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Thermal Properties of Spin-Wave Impurity States

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The effect of dilute magnetic impurities on the thermal properties of an ideal simple cubic spin-$\frac{1}{2}$ Heisenberg ferromagnet has been investigated using the thermal-Green's-function procedure with a simple random-phase decoupling scheme. It is shown that for a small ratio ϵ of impurity-host to host-host exchange, low-lying "s-type" virtual spin-wave states result which cause a large density of states to occur at low energies. These low-energy states lead to an accumulation of spin disorder at and near the impurity site. Consequently the impurity magnetization decreases far more rapidly than that of the host. This effect is accompanied by a large increase in the low-temperature spin-wave specific heat. Analytic solutions to the Green's-function equations are calculated for temperatures near 0 and near T_c, the Curie temperature. Self-consistent numerical solutions are presented for both the magnetization and the spin-wave specific heat as a function of temperature. For small ϵ the impurity magnetization is approximated by the Brillouin function

$$m_I=\mu_\beta \tanh\{\mu_\beta H+6J'\langle S_1{}^z\rangle/kT\},$$

where J' is host-impurity exchange and $\langle S_1{}^z\rangle$ is the thermal average for the impurity nearest-neighbor spins. $\langle S_1{}^z\rangle$ is found to be depressed from the bulk value by an amount which increases with temperature and is about 0.84 of the bulk value as $T\rightarrow T_c$.

I. INTRODUCTION

In a previous paper,[1] WCI, the effect of dilute impurities on the spin-wave spectrum of an ideal Heisenberg ferromagnet was investigated. It was shown that localized spin-wave states above the spin-wave band as well as virtual states within the band could be formed for reasonable ratios ϵ of impurity exchange to host exchange. In WCI the dependence of the impurity-state energy and lifetime on the impurity spin and exchange were calculated at low temperatures where simple spin-wave theory is valid. Different kinds of impurity states were classified according to their transformation properties. For the simple cubic structure s-, p- and d-like states result for nearest-neighbor (N.N.) coupling. The low-lying virtual s-like states are of particular importance to the thermodynamic behavior of the impure ferromagnet since these states give rise to a large density of states at low energies where the host density of states is very small. Consequently, a large spin disorder can accumulate in the vicinity of the impurity resulting in a local decrease in magnetization. Such an effect has been noted experimentally by Jaccarino, *et al.*,[2] who proposed that the virtual spin-wave state could be described by the simple molecular-field model. A theoretical justification of this proposal has been discussed by Callen *et al.*[3] They have reported the qualitative results of a thermal Green's function calculation of the magnetization of a spin impurity in a ferromagnetic host. Using a picture based on spin-wave scattering, the effect of different impurity-host exchanges and spin on the spectral weight function is discussed. The results of the magnetization calculation in the present paper are qualitatively in agreement with these ideas. One can also expect a large increase in the spin-wave specific heat at low temperatures. Both of these effects can be quite dramatic when the impurity exchange is substantially weaker than that between host spins. Localized modes split off above the top of the spin-wave band are of far less importance to the thermodynamic properties since large thermal energies are required to excite these states and since they cause only a negligible perturbation on the host density of states. In this paper we derive the effects of virtual spin-wave impurity states on the thermal behavior of the Heisenberg ferromagnet in some detail. Calculations show that the magnetization at and near an impurity site for a spin-$\frac{1}{2}$ system can deviate drastically from the bulk magnetization when $\epsilon<0.5$. Larger impurity spins can be expected to display this behavior for larger ϵ values. Calculations also show that the total bulk spin-wave specific heat can be increased significantly. For example, with a 1% solution of a weakly coupled impurity ($\epsilon\sim0.25$) the specific heat of the impure ferromagnet can exceed that of the pure ferromagnet by 12% at temperatures on the order of one tenth of the Curie point. In this case the specific heat departs radically from the usual low temperature expansion, $\alpha T^{3/2}+\beta T^{5/2}\cdots$. For weak exchange the impurity magnetization is very closely approximated by a Brillouin function for spin $\frac{1}{2}$, tanh $(6J'\langle S_1{}^z\rangle/kT)$, where J' is the impurity exchange with the host and $\langle S_1{}^z\rangle$ is the thermal average of the spin of the impurity N.N. The departure of the N.N. spins from host behavior increases with temperature and near the Curie temperature can amount to as much as 16% depression.

In Sec. II we formulate the problem of the thermal behavior of a spin-$\frac{1}{2}$ Heisenberg ferromagnet, having a spin-$\frac{1}{2}$ impurity whose exchange with the host differs from the host-host exchange, in terms of the two-time Green's function. The Green's function procedure itself is not discussed in this paper. (The reader

[1] T. Wolfram and J. Callaway, Phys. Rev. 130, 2207 (1963).
[2] V. Jaccarino, L. R. Walker, and G. K. Wertheim, Phys. Rev. Letters 13, 752 (1964).
[3] H. Callen, D. Hone, and A. Heeger, Phys. Letters 17, 233 (1965).

is referred to one of the many excellent review papers[4] on the topic.) A set of three simultaneous integral equations are derived using a simple random-phase decoupling scheme. These equations determine the spectral intensity function (and consequently all the thermodynamic properties) of the impurity spin, its nearest neighbors and the more distant neighbor spins. These equations are derived for N.N. coupling with the assumption (which is heuristically substantiated) that the thermal expectation value for the spins of the second neighbors are not significantly affected by the presence of the impurity.

In Sec. III the weakly coupled impurity is discussed. The reduced spectral function for the impurity is obtained and found to become sharper as the temperature increases. Asymptotic solutions of the set of equations are obtained for temperatures near the Curie point T_c. These results indicate that the ratio σ_1 of the thermal average of the impurity N.N. spin to the host thermal average deviates at most about 16% from unity. For small ϵ the ratio σ_0 of the impurity spin to the host spin is shown to tend to $\frac{3}{2}\epsilon\sigma_1$ as $T\rightarrow T_c$. Approximate solutions are derived for low temperatures. It is shown that the magnetization and specific heat of the weakly coupled impurity contains an exponential term in addition to the usual $T^{3/2}$ term. Numerical results for the entire temperature domain are presented. Both magnetization and specific heat calculations are presented.

Section IV contains a discussion of the experimental results obtained by Jaccarino *et al.*[2] for Mn in Fe. It is suggested that the thermal properties of the spin-wave impurity states of rare-earth ions in transition ferromagnets could be conveniently studied making use of the Mössbauer effect.

