Interpolation Theory of Ferromagnetic Heisenberg Model*

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This is the sequel to an earlier paper which gave a complete formulation of an interpolation theory of ferromagnetism based on the Green's-function method and the simple Tyablikov decoupling scheme. Numerical calculations of the energy and specific heat have been carried out for a few simple spin-wave models, and the results are compared with those deduced from other theories. It is found in general that the performance of the interpolation theory is poor for $S=\frac{1}{2}$ but becomes better for $S=1$ or higher. Also, the theory makes a large error around the critical temperature for all spins. The spin-disorder contribution to the transport coefficients of a ferromagnetic metal are studied for a parabolic model of the spin-wave spectrum, and the results are comparable qualitatively with the experiments.

I. INTRODUCTION

A RELIABLE interpolation theory of ferromagnetism is useful in understanding many experimental observations at temperatures where rigorous analysis is impossible at present; for instance, in the temperature region below—but not small compared with—the Curie point. The most widely used interpolation scheme is the Weiss molecular-field theory, but the shortcoming of this theory is that it ignores completely the transverse spin correlations and the short-range correlations above the Curie temperature. Tyablikov derived a different interpolation method for $S=\frac{1}{2}$ based on the study of two-spin Green's functions.[1] He showed that by making a suitable decoupling approximation to the three-spin Green's functions, one can solve the two-spin Green's functions in closed form at all temperatures. The result is an interpolation theory which agrees with the rigorous asymptotic analysis at both very high- and very low-temperature regions. This method has been generalized to higher spins, and different types of decoupling schemes have been proposed to improve the accuracy.[2-4] In all of these discussions, attention was focused on comparing the interpolation theory with the rigorous theories in the extremely high- and low-temperature regions, and comparing the Curie temperature with other approximate theories. No detailed study of the energy and specific heat was attempted because the longitudinal correlation functions of the spins, which are necessary for this study, are not given directly by this theory.[5] One of the authors

(SHL) derived these longitudinal correlation functions in a manner consistent with the Tyablikov approximation.[6] He also outlined the complete interpolation scheme for all the thermodynamical quantities for a Heisenberg ferromagnet and the spin-disorder contribution to the electrical resistivity of a ferromagnetic metal. The structure of the theory is extremely complicated, and the numerical analysis has just been completed. This paper gives a final report of this work.

II. SUMMARY OF PREVIOUS RESULTS

We study a simple isotropic Heisenberg model without external field. The Hamiltonian may be written as

$$H = -\sum_{ij} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j, \qquad (1)$$

where the interaction energy J_{ij} may be long- or short-ranged. If we define the Fourier transform of J_{ij} by

$$J(\mathbf{q}) = \sum_j J_{ij}\exp(-i\mathbf{q}\cdot\mathbf{R}_{ij}), \qquad (2)$$

then the spin-wave spectrum at an arbitrary temperature is, in the Tyablikov approximation,

$$\omega_\mathbf{q} = 2\sigma[J(0)-J(\mathbf{q})]\equiv 2\sigma J(0, \mathbf{q}), \qquad (3)$$

where σ is the saturation magnetization per spin and the units used are such that $\hbar=1$. We point out here that the proportionality of the spin-wave energy with the magnetization has recently been observed by Møller and Houmann in Tb at moderately high temperatures.[7]

For the general spin problem, the magnetization σ is solved from the following set of equations:

$$\sigma = \frac{S\Phi^{2S+1}+(S+1)(1+\Phi)^{2S+1}}{(1+\Phi)^{2S+1}-\Phi^{2S+1}} - (1+\Phi), \qquad (4)$$

$$\Phi = N^{-1}\sum_\mathbf{q} N(\omega_\mathbf{q}), \qquad (5)$$

$$N(\omega_\mathbf{q}) = [\exp(\beta\omega_\mathbf{q})-1]^{-1}, \qquad (6)$$

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[1] N. N. Bogolyubov and S. V. Tyablikov, Dokl. Akad. Nauk SSSR **126**, 53 (1959) [English transl.: Soviet Phys.—Doklady **4**, 604 (1959)].

[2] Yu. A. Izyumov and E. N. Yakovlev, Fiz. Met. i Metalloved. **9**, 667 (1960); K. Kawasaki and H. Mori, Progr. Theoret. Phys. (Kyoto) **25**, 1045 (1961); R. A. Tahir-Kheli and D. ter Haar, Phys. Rev. **127**, 88 (1962).

[3] H. B. Callen, Phys. Rev. **130**, 890 (1963).

[4] J. A. Copeland and H. A. Gersch, Phys. Rev. **143**, 236 (1966).

[5] The longitudinal correlation functions derived by R. A. Tahir-Kheli and H. B. Callen [J. Appl. Phys. **35**, 956 (1964); Phys. Rev. **135**, A679 (1964)] are not consistent with rotational invariance above the Curie temperature. See discussion in Ref. 6. The zz correlation function used by Copeland and Gersch, Ref. 4, is subject to the same criticism.

[6] S. H. Liu, Phys. Rev. **139**, A1522 (1965).

