# Green's-Function Theory of Ferrimagnetism, with an Application to Magnetite*

ROGER E. MILLS, RICHARD P. KENAN, AND FREDERICK J. MILFORD
*Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio*
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A Green's-function theory of magnetic properties of an $n$-sublattice ferrimagnet is derived in the random-phase approximation. The magnitude and relative orientation of the sublattice magnetizations, the renormalized magnon spectra, the zero-point motion and the Curie temperature as functions of the spin magnitudes, the exchange constants and the geometry are derived. These properties have been computed for magnetite. It is concluded that magnitudes of the exchange constant $J_{AB}$ between sites of tetrahedral and octahedral coordination of about $2.5\times10^{-3}$ eV above 119°K, and about $1\times10^{-3}$ eV below that temperature, are consistent with present experimental data for magnetite.

## 1. INTRODUCTION

EARLIER studies of magnetite have not led to a satisfactory determination of the exchange constants which characterize the magnetic properties of this substance. Linear spin-wave theories for magnetite[1–8] have been used to fit experimental data for the low-temperature specific heat,[9,10] the thermal conductivity,[11] and the acoustical and optical magnon spectra observed at room temperature.[12] The exchange constant between sites of tetrahedral and octahedral coordination $J_{AB}$, has been found to be about an order of magnitude greater than any of the other constants. However, the data for the specific heat require for $J_{AB}$ the value $0.44\times10^{-3}$ eV[9] or $1.1\times10^{-3}$ eV,[10] while the spectra require the value $2.4\times10^{-3}$ eV.[6] The result of the thermal-conductivity evaluation is not conclusive since it requires other parameters which can, at present, only be estimated. The experimental value of the Curie temperature[13] can be used in an expression for $T_c$ from molecular field theory[5] to calculate the value $1.6\times10^{-3}$ eV for $J_{AB}$, a result which does not clearly favor any of the other values. The fact that the linear spin-wave theories and the molecular field theory ignore the effect of statistical and dynamical correlations of the spins at higher temperatures indicates that the fit to the spectral data may need correction. The attempt at comparing high- and low-temperature data may be frustrated by a phase transition at 119°K in which the magnetite goes from a fcc structure to an orthorhombic structure upon cooling. Part of the purpose of the present paper is to report on a calculation of the renormalized magnon spectra and the thermodynamic properties of magnetite.

A two-time Green's-function theory of ferrimagnets with an isotropic Hamiltonian is derived in Sec. 2. This theory has been developed as a generalization of theories of ferromagnets due to Tahir-Kheli and ter Haar[14] and to Callen.[15] While this work was in progress, related papers on antiferromagnets were published by Hewson and ter Haar[16] and by Lines.[17] The present theory obtains generalizations of the spin-wave spectra and Curie temperatures derived by these older theories. It is shown that the zero-point motion of a magnetic system is described in a Green's function theory in a very simple manner which reflects directly the physical nature of the phenomenon. It is recognized here that in the absence of an external field the alignment of a magnetic system is not specified *a priori*, but, through the renormalization, the relative ordering of the sublattice magnetizations can be predicted correctly for a given choice of the exchange constants, independently of any preassigned choice of positive $z$ direction for a sublattice. Contact with the earlier results[14–17] is made in Sec. 3 where a brief application of the theory is made in the cases of simple ferromagnetism and two-sublattice antiferromagnetism. These applications illustrate some of the details of the theory and exhibit their physical significance. Results of calculations of the sublattice magnetizations and the Curie temperature of magnetite are given in Sec. 4 together with a comparison with experimental data. A summary and conclusions are presented in Sec. 5. Mathematical details concerning aspects of the approximations which have been used have have been relegated to Appendices.

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## 2. TWO-TIME GREEN'S-FUNCTION THEORY OF FERRIMAGNETS

The ferrimagnets described in this section are those whose Hamiltonian can be expressed in the form

$$\mathcal{H}=-\mu\mathbf{H}\cdot\sum_{\alpha m} g_\alpha \mathbf{S}_{\alpha m}+\sum_{\alpha\beta,mn} J_{\alpha m,\beta n}\mathbf{S}_{\alpha m}\cdot\mathbf{S}_{\beta n}, \quad (2.1)$$

in which $\mu$ is the Bohr magneton, $H$ is a uniform, external field, $\mathbf{S}_{\alpha m}$ is a spin operator situated on site $m$ of sublattice $\alpha$, $g_\alpha$ is the $g$ factor for the sublattice $\alpha$, and $J_{\alpha m,\beta n}$ is the exchange energy between atoms on sites $\mathbf{r}_{\alpha m}$ and $\mathbf{r}_{\beta n}$.[18] A positive value of $J_{\alpha m,\beta n}$ corresponds to antiferromagnetic coupling. It is assumed that all of the atoms on sublattice $\alpha$ are identical, with spin magnitude $S_\alpha$. No restrictions are placed on the number of sublattices, or the number of the sites on a sublattice. It should be noted that sublattices are to be distinguished here on a basis of differences in local magnetic characteristics and not merely differences in geometrical or chemical characteristics.

The commutation rules obeyed by the spin operators are, with

$$S_{\alpha m}{}^{\pm}=S_{\alpha m}{}^{x}\pm iS_{\alpha m}{}^{y}, \quad (2.2)$$

$$[S_{\alpha m}{}^{z},S_{\beta n}{}^{\pm}]_-=\pm S_{\alpha m}{}^{\pm}\delta_{\alpha\beta}\delta_{mn}, \quad (2.3a)$$

and

$$[S_{\alpha m}{}^{+},S_{\beta n}{}^{-}]_-=2S_{\alpha m}{}^{z}\delta_{\alpha\beta}\delta_{mn}. \quad (2.3b)$$

The ferrimagnets considered here have no preferred direction in the absence of an external field, so any uniform nonzero $H$, however small, will be taken as defining the direction of the $z$ axis. The internal energy is then

$$\langle\mathcal{H}\rangle=-\mu H\sum_{\alpha m}g_\alpha\sigma_\alpha+\tfrac{1}{2}\sum_{\alpha\beta}\sum_{mn}J_{\alpha m,\beta n}\times\langle S_{\alpha m}{}^{-}S_{\beta n}{}^{+}+S_{\alpha m}{}^{+}S_{\beta n}{}^{-}+2S_{\alpha m}{}^{z}S_{\beta n}{}^{z}\rangle. \quad (2.4)$$

Here $\langle\cdots\rangle$ denotes the expectation value with respect to the canonical ensemble, and $\sigma_\alpha=\langle S_{\alpha j}{}^{z}\rangle$. The site label $j$ can be neglected because of the translational invariance of the lattice. The random-phase approximation (RPA) is obtained by ignoring the correlations of $S_{\alpha j}{}^{z}$ with other operators in expectation values. The longitudinal correlation functions in (2.4) are approximated by

$$\langle S_{\alpha m}{}^{z}S_{\beta n}{}^{z}\rangle\approx\sigma_\alpha\sigma_\beta. \quad (2.5)$$

The transverse correlation functions in (2.4) will be expressed in terms of an integral representation involving a spectral function which can be obtained from a set of Green's functions. Consider now the expectation value $\langle S_{\alpha m}{}^{-}(t)S_{\beta n}{}^{+}(t')\rangle$, where the operators are in the Heisenberg picture. Invariance of the system under translations of the lattice or of the origin of the time scale implies that this expectation value must depend only on the differences $\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n}$ and $t-t'$. Let $E_\mu$ be the eigenvalue of the eigenstate $|E_\mu\rangle$ of $\mathcal{H}$, and let $Z$ equal $\mathrm{Tr}(e^{-\beta\mathcal{H}})$. Then

$$\langle S_{\alpha m}{}^{-}(t')S_{\beta n}{}^{+}(t)\rangle=Z^{-1}\sum_{\mu,\nu}e^{-\beta E_\nu}e^{i(E_\mu-E_\nu)(t-t')}\langle E_\nu|S_{\alpha m}{}^{-}|E_\mu\rangle\langle E_\mu|S_{\beta n}{}^{+}|E_\nu\rangle$$
$$=\frac{2\sigma_\alpha}{N}\sum_{\mathbf{k}}e^{+i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})}\int_{-\infty}^{\infty}d\omega\frac{\rho_{\alpha\beta}(\mathbf{k},\omega)e^{-i\omega(t-t')}}{e^{\beta\omega}-1}, \quad (2.6)$$

where $N$ is the number of sites on a sublattice and

$$\rho_{\alpha\beta}(\mathbf{k},\omega)\equiv\frac{1}{2\sigma_\alpha NZ}\sum_{r_{\alpha m},r_{\beta n}}e^{-i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})}\sum_{\mu,\nu}(e^{-\beta E_\mu}-e^{-\beta E_\nu})\langle E_\mu|S_{\beta n}{}^{+}|E_\nu\rangle\langle E_\nu|S_{\alpha m}{}^{-}|E_\mu\rangle\delta(\omega-E_\nu+E_\mu) \quad (2.7)$$

is the spectral function. (Here $\hbar=1$.) A sum rule follows by direct evaluation:

$$\int_{-\infty}^{\infty}d\omega\,\rho_{\alpha\beta}(\mathbf{k},\omega)=\frac{1}{2\sigma_\alpha N}\sum_{r_{\alpha m},r_{\beta n}}e^{-i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})}\langle[S_{\beta n}{}^{+},S_{\alpha m}{}^{-}]_-\rangle=\delta_{\alpha\beta}. \quad (2.8)$$

Similarly,

$$\langle S_{\alpha m}{}^{+}(t)S_{\beta n}{}^{-}(t')\rangle=\frac{2\sigma_\beta}{N}\sum_{k}e^{-i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})}\int_{-\infty}^{\infty}d\omega\frac{\rho_{\beta\alpha}(\mathbf{k},\omega)e^{-i\omega(t-t')}}{1-e^{-\beta\omega}}. \quad (2.9)$$

Then $\langle\mathcal{H}\rangle$ can be obtained by taking the limit of (2.6) and (2.9) as $t\to t'$ and substituting the result into (2.4):

$$\langle\mathcal{H}\rangle=-\mu HN\sum_\alpha g_\alpha\sigma_\alpha+2\sum_{\alpha,\beta}\sum_{mn}J_{\alpha m,\beta n}\times\left\{\frac{1}{N}\sum_{\mathbf{k}}\int_{-\infty}^{\infty}d\omega\left[\frac{\sigma_\alpha\rho_{\alpha\beta}(\mathbf{k},\omega)e^{i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})}}{e^{\beta\omega}-1}+\frac{\sigma_\beta\rho_{\beta\alpha}(\mathbf{k},\omega)e^{-i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})}}{1-e^{-\beta\omega}}\right]+\sigma_\alpha\sigma_\beta\right\}. \quad (2.10)$$

[18] The symbol $\beta$ in a subscript here always refers to a sublattice, while in an exponent or coth( ) it always denotes $(\kappa T)^{-1}$, where $\kappa$ is the Boltzmann constant and $T$ the absolute temperature.

The sums $\sum_{m,n}$ can be divided into contributions from the nearest neighbors, next-nearest neighbors, etc. Only nearest-neighbor (nn) contributions will be considered in the present paper. Then the $\sum_{m,n}$ can be incorporated in structure factors

$$\gamma_{\alpha\beta}(\mathbf{k})=\sum_{(\mathrm{nn})}\exp[i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})], \quad (2.11)$$

and (2.10) becomes

$$\langle\mathcal{H}\rangle=-\mu HN\sum_\alpha g_\alpha\sigma_\alpha+N\sum_{\alpha,\beta}\sigma_\alpha J_{\alpha\beta}\Big\{\sigma_\alpha\gamma_{\alpha\beta}(0)+(1/N)\sum_k\gamma_{\alpha\beta}(\mathbf{k})\int_{-\infty}^{\infty}d\omega\,\rho_{\beta\alpha}(\mathbf{k},\omega)\coth\tfrac{1}{2}\beta\omega\Big\}. \quad (2.12)$$

There are two sets of quantities which remain to be determined, the $\sigma_\alpha$ and the $\rho_{\alpha\beta}(\mathbf{k},\omega)$.