In Appendix A the normalization of the reduced spectral functions is discussed. It is shown that the decoupling and approximations used in the derivation of the integral equations for the thermal behavior of the system does not destroy the normalization of the spectral function. Appendix B contains a highly simplified derivation of the low-temperature behavior of the impurity magnetization and internal energy.

II. GREEN'S FUNCTIONS FOR THE IMPURE FERROMAGNET

In this section we develop a set of self-consistent Green's function equations which describe the temperature dependence of the magnetization of the impurity and its nearest neighbors and the unperturbed more distant spins.

We consider a ferromagnetic lattice of N spins described by the Heisenberg exchange Hamiltonian $\mathcal{H}^0$,

$$\mathcal{H}^0=-\mu_\beta H\sum_f S_f^z-\tfrac{1}{2}\sum_{f_1f_2\alpha} J(f_1-f_2)S_{f_1}^\alpha S_{f_2}^\alpha, \quad (2.1)$$

[4] See, for example, D. N. Zubarev, Usp. Fiz. Nauk. **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

where S_f^α is the α component of the spin localized at the lattice site f, $J(f_1-f_2)$ is the exchange integral (assumed >0) which describes the interactions of spins at f_1 and f_2, H is the external magnetic field (parallel to the z axis), and μ_B is the Bohr magneton. The convention $J(0)=0$ is adopted so that the double sum over f_1 and f_2 need not be restricted. If an "impurity" spin is substituted at the $f=0$ site with exchange $J'(f)$ with the host spins, then the spin Hamiltonian for the perturbed system is

$$\mathcal{H}=\mathcal{H}^0-\sum_{f\alpha}\Delta J(f)S_0^\alpha S_f^\alpha,$$
$$\Delta J=J'(f)-J(f). \quad (2.2)$$

Throughout this paper we shall make the simplifying assumptions that we are dealing with a spin-$\frac{1}{2}$ simple-cubic system (the impurity also has spin $\frac{1}{2}$) and that only the nearest-neighbor exchange integral is nonzero. These assumptions greatly simplify the mathematics without destroying the qualitative features we wish to study. The Hamiltonian (2.2) may be written in terms of the usual spin-deviation operators b_f and $b_f^\dagger$ which destroy and create, respectively, a unit of spin disorder at the lattice site f,

$$\mathcal{H}=\mathcal{H}^0-\Delta J\sum_g[(1-2n_g)(1-2n_0)+2(b_g^\dagger b_0+b_0^\dagger b_g)],$$
$$\mathcal{H}^0=-N(\mu_\beta H+3J)+(2\mu_\beta H+12J)\sum_f b_f^\dagger b_f-2J\sum_{fg}b_f^\dagger b_{f+g}-2J\sum_{fg}n_fn_{f+g}. \quad (2.3)$$

The symbol g in (2.2) and elsewhere in this paper refers to the 6 simple cubic nearest-neighbors vectors and $J=J(g)$, $\Delta J=\Delta J(g)$. The spin-deviation operators are defined by

$$S_f^x=b_f+b_f^\dagger,\quad S_f^y=i(b_f^\dagger-b_f),\quad S_f^z=1-2b_f^\dagger b_f, \quad (2.4)$$

and satisfy the commutation relations

$$[b_{f_1},b_{f_2}^\dagger]=(1-2n_{f_1})\delta_{f_1f_2},\quad n_f=b_f^\dagger b_f,\quad [b_{f_1},b_{f_2}]=[b_{f_1}^\dagger,b_{f_2}^\dagger]=0,\quad b_f^2=(b_f^\dagger)^2=0. \quad (2.5)$$

The temperature dependence of the magnetization is determined by the (thermal) average number of spin deviations $\langle n_f\rangle$ for the grand canonical ensemble. This function is conveniently obtained from the two-time Green's function procedure. Since this method has been reviewed by numerous authors[4] we shall not include a detailed discussion in this paper. The essential features necessary for our calculation are simply listed below

$$\langle n_f\rangle=\int_{-\infty}^{\infty}J_{ff}(\omega)d\omega\,, \tag{2.6a}$$

$$J_{f_1f_2}(\omega)=\lim_{\epsilon\to 0}i\{G_{f_1f_2}(\omega+i\epsilon)-G_{f_1f_2}(\omega-i\epsilon)\}/e^{\omega/kT}-1\,, \tag{2.6b}$$

$$\begin{aligned}G_{f_1f_2}(\omega)&=G_{f_1f_2}{}^{r}(\omega)\quad \mathrm{Im}\omega>0\,,\\ &=G_{f_1f_2}{}^{a}(\omega)\quad \mathrm{Im}\omega<0\,,\end{aligned} \tag{2.6c}$$

$$G_{f_1f_2}{}^{(r,a)}(t)=\int_{-\infty}^{\infty}G_{f_1f_2}{}^{(r,a)}(\omega)e^{-i\omega t}d\omega\,, \tag{2.6d}$$

$$\begin{aligned}G_{f_1f_2}{}^{(r,a)}(t)&\equiv\langle\langle b_{f_1}(t);b_{f_2}(0)\rangle\rangle_{(r,a)}\\ &=\mp i\theta(\pm t)\langle[b_{f_1}(t),b_{f_2}{}^{\dagger}(0)]\rangle\,,\end{aligned} \tag{2.6e}$$

where the upper sign goes with r and the lower with a, Imω is the imaginary part of ω, $\theta(t)$ is the unit step function,

$$\begin{aligned}\theta(t)&=1\quad t>0\\ &=0\quad t<0\\ d/dt\theta(t)&=\delta(t)\,.\end{aligned} \tag{2.7}$$

and we use units such that $\hbar=1$. The bracket $\langle O\rangle$ indicates an average of the operator O over the grand canonical ensemble,

$$\langle O\rangle\equiv\mathrm{Tr}\{\exp(-\mathcal{H}/kT)O\}/\mathrm{Tr}\{\exp(-\mathcal{H}/kT)\}\,. \tag{2.8}$$

The Green's functions $G_{f_1f_2}$ are obtained from their equations of motion,

$$\begin{aligned}i(d/dt)G_{f_1f_2}(t)&=\delta(t)\langle[b_{f_1}(t),b_{f_2}(0)]\rangle\\ &\quad+\langle\langle i(d/dt)b_{f_1}(t);b_{f_2}(0)\rangle\rangle\,,\\ i(d/dt)b_f&=[b_f,\mathcal{H}]\,.\end{aligned} \tag{2.9}$$

It is also convenient to define the function $A_f(\omega)$,

$$A_f(\omega)=2G_{ff}(\omega)/\langle[b_f,b_f{}^{\dagger}]\rangle\,. \tag{2.10}$$

The imaginary part of $A_f(\omega)$ is a reduced spectral function whose integral is normalized to unity

$$\int_{-\infty}^{\infty}d\omega\,\mathrm{Im}A_f(\omega)=1\,. \tag{2.11}$$

In the above $[A,B]$ is the commutator $AB-BA$.