[7] H. B. Møller and J. C. Houmann, in a paper presented in the Conference on Rare Earths at the University of Durham, England, 1966.

where N is the total number of spins and $\beta=(k_BT)^{-1}$. The Curie temperature is found from setting $\sigma \to 0$. The result is

$$[k_BT_c]^{-1}=[3/2S(S+1)]N^{-1}\sum_q [J(0,\,q)]^{-1} \quad (7)$$

where $J(0,\,q)$ was defined in Eq. (3). Above the Curie point we must solve for σ in the presence of an external field H_e and define the paramagnetic susceptibility per spin by

$$\chi=\lim_{H_e \to 0} \sigma/g\mu_B H_e,$$

where g is the gyromagnetic ratio and μ_B is the Bohr magneton. Then the equation for χ is

$$\chi^{-1}=[3/S(S+1)](N\beta)^{-1}\sum_q [1+2\chi J(0,\,q)]^{-1}. \quad (8)$$

As shown in Ref. 6, the important quantities in the theory are the two spin correlation functions. These are more easily expressed in terms of spatial Fourier com-

ponents of the spins. If we define

$$\mathbf{S}_q=N^{-1}\sum_i \mathbf{S}_i \exp(-i\mathbf{q}\cdot\mathbf{R}_i), \quad (9)$$

then the correlation functions may be written, in terms of their spectral representations

$$\langle S_{-q}{}^-(t)S_q{}^+(0)\rangle=\int \frac{d\omega}{2\pi}J_-(\mathbf{q},\,\omega)\,\exp(-i\omega t),$$

$$\langle S_{-q}{}^+(t)S_q{}^-(0)\rangle=\int \frac{d\omega}{2\pi}J_+(\mathbf{q},\,\omega)\,\exp(-i\omega t),$$

$$\langle S_{-q}{}^z(t)S_q{}^z(0)\rangle=\int \frac{d\omega}{2\pi}J_z(\mathbf{q},\,\omega)\,\exp(-i\omega t), \quad (10)$$

where

$$J_-(\mathbf{q},\,\omega)=-[4\pi\sigma/N(1-\exp(-\beta\omega))]\delta(\omega+\omega_q),$$

$$J_+(\mathbf{q},\,\omega)=[4\pi\sigma/N(1-\exp(-\beta\omega))]\delta(\omega-\omega_q),$$

and

$$J_z(\mathbf{q},\,\omega)=[s_q{}^{(1)}(-i\omega+\delta)-s_q{}^{(1)}(-i\omega-\delta)]/N(1-\exp(-\beta\omega)). \quad (11)$$

In the expression for $J_z(\mathbf{q},\,\omega)$, the quantity $s_q{}^{(1)}$ as a function of the imaginary frequency is given by

$$s_q{}^{(1)}(\omega_n)=\frac{\xi}{N}\sum_k \frac{N(\omega_k)-N(\omega_{k-q})}{i\omega_n+\omega_{k-q}-\omega_k}\left\{1+\frac{2\eta}{N}\sum_k \frac{(\omega_q-\omega_{k-q})[N(\omega_k)-N(\omega_{k-q})]}{i\omega_n+\omega_{k-q}-\omega_k}\right\}^{-1}, \quad (12)$$

where

$$\eta=S(S+1)^{-1}\left[\sigma+1+\Phi-\frac{(2S+1)\lambda}{(1+\Phi)^{2S+1}-\Phi^{2S+1}}\right],$$

and

$$\xi=(1+\Phi)^{2S-1}[(1+\Phi)^{2S+1}-\Phi^{2S+1}]^{-1}\left\{\sum_{n=1}^{2S-1}\frac{n(2S-n+1)}{(n+1)(2S-n)}\left(\frac{\Phi}{1+\Phi}\right)^{n-1}\right.$$

$$\times\left[1+\Phi+n-S+\sigma-\frac{(2S+1)\Phi^{2S-n}(1+\Phi)^{n+1}}{(1+\Phi)^{2S+1}-\Phi^{2S+1}}\right]+\frac{2S}{(2S+1)^2}\left(\frac{\Phi}{1+\Phi}\right)^{2S-1}$$

$$\times\left.\left[\Phi-S+\sigma-\frac{(2S+1)[\rho+(1+\Phi)^{2S+1}]}{(1+\Phi)^{2S+1}-\Phi^{2S+1}}\right]\right\},$$

$$\rho=-\sum_{n=0}^{2S}\frac{2S+1}{n+1}(1+\Phi)^{2S-n},$$

$$\lambda=\Phi^S(1+\Phi)^{S+1}, \quad \text{if } S=\text{integer},$$

$$=\sum_{n=0}^{2S+1}\binom{S+1}{2S-n+1}\Phi^n, \quad \text{if } S=\text{half-odd integer}.$$

The result for $s_q{}^{(1)}$ given in Ref. 6, Eq. (52) is in error. The explicit expression for the spectral density function $J_z(\mathbf{q},\,\omega)$ is

$$J_z(\mathbf{q},\,\omega)=[2\xi/N(1-\exp(-\beta\omega))](BC-AD)/(C^2+D^2), \quad (11')$$

where

$$A = N^{-1} \sum_k \frac{N(\omega_k) - N(\omega_{k-q})}{\omega + \omega_{k-q} + \omega_k},$$

$$B = (\pi/N) \sum_k [N(\omega_{k-q}) - N(\omega_k)]\delta(\omega + \omega_{k-q} - \omega_k),$$

$$C = 1 + \frac{2\eta}{N} \sum_k \frac{(\omega_q - \omega_{k-q})[N(\omega_k) - N(\omega_{k-q})]}{\omega + \omega_{k-q} - \omega_k},$$

$$D = (2\pi\eta/N) \sum_k (\omega_q - \omega_{k-q})[N(\omega_k) - N(\omega_{k-q})]\delta(\omega + \omega_{k-q} - \omega_k). \tag{11''}$$

In the actual calculation we evaluate the functions A, B, C, and D for an assumed spin-wave spectrum. Then from Eqs. (11') and (10) we obtain the value of the longitudinal correlation function.

In the paramagnetic-temperature region, the correlation functions are greatly simplified; they are

$$\langle S_{-q}{}^+(t) S_q{}^-(0) \rangle = \langle S_{-q}{}^-(t) S_q{}^+(0) \rangle$$
$$= 2\chi/\{N\beta[1 + 2\chi J(0, \mathbf{q})]\},$$

$$\langle S_{-q}{}^z(t) S_q{}^z(0) \rangle = \chi/\{N\beta[1 + 2\chi J(0, \mathbf{q})]\}. \tag{13}$$

In terms of these correlation functions we can write the energy of the system as

$$E = -N \sum_q J(\mathbf{q}) \langle \mathbf{S}_{-q} \cdot \mathbf{S}_q \rangle, \tag{14}$$

where for $\mathbf{q} = 0$ we have in particular

$$\langle S_0{}^z S_0{}^z \rangle = \sigma^2. \tag{15}$$

Hence, if the spin-wave spectrum is given, it is possible to calculate the energy of the system. From this result we can evaluate the specific heat, entropy, and other thermodynamic functions.