The $\sigma_\alpha$ can be obtained with a moment-generating function like that discussed by Callen.[15] The pertinent details of Callen's theorem on the moment generating function are discussed in Appendix A. It is noted here that under conditions which are satisfied in the RPA, a moment generating function for sublattice $\alpha$, $\Omega_\alpha(a)$, can be expressed as a function of a number $\Phi_\alpha$ and of a parameter $a$:

$$\Omega_\alpha(a)\equiv\langle\exp(aS_\alpha{}^z)\rangle=\frac{{\Phi_\alpha}^{2S_\alpha+1}e^{-S_\alpha a}-(1+\Phi_\alpha)^{2S_\alpha+1}e^{(S_\alpha+1)a}}{[{\Phi_\alpha}^{2S_\alpha+1}-(1+\Phi_\alpha)^{2S_\alpha+1}][(1+\Phi_\alpha)e^a-\Phi_\alpha]}. \quad (2.13)$$

The number $\Phi_\alpha$ is given under the same conditions by

$$\Phi_\alpha\equiv\langle S_{\alpha m}{}^-S_{\alpha m}{}^+\rangle/2\sigma_\alpha \quad (2.14)$$

$$=N^{-1}\sum_{\mathbf{k}}\int_{-\infty}^{\infty}d\omega\frac{\rho_{\alpha\alpha}(\mathbf{k},\omega)}{e^{\beta\omega}-1}. \quad (2.15)$$

$\Phi_\alpha$ has the form of an expectation value for a magnon number operator associated with sublattice $\alpha$.[19] From (2.14), this expectation value is closely related to the number of spin deviations on sublattice $\alpha$. From (2.13),

$$\sigma_\alpha=\left.\frac{d\Omega_\alpha}{da}\right|_{a=0}=S_\alpha-\Phi_\alpha+\frac{(2S_\alpha+1){\Phi_\alpha}^{2S_\alpha+1}}{[(1+\Phi_\alpha)^{2S_\alpha+1}-{\Phi_\alpha}^{2S_\alpha+1}]}. \quad (2.16)$$

Thus, the basic quantities which remain to be determined are the spectral functions, $\rho_{\alpha\beta}(\mathbf{k},\omega)$. The manner in which the spectral functions follow from a set of Green's functions is described below but first it is important to understand some qualitative features concerning the computation of the $\sigma_\alpha$.

A theory of ferrimagnets should have the capacity to predict the relative orientation of the spins on the various sublattices. This is inherent in $\Phi_\alpha$ and $\sigma_\alpha(\Phi_\alpha)$. From (2.15)

$$\Phi_\alpha{}'\equiv-1-\Phi_\alpha=-\langle[S_{\alpha m}{}^+,S_{\alpha m}{}^-]_-+S_{\alpha m}{}^-S_{\alpha m}{}^+\rangle/2\sigma_\alpha=-\langle S_{\alpha m}{}^+S_{\alpha m}{}^-\rangle/2\sigma_\alpha. \quad (2.17)$$

If the signs of the $y$ and $z$ axes are reversed for sublattice $\alpha$ alone, $\Phi_\alpha{}'$ has the form of (2.15) again. Thus, $\Phi_\alpha{}'$ is the characteristic number associated with the sublattice $\alpha$ when the sign convention for $+z$ is inverted.[21] The $\sigma_\alpha{}'$ obtained from (2.17) with $\Phi_\alpha{}'$ are related to the $\sigma_\alpha$ from (2.16) with $\Phi_\alpha$ by

$$\sigma_\alpha(\Phi_\alpha)=-\sigma_\alpha{}'(\Phi_\alpha'). \quad (2.18)$$

Thus, the sign of $\sigma_\alpha$ relative to the remaining $\sigma_\beta$'s is the same regardless of the convention taken for $+z$ on the $\alpha$ sublattice.

It may be verified by evaluation that for some $\Phi_\alpha$ on the interval $(-1, 0)$, $|\sigma_\alpha|$ is in excess of $S_\alpha$ (and in fact is so for all such $\Phi_\alpha$ if $S_\alpha$ is half-odd-integral), and hence such values of $\Phi_\alpha$ must be unphysical. It has not yet been possible to verify that such unphysical values of $\Phi_\alpha$ will not be predicted by this theory, but they have not occurred in any calculations with $\mathbf{H}=0$.

It is expected that in some cases, e.g., that of the antiferromagnet,[22] the value of $|\sigma_\alpha|$ will differ somewhat from $S_\alpha$ at the absolute zero of temperature. If one sets $T=0$ in (2.15), then

$$\Phi_\alpha(T=0)=-N^{-1}\sum_{\mathbf{k}}\int_{-\infty}^{0}d\omega\rho_{\alpha\alpha}(\mathbf{k},\omega). \quad (2.19)$$

The zero-point deviation of $\sigma_\alpha$ is obtained by evaluating (2.16) using the value of $\Phi_\alpha$ given by (2.19). The origin of the "negative frequencies" which are required if $\Phi_\alpha$ in (2.19) is to be nonzero can be ascertained by considering the zero temperature limit of $\rho_{\alpha\alpha}$. It follows from (2.7) that

$$\rho_{\alpha\alpha}(\mathbf{k},\omega)\,|_{T=0}=[2\sigma_\alpha(0)N]^{-1}\sum_{r_{\alpha m},r_{\beta n}}\exp[-i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})]\times\sum_\nu\{\langle E_0|S_{\alpha n}{}^+|E_\nu\rangle\langle E_\nu|S_{\alpha m}{}^-|E_0\rangle\delta(\omega-E_\nu+E_0)-\langle E_\nu|S_{\alpha n}{}^+|E_0\rangle\langle E_0|S_{\alpha m}{}^-|E_\nu\rangle\delta(\omega-E_0+E_\nu)\}, \quad (2.20)$$

where $|E_0\rangle$ represents the ground state. The spin deviations included in the first term in the curly brackets

[19] The terms spin wave and magnon are sometimes used in the literature as though they were synonymous and sometimes as though they were distinct in meaning. Here, for definiteness, the term spin wave is taken to refer to the mode of propagation of spin deviations as observed in the direct lattice, while the term magnon is used to refer to the components in the reciprocal lattice of a spin wave. This is precisely analogous to the distinction discussed by Ziman (Ref. 20) between phonons and vibrations of a solid, or between photons and vibrations of an electromagnetic field.

[20] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 16.

[21] It is clear from this that while $\Phi_\alpha$ or $\Phi_\alpha{}'$ have the *form* of an expectation value of a magnon number operator, the name magnon number function which is used herein for $\Phi_\alpha$ can be taken only loosely unless $\Phi_\alpha$ is further specified so as to be positive.

[22] P. W. Anderson, Phys. Rev. 83, 1260 (1951); 86, 694 (1952).

are associated with excitations of system from the ground state, while the second term includes de-excitations to the ground state. Only the latter term contributes to (2.19). If the ground state is perfectly ordered, then, depending on the convention for $+z$, $\Phi_\alpha$ is zero directly, or is $-1$ after a cancellation of factors. (Note that $\sigma_\alpha(0)$ is given by $\frac{1}{2}\langle E_0|S_\alpha{}^+S_\alpha{}^- + S_\alpha{}^-S_\alpha{}^+|E_0\rangle$.) The value of $\sigma_\alpha$ which follows from (2.16) is then $\pm S_\alpha$, respectively. On the other hand, if the ground state is not perfectly ordered, the $\sigma_\alpha(0)$ in the denominator of $\rho_{\alpha\alpha}$ is not canceled after the $\omega$ integration and $\Phi_\alpha$ is neither 0 nor $-1$. Hence $|\sigma_\alpha|$ differs from $S_\alpha$.

It is clear that the sign which is carried by a frequency $\omega$ is of mathematical origin since that sign can be altered by changing the $+z$ convention for the sublattices. It would be a mistake to set positive the signs of all frequencies on the ground that such a situation would be more physical, for to do so would be to discard the feature of the theory whereby the relative orientation of the sublattice magnetizations is given through a self-consistent calculation. It is possible in this theory to talk of holes and particles associated with frequencies of different signs, but the arbitrariness of the designation makes this hardly seem worthwhile.

Now, to determine the spectral functions, consider a set of Green's functions which are defined as

$$\langle\langle S_{\beta n}{}^+(t); S_{\alpha m}{}^-(t')\rangle\rangle \equiv -i\Theta(t-t')\langle[S_{\beta n}{}^+(t), S_{\alpha m}{}^-(t')]_-\rangle. \quad (2.21)$$

$\Theta(t-t')$ is the Heaviside unit function. With (2.6) and (2.9) this becomes

$$\langle\langle S_{\beta n}{}^+(t); S_{\alpha m}{}^-(t')\rangle\rangle_r = -2i\Theta(t-t')\frac{\sigma_\alpha}{N}\sum_{\mathbf{k}} e^{+i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})} \times\int_{-\infty}^{\infty} d\omega\rho_{\alpha\beta}(k,\omega)e^{-i\omega(t-t')}. \quad (2.22)$$

The Fourier transform of this function is

$$G_{\beta\alpha}(\mathbf{k},\omega)\equiv\frac{1}{N}\sum_{\mathbf{r}_{\alpha m},\mathbf{r}_{\beta n}} e^{i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})} \times\int_{-\infty}^{\infty} d(t-t')e^{+i\omega(t-t')}\langle\langle S_{\beta n}{}^+(t); S_{\alpha m}{}^-(t')\rangle\rangle \quad (2.23)$$

or

$$G_{\beta\alpha}(\mathbf{k},\omega+i\epsilon) = -2\sigma_\alpha\int_{-\infty}^{\infty} d\omega\frac{\rho_{\alpha\beta}(\mathbf{k},\omega')}{\omega'-\omega-i\epsilon}. \quad (2.24)$$

Here and elsewhere, $\epsilon$ is a vanishingly small positive quantity. The spectral function $\rho_{\alpha\beta}(\mathbf{k},\omega)$ is thus proportional to the imaginary part of $G_{\alpha\beta}(\mathbf{k},\omega)$ on the real $\omega$ axis:

$$\rho_{\alpha\beta}(\mathbf{k},\omega) = -\frac{1}{2\pi\sigma_\alpha}\mathrm{Im}G_{\beta\alpha}(\mathbf{k},\omega+i\epsilon). \quad (2.25)$$

Information about the Green's functions follow from their equations of motion. Since the operators are in the Heisenberg picture, the time derivative of a typical operator is given as follows:

$$i\frac{\partial S_{\beta n}{}^+(t)}{\partial t} = [S_{\beta n}{}^+(t),\mathcal{H}]_- = +\mu H g_\beta S_{\beta n}{}^+(t) + 2\sum_{\xi,l} J_{\beta n,\xi l} \times[S_{\beta n}{}^z S_{\xi l}{}^+ - S_{\beta n}{}^+ S_{\xi l}{}^z](t). \quad (2.26)$$

Then, if $B(t')$ is some product of components of the spin operators,

$$i\frac{\partial}{\partial t}\langle\langle S_{\beta n}{}^+(t); B(t')\rangle\rangle = \delta(t-t')\langle[S_{\beta n}{}^+(t), B(t')]_-\rangle + \langle\langle[S_{\beta n}{}^+(t),\mathcal{H}(t)]_-; B(t')\rangle\rangle. \quad (2.27)$$

