sigma_x^{(i)} \sigma_x^{(j)} + \left(\frac{1}{4}\right) \sum_{i \neq j} [\sigma_x^{(i)} \sigma_x^{(j)} + \sigma_y^{(i)} \sigma_y^{(j)}] S_z^2 = (N/4) + \left(\frac{1}{4}\right) \sum_{i \neq j} \sigma_z^{(i)} \sigma_z^{(j)}.$$

Combining, we have

$$2(\mathbf{S}^2 - S_z^2) - N = \frac{1}{2} \sum_{i \neq j} (\sigma_x^{(i)} \sigma_x^{(j)} + \sigma_y^{(i)} \sigma_y^{(j)}). \quad (\text{B4})$$

Now, in any eigenstate of S_x the means of the two terms on the right of Eq. (B4) are the same, so for the state Ψ_0 for which \mathbf{S}^2 is $S(S+1)$ and S_z is S ,

$$\langle \Psi_0, \sum_{i \neq j} \sigma_y^{(i)} \sigma_y^{(j)} \Psi_0 \rangle = 2S - N. \quad (\text{B5})$$

Combining (B5), (B3), (B2), and (B1) we have, therefore,

$$\langle s_y^{(k)} \Psi_0, s_y^{(k)} \Psi_0 \rangle = 2S + \delta, \quad (\text{B6})$$

where δ is $O(k^2)$ as $k \rightarrow 0$ and $O(1)$ as N and the size of the crystal become infinite at fixed k .

Next consider the mean energy \bar{E}_k of $s_y^{(k)}\Psi_0$, given by

$$\begin{aligned} \bar{E}_k(s_y^{(k)}\Psi_0, s_y^{(k)}\Psi_0) &= \langle s_y^{(k)}\Psi_0, H s_y^{(k)}\Psi_0 \rangle \\ &= E_0(s_y^{(k)}\Psi_0, s_y^{(k)}\Psi_0) + \langle \Psi_0, s_y^{(k)+} [H s_y^{(k)} - s_y^{(k)} H] \Psi_0 \rangle. \quad (\text{B7}) \end{aligned}$$

Only the kinetic energy operator contributes to the commutator; in atomic units we have

$$\begin{aligned} s_y^{(k)+} [H s_y^{(k)} - s_y^{(k)} H] &= k^2 s_y^{(k)+} s_y^{(k)} \\ &\quad - 2i\mathbf{k} \cdot \sum_{i,j} \sigma_y^{(i)} \sigma_y^{(j)} \exp[i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \nabla_j. \quad (\text{B8}) \end{aligned}$$

It is clear at this point that the \bar{E}_k given by Eq. (B7) will be $E_0 + O(k^2)$ if Ψ_0 has any symmetry property which requires \bar{E}_k and \bar{E}_{-k} to be the same. To evaluate the coefficient of k^2 explicitly for the case where Ψ_0 is the ground state of an insulator we may take this symmetry property to be invariance under Wigner's

TABLE I. Group-theoretical restrictions on the lengths of components of $\mathbf{s}^{(k)}\Psi_0$.

Subspace Wave function	(S-1)	S	(S+1)
$(s_x^{(k)} + is_y^{(k)})\Psi_0$	0	0	L_+
$s_x^{(k)}\Psi_0$	0	L_0	$L_+/(2S+2)^\dagger$
$(s_x^{(k)} - is_y^{(k)})\Psi_0$	L_-	$L_0/(2S)^\dagger$	$L_+/\{(S+1)(2S+1)\}^\dagger$

time-reversal operation,¹⁷ and shall accordingly replace the second term on the right of Eq. (B8), which we may call G , by the average of G , the time-reversed operator, and the adjoints of these, the latter averaging being permissible since the mean value of G must be real. The result is

$$G \rightarrow \mathbf{k} \cdot \sum_{i,j} \sigma_y^{(i)} \sigma_y^{(j)} (\sin[\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \nabla_j - \nabla_j \sin[\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)]) \\ = -k^2 \sum_{i \neq j} \sigma_y^{(i)} \sigma_y^{(j)} \cos[\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)]. \quad (\text{B9})$$