The difficulty with this calculation is in the complexity of the zz correlation function below the Curie temperature. In order that the numerical analysis may be carried out by the high-speed computer in a finite amount of time, we adopted a very simple model for the spin-wave spectrum, i.e.,

$$J(0) - J(q) = aq^2, \tag{16}$$

for $q \leq q_0$. The size of q_0 is chosen such that the states contained in the phase space are the same as the number of spin-wave degrees of freedom, namely N. This will be called the parabolic model, and its advantage is that the angular integration appearing in Eq. (11'') can be easily carried out. We also limit our attention to the cases $S = \frac{1}{2}$, $S = 1$, and $S = \infty$. In the last case we take the limit $S \to \infty$, $[J(0) \to 0$, but $J(0)S^2 \to$ constant$]$. Some of the equations listed above are simplified. For $S = \frac{1}{2}$:

$$\sigma = \frac{1}{2}(1 + 2\Phi),$$
$$\eta = 2\sigma,$$
$$\xi = 4\sigma^2; \tag{17}$$

$S = 1$:
$$\sigma = (1 + 2\Phi)/(1 + 3\Phi + 3\Phi^2),$$
$$\eta = (2 + 3\Phi)/2(1 + 3\Phi + 3\Phi^2),$$
$$\xi = 2(1 + \Phi)(1 + 3\Phi)/(1 + 3\Phi + 3\Phi^2)^2; \tag{18}$$

and for $S = \infty$:
$$\sigma/S = m, \qquad T/T_c = t,$$
$$m = \coth(3m/t) - t/3m,$$
$$kT_c = \lim \frac{2S^2}{3/N} \sum_q [J(0) - J(\mathbf{q})]^{-1},$$
$$\eta = \lim 3m/2S,$$
$$\xi = 1 - (3m/t)^2 \operatorname{csch}^2(3m/t)^2. \tag{19}$$

We shall also discuss some of the results derived from the Callen decoupling method. The main difference between the predictions of the two theories is that the spin-wave energy in Callen theory is given by

$$\omega_q = 2\sigma[J(0, \mathbf{q}) + (\sigma/NS)^2 \sum_k J(\mathbf{k}, \mathbf{k} - \mathbf{q})N(\omega_k)]. \tag{20}$$

Consequently, the Curie temperature is solved from the equations

$$(k_B T_c)^{-1} = [3/2S(S+1)]N^{-1} \sum_q E_q{}^{-1},$$

$$E_q = J(0, \mathbf{q}) + (2NS^2)^{-1} \sum_k J(\mathbf{k}, \mathbf{k} - \mathbf{q})(k_B T_c/E_k). \tag{21}$$

The susceptibility above the Curie point satisfies

$$\chi^{-1} = [3/S(S+1)](N\beta)^{-1} \sum_q [1 + 2\chi E_q(T)]^{-1},$$

where

$$E_q(T) = J(0, \mathbf{q})$$
$$+ (\chi/\beta NS^2) \sum_k J(\mathbf{k}, \mathbf{k} - \mathbf{q})/[1 + 2\chi E_k(T)]. \tag{22}$$

The zz correlation function below the Curie point is difficult to write down, but above the Curie point the rotational invariance of the correlation functions implies that

$$\langle S_{-q}{}^+ S_q{}^- \rangle = \langle S_{-q}{}^- S_q{}^+ \rangle$$
$$= 2\langle S_{-q}{}^z S_q{}^z \rangle$$
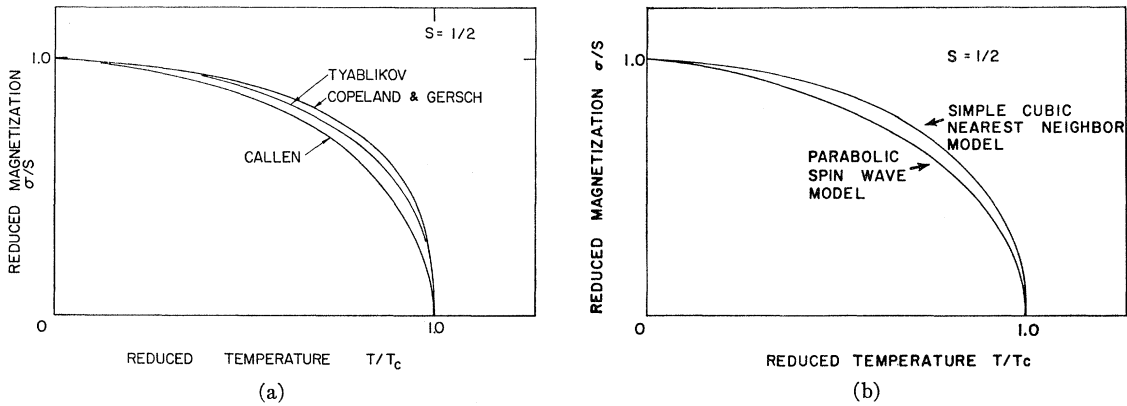$$= 2\chi/N\beta[1 + 2\chi E_q]. \tag{23}$$

Fig. 1. The magnetization curves for some simple spin-wave models: (a) The fcc nearest-neighbor-interaction model calculated on the basis of the three decoupling approximations. (b) The simple-cubic nearest-neighbor model and the parabolic model calculated by using the Tyablikov approximation.

The discussion will be limited to the predictions in the paramagnetic region.

Copeland and Gersch[4] proposed a third decoupling scheme. In their theory the spin-wave energy is given by the expression

$$\omega_q = 2\sigma[J(0, q) + (\sigma^3/2S^4) \sum_k J(k, k-q)N(\omega_k)].$$

The consequences of this assumption are discussed in some detail in Ref. 4.