The random-phase approximation for this equation is obtained by replacing by their expectation values the factors of $S^z$ which appear in the commutator of the last term of (2.27). Thus

$$\sum_{\xi,l}\left\{\left[i\frac{\partial}{\partial t} - \mu g_\beta H + 2\sum_{\xi,p} J_{\beta n,\xi p}\sigma_\xi\right]\delta_{\beta n,\xi l} - 2J_{\beta n,\xi l}\sigma_\beta\right\} \times\langle\langle S_{\xi l}{}^+(t); B(t')\rangle\rangle = \delta(t-t')\langle[S_{\beta n}{}^+(t), B(t)]_-\rangle. \quad (2.28)$$

This equation of motion is in the form of a product of a matrix independent of $B(t)$ and one which depends on $B(t)$. The operator $B(t)$ has been used here to facilitate the argument in Appendix A. It can now be replaced by $S_{\alpha m}{}^-(t)$ to obtain the equation of motion of the Green's function which is desired. The commutator on the right-hand side of (2.28) becomes just $2\delta_{\alpha\beta}\delta_{mn}\sigma_\beta$ and the exchange terms are restricted to nearest-neighbor terms. Introduction of the Fourier transform of the Green's function then gives

$$\sum_\xi\{[\omega - \mu g_\beta H + 2\sum_\xi J_{\beta\xi}\gamma_{\beta\xi}(0)\sigma_\xi]\delta_{\beta\xi} - 2J_{\beta\zeta}\sigma_\beta\gamma_{\beta\zeta}(k)\}G_{\zeta\alpha}(\mathbf{k},\omega) = 2\sigma_\beta\delta_{\beta\alpha}. \quad (2.29)$$

This is in the form of a matrix equation,

$$\sum_\zeta[\omega I - \mathcal{J}(\mathbf{k})]_{\beta\zeta}G_{\zeta\alpha}(\mathbf{k},\omega) = 2\delta_{\beta\alpha}\sigma_\beta. \quad (2.30)$$

$\mathcal{J}(\mathbf{k})$ is a matrix whose elements may be obtained from (2.29) by inspection. Then

$$G_{\beta\alpha}(\mathbf{k},\omega) = 2[\omega I - \mathcal{J}(\mathbf{k})]^{-1}{}_{\beta\alpha}\sigma_\alpha, \quad \text{(no sum on } \alpha). \quad (2.31)$$

If the Green's functions are evaluated in terms of the original spectral functions with discrete spectra, it is found that as functions of a complex $\omega$ they have only simple poles on the real axis. The poles of $G_{\beta\alpha}(\mathbf{k},\omega)$ given in (2.31) are the roots, $\omega_l(\mathbf{k})$ of

$$\mathrm{Det}[\omega I - \mathcal{J}(\mathbf{k})] = 0. \quad (2.32)$$

Only distinct zeros are to be considered when a partial-fraction expansion of $G_{\beta\alpha}$ is made since the poles are simple. Denote by $R_{\beta\alpha,l}(\mathbf{k})$ the residue of $[\omega I - \mathcal{J}(\mathbf{k})]^{-1}{}_{\beta\alpha}$

at $\omega_l$:

$$R_{\beta\alpha,l}(\mathbf{k})\equiv\lim_{\omega\to\omega_l}(\omega-\omega_l(\mathbf{k}))[\omega I-\mathcal{J}(\mathbf{k})]^{-1}{}_{\beta\alpha}. \quad (2.33)$$

The inverse element may be written

$$[\omega I-\mathcal{J}(\mathbf{k})]^{-1}{}_{\beta\alpha}=\sum_l R_{\beta\alpha,l}(\mathbf{k})/[\omega-\omega_l(\mathbf{k})]. \quad (2.34)$$

Equations (2.25), (2.31), and (2.34) give

$$\rho_{\alpha\beta}(\mathbf{k},\omega)=\sum_l R_{\beta\alpha,l}(\mathbf{k})\delta(\omega-\omega_l(\mathbf{k})). \quad (2.35)$$

The sum rule (2.8) gives

$$\sum_l R_{\beta\alpha,l}(\mathbf{k})=\delta_{\alpha\beta}. \quad (2.36)$$

A physical interpretation of these quantities may be obtained by substituting (2.35) in (2.22).

$$\langle\langle S_{\beta n}{}^{+}(t);S_{\alpha m}{}^{-}(t')\rangle\rangle = -2\sigma_\alpha i\Theta(t-t')N^{-1}\sum_{\mathbf{k}}\sum_l R_{\beta\alpha,l}(\mathbf{k}) \times\exp i[\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\beta n})-\omega_l(\mathbf{k})(t-t')]. \quad (2.37)$$

Thus spin deviations associated with sublattices $\alpha$ and $\beta$ can be represented as a superposition of waves of wave number $\mathbf{k}$, frequency $|\omega_l(\mathbf{k})|$ and amplitude $|R_{\beta\alpha,l}(\mathbf{k})|$. The $\omega_l(\mathbf{k})$ and, from (2.33), the $R_{\beta\alpha,l}(\mathbf{k})$, need not all be positive. The sign of $\omega_l(\mathbf{k})$ indicates in (2.37) the direction in which that mode propagates, and the sign of $R_{\beta\alpha,l}(\mathbf{k})$ indicates the phase of the mode relative to the other modes.

The roots $\omega_l(\mathbf{k})$ involve the $\sigma_\alpha$ through the elements $\mathcal{J}(\mathbf{k})_{\beta\alpha}$. The quantities $\sigma_\alpha$ are to be obtained from (2.16) with the numbers $\Phi_\alpha$. These in turn depend on the $\omega_l(\mathbf{k})$, for from (2.15) and (2.35),

$$\Phi_\alpha=N^{-1}\sum_{\mathbf{k}}\sum_l R_{\alpha\alpha,l}(\mathbf{k})/[\exp\beta\omega_l(\mathbf{k})-1]. \quad (2.38)$$

This and (2.16) then give a set of implicit equations to be solved for the $\sigma_\alpha$. Self-consistent solutions can be obtained by iteration from a suitable set of initial values.

The approximate energy (2.12) can also be simplified directly using (2.35):

$$\langle\mathcal{H}\rangle=-\mu HN\sum_\alpha g_\alpha\sigma_\alpha+N\sum_{\alpha,\beta}\sigma_\alpha J_{\alpha\beta}\Big\{\sigma_\beta\gamma_{\alpha\beta}(0) +N^{-1}\sum_{\mathbf{k}}\sum_l\gamma_{\alpha\beta}(\mathbf{k})R_{\beta\alpha,l}(\mathbf{k})\coth\frac{\beta\omega_l(\mathbf{k})}{2}\Big\}. \quad (2.39)$$

In principle, the specific heat and susceptibilities can be obtained by appropriate differentiation of (2.39). However $\langle\mathcal{H}\rangle$ depends on $H$ or $T$ not only explicitly, but also implicitly through the $\sigma_\alpha$. Since this implicit dependence is very complicated, it appears that it would be simpler in practice to obtain self-consistent $\sigma_\alpha$ for a suitable set of values of $H$ (or $T$) and then evaluate the derivatives numerically.

There exists a temperature, which will be called the Curie temperature, at which the sublattice magnetization simultaneously vanish in the absence of an external magnetic field. It was shown above that a sign convention for each sublattice can be chosen so that $\sigma_\alpha$ is positive. Suppose, for the moment, that such choices have been made. The function $\sigma_\alpha(\Phi_\alpha)$ has a negative first derivative and a positive second derivative with respect to $\Phi_\alpha$, for all positive $\Phi_\alpha$. Thus $\sigma_\alpha(\Phi_\alpha)$ decreases monotonically from $S_\alpha$ to zero as $\Phi_\alpha$ increases without bound from zero. Since the sum of the residues is bounded according to (2.36), (2.38) shows that $\Phi_\alpha$ becomes unbounded only when the $\omega_l(\mathbf{k})$ vanish. The elements of $\mathcal{J}(\mathbf{k})$ are linear and homogeneous in the $\sigma_\alpha$ in the absence of a magnetic field, and so the $\omega_l(\mathbf{k})$ are linear, homogeneous functions of the $\sigma_\alpha$. Thus the vanishing of the $\sigma_\alpha$ implies the vanishing of the $\omega_l(\mathbf{k})$ which in turn implies that the $\Phi_\alpha$ increase without bound. This implies again that the $\sigma_\alpha$ vanish, so a self-consistent solution is obtained.

Physically, a large $\Phi_\alpha$ corresponds to a large magnon population on sublattice $\alpha$ and when this increases without limit, an instability in the ordering of the spins on the sublattice is indicated. In asserting that there exists a temperature at which the sublattice magnetizations simultaneously vanish, one assumes that the normal modes represented by the $\omega_l(\mathbf{k})$ involve contributions from all the sublattices. If there were to exist sets of the sublattices which are not coupled by any of the normal modes, then each of these disjoint sets would be expected to have a distinct Curie temperature.

An expression for the temperature at which this occurs can be derived by considering the ratios $\sigma_\alpha/\sigma_r$ of the sublattice magnetizations to some particular one of them which is taken as a reference. Define $\sigma_{\alpha r}$ and $\omega_{r,l}$:

$$\sigma_{\alpha r}=\sigma_\alpha/\sigma_r, \quad (2.40)$$

$$\omega_{r,l}\equiv\omega_l/\sigma_r. \quad (2.41)$$

Then the $\omega_{r,l}$ and the $R_{\alpha\beta,l}$ are functions only of the $\sigma_{\alpha r}$.

The asymptotic forms of (2.16) and (2.38) for large $\Phi_\alpha$ and small $\sigma_\alpha$ give

$$\sigma_\alpha\sim S_\alpha(S_\alpha+1)/3\Phi_\alpha\sim\sigma_r\beta[S_\alpha(S_\alpha+1)/3\Phi_{\alpha r}], \quad (2.42)$$

where $\Phi_{\alpha r}$ is defined by

$$\Phi_\alpha\sim 1/N\beta\sigma_r\sum_{k,l}R_{\alpha\alpha,l}(\mathbf{k})/\omega_{r,l}(\mathbf{k})=\Phi_{\alpha r}/\beta\sigma_r. \quad (2.43)$$

The Curie temperature is determined by the condition that $\sigma_{rr}$ be unity. Thus

$$\tau_c=1/\kappa\beta_c=S_r(S_r+1)/3\kappa\Phi_{rr}. \quad (2.44)$$

The $\sigma_{\alpha r}$ needed for the evaluation of $\Phi_{rr}$ are obtained as the solutions of a set of implicit equations,

$$\sigma_{\alpha r}=S_\alpha(S_\alpha+1)\Phi_{rr}/S_r(S_r+1)\Phi_{\alpha r}. \quad (2.45)$$

It is concluded in Appendix A that better approximations to the equation of motion for $S_\alpha{}^{+}$ will still satisfy conditions necessary for the validity of much of the theory presented in this section. It may be that the

inverse elements $[\omega I-\mathcal{J}(\mathbf{k})]^{-1}_{\alpha\beta}$ so obtained are not such that the $\omega_l(\mathbf{k})$ vanish as the $\sigma_\alpha$ go to zero. The present derivation of a Curie temperature will not hold then. Note, however, that the restriction to nearest-neighbor exchange integrals applied in going from (2.11) to (2.12), and in writing (2.29), can be lifted without changing in any essential way the validity of the arguments above which pertain to the RPA. This is also true if anisotropy coefficients are applied to the transverse or longitudinal terms of $\mathcal{H}$, and so the theory described above is applicable to more general cases than are considered here.