In order to determine the new Green's function which appears on the right-hand side of (2.9), one must calculate its time rate of change and consequently a system of simultaneous differential equations result. The system, in general, does not close on itself and one must "decouple" the set by approximating higher order Green's functions. A number of decoupling schemes have been suggested; however, in this paper we use the simple procedure outlined in Ref. 4, namely,

$$\langle\langle n_{f_1}(t)b_{f_2}(t);b_{f_3}{}^{\dagger}(0)\rangle\rangle\to\langle n_{f_1}\rangle\langle\langle b_{f_2}(t);b_{f_3}{}^{\dagger}(0)\rangle\rangle\,, \tag{2.12}$$

where the arrow means "replaced by." This procedure, while crude, leads to a qualitatively good description of the ferromagnetic state over the entire temperature range. The procedure outlined above gives the following Green's functions for the impure ferromagnet

$$\begin{aligned}\omega G_{f_1f_2}&=(2\pi)^{-1}\langle S_{f_1}{}^{z}\rangle\delta_{f_1f_2}+2\mu_\beta HG_{f_1f_2}(\omega)\\ &\quad-2J\sum_g\langle S_{f_1}{}^{z}\rangle G_{f_1+g,f_2}(\omega)\\ &\quad+2J\sum_g\langle S_{f_1+g}{}^{z}\rangle G_{f_1f_2}(\omega)+F_{f_1f_2}(\omega)\,,\end{aligned} \tag{2.13}$$

where

$$\begin{aligned}(f_1\neq 0)\,,\quad F_{f_1f_2}(\omega)&=-2\Delta J\sum_g[\langle S_{f_1}{}^{z}\rangle G_{0f_2}(\omega)\\ &\qquad-\langle S_0{}^{z}\rangle G_{f_1f_2}(\omega)]\delta_{f_1g}\\ (f_1=0)\,,\quad F_{0f_2}(\omega)&=2\Delta J\sum_g[\langle S_g{}^{z}\rangle G_{0f_2}(\omega)\\ &\qquad-\langle S_0{}^{z}\rangle G_{gf_2}(\omega)]\,.\end{aligned} \tag{2.14}$$

In the absence of the impurity, $\langle S_f{}^z\rangle$ is independent of f since $\mathcal{H}^0$ is translationally invariant. This property is destroyed by the impurity perturbation and one expects physically that the magnetization at and near the impurity will deviate from that of the "perfect" ferromagnet. More distant sites should, however, be unaffected by the perturbation. Calculations to be discussed later in this paper suggest that in the case of the strong perturbation $[J'(g)=0]$ the second nearest neighbors of the impurity deviate from host behavior only very slightly even at the Curie temperature. We therefore assume that $\langle S_f\rangle$ will be independent of f whenever $|f|>|g|$. If we write $\langle S_f{}^z\rangle=\langle S^z\rangle$ for $|f|>|g|$ then we must determine the quantities $\langle S_0{}^z\rangle$, $\langle S_g{}^z\rangle$ and $\langle S^z\rangle$. Because of symmetry $\langle S_g{}^z\rangle\equiv\langle S_1{}^z\rangle$ will be the same for all nearest neighbors so that there are only three functions to determine: $\langle S_0{}^z\rangle$, $\langle S_1{}^z\rangle$, and $\langle S^z\rangle$. The system of Green's function equations (2.13) may be written as the matrix equation

$$-4J\langle S^z\rangle(M+\Delta M)\mathbf{G}_{f_2}=\omega\mathbf{G}_{f_2}+(2\pi)^{-1}\boldsymbol{\varrho}_{f_2}\,, \tag{2.15}$$

where the matrix M is defined by

$$\begin{aligned}M_{ff}&=[12J\langle S^z\rangle+2\mu_\beta H]/[-4J\langle S^z\rangle]\,,\\ M_{f,f+g}&=-\tfrac{1}{2}\,,\end{aligned}$$

and all other matrix elements are zero. ΔM contains the induced perturbation in nearest-neighbor magnetization as well as the direct impurity perturbation. It also contains the effect of nearest-neighbor deviations on the remainder of the host. If we assume that only the impurity and its nearest neighbors are perturbed and that more distant neighbors are unperturbed then ΔM has only a 7×7 block of nonvanishing elements

$$\begin{aligned}-4J\langle S^z\rangle\Delta M_{00}&=12J'\langle\Delta S_1{}^z\rangle+12\Delta J\langle S^z\rangle\,,\\ -4J\langle S^z\rangle\Delta M_{0g}&=-2J'\langle\Delta S_0{}^z\rangle-2\Delta J\langle S^z\rangle\,,\\ -4J\langle S^z\rangle\Delta M_{g0}&=-2J'\langle\Delta S_1\rangle-2\Delta J\langle S^z\rangle\,,\\ -4J\langle S^z\rangle\Delta M_{gg}&=2J'\langle\Delta S_0\rangle+2\Delta J\langle S^z\rangle\,,\end{aligned} \tag{2.16}$$

where $\langle\Delta S_i^z\rangle=\langle S_i^z-S^z\rangle$ is the deviation from host behavior. The source vector $\boldsymbol{\varrho}_{f_2}$ is a column vector of zeros except for the f_2 row which has value $\langle S_{f_2}^z\rangle$. The vector $\mathbf{G}_{f_2}$ has components $G_{f_1f_2}(\omega)$ and we adopt the convention that the first seven rows correspond to the impurity and its 6 neighbors in the order (1,0,0), (−1, 0, 0), (0,1,0), (0, −1, 0), (0,0,1) and (0, 0, −1). Equation (2.15) is easily solved to give

$$-4J\langle S^z\rangle\mathbf{G}_{f_2}=(M-\zeta+\Delta M)^{-1}\boldsymbol{\varrho}_{f_2}/2\pi$$
$$=-(I-\mathcal{G}^0(\mathcal{E})\Delta M)^{-1}\mathcal{G}^0(\mathcal{E})\boldsymbol{\varrho}_{f_2}/2\pi, \quad (2.17)$$