III. RESULTS OF NUMERICAL ANALYSIS

Figure 1 shows some magnetization curves obtained from the various decoupling theories. In Fig. 1(a) we compare the magnetization curves for an fcc nearest-neighbor-interaction model calculated on the basis of the three types of decoupling approximations. Generally speaking, the curves agree with each other quite well except near the Curie temperature. In Fig. 1(b) the magnetization curve for the parabolic model is compared with that of a simple cubic model with nearest-neighbor interactions both calculated by using the Tyablikov approximation. It is apparent that the error introduced by making the parabolic spectrum approximation is of the same order of magnitude as the uncertainty in the decoupling approximation itself. Just below the Curie point the temperature dependence of the magnetization is found to be, for an arbitrary spin-wave model,

$$\sigma \sim (T_c - T)^{1/2},$$ (24)

in agreement with the Weiss molecular-field theory and the Landau theory of second-order phase transition.[8] Just above the Curie temperature the suscepti-

bility has the temperature dependence

$$\chi \sim (T - T_c)^{-2},$$ (25)

which disagrees with the prediction

$$\chi \sim (T - T_c)^{-1}$$

of the classical theory. This peculiar temperature dependence of χ has important influence on the accuracy of the interpolation theory in the region above T_c.

The Curie temperatures predicted by the Tyablikov and Callen theories for some cubic near-neighbor-interaction models are tabulated in Ref. 3.

It was shown in Ref. 6 that the static-spin correlation functions should satisfy the sum rule:

$$\sum_q \langle S_{-q} \cdot S_q \rangle = S(S+1).$$ (26)

It is easy to show that the sum rule is satisfied by the correlation functions in Eq. (13) above the Curie temperature. Below the Curie temperature, the left-hand side of Eq. (26) is evaluated numerically for the parabolic model. The results are depicted in Fig. 2. The
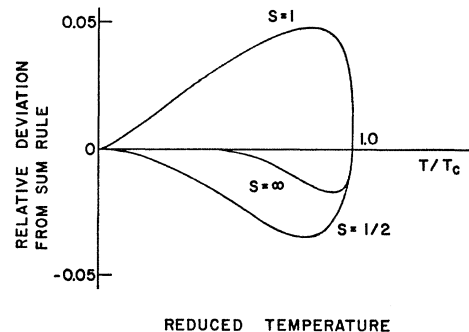
[8] See L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), Chap. 16.

Fig. 2. The deviation from the spin sum rule for the parabolic model with different S values. The deviation is a measure of the accuracy of the Tyablikov decoupling approximation.

ordinate represents the relative deviation from the sum rule defined by

$$\left[\sum_q \langle \mathbf{S}_{-q} \cdot \mathbf{S}_q \rangle - S(S+1)\right]/S(S+1),$$

and the abscissa is the reduced temperature. It can be seen that the sum rule is satisfied to within 5% for $S=\frac{1}{2}$ and 1, and to within 2% for $S=\infty$. In all cases the largest deviation occurs just below the Curie temperature. This is not surprising, because it has been shown by Wallace that the Tyablikov approximation should break down near the critical temperature.[9]

The results of the energy calculation are shown in Fig. 3. The ordinate is in reduced unit defined by $E/NJ(0)S^2$. One can see that for $S=\frac{1}{2}$, the theory gives a critical-point energy lower than the ground-state energy, and the specific heat is negative for a wide range of temperatures below T_c. One might wonder if this difficulty arises from the parabolic spin-
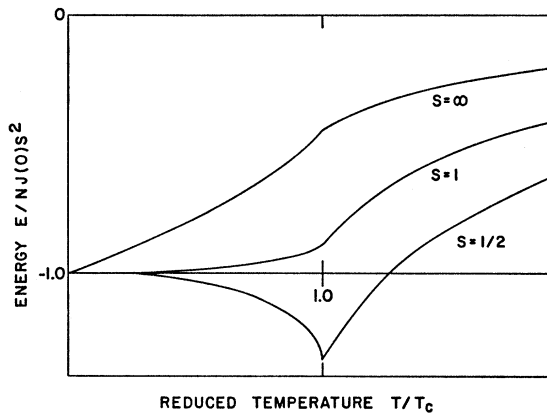

FIG. 3. The energy of the parabolic model according to the interpolation theory.

wave spectrum. In Table I we tabulate the energy difference between the critical point and absolute zero for three cubic nearest-neighbor-interaction models with $S=\frac{1}{2}$. The interaction constant is denoted by J and the number of nearest neighbors by z. It shows that the simple cubic model has the same difficulty. The energy difference is calculated in the following way. At the Curie point

$$\langle S_{-q}{}^x S_q{}^x \rangle = \langle S_{-q}{}^y S_q{}^y \rangle$$
$$= \langle S_{-q}{}^z S_q{}^z \rangle$$
$$= kT_c/2J(0, q),$$

which are easily obtained from Eq. (13) by taking the limit $\beta=1/kT_c$, $\chi\to\infty$. Hence, from Eq. (14) we find

$$E_c = -\tfrac{3}{2}NkT_c \sum_q J(q)/J(0, q).$$

[9] D. C. Wallace, Phys. Rev. **152**, 261 (1966).

TABLE I. $E_c - E_0$ for cubic models.