## 3. FERROMAGNETISM AND SIMPLE ANTIFERROMAGNETISM

The application of the theory developed in the previous section is straightforward in the case of a simple lattice, or of a two sublattice system. It will be discussed here to illustrate several features of the theory before discussing the more complicated case of magnetite.

The case of a simple ferromagnet involves only one spin species, and the exchange integral $J$ is negative. Only one root of (2.32) occurs, which is, from (2.29),

$$\omega(\mathbf{k})=\mu gH-2J\sigma[\gamma(0)-\gamma(\mathbf{k})]. \tag{3.1}$$

From either (2.33) or (2.36), the only residue has the constant value unity. The spectral function is just $\delta(\omega-\omega(\mathbf{k}))$, and so the magnon number function is

$$\Phi=N^{-1}\sum_{\mathbf{k}}(\exp\beta\{\mu gH-2J\sigma[\gamma(0)-\gamma(\mathbf{k})]\}-1)^{-1}. \tag{3.2}$$

The substitution of this relation into (2.16) then gives an implicit equation for the magnetization, $\sigma$. The structure factor $\gamma(\mathbf{k})$, of course, depends only on the lattice geometry. The magnetization $\sigma$ may be taken as either negative or positive in the absence of an external field. Substitution of the expression (3.2) for $\Phi$ into (2.16) then gives a value of $\sigma$ consistent with whichever choice has been made. If $\sigma$ is chosen to be positive, $\Phi$ has the value zero at zero temperature: the ground state of a ferromagnet is perfectly ordered. If $\sigma$ is chosen to be negative, $\Phi$ becomes $-1$, and again perfect ordering is predicted in the ground state.

The Curie temperature is given directly by the evaluation of (2.40)–(2.44).

$$\frac{1}{T_c}=\frac{-3\kappa}{2JS(S+1)N}\sum_{\mathbf{k}}[\gamma(0)-\gamma(\mathbf{k})]^{-1}. \tag{3.3}$$

This agrees with the results previously obtained by other authors.[14,15]

A description of antiferromagnetism is obtained as a special case of a ferrimagnet with two sublattices. The roots of (2.32) are, in terms of the elements of $\mathcal{J}(\mathbf{k})$, for two sublattices

$$\omega_\pm(k)=\tfrac{1}{2}(\mathcal{J}_{11}+\mathcal{J}_{22})\pm\{\tfrac{1}{4}(\mathcal{J}_{11}-\mathcal{J}_{22})^2+\mathcal{J}_{12}\mathcal{J}_{21}\}^{1/2}. \tag{3.4}$$

The residues are given by

$$R_{11\pm}=R_{22\mp}=\tfrac{1}{2}\pm\frac{(\mathcal{J}_{11}-\mathcal{J}_{22})}{2(\omega_+-\omega_-)}$$

$$=-\frac{1}{2}\left\{1\pm\left[1+\frac{4\mathcal{J}_{12}\mathcal{J}_{21}}{(\mathcal{J}_{11}-\mathcal{J}_{22})^2}\right]^{-1/2}\right\}. \tag{3.5}$$

$$R_{12\pm}=\pm\mathcal{J}_{12}/(\omega_+-\omega_-), \tag{3.6}$$

$$R_{21\pm}=\pm\mathcal{J}_{21}/(\omega_+-\omega_-). \tag{3.7}$$

The spectral functions which follow give for $\alpha=1$ or 2

$$\Phi_{\alpha\alpha}=\frac{1}{2N}\sum_k\left\{b(\omega_+)+b(\omega_-)\right.$$

$$\left.+(-1)^{\alpha+1}\frac{\mathcal{J}_{11}-\mathcal{J}_{22}}{\omega_+-\omega_-}[b(\omega_+)-b(\omega_-)]\right\}, \tag{3.8}$$

where

$$b(\omega)=[\exp(\beta\omega)-1]^{-1}. \tag{3.9}$$

Consider the special two sublattice system in which a spin on one sublattice has nearest neighbors only on the other sublattice. Then $J_{11}$ and $J_{22}$ are zero, and the matrix $\mathcal{J}(\mathbf{k})$ reads, with $J=J_{12}$, $\gamma_{12}=\gamma$.

$$\mathcal{J}(\mathbf{k})=\begin{pmatrix}\mu g_1H-2J\sigma_2\gamma(0) & 2J\sigma_1\gamma(\mathbf{k})\\ 2J\sigma_2\gamma(\mathbf{k})^* & \mu g_2H-2J\sigma_1\gamma(0)\end{pmatrix}. \tag{3.10}$$

If the distinction between the sublattices disappears, the $\omega_\pm(\mathbf{k})$ become the $\omega(\mathbf{k})$ of (3.1), and the case for simple ferromagnetism is recovered, as expected.

If the only distinction between the sublattices is the magnetic ordering, i.e., $S_1=S_2$, the case of simple antiferromagnetism is obtained. The statement

$$\sigma_1=-\sigma_2 \tag{3.11}$$

leads to a self-consistent solution, for then

$$\omega_\pm=\mu gH\pm 2|J\sigma_1|\{|\gamma(0)|^2-|\gamma(\mathbf{k})|^2\}^{1/2}. \tag{3.12}$$

If $H=0$, $\omega_+=-\omega_-$ and from (3.8)

$$\Phi_\alpha=-\tfrac{1}{2}+\frac{(-1)^{\alpha+1}}{2N}\operatorname{sgn}(J\sigma_1)$$

$$\times\sum_{\mathbf{k}}\left\{[1-|\gamma(\mathbf{k})/\gamma(0)|^2]^{-1/2}\coth\frac{\beta\omega_+}{2}\right\}. \tag{3.13}$$

It has been pointed out in Sec. 2 that $\Phi$ must not be in the interval $(-1, 0)$ if the $\sigma$ are to be assured to have physical values. The sum exceeds $N$, so this requirement is met. If $J<0$, no self-consistent solution follows when (3.13) is substituted into (2.16). However, if $J>0$, then it is found that the magnitudes of $\sigma_1$ and $\sigma_2$ are equal, and that each may have either sign, in such a way that (3.11) is satisfied. Thus, $J$ may be dropped from (3.13).

The zero-point deviation of the sublattice magnetizations follows from (2.16) and (3.13) upon letting $\beta$ go to infinity.

$$\Phi_\alpha|_{T=0}=-\tfrac{1}{2}+\frac{(-1)^{\alpha+1}}{2N}\,\mathrm{sgn}(\sigma_1)\times\textstyle\sum_{\mathbf{k}}[1-|\gamma(\mathbf{k})/\gamma(0)|^2]^{-1/2}. \quad (3.14)$$

The same result follows from direct evaluation of (2.19). In this approximation, the zero-point deviation, from (2.16), depends only on the spin magnitude $S$ and the geometry of the sublattices.

The Curie (or Néel) temperature can also be directly expressed in this case since the ratio of the sublattice magnetizations is $-1$. Thus, (2.40)–(2.44) gives

$$\frac{1}{T_N}=\frac{3\kappa}{S(S+1)JN}\textstyle\sum_{\mathbf{k}}[1-|\gamma(\mathbf{k})/\gamma(0)|^2]^{-1}. \quad (3.15)$$

This also is in agreement with previous results of other authors.[16,17]

The propagation of the spin waves on a sublattice is also of interest. The Eq. (2.37) for the Green's functions becomes for simple antiferromagnetism

$$\langle\langle S_{\alpha n}{}^{+}(t);S_{\alpha m}{}^{-}(t')\rangle\rangle=-\frac{i\sigma_\alpha\Theta(t-t')}{N}\textstyle\sum_{\mathbf{k}}\exp i\mathbf{k}\cdot(\mathbf{r}_{\alpha m}-\mathbf{r}_{\alpha n})[\{[1-|\gamma(\mathbf{k})/\gamma(0)|^2]^{-1/2}+(-1)^{\alpha+1}\}$$
$$\times\exp[-i\omega_+(\mathbf{k})(t-t')]-\{[1-|\gamma(\mathbf{k})/\gamma(0)|^2]^{-1/2}-(-1)^{\alpha+1}\}\exp[i\omega_+(\mathbf{k})(t-t')]]. \quad (3.16)$$

The propagation of a spin deviation from $\mathbf{r}_{\alpha m}$ to $\mathbf{r}_{\alpha n}$ is thus given as a superposition of pairs of waves of wave number $\mathbf{k}$. The waves in each pair travel in opposite directions, generally have unequal amplitudes, and are 180° out of phase. The inversion symmetry of antiferromagnetism has not been lost in spite of the unequal amplitudes. A wave of given $\mathbf{k}$, amplitude, and direction on one sublattice is matched by a wave of the same $\mathbf{k}$ and amplitude, but of opposite direction, on the other sublattice.

## 4. APPLICATION TO MAGNETITE

Magnetic properties of the ferrite magnetite ($Fe_3O_4$) have been treated previously in the approximation of linear spin waves.[1–8] The calculation of these properties in terms of the renormalized spin-wave theory of Sec. 2 is the subject of this section.

In its ordered phase, magnetite can be described approximately as being composed of six interpenetrating fcc sublattices. This is illustrated in Fig. 1 of the paper by Glasser and Milford (GM).[6] The enumeration of the sublattices given there is also used here. It is adequate to the present purpose to note that two of the sublattices, 5 and 6, are occupied by ferric ions whose nearest neighbors have tetrahedral coordination (type $A$). The remaining four sublattices involve sites for which the nearest neighbors have octahedral coordination. Ferric ions (type $B1$) occupy two of these sublattices, 1 and 2, while ferrous ions (type $B2$) are on the remaining ones, 3 and 4. The spin magnitudes are $S_A=S_{B1}=2.5$, $S_{B2}=2$. The structure factors (2.11) for magnetite can be computed using information given in the Appendix of GM.