where

$$\zeta=\omega/-4J\langle S^z\rangle,$$
$$\mathcal{E}=\zeta-M_{ff}=\zeta+3+\mu_\beta H/2J\langle S^z\rangle,$$

and

$$\mathcal{G}^0(\mathcal{E})=(\zeta-M)^{-1}.$$

The spin-wave Green's function $\mathcal{G}^0(\mathcal{E})$ has been discussed in WCI and its elements are given by

$$[\mathcal{G}^0(\mathcal{E})]_{f_1,f_2}=\frac{1}{N}\sum_q\frac{\exp[i\mathbf{q}\cdot(\mathbf{f}_1-\mathbf{f}_2)]}{(\mathcal{E}-\mathcal{E}\mathbf{q})} \quad (2.18)$$

with

$$\mathcal{E}\mathbf{q}=\tfrac{1}{2}\sum_{\mathbf{g}}\cos(\mathbf{q}\cdot\mathbf{g}). \quad (2.19)$$

The numerical values of the matrix elements of $\mathcal{G}^0$ are tabulated in WCI. The matrix given in (2.17) is most easily constructed by first transforming to s, p and d-like symmetry coordinates and transforming back after construction of the inverse. The transformation is also given in WCI. The results are

$$-4J\langle S^z\rangle G_f\equiv G_{ff}(\mathcal{E})=(2\pi)^{-1}\langle S^z\rangle\mathcal{G}_{00}(\mathcal{E}),\qquad |f|>|g|, \quad (2.20)$$

$$-4J\langle S^z\rangle G_0\equiv G_{00}(\mathcal{E})=(2\pi)^{-1}\langle S_0^z\rangle\{\mathcal{G}_{00}(\mathcal{E})-2\Delta M_{gg}\mathcal{G}_{01}(\mathcal{E})\}/\det A, \quad (2.21)$$

$$-4J\langle S^z\rangle G_g\equiv G_{gg}(\mathcal{E})=(2\pi)^{-1}\langle S_1^z\rangle\times\left\{\tfrac{1}{3}\mathcal{G}_{01}(\mathcal{E})(\mathcal{E}-\Delta M_{00})/\det A+\frac{1}{2}\frac{[\mathcal{G}_{00}(\mathcal{E})-\mathcal{G}_{03}(\mathcal{E})]}{1-\Delta M_{gg}[\mathcal{G}_{00}(\mathcal{E})-\mathcal{G}_{03}(\mathcal{E})]}+\frac{\tfrac{1}{3}[\mathcal{G}_{00}(\mathcal{E})+\mathcal{G}_{03}(\mathcal{E})-2\mathcal{G}_{02}(\mathcal{E})]}{1-\Delta M_{gg}[\mathcal{G}_{00}(\mathcal{E})+\mathcal{G}_{03}(\mathcal{E})-2\mathcal{G}_{02}(\mathcal{E})]}\right\}, \quad (2.22)$$

where

$$\mathcal{G}_{00}(\mathcal{E})=[\mathcal{G}^0(\mathcal{E})]_{(0,0,0),(0,0,0)},$$
$$\mathcal{G}_{01}(\mathcal{E})=[\mathcal{G}^0(\mathcal{E})]_{(0,0,0),(1,0,0)},$$
$$\mathcal{G}_{02}(\mathcal{E})=[\mathcal{G}^0(\mathcal{E})]_{(0,0,0),(1,1,0)}, \quad (2.23)$$
$$\mathcal{G}_{03}(\mathcal{E})=[\mathcal{G}^0(\mathcal{E})]_{(0,0,0),(2,0,0)},$$

and

$$\det A=1-6\mathcal{G}_{01}(\mathcal{E})(\Delta M_{g0}+\Delta M_{0g})-2\Delta M_{gg}\mathcal{E}\mathcal{G}_{01}(\mathcal{E})-\mathcal{G}_{00}(\mathcal{E})\Delta M_{00}. \quad (2.24)$$

When $J'=J$, (2.21) and (2.22) become identical with (2.20). This fact is easily verified using the identities derived in WCI:

$$\mathcal{G}_{01}(\mathcal{E})=\tfrac{1}{3}(\mathcal{E}\mathcal{G}_{00}-1), \quad (2.25)$$

and

$$\mathcal{G}_{00}(\mathcal{E})+\mathcal{G}_{03}(\mathcal{E})+4\mathcal{G}_{02}(\mathcal{E})=2\mathcal{E}\mathcal{G}_{01}(\mathcal{E}). \quad (2.26)$$

Equation (2.20) is just the Green's function for an unperturbed host ferromagnet. The self-consistent equation for the spin as a function of temperature is found using (2.6) to be

$$\frac{1}{2}\frac{\langle 1-S^z\rangle}{\langle S^z\rangle}=\frac{1}{\pi}\int_{+\infty}^{-\infty}\frac{\operatorname{Im}\mathcal{G}_{00}(\mathcal{E})d\mathcal{E}}{e^{\beta(3-\mathcal{E})}-1}=\int_{-3}^{+3}\frac{d\mathcal{E}N_0(\mathcal{E})}{e^{\beta(3-\mathcal{E})}-1}, \quad (2.27)$$

since the spin-wave band extends from 3 to −3 in $\mathcal{E}$ space. It is also important to note that in this form the renormalization of the spin-wave energy is apparent only in the temperature factor β. Thus in (2.27) the spin-wave band ($|\mathcal{E}|\leq 3$) remains fixed and the factor β varies with temperature. The thermal behavior of the impurity spin is determined by (2.21) which gives

$$\frac{\tfrac{1}{2}\langle 1-S_0^z\rangle}{\langle S_0^z\rangle}=\int_{-3}^{+3}\frac{d\mathcal{E}\sigma_0\epsilon^2N_0(\mathcal{E})}{(c+bR_0)^2+(\pi bN_0)^2}\times\frac{1}{e^{\beta(3-\mathcal{E})}-1}, \quad (2.28)$$

with

$$c=\tfrac{1}{3}[(\mathcal{E}-3)-(\mathcal{E}-3)\epsilon\sigma_0+3\epsilon\sigma_1],$$
$$b=-\tfrac{1}{3}(\mathcal{E}-3)[(\mathcal{E}-3)-\mathcal{E}\epsilon\sigma_0+3\epsilon\sigma_1],$$
$$\epsilon=J'/J,$$
$$\sigma_0=\langle S_0^z\rangle/\langle S^z\rangle,$$
$$\sigma_1=\langle S_1^z\rangle/\langle S^z\rangle, \quad (2.29)$$
$$\beta=4J\langle S^z\rangle/kT,$$
$$N_s=\pi^{-1}\operatorname{Im}\mathcal{G}_{0s}(\mathcal{E})\quad\text{for}\quad\operatorname{Im}(\mathcal{E})>0,$$
$$R_s=\operatorname{Re}\mathcal{G}_{0s}(\mathcal{E}).$$