Combining with Eqs. (B8) and (B7) and the previous evaluation of Eq. (B2), we have, finally,

$$\bar{E}_k = E_0 + (N/2S)k^2 \quad (\text{B10})$$

to within an error which is $O(k^4)$ as $k \rightarrow 0$, and $O(N^{-1})$ as $N \rightarrow \infty$.

A slight extension of the argument leading to Eq. (B6) enables us to calculate the orders of magnitude of the portions of $\mathbf{s}^{(k)}\Psi_0$ which have spins $(S-1)$, S , and $(S+1)$. Remembering that Ψ_0 has $S_x = S$, we can use the group-theoretical relations between the different matrix elements of a vector operator¹⁸ to express the lengths of the projections of the various $s_\mu^{(k)}\Psi_0$ ($\mu = x, y, z$) onto the subspace of spin S' in terms of a single constant dependent on S' , as shown in Table I. The entries in the table are the values of the square root of the normalization integral of the projection of the wave function indicated at the left of each row onto the subspace of the spin indicated in each column. Without further assumptions regarding the nature of the state Ψ_0 we can say nothing about the values of the constants L_+ , L_0 , L_- . However, if Ψ_0 has the property of having no long-range correlations between x - and y -components of spin density we can evaluate them by the method used for Eq. (B6). We have

$$(s_x^{(k)} + is_y^{(k)})^\dagger (s_x^{(k)} + is_y^{(k)}) = 2N - 4S_x \\ + \sum_{i \neq j} (\sigma_x^{(i)} \sigma_x^{(j)} + \sigma_y^{(i)} \sigma_y^{(j)}) \cos[\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \\ - \sum_{i \neq j} (\sigma_x^{(i)} \sigma_y^{(j)} - \sigma_y^{(i)} \sigma_x^{(j)}) \sin[\mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_i)]. \quad (\text{B11})$$

The square of the quantity L_+ of Table I is the expectation value of (B11). If Ψ_0 has the property just mentioned and has in addition any symmetry property which requires this to be the same for \mathbf{k} and $-\mathbf{k}$, this expectation value is given to within an error of order Nk^2 by setting the cosine equal to unity and the sine to zero in (B11); using (B4) this gives

$$L_+^2 = O(Nk^2). \quad (\text{B12})$$

A similar argument using the operator $s_x^{(k)} + s_y^{(k)}$ gives a value for $L_0^2 + L_+^2/(2S+2)$; neglecting the second of these terms, we find

$$L_0^2 = O(Nk^2). \quad (\text{B13})$$

The operator $(s_x^{(k)} - is_y^{(k)})^\dagger (s_x^{(k)} - is_y^{(k)})$ differs from the right of (B11) only in having a plus sign for the term $4S_x$; its mean value gives $[L_-^2 + (2L_0^2/S) + L_+^2/(S+1)(2S+1)]$, and since the last two of these terms are negligible compared with the first, we have

$$L_-^2 = 8S + O(Nk^2). \quad (\text{B14})$$

It is now very easy to show that the lack of long-range correlations between x - and y -components of spin density, which we have assumed in deriving the preceding equations, especially Eq. (B12), cannot be valid for states with spin waves excited. For suppose Ψ_0 to be a state with no spin waves excited, so that Eqs. (B12), (B13), and (B14) apply to it. Then

$$(s_x^{(k)} - is_y^{(k)})\Psi_0/L_- = \Psi_1 + O(k), \quad (\text{B15})$$

where Ψ_1 is a state of spin $(S-1)$, which, for the case where Ψ_0 is the ground state of an insulator, differs only by $O(k)$ from the normalized eigenfunction of the lowest spin-wave band. Taking the scalar product of (B15) with Ψ_1 and using the properties of adjoint operators,

$$[(s_x^{(-k)} + is_y^{(-k)})\Psi_1, \Psi_0] = L_- [1 + O(k)] = O(N^\dagger),$$

whence it is obvious that the length of $[(s_x^{(-k)} + is_y^{(-k)})\Psi_1]$ is $O(N^\dagger)$, rather than $O(N^\dagger k)$ as it would be if Eq. (B12) applied to it.