The matrix $\omega I-\mathcal{J}(\mathbf{k})$ of (2.30) has in this case a determinant which is a sixth-order polynominal in $\omega$ and whose zeros are not generally available in any simple analytic form. However, as shown in GM, the polynominal in $\omega$ can be factored readily if the only nonzero exchange integral is that between sites on the $A$ and $B$ type sublattices $J_{AB}$. Then for $\mathbf{H}=0$, the six roots have the form

$$\begin{bmatrix}\omega_1\\ \omega_2\\ \omega_3\\ \omega_4\end{bmatrix}=\begin{bmatrix}\frac{1}{2}\\ \frac{1}{2}\\ \frac{1}{2}\\ \frac{1}{2}\end{bmatrix}(\mathcal{J}_{11}+\mathcal{J}_{55})+\begin{bmatrix}+\frac{1}{2}\\ -\frac{1}{2}\\ +\frac{1}{2}\\ -\frac{1}{2}\end{bmatrix}\left\{(\mathcal{J}_{11}-\mathcal{J}_{55})^2+2B+\begin{bmatrix}+2\\ +2\\ -2\\ -2\end{bmatrix}(B^2-4C)^{1/2}\right\}^{1/2}, \quad \begin{matrix}(4.1a)\\ (4.1b)\\ (4.1c)\\ (4.1d)\end{matrix}$$

$$\omega_5=\omega_6=\mathcal{J}_{11}, \quad (4.1e)$$

where

$$\mathcal{J}_{11}=-6J_{AB}(\sigma_5+\sigma_6), \quad (4.2)$$

$$\mathcal{J}_{55}=-6J_{AB}(\sigma_1+\sigma_2+\sigma_3+\sigma_4), \quad (4.3)$$

$$B=4J_{AB}{}^2(\sigma_5+\sigma_6)\sum_{\alpha=1}^{4}\sigma_\alpha|\gamma_{\alpha5}|^2, \quad (4.4)$$

and

$$C=16J_{AB}{}^4\sigma_5\sigma_6\sum_{\alpha<\beta}^{4}\sigma_\alpha\sigma_\beta(\mathrm{Im}\gamma_{\alpha5}\gamma_{\beta5}{}^*)^2. \quad (4.5)$$

The fact that $\gamma_{\alpha 6}$ is the complex conjugate of $\gamma_{\alpha 5}$ has been used in writing (4.4) and (4.5). The products of the structure factors which are needed are listed here.

$$|\gamma_{15}|^2=3+2\cos\tfrac{1}{2}a(k_x+k_y)+2\cos\tfrac{1}{2}a(k_x-k_z)+2\cos\tfrac{1}{2}a(k_y+k_z) \tag{4.6}$$

$$|\gamma_{25}|^2=3+2\cos\tfrac{1}{2}a(k_x+k_y)+2\cos\tfrac{1}{2}a(k_x+k_z)+2\cos\tfrac{1}{2}a(k_y-k_z) \tag{4.7}$$

$$|\gamma_{35}|^2=3+2\cos\tfrac{1}{2}a(k_x-k_y)+2\cos\tfrac{1}{2}a(k_x-k_z)+2\cos\tfrac{1}{2}a(k_y-k_z) \tag{4.8}$$

$$|\gamma_{45}|^2=3+2\cos\tfrac{1}{2}a(k_x-k_y)+2\cos\tfrac{1}{2}a(k_x+k_z)+2\cos\tfrac{1}{2}a(k_y+k_z) \tag{4.9}$$

$$\mathrm{Im}\gamma_{15}\gamma_{25}^*=2[\sin\tfrac{1}{4}a(3k_x+k_y)+\sin\tfrac{1}{4}a(k_x-k_y)-\sin\tfrac{1}{4}a(k_x+3k_y)] \tag{4.10}$$

$$\mathrm{Im}\gamma_{35}\gamma_{45}^*=2[\sin\tfrac{1}{4}a(3k_x-k_y)+\sin\tfrac{1}{4}a(k_x+k_y)-\sin\tfrac{1}{4}a(k_x-3k_y)] \tag{4.11}$$

$$\mathrm{Im}\gamma_{15}\gamma_{35}^*=2[\sin\tfrac{1}{4}a(3k_x-k_z)+\sin\tfrac{1}{4}a(k_x+k_z)-\sin\tfrac{1}{4}a(k_x-3k_z)] \tag{4.12}$$

$$\mathrm{Im}\gamma_{25}\gamma_{45}^*=2[\sin\tfrac{1}{4}a(3k_x+k_z)+\sin\tfrac{1}{4}a(k_x-k_z)-\sin\tfrac{1}{4}a(k_x+3k_z)] \tag{4.13}$$

$$\mathrm{Im}\gamma_{15}\gamma_{45}^*=2[\sin\tfrac{1}{4}a(3k_y+k_z)+\sin\tfrac{1}{4}a(k_y-k_z)-\sin\tfrac{1}{4}a(k_y+3k_z)] \tag{4.14}$$

$$\mathrm{Im}\gamma_{25}\gamma_{35}^*=2[\sin\tfrac{1}{4}a(3k_y-k_z)+\sin\tfrac{1}{4}a(k_y+k_z)-\sin\tfrac{1}{4}a(k_y-3k_z)]. \tag{4.15}$$

The parameter $a$ in (4.6)–(4.15) is the lattice constant.

There are five distinct zeros $\omega_l(\mathbf{k})$ given in (4.1). The residues, $R_{\alpha\alpha,l}(\mathbf{k})$ associated with these zeros are listed below.

$\alpha,l=1, 2, 3, 4$:

$$R_{\alpha\alpha,l}(\mathbf{k})=4J_{AB}^2\sigma_\alpha[(\sigma_5+\sigma_6)|\gamma_{\alpha 5}|^2(\omega_l-\mathcal{J}_{11})(\omega_l-\mathcal{J}_{55})-4J_{AB}^2\sigma_5\sigma_6\sum_{\beta=1}^{4}\sigma_\beta(\mathrm{Im}\gamma_{\alpha 5}\gamma_{\beta 5}^*)^2]/\prod_{i=1;\neq l}^{5}(\omega_l-\omega_i). \tag{4.16}$$

$\alpha=5, 6;\quad l=1, 2$:

$$R_{\alpha\alpha,l}(\mathbf{k})=(\omega_l-\mathcal{J}_{11})[-\tfrac{1}{2}B+\tfrac{1}{2}(B^2-4C)^{1/2}+4J_{AB}^2\sigma_\alpha\sum_{\beta=1}^{4}\sigma_\beta|\gamma_{\beta 5}|^2]/\prod_{i=1;\neq l}^{4}(\omega_l-\omega_i). \tag{4.17}$$

$\alpha=5, 6;\quad l=3, 4$:

$$R_{\alpha\alpha,l}(\mathbf{k})=(\omega_l-\mathcal{J}_{11})[-\tfrac{1}{2}B-\tfrac{1}{2}(B^2-4C)^{1/2}+4J_{AB}^2\sigma_\alpha\sum_{\beta=1}^{4}\sigma_\beta|\gamma_{\beta 5}|^2]/\prod_{i=1;\neq l}^{4}(\omega_l-\omega_i). \tag{4.18}$$

$\alpha=1, 2, 3, 4;\quad l=5$:

$$R_{\alpha\alpha,5}(\mathbf{k})=1-16J_{AB}^2\sigma_5\sigma_6\sum_{\beta=1}^{4}\sigma_\alpha\sigma_\beta(\mathrm{Im}\gamma_{\alpha 5}\gamma_{\beta 5}^*)^2/\prod_{i=1}^{4}(\omega_5-\omega_i), \tag{4.19}$$

$\alpha=5, 6;\quad l=5$:

$$R_{55,5}(\mathbf{k})=R_{66,5}(\mathbf{k})=0. \tag{4.20}$$

These expressions can be used to write the explicit forms for the magnon-number functions, $\Phi_\alpha$. However, a simplification follows immediately in this approximation, for a self-consistent solution of these $\Phi_\alpha$ and (2.17) is expressed by

$$\sigma_1=\sigma_2=\sigma_{B1}, \tag{4.21}$$

$$\sigma_3=\sigma_4=\sigma_{B2}, \tag{4.22}$$

and

$$\sigma_5=\sigma_6=\sigma_A: \tag{4.23}$$

the six sublattice magnetizations are equal pairwise when only $J_{AB}$ is nonzero. Any difference between $\sigma_5$ and $\sigma_6$ must arise from a difference between $\Phi_5$ and $\Phi_6$ since $S_5=S_6=S_A$. However

$$\Phi_5-\Phi_6=\frac{1}{N}\sum_{\mathbf{k},l}(R_{55,l}-R_{66,l})/(e^{\beta\omega_l}-1), \tag{4.24}$$

and, from (4.17)–(4.19), the difference of the residues is zero ($l=5$) or proportional to $\sigma_5-\sigma_6$($l=1, 2, 3, 4$). Thus (4.23) and the vanishing of $\Phi_5-\Phi_6$ are consistent with one another. This result is physically reasonable, for if only $J_{AB}$ is nonzero, sites 5 and 6 are in exactly the same environment.

The spins on the octahedral sites are not in identical environments even if only $J_{AB}$ is nonzero, but the symmetry of their environments is such that the sums over the reciprocal lattice give identical contributions, and (4.21) and (4.22) give self-consistent results. The different environments are manifested in the zeros and the residues through the functions in (4.6)–(4.15). Note that reversal of the $z$ axis has the same effect on these functions as performing the permutation (12)(34) on the sublattice labels. Then if (4.21) and (4.22) hold, $B$ and $C$, and also the $\omega_l(\mathbf{k})$, are invariant under reversal

of the $z$ axis, but the permutation (12)(34) operates on the residues. Let $\Phi_{\alpha\pm}$ denote that portion of $\Phi_\alpha$ which is obtained by summing over that portion of the Brillouin zone for which $k_z=\pm|k_z|$, respectively. Then, taking $\Phi_1$ and $\Phi_2$, for example,

$$\Phi_1=\Phi_{1+}+\Phi_{1-}=\Phi_{1+}+\Phi_{2+}=\Phi_2. \quad (4.25)$$

Similarly, $\Phi_3=\Phi_4$. Since $S_1=S_2=S_{B1}$ and $S_3=S_4=S_{B2}$, the equalities (4.21) and (4.22) give self-consistent solutions.

It should be emphasized that (4.21)–(4.23) are only sufficient conditions for self-consistent solutions. The possibility has not been excluded that other self-consistent solutions might exist. However, the reduction to $\sigma_{B1}$ and $\sigma_{B2}$ was first found numerically from the convergence of results of iterative computations using the residues (4.16)–(4.20) with (4.23), and so it appears that (4.21) and (4.22) give stable solutions, at the least.

Even with the reduction from six to three coupled implicit equations for the $\sigma_\alpha$ which is allowed by (4.21)–(4.23), the complexity of the problem is such that a digital computer is needed to obtain a solution. The sums over the first Brillouin zone are converted to triple integrals, which are in turn approximated by Gaussian quadratures. More accurate results are obtained by integrating over the precise Brillouin zone, but good first approximations are obtained if the accurate structure factors are replaced by their averages over the unit sphere.

$$\gamma_{\alpha\beta}(\mathbf{k})\rightarrow\gamma(k)=\frac{1}{4\pi}\int d\Omega\gamma_{\alpha\beta}(\mathbf{k})=3\,\sin\delta k/\delta k\,, \quad (4.26)$$

where $\Omega$ is the solid angle, $k^2=k_x^2+k_y^2+k_z^2$, and, for the spinel lattice $\delta=11^{1/2}(a/8)$. It is shown in Appendix B that (4.26) gives a considerable simplification in the basic equations. The triple quadrature needed with the accurate structure factors is reduced to a single one, over $k$, since angular integrations become trivial in calculating the $\Phi_\alpha$. The upper limit on the remaining integration is adjusted to preserve the normalization $\sum_{\mathbf{k}}1=N$. The agreement of the results obtained using the averaged and the accurate structure factors is so good that only a few calculations have been done with the accurate structure factors to spot-check the accuracy of the more numerous calculations using (4.26). All calculations[23] have been done in terms of a dimensionless temperature parameter,

$$\tau=kT/12J_{AB}. \quad (4.27)$$

Typical results for the sublattice magnetizations are given in Table I. The good agreement between the two sets at smaller values of $\tau$ is apparent. Similar calculations were also performed to obtain the predicted value of the Curie temperature. These numbers and the ratios of the sublattice magnetizations from the two calculations are compared in Table II. It might be argued that calculations based on the ordered lattice should not be applied above the transition temperature, 119°K, and particularly not near the Curie temperature, 848°K. However averaging of the values of $S_{B1}$ and $S_{B2}$ to simulate the effects of disordering gives a value of $\tau_C$ for the averaged structure factors which is very

TABLE I. Sublattice magnetizations for various values of $\tau$.