$$\frac{\tfrac{1}{2}\langle 1-S_1^z\rangle}{\langle S_1^z\rangle}=\int_{-3}^{+3}d\mathcal{E}\left\{\frac{1}{3}\frac{[cN_1+b(R_0N_1+N_0R_1)](\mathcal{E}-\Delta M_{00})}{(c+bR_0)^2+(\pi bN_0)^2}+\frac{\tfrac{1}{2}(N_0-N_3)}{[1-\Delta M_{gg}(R_0-R_3)]^2+[\pi\Delta M_{gg}(N_0-N_3)]^2}+\frac{\tfrac{1}{3}(N_0+N_3-2N_2)}{[1-\Delta M_{gg}(R_0+R_3-2R_2)]^2+[\pi\Delta M_{gg}(N_0+N_3-2N_2)]^2}\right\}\frac{1}{e^{\beta(3-\mathcal{E})}-1}. \quad (2.30)$$

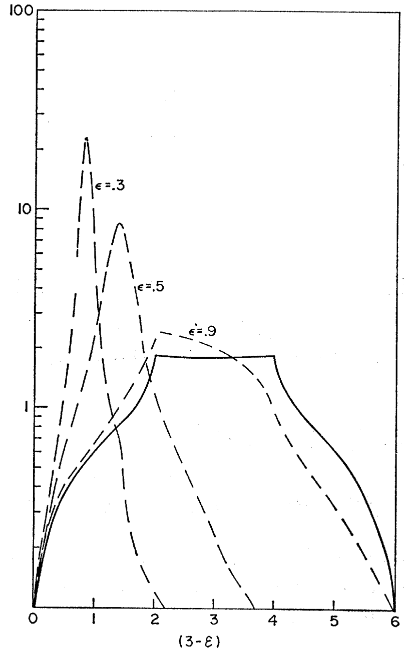

FIG. 1. The transition of the reduced spectral function from the host density towards the δ-function behavior with decreasing ε. The ordinate is $2\pi\,\mathrm{Im}A_0(\mathcal{E})$ and the solid curve is for $\epsilon=1$.

Equations (2.27), (2.28), and (2.30) are self-consistent, simultaneous integral equations. In WCI it was shown that the vanishing of $c+bR_0$ corresponds to the occurrence of an s-like spin-wave impurity continuum resonance state whose width is proportional to N_0. Similarly, the vanishing of $1-\Delta M_{gg}(R_0-R_3)$ or $1-\Delta M_{gg}(R_0+R_3-2R_2)$, [Eq. (2.30)], corresponds to p and d-like resonances. It is clear that the thermal behavior of the impurity spin is governed principally by the s-state resonance, while the nearest-neighbor spins have contributions from all three types of states. However, since $\langle S_0^z\rangle$ is coupled to $\langle S_1^z\rangle$ the impurity will have a weak dependence on the p and d resonances as well. It should also be noted that in the case that true localized modes occur above the top of the spin-wave band (i.e., when any of the above mentioned factors vanish for $\mathcal{E}<-3$) we must add additional terms of the form $\{\exp[4J\langle S^z\rangle(3-\mathcal{E}_L)/kT]-1\}^{-1}$ to (2.28) and (2.30) for each localized mode with energy $\mathcal{E}_L$. In this paper we are principally interested in continuum resonance states. For $\epsilon\leq 1$ no localized modes can occur. The energy and width of the various types of spin-wave impurity states at $T=0$ as a function of ϵ and spin mismatch are discussed in WCI.

III. SOLUTIONS OF THE COUPLED EQUATIONS

A. Weak-Coupling Limit ($\epsilon\ll 1$)

The reduced spectral function for the impurity $\mathrm{Im}A_0(\mathcal{E})$ gives the effective density of states per impurity spin. It is easily seen to tend to $N_0(\mathcal{E})$ as $\epsilon\to 1$. In the other limit, as $\epsilon\to 0$, $\mathrm{Im}A_0(\mathcal{E})$ approximates a Dirac δ function with its peak near $3-\mathcal{E}=3\epsilon\sigma_1$. This limit is most conveniently obtained from the Green's function. From (2.21) and (2.16) we have

$$G_0(\mathcal{E})=\frac{\langle S_0^z\rangle}{2\pi}\left(3\epsilon\sigma_1-(3-\mathcal{E})-\frac{\epsilon^2(\mathcal{E}\mathcal{G}_{00}-1)\sigma_0\sigma_1}{\frac{1}{3}[\mathcal{G}_{00}(3-\mathcal{E})+1]+(\epsilon\sigma_0/3)(\mathcal{E}\mathcal{G}_{00}-1)}\right)^{-1}. \quad (3.1)$$

For sufficiently small ϵ this gives $\mathrm{Im}A_0(\mathcal{E})\to\delta[(3-\mathcal{E})-3\epsilon\sigma_1]$. One must exercise some care, however, in using this result. It is in fact qualitatively incorrect to use this at very low temperatures because the exact behavior of the Green's function at the bottom of the spin-wave band ($\mathcal{E}=3$) must be preserved. For very small but finite ϵ (3.1) gives approximately

$$G_0(\mathcal{E})=\frac{\langle S_0^z\rangle}{2\pi}\times\frac{1}{3\epsilon\sigma_1-(3-\mathcal{E})-3\epsilon^2\sigma_0\sigma_1(3\mathcal{G}_{00}-1)+O(\epsilon^3)},$$

$$\mathrm{Im}A_0(\mathcal{E})=\frac{\langle S_0^z\rangle}{\pi}\times\frac{\Gamma(\mathcal{E})}{[3\epsilon\sigma_1-(3-\mathcal{E})-P(\mathcal{E})]^2+[\Gamma(\mathcal{E})]^2}, \quad (3.2)$$

$$\Gamma(\mathcal{E})=9\pi\epsilon^2\sigma_0\sigma_1N_0(\mathcal{E}),$$

$$P(\mathcal{E})=3\pi\epsilon^2\sigma_0\sigma_1[3R_0(\mathcal{E})-1].$$

Thus the reduced spectral function is in the form of a Breit-Wigner shape with width proportional to $N_0(\mathcal{E})$, the host density of states. The peak at $(3-\mathcal{E})=3\epsilon\sigma_1$ (or $\omega=12J'\langle S_1\rangle$) is displaced slightly according to