Model	sc	bcc	fcc
$(E_c - E_0)/NzJ$	-0.005	0.04	0.05

For cubic lattices with nearest-neighbor interaction

$$J(q) = Jz\gamma(q),$$

where

$$\gamma(q) = \tfrac{1}{3}[\cos aq_x + \cos aq_y + \cos aq_z], \quad \text{for sc}$$
$$= \tfrac{1}{3}[\cos\tfrac{1}{2}aq_x \cos\tfrac{1}{2}aq_y + \cos\tfrac{1}{2}aq_y \cos\tfrac{1}{2}aq_z$$
$$\qquad + \cos\tfrac{1}{2}aq_z \cos\tfrac{1}{2}aq_x], \quad \text{for fcc}$$
$$= \cos\tfrac{1}{2}aq_x \cos\tfrac{1}{2}aq_y \cos\tfrac{1}{2}aq_z, \quad \text{for bcc.}$$

The domain of integration over q is the first Brillouin zone. The Curie temperature which appears in the energy expression may be related to the quantity Jz by Eq. (7). The ground-state energy is

$$E_0 = -NJzS^2.$$

From these results the quantity $(E_c - E_0)/NzJ$ is readily computed. If we use the relations in Eqs. (20), (21), and (23), we can calculate the above energy difference in the Callen decoupling scheme. In fact, both the Tyablikov and the Callen decoupling approximation yield the same answer. One must conclude from these evidences that the negative specific-heat difficulty comes from the decoupling approximation.

For large S, the energy curves look more or less like what we would expect. The variation of the energy above the Curie point comes from the short-range ordering of the spins. In Table II we compare the energy difference in Table I for the face-centered cubic (fcc) model as obtained by the Tyablikov approximation, the Callen approximation, and the Domb and Sykes extrapolation.[10] The energies are normalized differently from Table I. For $S=\frac{1}{2}$, both decoupling approximations give too small a difference, but for $S=1$ and higher, the approximate results are reasonably accurate. Therefore, as far as the energy calculation is concerned, the interpolation theory works well only for $S=1$ or higher.

TABLE II. $(E_c - E_0)/Nk_BT_c$ versus S for fcc.

	Tyablikov	Callen	Domb and Sykes
$S=\frac{1}{2}$	0.055	0.124	0.297
1	0.492	0.429	0.551
∞	1.502	1.398	1.406

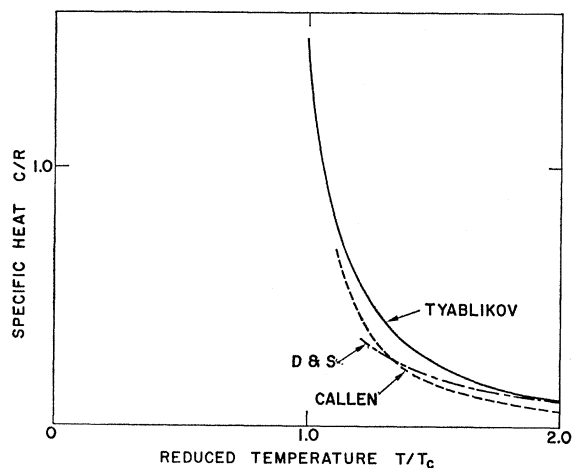[10] C. Domb and M. F. Sykes, Phys. Rev. **128**, 168 (1962).

FIG. 4. The specific heat above the Curie temperature for a fcc nearest-neighbor model. Note that the Tyablikov and Callen decoupling schemes overestimate the short-range-order effect immediately above the Curie point.

Figure 4 shows the specific-heat curves above the Curie temperature as calculated by using the two approximate theories and the Domb and Sykes formula for an fcc model with $S=\frac{1}{2}$. The approximate curves do not diverge at T_c but decrease rather slowly with increasing temperature, and the extrapolated curve of Domb and Sykes is singular at T_c but drops very rapidly. As a result, there is a region above T_c where the interpolation theory gives too high a value for the specific heat. This particular feature is connected with the peculiar temperature dependence of χ just above T_c, Eq. (25), and is independent of the spin value.[11]

To summarize, we have demonstrated by numerical calculation on a simple, parabolic model that the interpolation theory based on the Tyablikov approximation gives poor answer for the energy when $S=\frac{1}{2}$. The Callen decoupling scheme does not give a substantial improvement. For large spins the interpolation theory works better although the specific heat is too high in a temperature range above the Curie point.

IV. TRANSPORT COEFFICIENTS

A. Electrical Resistivity

Using the free-electron model, the parabolic spin-wave model, and the s-d exchange model between the conduction electrons and the localized spins, we showed in Ref. 6 that the spin-disorder contribution to the resistivity of a ferromagnetic metal is given by

$$\rho = \text{const} \times \int_{-\infty}^{\infty} d\omega \int_{0}^{2k_F} q^3 dq \, \frac{\beta \omega J(q, \omega)}{\exp(\beta \omega) - 1}, \quad (27)$$

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[11] The authors are indebted to Dr. Duk-Joo Kim for this remark.

where

$$J(q, \omega) = \tfrac{1}{2} J_+(q, \omega) + \tfrac{1}{2} J_-(q, \omega) + J_z(q, \omega).$$

Because of the simple spin-wave model we adopted, the spectral density functions have no dependence on the angle of $\mathbf{q}$. For simplicity we have only analyzed the case $2k_F \leq q_0$ to avoid the difficulty of umklapp scattering in electron–spin-wave interactions. In Figs. 5 and 6 we plot the resistivity curves for $S=\frac{1}{2}$ and $S=\infty$, respectively, for $R=0.35$ and 0.45, $R=k_F/q_0$. Roughly q_0 corresponds to the size of the first Brillouin zone so both these R values correspond to almost-half-filled conduction bands. It is difficult to make any quantitative comparison with the experiments because of the highly idealized model used in the calculation. One can only say that the general shapes of the curves resemble the measured ones except near the Curie point. Again, the wrong temperature dependence of χ just above the Curie point gives rise to a much too slow variation of the resistivity.[12]