| | Accurate structure factors[a] | | | Averaged structure factors[a] | | |
|---|---|---|---|---|---|---|
| $\tau$ | $\sigma_A$ | $\sigma_{B1}$ | $\sigma_{B2}$ | $\sigma_A$ | $\sigma_{B1}$ | $\sigma_{B2}$ |
| 0 | 2.4409 | −2.4884 | −1.9951 | 2.4488 | −2.4716 | −1.9773 |
| 0.05 | | | | 2.4483 | −2.4710 | −1.9768 |
| 0.1 | | | | 2.4472 | −2.4698 | −1.9759 |
| 0.2 | | | | 2.4442 | −2.4663 | −1.9731 |
| 0.3 | | | | 2.4403 | −2.4609 | −1.9686 |
| 0.4 | | | | 2.4355 | −2.4521 | −1.9612 |
| 0.5 | | | | 2.4298 | −2.4384 | −1.9492 |
| 0.6 | | | | 2.4227 | −2.4193 | −1.9319 |
| 0.7 | | | | 2.4137 | −2.3947 | −1.9094 |
| 0.8 | | | | 2.4022 | −2.3652 | −1.8821 |
| 0.9 | | | | 2.3879 | −2.3312 | −1.8505 |
| 1.0 | 2.3608 | −2.3052 | −1.8298 | 2.3702 | −2.2930 | −1.8150 |
| 1.1 | | | | 2.3488 | −2.2509 | −1.7759 |
| 1.2 | | | | 2.3234 | −2.2049 | −1.7334 |
| 1.3 | | | | 2.2937 | −2.1551 | −1.6877 |
| 1.4 | | | | 2.2593 | −2.1015 | −1.6390 |
| 1.5 | | | | 2.2199 | −2.0440 | −1.5872 |
| 1.6 | | | | 2.1749 | −1.9822 | −1.5323 |
| 1.7 | | | | 2.1237 | −1.9160 | −1.4741 |
| 1.8 | | | | 2.0656 | −1.8449 | −1.4127 |
| 1.9 | | | | 1.9997 | −1.7683 | −1.3474 |
| 2.0 | 1.9074 | −1.6853 | −1.2832 | 1.9249 | −1.6856 | −1.2781 |
| 2.1 | | | | 1.8397 | −1.5957 | −1.2039 |
| 2.2 | | | | 1.7424 | −1.4973 | −1.1239 |
| 2.3 | | | | 1.6303 | −1.3884 | −1.0369 |
| 2.4 | | | | 1.4999 | −1.2662 | −0.94088 |
| 2.5 | 1.3185 | −1.1150 | −0.82862 | 1.3453 | −1.1262 | −0.83261 |
| 2.6 | | | | 1.1566 | −0.96053 | −0.70648 |
| 2.7 | | | | 0.91230 | −0.75191 | −0.55021 |
| 2.8 | 0.0966 | −0.0791 | −0.0578 | 0.54137 | −0.44296 | −0.32248 |
| | | $\tau_C=2.8044$ | | | | |
| 2.81 | | | | 0.48710 | −0.39828 | −0.28780 |
| 2.82 | | | | 0.42557 | −0.34773 | −0.25288 |
| 2.83 | | | | 0.35300 | −0.28823 | −0.20951 |
| 2.851 | | | | 0.07020 | −0.05723 | −0.04156 |
| | | | | | $\tau_C=2.8518$ | |

[a] Averaging of the structure factors affects the accuracy seriously only for $\tau/\tau_C\geq 0.9$. Much more computer time was required for the more accurate calculation but a few values of the $\sigma_\alpha$ were computed in that way to establish the reliability of the less accurate calculation.

[23] Programs for these computations were written for a CDC G-20 using a FORTRAN compiler. The zero-temperature results were obtained with the averaged structure factors by iteration using $S_A$, $-S_{B1}$ and $-S_{B2}$ as initial values of the $\sigma_\alpha$. Values of the $\sigma_\alpha$ at successively higher $\tau$ were obtained using the $\sigma_\alpha$ from lower $\tau$ as initial values for the iterations. Calculations were made for 42 values of $\tau$ up to the Curie temperature. At low $\tau$, convergence was obtained to 1 ppm in three or four iterations, while very near $\tau_C$, at $\tau=2.851$, 5500 iterations gave convergence to within 30 ppm. The three-dimensional quadratures used with the accurate structure factors and correct Brillouin-zone configuration made the more accurate calculation much slower. The symmetry of the equations made it possible to reduce the integration to one quadrant of the zone. A considerable saving was also obtained by tabulating the functions of the structure functions over one octant (the maximum needed) for each integration mesh. The mesh was refined sufficiently to assure that it had no distinguishable effect on the calculations. Self-consistency was obtained to within 100 ppm in up to 9 iterations from the values of the averaged calculation. Calculation of the Curie temperature using the accurate structure factors and the precise Brillouin zone proceeded in an analogous manner from the explicit results obtained with the averaged structure factors.

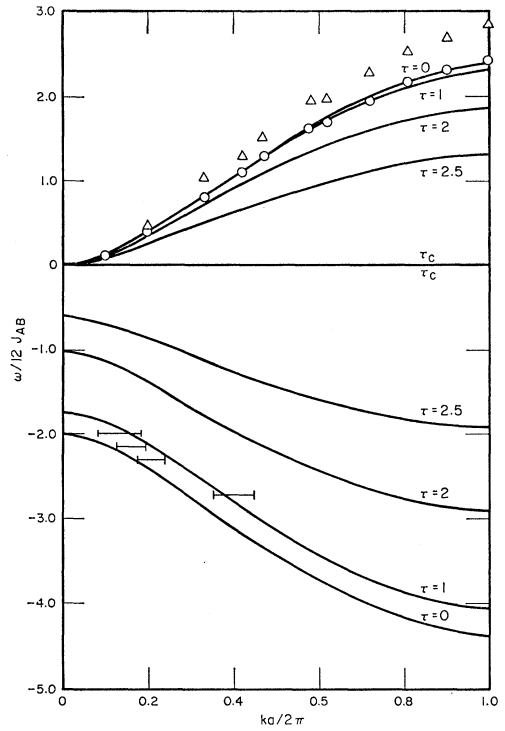


FIG. 1. Renormalized magnon spectra. The solid lines represent doints computed with the averaged structure factors at the dimensionless temperature $\tau=\kappa T/12J_{AB}$. The circles and bars represent the measured values of the acoustical and optical magnon spectra, respectively (Ref. 12), plotted using $J_{AB}=2.55\times10^{-3}$ eV. The triangles represent the same data for the acoustical mode plotted using the value $J_{AB}=2.13\times10^{-3}$ eV obtained from the Curie temperature.

nearly that given in Table II. The sublattice magnetizations are also averaged when $S_B=\frac{1}{2}(S_{B1}+S_{B2})$ is used. It should be noted that if the exchange integral, $J_{AB}$, is evaluated using the experimental Curie temperature

TABLE II. Curie temperature and ratios of sublattice magnetizations.

| Accurate structure factors | Averaged structure factors |
|---|---|
| $\tau_C$ 2.8044 | 2.8518 |
| $\sigma_{B1}/\sigma_A$ −0.81532 | −0.81849 |
| $\sigma_{B2}/\sigma_{B1}$ 0.72605 | 0.73061 |

and the more accurate value of $\tau_C$, then

$$J_{AB}=2.13\times10^{-3}\text{ eV(Curie temperature)}. \quad (4.28)$$

The renormalized dispersive modes computed using the averaged structure factors are plotted for various values of $\tau$ in Fig. 1. The corresponding graphs for the nondispersive modes follow from the data of Table I and Eq. (B4). The spectra computed with the accurate structure factors have been shown by GM to be nearly isotropic.[6] Their results correspond to the low-temperature case here. The acoustical and optical magnon spectral data[12] have also been plotted in Fig. 1, using energy units of $12J_{AB}$ where

$$J_{AB}=2.55\times10^{-3}\text{ eV (spectral data)}. \quad (4.29)$$

This value was chosen in order to position the acoustical spectral datum at $ka/2\pi\approx0.7$ as shown in Fig. 1. The remainder of the data fell as shown. With (4.29), room temperature corresponds to $\tau\approx0.85$, in reasonable agreement with the optical spectra. (Since the experimental data yields only the magnitude of the roots, $|\omega_l|$, the liberty has been taken of attaching signs in accord with the theory.) The comparison of the theory and experiment is good, but is neither unique nor optimized. The effect of altering $J_{AB}$ has been illustrated in Fig. 1 by plotting the acoustical spectral data using the value of $J_{AB}$ obtained from the Curie temperature. Even at smaller wave numbers, the difference is quite

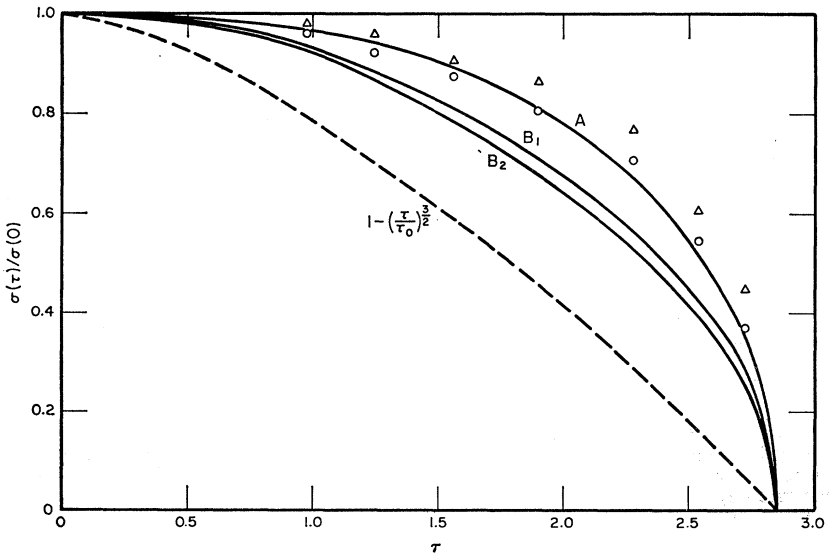


FIG. 2. The sublattice magnetizations, normalized to the zero-temperature values, are plotted against the dimensionless temperature. The dashed curve represents the corresponding values from the Bloch $T^{3/2}$ law. The triangles and circles represent data for $\sigma_A$ and $\sigma_B$, respectively, obtained by Riste and Tenzer from neutron-diffraction data (Ref. 24).

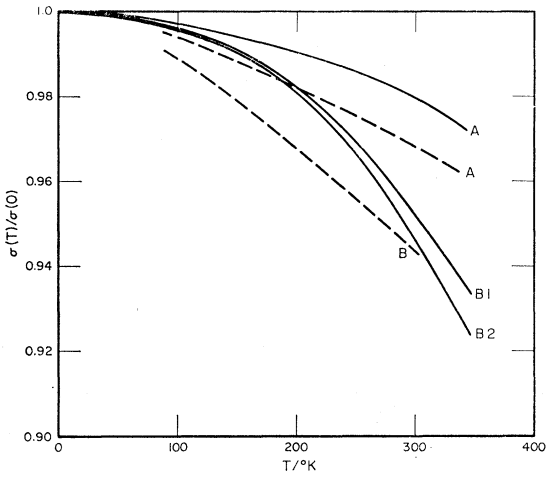


FIG. 3. Normalized sublattice magnetization $\sigma(T)/\sigma(0)$ versus $T$. The solid lines represent calculated values. The broken lines are from Fig. 3 of Boyd (Ref. 25).

distinct. The fits using the spectral data and the Curie temperature are more nearly consistent in the RPA than are the fits from linear spin-wave theory and the molecular field theory.

A comparison is given in Fig. 2 of the values of $\sigma_\alpha(\tau)/\sigma_\alpha(0)$ computed with the present theory, with the $T^{3/2}$ law, and the neutron scattering data obtained by Riste and Tenzer.[24] The latter has been plotted using the value of $J_{AB}$ obtained from the Curie temperature. The RPA curves are somewhat better "squared-up" than is the $T^{3/2}$ curve, but the correction is still not adequate.