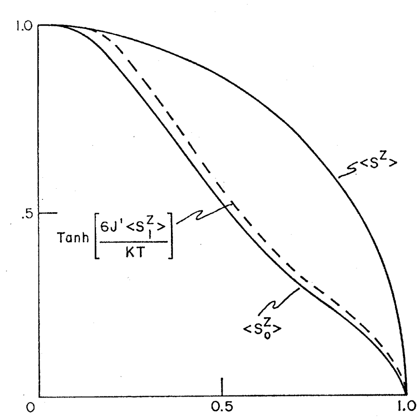

FIG. 2. The thermal behavior of the impurity spin $\langle S_0^z\rangle$ for $\epsilon=0.25$ as a function of the reduced temperature $\tau=T/T_c$. The unperturbed host thermal average $\langle S^z\rangle$ is also shown. The dashed curve, a plot of the Brillouin function for spin $\frac{1}{2}$, compares quite well with the calculated impurity spin.

$[R_0(\mathcal{E})-1]$. Since $R_0<1$ the shift is to lower energy. The δ-function approximation gives

$$\langle S_0^z\rangle=\tanh(6J'\langle S_1\rangle/kT) \quad \text{(weak coupling, } \epsilon \text{ small).} \quad (3.3)$$

Equation (3.3) is valid for $6J'/kT\lesssim 1$ (but is not valid when $6J'/kT\gg 1$) and shows that the impurity magnetization decreases according to the Brillouin function with an effective field equal to the impurity-exchange field with the nearest neighbors. A similar expression has been suggested by Jaccarino *et al.*,[2] for dilute concentrations of Mn in ferromagnetic iron (see Sec. IV), and the validity of this result has been stressed by Callen *et al.*[3] The approach of $\mathrm{Im}A_0(\mathcal{E})$ to the δ function as ϵ is decreased is shown in Fig. 1. One also notes from (3.2) that the effective width Γ is proportional to σ_0 and σ_1 and that consequently the peak width narrows and peak height grows as the temperature increases. This feature persists for finite ϵ as can be seen in Fig. 5. The shift in the peak is also evident. In general, the set of Eqs. (2.27), (2.28), and (2.30) can only be solved numerically. However, asymptotic solutions can be obtained near $T=0$ and near the Curie temperature. The numerical solutions of (2.27), (2.28), and (2.30) as a function of temperature are shown in Figs. 2, 3, and 4.

B. Solutions Near the Curie Temperature

In this section we obtain solutions for (2.27), (2.28), and (2.30) as $T\to T_c$. The above equations all have integrals of the form

$$I(\beta)=\int_{+\infty}^{-\infty} d\mathcal{E}\,\mathrm{Im}A_j(\mathcal{E})/e^{\beta(3-\mathcal{E})}-1\,, \qquad (3.4)$$

where $\mathrm{Im}A_j(\mathcal{E})$, the reduced spectral function, is the imaginary part of an analytic function of complex $\mathcal{E}$

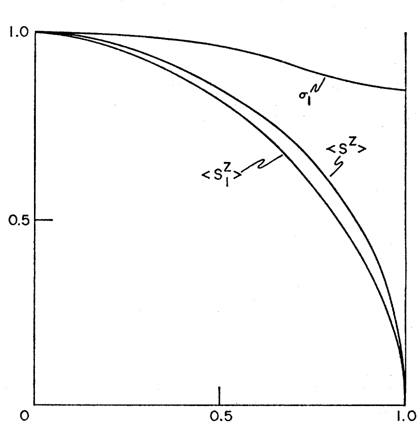

FIG. 3. The thermal behavior of the nearest-neighbor spins $\langle S_1^z\rangle$ (for $\epsilon=0$) as a function of τ, the reduced temperature T/T_c along with the host $\langle S^z\rangle$. The upper curve is the ratio $\sigma_1=\langle S_0^z\rangle/\langle S^z\rangle$.

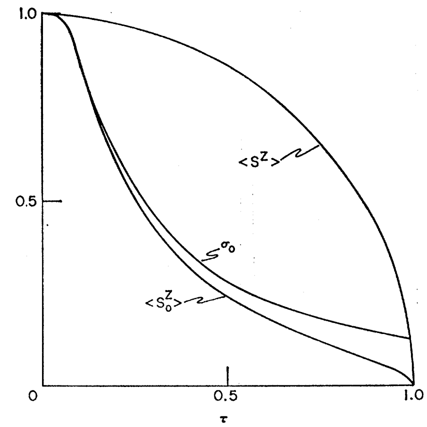

FIG. 4. The thermal behavior of the impurity spin $\langle S_0^z\rangle$ for $\epsilon=0.1$ as a function of the reduced temperature $\tau=T/T_c$ along with the host spin $\langle S^z\rangle$. The ratio $\sigma_0=\langle S_0^z\rangle/\langle S^z\rangle$ is also shown.

and vanishes outside of the spin-wave band. As $T\to T_c$, $\beta\to 0$ (since $\beta\alpha\langle S^z\rangle$) and it is convenient to expand $I(\beta)$ as,

$$I(\beta)=\frac{\pi}{\beta}\,\mathrm{Re}A_j(\mathcal{E}=3)-\tfrac{1}{2}+\frac{\beta}{12}\int_{+\infty}^{-\infty} d\mathcal{E}\,\mathrm{Im}A_j(\mathcal{E})(3-\mathcal{E})+O(\beta^2)\,. \qquad (3.5)$$

In obtaining (3.5) we have made use of the dispersion relation

$$\frac{1}{\pi}\int_{+\infty}^{-\infty} d\mathcal{E}\,\mathrm{Im}A_j(\mathcal{E})/(\mathcal{E}'-\mathcal{E})=\mathrm{Re}A_j(\mathcal{E}')\,, \qquad (3.6)$$

as well as the normalization condition,

$$\int_{+\infty}^{-\infty} d\mathcal{E}\,\mathrm{Im}A_j(\mathcal{E})=1\,. \qquad (3.7)$$

[The fact that (3.7) holds for the approximate $A_j(\mathcal{E})$ calculated here is discussed in Appendix A.]