B. Thermal Conductivity and Thermoelectric Power

In addition to the electrical resistivity, the spin disorder also contributes to the electronic thermal resistance and the thermoelectric power of a ferromagnetic metal. These effects were first discussed by Kasuya[13] on the basis of s-d exchange interaction in the molecular-field approximation and the spin-wave approximation. We study this problem here using the interpolation scheme with special emphasis on the region near the Curie point. In the following calculation the splitting of the conduction band is ignored so the results do not apply at very low temperatures. We also assume that the spin system is in thermal equilibrium.
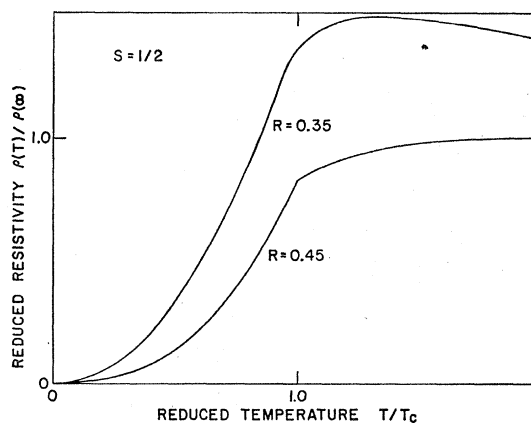

FIG. 5. The calculated spin-disorder resistivity for the parabolic model with $S=\frac{1}{2}$ and two different sizes of the Fermi sphere.

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[12] For comparison with other approximate calculations, see P.-G. deGennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958); D. J. Kim, Progr. Theoret. Phys. (Kyoto) **31**, 921 (1964).

[13] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **22**, 227 (1959).

As a result, the interesting effects of magnon thermal conduction[14] and magnon drag[15] are excluded from consideration.

In the presence of a temperature gradient ∇T and a gradient of the electrochemical potential $\nabla\mu$, the Boltzmann transport equation becomes[16]

$$(\partial f_k/\partial t)_{\text{field}} + (\partial f_k/\partial t)_{\text{coll}} = 0, \qquad (28)$$

where

$$(\partial f_k/\partial t)_{\text{field}} = -\mathbf{v}\cdot[(\epsilon_k-\mu/T)\nabla T - \nabla\mu](\partial f_k/\partial\epsilon_k), \qquad (29)$$

and[6]

$$(\partial f_k/\partial t)_{\text{coll}} = \tfrac{1}{4}I^2\int_{-\infty}^{\infty} d\omega \sum_{k'} \delta(\epsilon_k-\epsilon_{k'}-\omega)J(q,\omega)$$
$$\times[f_k(1-f_{k'})-\exp(-\beta\omega)f_{k'}(1-f_k)]. \qquad (30)$$

In the above equations $\epsilon_k=k^2/2m$, $\mathbf{v}=\mathbf{k}/m$, m is the electron mass, $\mathbf{q}=\mathbf{k}-\mathbf{k}'$, and $\mu=$ chemical potential. Since we deal with an isotropic system, the gradients ∇T and $\nabla\mu$ are in the same direction. A unit vector in this direction is denoted by $\mathbf{u}$. Following the standard variational method, we assume the form of the distribution function to be

$$f_k=f_0(\epsilon_k) - (a_0-a_1\eta)\mathbf{k}\cdot\mathbf{u}[\partial f_0(\epsilon_k)/\partial\epsilon_k], \qquad (31)$$

where a_0 and a_1 are constants and $\eta=\beta(\epsilon_k-\mu)$. We substitute this into the Boltzmann equation and keep only those terms that are linear in the temperature gradient. This gives the following equation for a_0 and a_1:

$$-\mathbf{v}\cdot\mathbf{u}[\eta k_B\nabla T-\nabla\mu][\partial f_0(\epsilon_k)/\partial\epsilon_k] = \tfrac{1}{4}\beta I^2$$
$$\times\int d\omega \sum_{k'} [a_0\mathbf{q}\cdot\mathbf{u}-a_1(\mathbf{k}\eta-\mathbf{k}'\eta')\cdot\mathbf{u}]f_0(\epsilon_k)[1-f_0(\epsilon_k-\omega)]$$
$$\times J(q,\omega)\delta(\epsilon_k-\epsilon_{k'}-\omega). \qquad (32)$$
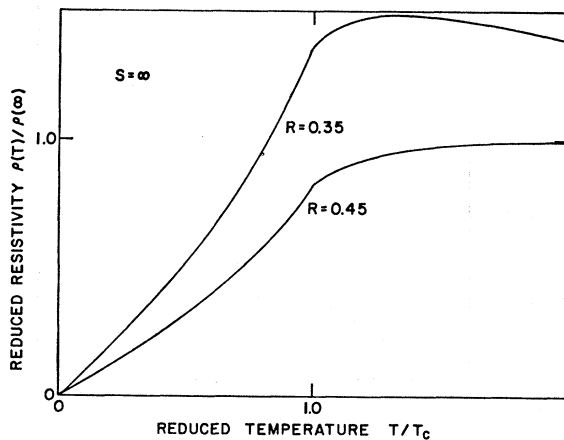

FIG. 6. The calculated spin-disorder resistivity for the parabolic model with $S=\infty$ and two different sizes of the Fermi sphere.

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If one multiplies both sides of Eq. (32) by $\mathbf{k}\cdot\mathbf{u}$ and integrates over $\mathbf{k}$, one obtains

$$k_B R_1\nabla T-R_0\nabla\mu = P_1a_0-P_2a_1, \qquad (33)$$

where k_B is the Boltzmann constant and the integrals R_n are defined by

$$R_n = -\sum_k (\mathbf{v}\cdot\mathbf{u})(\mathbf{k}\cdot\mathbf{u})\eta^n[\partial f_0(\epsilon_k)/\partial\epsilon_k]. \qquad (34)$$

The integrals P_1 and P_2 are given by

$$P_1 = \tfrac{1}{2}\beta\sum_{kk'} (\mathbf{q}\cdot\mathbf{u})^2 W(\mathbf{k},\mathbf{k}'), \qquad (35)$$

$$P_2 = \tfrac{1}{2}\beta\sum_{kk'} \mathbf{q}\cdot\mathbf{u}(\mathbf{k}\eta-\mathbf{k}'\eta)\cdot\mathbf{u}W(\mathbf{k},\mathbf{k}'), \qquad (36)$$

where

$$W(\mathbf{k},\mathbf{k}') = \tfrac{1}{4}I^2\int d\omega\, J(q,\omega)\delta(\epsilon_k-\epsilon_{k'}-\omega)f_0(\epsilon_k)$$
$$\times[1-f_0(\epsilon_k-\omega)].$$