The need for better correction is also apparent from comparison with NMR data obtained by Boyd[25] at intermediate temperatures, as shown in Fig. 3. Notice that no discontinuities are seen in Boyd's curves at the phase transition temperature, 119°K. The curves of $\sigma_A(T)/\sigma_A(0)$ in Fig. 4 have been plotted using for $T<119$°K the values of $J_{AB}$ obtained from the specific heat measurements of Kouvel[9] and of Dixon *et al.*,[10] while the curve for $T>119$°K has been plotted using the value of $J_{AB}$ obtained from the Curie temperature. A distinct discontinuity is observable in either case, although it is much reduced using the larger $J_{AB}$ from the specific-heat data.[26] (It is interesting to note that Domenicali[28] has observed a field and orientation-dependent change in the bulk magnetization of single crystals of magnetite upon warming or cooling through temperatures in the neighborhood of 119°K.) If the "squaring-up" of the magnetization curves were improved, however, the amount of the discontinuities in Fig. 4 would be reduced, and might even become undetectable.

It is laborious but straightforward to express $\langle\mathcal{H}\rangle$ more explicitly for magnetite. The result, given below without proof, is more compact than might be expected thanks to a considerable amount of recombination of the residues, $R_{\alpha\beta}$.

$$\langle\mathcal{H}\rangle=-\mu H_z N\sum_\alpha g_\alpha\sigma_\alpha-8NZJ_{AB}\sigma_A(\sigma_{B1}+\sigma_{B2})$$
$$-8J_{AB}{}^2\sigma_A\sum_k \mathrm{Re}[\sigma_{B1}(\gamma_{15}{}^2+\gamma_{25}{}^2)$$
$$+\sigma_2(\gamma_{35}{}^2+\gamma_{45}{}^2)]/(B^2-4C)^{1/2}$$
$$\times\left\{\frac{B+(B^2-4C)^{1/2}}{\omega_1-\omega_2}\left(\coth\frac{\beta\omega_1}{2}-\cot\frac{\beta\omega_2}{2}\right)\right.$$
$$\left.-\frac{B-(B^2-4C)^{1/2}}{\omega_3-\omega_4}\left(\coth\frac{\beta\omega_3}{2}-\coth\frac{\beta\omega_4}{2}\right)\right\}, \quad (4.30)$$

where $z$ is the number of nearest neighbors. Note that

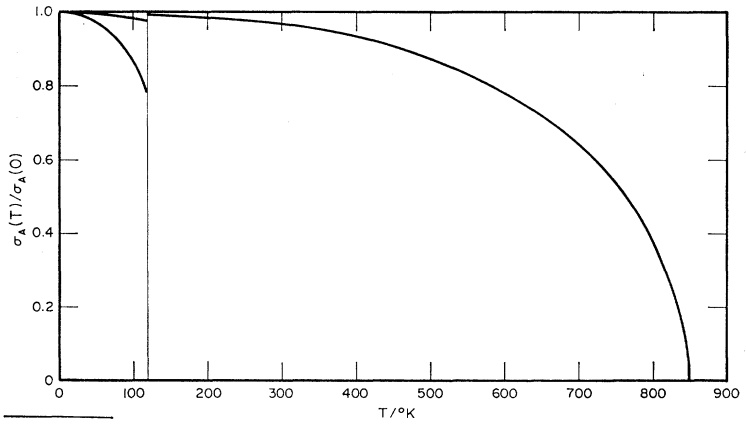


FIG. 4. The normalized sublattice magnetizations $\sigma(T)/\sigma(0)$ are plotted versus $T$ using, for $T>119$°K, the value of $J_{AB}$ obtained from the Curie temperature, and, for $T<119$°K, the values of $J_{AB}$ obtained from the specific heat data (Refs. 9–10). The discontinuity in the curve is only reduced, but not eliminated, by changing from the values of $J_{AB}$ from Kouvel's data (Ref. 9) to the value of $J_{AB}$ from the data of Dixon *et al.* (Ref. 10).

[24] T. Riste and L. Tenzer, J. Phys. Chem. Solids, **19**, 117 (1961).
[25] E. L. Boyd, Phys. Rev. **129**, 1961 (1963).
[26] This comment should not be construed as favoring either value. Indeed, Kouvel's value (Ref. 9) of the specific heat appears to be more nearly compatible than is the value of Dixon *et al.* (Ref. 10) with values of the specific heat of the substances $Ni_{1-x}Fe_{2+x}O_4$ measured by Pollack and Atkins, (Ref. 27) but the extrapolation which is required is rather large.
[27] S. R. Pollack and K. R. Atkins, Phys. Rev. **125**, 1248 (1962).
[28] C. A. Domenicali, Phys. Rev. **78**, 458 (1950).

the nondispersive mode $\omega_5$ does not contribute to $\langle \mathcal{H} \rangle$. A calculation of the specific heat, $C$, based on this expression shows that at low temperatures the value of $C$ obtained in the linear spin wave calculations[7] will not be changed appreciably even though (4.30) is more complicated than the $\langle \mathcal{H} \rangle$ of the simple-harmonic-oscillator model of that calculation.

## 5. SUMMARY AND CONCLUSIONS

A theory has been derived which gives for a ferrimagnet of $n$ sublattices the renormalized magnon spectra in the RPA. The magnon spectra and the sublattice magnetizations are obtained as self-consistent solutions to a set of $n$-coupled implicit equations. The ratios of the sublattice magnetization at the Curie temperature are obtained as the self-consistent solutions of a second set of $n$-coupled implicit equations. The Curie temperature itself is determined as a function of these ratios of the sublattice magnetizations. The zero-point motion and the relative signs of the sublattice magnetizations follow from the theory. It has been shown that older results for simple ferro- and antiferromagnets follow as special cases. The magnons considered here all have infinite lifetime, but magnons of given wave number are found to differ, in general, in their amplitudes, their directions, and their phases, from sublattice to sublattice.

Calculations based on the general theory have been made of properties of the magnetic insulator, magnetite ($Fe_3O_4$). The acoustical and optical magnon spectra are found to be in good agreement with experimental data for the exchange constant given in (4.29). This value of $J_{AB}$ is in reasonable, but not good, agreement with a value (4.28) obtained by matching the theoretical and experimental Curie temperatures. The values of $J_{AB}$ based on data taken above 119°K are found to differ significantly from values of $J_{AB}$ obtained from either measurements of the low-temperature specific heat.

The experimental data for magnetite is in need of further refinement, but even now it seems adequate to support the statement that theoretical interpretation of data taken above 119°K requires a value of $J_{AB}$ of about $2.5\times10^{-3}$ eV, while the low-temperature data requires a smaller $J_{AB}$, on the order of $1\times10^{-3}$ eV. It would be desirable to make measurements of one physical property of magnetite both above and below 119°K (for example, the magnon spectra) in order to obtain a better check.

It is shown in GM[6] that the magnon spectra predicted by linear spin-wave theory agrees better with the experimental results[12] if a small ferromagnetic coupling between the sites of octahedral coordination, $J_{BB}\approx -J_{AB}/10$, is included in the calculation. The same result is expected to hold in the present renormalized spin-wave theory. An estimate of the effect on $J_{BB}$ of the second-order transition at 119°K can be obtained by considering the data for the electrical conductivity of magnetite.[28–30] The reduction by nearly two orders of magnitude which this quantity undergoes upon cooling through the transition temperature, and the related ordering of the ferric and ferrous ions on the $B1$ and $B2$ sites, indicates that the overlap integrals of the electronic wave functions for these sites are considerably reduced. Thus it seems reasonable to expect that $J_{BB}$, which depends in part on a similar overlap of the electronic wave functions, is also reduced in magnitude in passing from above to below 119°K. Thus including $J_{BB}$ should not alter seriously the present results.

The quantitative change in the crystallographic configuration in passing from the fcc phase above 119°K to the orthorhombic phase below 119°K is quite small, and so it probably should not be expected that the change in the overlap of the electronic wave functions is due to a substantial change in the crystal-field splitting of the electronic energy levels. The wave functions for the $d$ electrons of the Fe ions are expected to be much larger in magnitude along certain directions than in others. Then if the wave functions are but little affected locally by the change in the crystal field, the change in orientation of the ions would lead to an alteration of the overlap of wave functions of electrons on different ions. This would be noticeable in $J_{AB}$ as well as in $J_{BB}$. Further investigation of this problem has been initiated.

The high-temperature values of $J_{AB}$ given in (4.28) and (4.29) may be more consistent with one another than the 20% difference in the numerical values would indicate. There is empirical evidence[31] that the exchange constants in magnetite, as in several other insulators, are proportional to the $-10/3$ power of the volume, $V$. Then $J_{AB}$ will depend on temperature, because of thermal expansion, in accord with the relation

$$J_{AB}(T)=J_{AB}(T_0)[1-10\alpha(T-T_0)], \qquad (5.1)$$

where $\alpha$ is the coefficient of linear expansion. If $T_0$ is taken to be the temperature of the spectral data, 300°K, and $\alpha$ as $16\times10^{-6}$/°K,[32] the value of $J_{AB}(T_C)$ is then calculated to be $2.3\times10^{-3}$ eV. This differs from the $J_{AB}$ of (4.28) by about 8%. The agreement is quite satisfactory considering the simplicity of the RPA used herein. Note also that temperature correction of the type stated in (5.1) will also improve the "squaring-up" of the RPA curve in Fig. 2, and will reduce the step in the magnetization curve in Fig. 4.

## ACKNOWLEDGMENT

The material included in this paper represents both an elaboration and an extension of brief accounts given

[29] E. J. W. Verwey and P. W. Haagman, Physica 8, 979 (1941).
[30] B. A. Calhoun, Phys. Rev. 94, 1577 (1954).
[31] D. Bloch, Ann. Phys. (Paris) (to be published).
[32] L. Néel, J. Phys. Radium 12, 258 (1951).

in earlier papers.[33,34] It is part of a continuing investigation of properties of magnetite sponsored by the Battelle Memorial Institute and the U. S. Air Force.

We would like to thank Dr. T. M. Holden and his associates for communicating their heat-capacity data[10] to us prior to publication and Dr. M. L. Glasser for helpful discussions. One of us (REM) would like to thank Professor H. B. Callen for constructive criticism concerning the description of the zero-point deviation and Dr. D. Bloch for an illuminating discussion concerning the volume dependence of exchange constants, and for providing Refs. 31 and 32.

## APPENDIX A

Consequences of Callen's theorem[15] for the moment-generating function defined in (2.13) are discussed in this Appendix. A number $\Phi_\alpha{}^C$ is defined as the ratio of two expectation values

$$\Phi_\alpha{}^C \equiv \langle \exp(aS_\alpha{}^z) S_\alpha{}^- S_\alpha{}^+ \rangle / \langle [S_\alpha{}^+, \exp(aS_\alpha{}^z) S_\alpha{}^-]_- \rangle . \quad \text{(A1)}$$

Then, in a manner exactly parallel to Callen's proof for a simple ferromagnet, the expectation values are expanded using the commutation relations (2.2) and (2.3) to obtain a relation between the moments $\langle (S_\alpha{}^z)^n \rangle$ for $n=0$, 1 and 2. These can be expressed as derivatives using the moment generating function, $\Omega_\alpha(a)$, since

$$\langle (S_\alpha{}^z)^n \rangle = (d/da)^n \Omega_\alpha(a) \big|_{a=0} . \quad \text{(A2)}$$

In this manner a second order differential equation for $\Omega_\alpha(a)$ is obtained which has the explicit solution (2.13), provided $\Phi_\alpha{}^C$ is independent of the variable $a$. In that event, $a$ may be set to zero in (A1) and then $\Phi_\alpha{}^C$ becomes the $\Phi_\alpha$ of (2.15).