Using (3.5) one obtains from (2.27),

$$\tfrac{1}{2}=kTR_0(3)/4J+J/kT[\langle S^z\rangle]^2+O([\langle S^z\rangle]^3)\,, \qquad (3.8)$$

for the unperturbed spins. In obtaining (3.8) we have used the fact that $\int d\mathcal{E}\mathcal{E}N_0(\mathcal{E})$ vanishes since $N_0(\mathcal{E})$ is an even function of $\mathcal{E}$. Setting $\langle S^z\rangle=0$ we obtain for the Curie temperature

$$T_c=2J/kR_0(3) \qquad (3.9)$$

and for small $\langle S^z\rangle$

$$\langle S^z\rangle\cong[3\tau(1-(\tau/\tau_c))]^{1/2}\,, \quad \tau=kT/6J\,. \qquad (3.10)$$

It is worth noting that the solution corresponding to

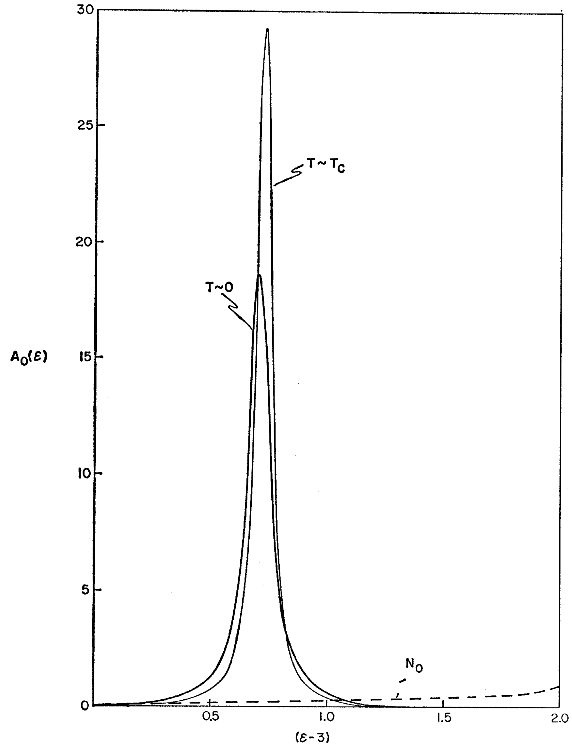

FIG. 5. The reduced spectral function $\mathrm{Im}A_0(\mathcal{E})$ for $\epsilon=0.25$. The heavy curve is for T near zero and the light curve is for T near T_c. The peak height increases with temperature and is slightly shifted. The dashed curve is the host density of states $N_0(\mathcal{E})$.

(3.10) in Ref. 4 is a mistranscription (see Ref. 5). Applying the same procedure to (2.28) and (2.30) yields the coupled equations

$$\sigma_0=\left\{\frac{R_0\epsilon\sigma_1}{R_0\epsilon\sigma_0+\frac{1}{3}(1-\epsilon\sigma_0)}\right\}_{\mathcal{E}=3},$$

$$\sigma_1=R_0\left\{\tfrac{1}{3}(3R_0-1)+\frac{\frac{1}{2}(R_0-R_3)}{1-\frac{1}{2}(1-\epsilon\sigma_0)(R_0-R_3)}+\frac{\frac{1}{3}(R_0+R_3-2R_2)}{1-\frac{1}{2}(1-\epsilon\sigma_0)(R_0+R_3-2R_2)}\right\}^{-1}_{\mathcal{E}=3}.$$

$$(T\rightarrow T_c). \tag{3.11}$$

The strongest perturbation on the nearest-neighbor spins (for $0\leq\epsilon\leq 1$) occurs when the impurity-exchange vanishes ($\epsilon=0$). In this case one obtains a value of $\sigma_1\approx 0.84$. Thus, in this case the thermal average for nearest-neighbor spins is about 16% lower than the very distant host spins as the Curie temperature is approached. One can expect that the effect of the first neighbors on the second neighbors would be to include a deviation of about $(0.16)^2$ or $2\frac{1}{2}$% from host behavior near the Curie temperature. σ_1 clearly tends to one as ϵ increases from zero. As one can see in Fig. 3, the deviation of σ_1 decreases as the temperature is lowered. It therefore appears to be a good approximation to ignore the second-neighbor deviations. Solving for σ_0 in terms of σ_1 gives

$$\sigma_0=\left(\frac{1}{\epsilon^2}+3\sigma_1\right)^{1/2}-\frac{1}{\epsilon}, \tag{3.12}$$

which for small ϵ gives the result that the σ_0 approaches the Curie temperature as $(\frac{3}{2})\epsilon\sigma_1\approx 1.26\epsilon$ using the value of 0.84 for σ_1, (The values of the R's and N's are given in WCI) and $R_0(3)\approx\frac{1}{2}$. For ϵ near 1, $\epsilon=1-\delta$, $\sigma_1\approx 1$

$$\sigma_0(T\rightarrow T_c)=1-\tfrac{1}{2}\delta.$$

The exact dependence of σ_0 and σ_1 on ϵ can be obtained from (3.11) but will not be calculated here.

C. Low-Temperature Solutions

In this section we investigate the solutions of (2.27), (2.28), and (2.30) in the limit of small temperatures.

We consider first the host behavior, (2.28), as $\beta\rightarrow\infty$. Using (2.19) we can expand $N_0(\mathcal{E})$ about $\mathcal{E}=3$ and find

$$N_0(\mathcal{E})=(\sqrt{2}\pi^2)^{-1}(3-\mathcal{E})^{1/2}+O[(3-\mathcal{E})^{3/2}]. \tag{3.13}$$

For sufficiently large β only the region near $\mathcal{E}=3$ contributes to the integral

$$\frac{\frac{1}{2}\langle 1-S^z\rangle}{\langle S^z\rangle}\simeq\frac{1}{\sqrt{2}\pi^2}\int_{-3}^{+3}\frac{d\mathcal{E}(3-\mathcal{E})^{1/2}}{e^{\beta(3-\mathcal{E})}-1}$$

$$\cong\left(\frac{1}{2\pi}\right)^{3/2}\beta^{-3/2}\zeta(\tfrac{3}{2}), \tag{3.14}$$

where ζ is the Riemann zeta function. Equation (3.14) leads to the well-known result that the saturation magnetization, M/M_0, behaves like $1-\alpha T^{3/2}$, $\alpha=(k/8\pi J)^{3/2}\zeta(\frac{3}{2})$.