Similarly, if one multiplies both sides of Eq. (32) by $\mathbf{k}\cdot\mathbf{u}\eta$ and integrates over $\mathbf{k}$, one obtains

$$k_B R_2\nabla T-R_1\nabla\mu = P_2a_0-P_3a_1, \qquad (37)$$

where

$$P_3 = \tfrac{1}{2}\beta\sum_{kk'} [(\mathbf{k}\eta-\mathbf{k}'\eta)\cdot\mathbf{u}]^2 W(\mathbf{k},\mathbf{k}'). \qquad (38)$$

From Eqs. (33) and (37), the constants a_0 and a_1 may be solved in terms of the gradients.

The electric current density is

$$j=V^{-1}\sum_k e\mathbf{v}\cdot\mathbf{u}f_k = V^{-1}(eR_0a_0-eR_1a_1) \qquad (39)$$

and the thermal current density is

$$U=V^{-1}\sum_k (\epsilon_k-\mu)\mathbf{v}\cdot\mathbf{u}f_k = \beta V^{-1}(R_1a_0-R_2a_1). \qquad (40)$$

In terms of the gradients, we can write

$$j=-L_{EE}\nabla\mu+L_{ET}\nabla T, \qquad (41)$$
$$U=-L_{TE}\nabla\mu+L_{TT}\nabla T, \qquad (42)$$

where

$$L_{EE}=e[R_1^2P_1-2R_0R_1P_2+R_0^2P_3]/DV_0,$$
$$L_{ET}=ek_B[R_1R_2P_1-(R_1^2+R_0R_2)P_2+R_0R_1P_3]/DV_0,$$
$$L_{TE}=k_BT[R_1R_2P_1-(R_1^2+R_0R_2)P_2+R_0R_1P_3]/DV_0,$$
$$L_{TT}=k_B^2T[R_2^2P_1-2R_1R_2P_2+R_1^2P_3]/DV_0,$$
$$D=P_1P_3-P_2^2. \qquad (43)$$

V_0 is the volume of the unit cell. If we set $j=0$, we find the thermoelectric power

$$S=\nabla\mu/e\nabla T=L_{ET}/eL_{EE}. \qquad (44)$$

Putting this into Eq. (42), we find the thermal conductivity
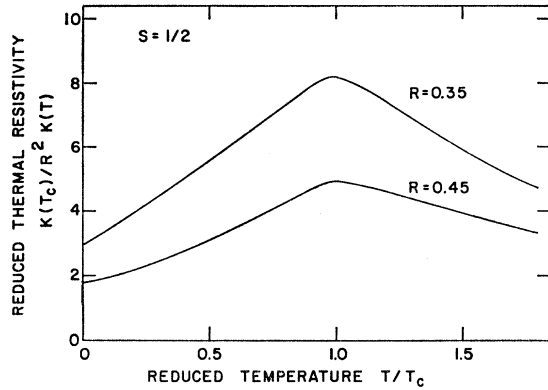
$$K=U/\nabla T=L_{TT}-L_{ET}L_{TE}/L_{EE}. \qquad (45)$$

FIG. 7. The calculated spin-disorder thermal resistivity for the parabolic model with $S=\frac{1}{2}$ and two sizes of the Fermi sphere.

It is straightforward to obtain the explicit expressions for R_n. The useful ones are

$$R_0 = V_0 k_F^3/3\pi^2,$$

$$R_1 = V_0 m k_F/6\beta,$$

$$R_2 = V_0 k_F^3/18. \tag{46}$$

The integrals P_1, P_2, and P_3 may be reduced by the technique described in detail by Ziman[17]; the results are

$$P_1 = (m^2 I^2 V_0{}^2/96\pi^4) I_{31},$$

$$P_2 = (m^3 I^2 V_0{}^2/96\pi^4\beta)[I_{13} + 16 k_F^2(\tfrac{1}{3}\pi^2 J_1 + \tfrac{1}{12}J_3)],$$

$$P_3 = (m^2 I^2 V_0{}^2/96\pi^4)[\tfrac{1}{3}\pi^2 I_{31} + k_F^2 I_{13} - \tfrac{1}{6}I_{33}], \tag{47}$$

where

$$I_{mn} = \int_0^{2k_F} q^m dq \int_{-\infty}^{\infty} J(q, \omega)\, \frac{(\beta\omega)^n d\omega}{\exp(\beta\omega) - 1},$$

$$J_n = \int_{-\infty}^{\infty} J(q, \omega)\, \frac{(\beta\omega)^n d\omega}{\exp(\beta\omega) - 1}.$$

A simple calculation shows that R_1 is smaller than R_0 and R_2 by a factor of the order $k_B T/\mu$, and P_2 is smaller than P_1 and P_3 by the same order. If we keep only the lowest-order quantities in $k_B T/\mu$, the expressions for K and S may be greatly simplified. The results are

$$K = k_B{}^2 T R_2{}^2/P_3 V_0$$

and

$$S = \frac{k_B}{e}\, \frac{R_1 R_3 P_1 - R_0 R_2 P_2 + R_0 R_1 P_3}{R_0{}^2 P_3}.$$

It is very difficult to evaluate these integrals at a general temperature. In the very-high-temperature limit $(T \gg T_c)$

$$P_1 \cong m^2 I^2 V_0{}^2 k_F{}^4 \chi/4\pi^3\beta,$$

$$P_2 \cong (2\pi^2/3\beta\mu) P_1,$$

$$P_3 \cong \tfrac{1}{6}\pi^2 P_1.$$

[17] Reference 16, pp. 403–407.