APPENDIX C. MEAN ENERGY OF $\partial\Psi_w/\partial R$

Let $\Psi_w(R)$ be the ground-state eigenfunction of the sum of the crystal hamiltonian and the perturbation (32). Its energy will be of the form $(E_0 + \Delta E)$, where E_0 is the energy of the unperturbed ground-state eigenfunction Ψ_0 and

$$\Delta E = -R^2 \sum_i |\Delta_{i0}|^2 / (E_i - E_0), \quad (\text{C1})$$

where Δ_{i0} is the matrix element of the perturbation connecting the eigenfunctions Ψ_0 and Ψ_i . Defining c_i as the coefficient of $R\Psi_i$ in Ψ_w , i.e.,

$$c_i = -\Delta_{i0} / (E_i - E_0), \quad (\text{C2})$$

we can rewrite Eq. (C1) as

$$\Delta E = R^2 \sum_i c_i \Delta_{i0}^*. \quad (\text{C3})$$

The mean value \bar{E} of the crystal hamiltonian in the state $\partial\Psi_w/\partial R$ is given by

$$\bar{E} - E_0 = -(\sum_i c_i \Delta_{i0}^*) / \sum_i |c_i|^2. \quad (\text{C4})$$

Applying the Schwarz inequality to Eq. (C4) and noting that the left side is >0 , we have

$$\bar{E} - E_0 \leq [(\sum_i |\Delta_{i0}|^2) / \sum_i |c_i|^2]^\dagger. \quad (\text{C5})$$

Likewise, applying the Schwarz inequality to Eq. (C3) and using Eq. (36) of the text,

$$A \geq \Omega M^2 / 8k^2 [(\sum_i |\Delta_{i0}|^2) (\sum_i |c_i|^2)]^\dagger. \quad (\text{C6})$$

The equality holds in Eqs. (C5) and (C6) if and only if $\Delta_{i0} \propto c_i$, i.e., if E_i is the same for all states for which $\Delta_{i0} \neq 0$. Now, if Ψ_0 satisfies the postulate (c) of Sec. IIB, regarding the absence of long-range correlations between x - and y -components of spin, we have from Eq. (B6) of Appendix B

$$\sum_i |\Delta_{i0}|^2 = \text{mean square of (32)} / R^2 = S + O(k^2). \quad (\text{C7})$$

Combining Eqs. (C5), (C6), and (C7) gives, therefore, with $M = 2S/\Omega$,

$$\bar{E} - E_0 \leq (2\Omega/S) A k^2 + O(k^4). \quad (\text{C8})$$

If the $O(k^4)$ in Eq. (C8) is to be merely that due to the $O(k^2)$ in Eq. (C7), the multidimensional vectors c and Δ must be parallel, as mentioned above. However, if $(\bar{E} - E_0)$ departs from the first term on the right of (C8) by this plus an additional amount of order k^4 , these two vectors may make a small angle of order k with each other, so that we have merely

$$\Delta_{i0} = -c_i (E_i - E_0) = -c_i \delta E + O(k), \quad (\text{C9})$$

where δE is some constant independent of i , but dependent on k and of order k^2 , so that $c_i \delta E$ is $O(k^{-1})$.

¹⁷ E. Wigner, Göttingen Nachrichten (1932), p. 546.

¹⁸ See for example E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Friedrich Vieweg und Sohr, Braunschweig, 1931), p. 264.