It is not obvious from (A1) that $\Phi_\alpha{}^C$ will be independent of $a$. It appears that in general it will not be so, but the arguments of Sec. 2 are readily modified to show that $\Phi_\alpha{}^C$ is independent of $a$ in the RPA. A spectral representation for $\Phi_\alpha{}^C$ similar to (2.15) is obtained upon replacing in (2.7) $2\sigma_\alpha$ by $\langle [S_\alpha{}^+, \exp(aS_\alpha{}^z) S_\alpha{}^-]_- \rangle$, and $S_\alpha{}^-$ by $\exp(aS_\alpha{}^z) S_\alpha{}^-$. The formal structure of the Green's function in (2.24) is preserved if these same replacements are made in (2.21) to (2.24). The equations of motion of the altered Green's functions have precisely the form of (2.27) and (2.28), with $B(t')$ being $\exp(aS_\alpha{}^z) S_\alpha{}^-(t')$. This leads at length to an equation in the form of (2.31) in which the inverse matrix element is exactly the same as in Sec. 2, and all the $a$ dependence is in the factor $\langle [S_\alpha{}^+, \exp(aS_\alpha{}^z) S_\alpha{}^-]_- \rangle$ which replaces the explicit $2\sigma_\alpha$. No such replacement occurs in the inverse matrix element. Then upon taking the imaginary part of the $a$-dependent Green's function, and using the analog of (2.25) to calculate the spectral function, it is seen that in the RPA the $a$-dependent terms factor out. Thus the spectral function, and so also $\Phi_\alpha{}^C$, is $a$ independent. Then (2.13) and (2.16) follow as valid.

It is apparent that whenever the $a$-dependent Green's functions can be put in the form of (2.31) with $2\sigma_\alpha$ replaced by $\langle [S_\alpha{}^+, \exp(aS_\alpha{}^z) S_\alpha{}^-] \rangle$, and $[\omega I - \mathcal{J}(\mathbf{k})]^{-1}{}_{\alpha\beta}$ independent of $a$ (as in the RPA), the corresponding spectral function will be $a$-independent. The $\Phi_\alpha{}^C$ which follows then implies (2.13). This includes also cases in which more complicated types of correlations are included in the approximation to the equation of motion of $S_\alpha{}^+$ which gives the form of $[\omega I - \mathcal{J}(\mathbf{k})]^{-1}{}_{\alpha\beta}$.[35]

## APPENDIX B

The equations given in Sec. 4 for the application to magnetite of this ferrimagnet theory are applicable to any ferrimagnet with the inverse spinel structure. The spherical averaging of the structure factors introduced in (4.26) gives equations which are much simpler, but still rather accurate. These latter equations will be given here. The reduction to three independent $\sigma_\alpha$ is also included in the equations which follow.

The function $C$ defined in (4.5) vanishes when (4.26) is adopted since all the structure factors are strictly real. In order to extract square roots in the expressions for the zeros, the signs of $\sigma_A$, $\sigma_{B1}$, and $\sigma_{B2}$ are assumed to be $+$, $-$, $-$, respectively. Then with $J_{AB}>0$,

$$\mathcal{J}_{11} = -12 J_{AB} \sigma_A < 0 , \quad \text{(B1)}$$

$$\mathcal{J}_{55} = -12 J_{AB} (\sigma_{B1} + \sigma_{B2}) > 0 , \quad \text{(B2)}$$

and

$$B = 16 J_{AB}{}^2 \sigma_A (\sigma_{B1} + \sigma_{B2}) \gamma(\mathbf{k})^2 < 0 . \quad \text{(B3)}$$

The frequencies (4.1) become

$$\omega_1 = \mathcal{J}_{55} , \quad \text{(B4a)}$$

$$\omega_2 = \omega_5 = \omega_6 = \mathcal{J}_{11} , \quad \text{(B4b)}$$

$$\omega_3(\mathbf{k}) = \tfrac{1}{2}(\mathcal{J}_{11} + \mathcal{J}_{55}) + \tfrac{1}{2}\{(\mathcal{J}_{11} - \mathcal{J}_{55})^2 + 4B\}^{1/2} , \quad \text{(B4c)}$$

$$\omega_4(\mathbf{k}) = \tfrac{1}{2}(\mathcal{J}_{11} + \mathcal{J}_{55}) - \tfrac{1}{2}\{(\mathcal{J}_{11} - \mathcal{J}_{55})^2 + 4B\}^{1/2} . \quad \text{(B4d)}$$

With the signs of the $\sigma_\alpha$ taken above, $\omega_1$ and $\omega_3 > 0$, while $\omega_2$ and $\omega_4 < 0$. Calculation of the residues is complicated only slightly by the fact that $\omega_2$ and $\omega_5$ have become degenerate so that only four distinct zeros now appear. It follows from the sum rule (2.36) that the residues should be added together for the zeros which

[33] R. E. Mills, R. P. Kenan, and F. J. Milford, Phys. Letters **12**, 173 (1964).

[34] R. E. Mills, R. P. Kenan, and F. J. Milford, J. Appl. Phys. **36**, 1131 (1965).

[35] This problem has been studied explicitly for a ferromagnet (Ref. 36). After the $a$-dependent Green's function and the factor $[\omega I - \mathcal{J}(\mathbf{k})]^{-1}$ are completely separated algebraically by a functional technique, it becomes obvious that in general the latter factor depends on the parameter $a$. It is then also apparent that (2.14) can be valid even in approximations in which, because of dynamical correlations, the magnons have a finite lifetime. The generality of (2.14) was also studied by Callen and Shtrikman (Ref. 37) in a comparison of theories of this type to molecular field theories.

[36] R. E. Mills, Bull. Am. Phys. Soc. **10**, 305, AC3 (1965).

[37] H. B. Callen and S. Shtrikman, Solid State Commun. **3**, 5 (1965).

have become degenerate. From (4.16)–(4.20), and writing $R_{B1,l}$ rather than $R_{11,l}=R_{22,l}$, etc.,

$$R_{Bi,1}(k)=0, \tag{B5a}$$

$$R_{Bi,2}(k)=1-\tfrac{1}{2}r_i, \tag{B5b}$$

$$R_{Bi,l}(k)=(-1)^{l+1}(r_i/2)\times[(\omega_l-\omega_1)/(\omega_3-\omega_4)],\quad l=3,4, \tag{B5c}$$

where

$$r_i=\sigma_{Bi}/(\sigma_{B1}+\sigma_{B2}),\quad i=1,2, \tag{B5d}$$

and

$$R_{A,1}(k)=\tfrac{1}{2}, \tag{B6a}$$

$$R_{A,2}(k)=0, \tag{B6b}$$

$$R_{A,l}(k)=(-1)^{l+1}(1/2)\times[(\omega_l-\omega_2)/(\omega_3-\omega_4)],\quad l=3,4. \tag{B6c}$$

The magnon-number functions reduce to

$$\Phi_A=\frac{1}{2N}\sum_k\left\{b(\omega_2)+\frac{1}{\omega_3-\omega_4}[(\omega_3-\omega_2)b(\omega_3)-(\omega_4-\omega_2)b(\omega_4)]\right\}, \tag{B7}$$

$$\Phi_{Bi}=\frac{1}{N}\sum_k\left\{b(\omega_1)-\frac{r_i}{2}\left(b(\omega_1)-\frac{1}{\omega_3-\omega_4}[(\omega_3-\omega_1)b(\omega_3)-(\omega_4-\omega_1)b(\omega_4)]\right)\right\}, \tag{B8}$$

with the $b(\omega)$ defined in (3.9). The $\sigma_A$, $\sigma_{B1}$ and $\sigma_{B2}$ then can be obtained by an iterative calculation.

Since $b(\omega)$ becomes 0 or $-1$ at zero temperature as $\omega$ is greater or less than zero,

$$\Phi_A|_{T=0}=\frac{1}{2N}\sum_k(\omega_3-\omega_2)/(\omega_3-\omega_4) \tag{B9}$$

$$\Phi_{Bi}|_{T=0}=-1-\frac{r_i}{2N}\sum_k(\omega_1-\omega_4)/(\omega_3-\omega_4). \tag{B10}$$

Now $\omega_1-\omega_4=\omega_3-\omega_2>0$, and so only one sum appears in (B9) and (B10). Also the magnon number functions at zero temperature are consistent with the initial choice of signs. Unlike the case of antiferromagnetism discussed in Sec. 3, determination of the zero-point deviation requires solution of implicit equations since the $r_i$ and the $\omega_l$ depend on the $\sigma_\alpha$. The sum in (B9) and (B10) is small, and so, from (2.16)–(2.18), the deviations from perfect ordering on the individual sublattices are small. To first order in these small quantities,

$$\Phi_A+[1+\Phi_{B1}]+[1+\Phi_{B2}]=0. \tag{B11}$$

The total magnetization is $S_A-S_{B1}-S_{B2}$, to first order in the small quantities $\Phi_\alpha$. This result can be seen from the data of Table I to hold for magnetite.

An explicit expression for the Curie temperature is found upon applying a bit of algebra to (2.40)–(2.44). The equations are combined to give a quadratic equation in $\sigma_{B2}/\sigma_{B1}$, from which

$$\sigma_{B2}/\sigma_{B1}=-\frac{1-S_{12}}{1+I_C}+\left[\left(\frac{1-S_{12}}{1+I_C}\right)^2+\frac{S_{12}}{S_{B2}}\right]^{1/2}, \tag{B12}$$

where $S_{Bi}$ is the spin magnitude of the $B_i$ ions,

$$S_{12}\equiv S_{B2}(S_{B2}+1)/[S_{B1}(S_{B1}+1)], \tag{B13}$$

and

$$I_C\equiv\frac{1}{N}\sum_k 9/(9-\gamma(k)^2). \tag{B14}$$

For inverse spinels, with $\gamma(k)$ from (4.26),

$$I_C=1.8784. \tag{B15}$$

Then

$$\tau_C=\frac{2}{3}\left(1+\frac{\sigma_{B2}}{\sigma_{B1}}\right)\left[\frac{S_{B1}(S_{B1}+1)S_A(S_A+1)}{(1+I_C)^2+2(1+I_C)\sigma_{B2}/\sigma_{B1}}\right]^{1/2} \tag{B16}$$

(Ref. 38).

Also

$$\sigma_A/\sigma_{B1}=-\frac{3\tau_C(1+I_C+2\sigma_{B2}/\sigma_{B1})}{2S_{B1}(S_{B1}+1)(1+\sigma_{B2}/\sigma_{B1})}. \tag{B17}$$

The values of these quantities for magnetite are given in the Table II of Sec. 4.

The expectation value of the Hamiltonian is given in this case by

$$\langle\mathcal{H}\rangle=-\mu H_z N\sum_\alpha g_\alpha\sigma_\alpha-8NJ_{AB}\sigma_A(\sigma_{B1}+\sigma_{B2})-32J_{AB}{}^2\sigma_A(\sigma_{B1}+\sigma_{B2})\times\sum_k\frac{\gamma^2(k)}{\omega_3-\omega_4}\left(\coth\frac{\beta\omega_3}{2}-\coth\frac{\beta\omega_4}{2}\right). \tag{B18}$$

Here again, as in (4.30), the nondispersive modes do not contribute. The physical origin of this curious fact has not been ascertained.

[38] The similarity of this result for $\tau_C$ to the corresponding ($J_{AB}\neq 0$) form of Kouvel's expression based on molecular-field theory should be noted.