Hence, the thermal conductivity

$$K = 4\pi k_F{}^2 k_B/27 m^2 I^2 V_0 \chi,$$

which is linear in temperature. The thermoelectric power reduces to the well-known formula for elastic s-wave scattering,

$$S = \pi^2 k_B{}^2 T/3e\mu.$$

At lower temperatures the thermal resistivity and thermoelectric power are calculated numerically for the simple model we used for the resistivity calculation. Figure 7 shows the reduced thermal resistivity $K(T_c)/K(T)$ for two different sizes of the Fermi sphere. For both curves a peak occurs around the Curie temperature. The calculation is not accurate enough at low temperatures because the conduction-band splitting is ignored. In a more careful calculation the thermal resistivity should vanish exponentially as $T \to 0°\text{K}$. For the entire specimen this part of the thermal resistivity is connected in series with the electron-phonon and electron-impurity scattering contributions and in parallel with the phonon and magnon conduction contributions. We then expect to see a dip in the total thermal conductivity around the Curie temperature. Experimental observations seem to indicate the existence of this behavior.[18] The rise in thermal conductivity above the ordering temperature can be understood as caused by the scattering of the electrons from the randomly oriented spins. At the Curie temperature, the expression for the thermal conductivity can be written as

$$K(T_c) = (8\pi^3 M V_0/\hbar k_B)\,(I/\mu)^2,$$

where $M = (2a)^{-1}$ is the spin-wave mass. For gadolinium we may take $I/\mu \cong 0.02$, $V_0 \cong 3\times10^{-23}$ cm^3, and
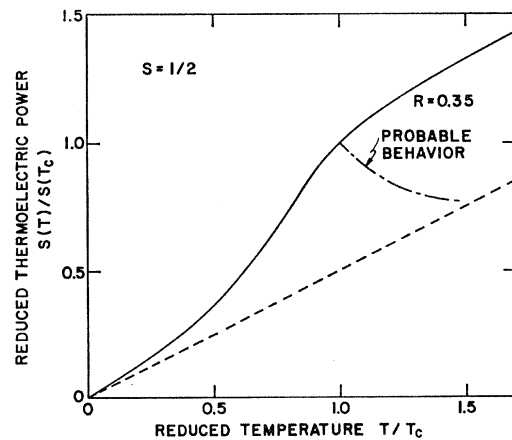

FIG. 8. The calculated spin-disorder thermoelectric power for the parabolic model with $S=\frac{1}{2}$ and $R=0.35$. The curve labeled "probable behavior" illustrates the probable result of a more accurate theory.

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a spin-wave mass equal to 10 times the electron mass. Then the spin-disorder part of the thermal conductivity at the Curie temperature is estimated to be about 0.5 W/°K cm. This agrees in order of magnitude with the observed value of 0.12 W/°K cm.[18]

In Fig. 8 we plot the thermoelectric power for the simple spin-wave model for $R=0.35$. The reduced thermoelectric power $S(T)/S(T_c)$ is quite insensitive to the size of R. The dotted line represents the elastic s-wave scattering limit. The computed curve does not reach this limit until a very high temperature is reached. This again demonstrates the fact that the interpolation theory overestimates the short-range-order effect. In a more accurate theory the behavior of $S(T)$ above the Curie point should approach the dotted line more rapidly as shown by the curve labeled "probable behavior." In reality, a peak in $S(T)$ around the Curie

point has been seen in several materials.[19] Generally one sees another peak at a lower temperature. It seems that the explanation of this peak in terms of the magnon drag effect is quite successful.[20] For an order-of-magnitude estimate we take $\mu=3.3$ eV for Gd.[21] We find the spin-disorder contribution to the thermoelectric power at the Curie point to be -4.5 $\mu V/°$K compared with the observed value of -2 $\mu V/°$K.

ACKNOWLEDGMENT

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Antiferromagnetic Transition in CoCl₂·6H₂O and Fisher's Relation*

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It is found that the zero-field heat capacity C_p and parallel susceptibility $\chi_{||}$ of the antiferromagnet CoCl₂·6H₂O obey Fisher's relation $C=A\partial(\chi T)/\partial T$ through the Néel point $T_N(0)$. The coefficient A is shown by a thermodynamic argument to yield the curvature of the antiferro-paramagnetic phase boundary in the $H-T$ plane for $H=0$. A parabola having the curvature deduced in this way is found to fit the observed phase boundary over a wide range of H and T.

I. INTRODUCTION

THE antiferro-paramagnetic phase transition occurring in CoCl₂·6H₂O at 2.29°K has been the subject of several investigations by magnetic,[1,2] thermal,[3,4] and resonance[5-8] techniques. Recently, we have reported[4] a series of measurements of the heat capacity C_p of CoCl₂·6H₂O performed near its zero-field Néel point $T_N(0)$ with high-temperature resolution. This work was the outgrowth of earlier less detailed observations which indicated[3] that C_p varied roughly as $\ln|T-T_N|$

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as one approached T_N. The same measurements had also shown that the spin entropy gained as T is raised above T_N is $0.36R$, slightly more than half that associated with complete disordering of the Co⁺⁺ spins $(S=\frac{1}{2})$, namely, $R \ln(2S+1) =0.69R$. This fact as well as the structure[9] of the material are consistent with the possibility that antiferromagnetism in CoCl₂·6H₂O may have a noticeably two-dimensional character. Since the effective spin of the Co⁺⁺ ion is $S=\frac{1}{2}$ and the moment quite anisotropic,[2] it is possible in addition that the behavior of CoCl₂·6H₂O might resemble that of a two-dimensional Ising model.[10] These characteristics, combined with its convenient Néel point, make CoCl₂·6H₂O an interesting substance in which to study details of a λ-type magnetic ordering transition. We wish to describe some conclusions of an essentially thermodynamic character which can be drawn from the heat-capacity data in combination with careful measurements of $\chi_{||}$ which we have also carried out at $T_N(0)$.

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