Next we consider the low-temperature behavior of the impurity magnetization. Equation (2.28) can be written as

$$\frac{\frac{1}{2}\langle 1-S_0\rangle}{\sigma_0\langle S_0\rangle}=\int_{-3}^{+3}\left(\frac{d\mathcal{E}}{e^{\beta(3-\mathcal{E})}-1}\right)\times\left(\frac{\epsilon^2N_0(\mathcal{E})}{(C+dR)^2+(\pi dN_0)^2}\right). \tag{3.15}$$

The second factor tends to $N_0(\mathcal{E})$ as $\mathcal{E}\rightarrow 3$. If ϵ is small the second term is also highly peaked about $\mathcal{E}=3-3\epsilon\sigma_1$. In fact, as $\epsilon\rightarrow 0$ the second factor was shown to tend to $\delta(3-\mathcal{E}-3\epsilon\sigma_1)$. For finite ϵ, however, the behavior near the origin ($\mathcal{E}$ near 3) cannot be ignored as far as the low-temperature limit is con-

[5] V. L. Bronch-Bruevich and S. V. Tyablikov, *The Green's Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), p. 185.

cerned. To get the qualitative behavior for $\epsilon \ll 1$ one approximates the second factor by (see Appendix B)

$$\epsilon^2 N_0(\mathcal{E})/(c+dR)^2+(\pi b N_0)^2 \approx N_0(\mathcal{E})+\delta(3-\mathcal{E}-3\epsilon\sigma_1)\,, \quad (3.16)$$

(for large β). One then obtains

$$\frac{\frac{1}{2}\langle 1-S_0\rangle}{\sigma_0\langle S_0^z\rangle} \simeq \frac{1}{(2\pi)^{3/2}}\beta^{-3/2}\zeta(\tfrac{3}{2})+\frac{1}{e^{3\epsilon\beta}-1}\,, \quad (3.17)$$

(where for large β, $\sigma_1 \to 1$). A slightly more sophisticated treatment is given in Appendix B which shows that (3.17) is qualitatively correct whenever the width Γ of the resonance is small compared to 3ϵ and $\Gamma\beta/2 \ll 1$. $\Gamma=(3\pi N_0 b)|_{\mathcal{E}=3-3\epsilon}=(1/\sqrt{2}\pi)(3\epsilon)^{5/2}$, the width is small compared to 3ϵ whenever $3\epsilon \ll 1$. In the extreme low-temperature limit the first term in (3.17) will dominate and the magnetization in this limit is identical to that of the host ferromagnet. On the other hand, for $\beta \sim 10$ (about $0.1T_c$) and $\epsilon \sim 0.2$, the two terms are approximately equal and for $\epsilon \sim 0.1$ the exponential term is larger by a factor of about 20. Thus a 1% concentration of impurities with $\epsilon \sim 0.1$ for example, could cause a 20% deviation in the bulk magnetization of temperature on the order of $0.1T_c$. (Numerical calculations verify the qualitative behavior but give different numerical factors.)

The presence of a low-lying s-state virtual state does not contribute significantly to the nearest-neighbor low-temperature behavior because the factor $(\mathcal{E}-\Delta M_{00})$ in (2.30) vanishes as the resonance $\mathcal{E}=3-3\epsilon$ is approached. Consequently $\langle S_1^z\rangle$ is only very slightly depressed from the host value at low temperatures.

D. Internal Energy and Specific Heat at Low Temperatures

The internal energy E of the host spins may be calculated from the expression

$$E/4J\langle S^z\rangle=\int_{-3}^{+3}(3-\mathcal{E})N_0(\mathcal{E})d\mathcal{E}/e^{\beta(3-\mathcal{E})}-1\,. \quad (3.18)$$

Following the procedure used in the previous sections leads to the low-temperature result

$$\frac{E}{4J}\to\frac{3}{2}\frac{\beta^{-5/2}}{(2\pi)^{3/2}}\zeta(\tfrac{5}{2})\,,\quad \beta\to\infty \quad (3.19)$$

and the low-temperature specific heat per host spin c_v^h

$$c_v^h\to\frac{15}{4}k\left(\frac{k}{4J}\right)^{3/2}\frac{\zeta(\frac{5}{2})}{(2\pi)^{3/2}}T^{3/2}\,,\quad \beta\to\infty\,. \quad (3.20)$$

The spin-wave specific heat of the impurity may be calculated from the reduced spectral function[6]

$$\frac{c_v^I}{4J}=\frac{d}{dT}\left\{-\langle S^z\rangle\int_{-3}^{+3}\frac{d\mathcal{E}(3-\mathcal{E})\,\mathrm{Im}A_0(\mathcal{E})}{e^{\beta(3-\mathcal{E})}-1}\right\}\,. \quad (3.21)$$

Using (3.16) we find the approximate low-temperature specific heat for the weakly coupled impurity to be

$$c_v^I\approx c_v^h 4J\frac{(3\epsilon)^2(J/kT^2)}{\sinh^2(6J'/kT)} \quad \text{for} \quad (4J/kT\gg 1)\,. \quad (3.22)$$

Equation (3.22) is valid for the same conditions for which (3.17) holds. The impurity term in (3.22) dominates c_v^h very rapidly as T increases from zero. For example for $\epsilon\sim 0.1$ at $T/T_c\sim 0.1$ ($\beta=10$) the second term is roughly a factor of 20 times as large as c_v^h. As a result the specific heat departs radically from the $T^{3/2}$ law. Numerical calculations of the exact expression given by (3.21) show that for the ϵ and T suggested above, the impurity contribution is actually 50 times larger than the host specific heat. This means that a 1% concentration of such impurities would give a 50% increase in the spin-wave specific heat of the bulk sample! This situation is analogous to the lattice specific heat anomaly due to a heavy mass virtual phonon state.[7] The phonon specific heat anomaly has been observed experimentally with Pb in Mg.[8]

E. Numerical Solutions

Equations (2.27), (2.28), and (2.30) were solved numerically by an iterative procedure as a function of temperature. The results are shown in Figs. 2, 3, and 4. In Fig. 2 we have compared the behavior of the Bril-

[6] In terms of the total crystal density of states

$$n=(\mathrm{Im}/\pi)\,\mathrm{Tr}(H^0+H^1-E)$$

one can write the crystal internal energy at temperature T as

$$W=\int\frac{dEn(E)}{e^{E/kT}-1,}\quad \text{where, of course,}\quad c_v=\partial W/\partial T.$$

In the lattice site representation, $n(E)$ is simply related to the diagonal elements of $\langle\langle a_{f_1};a_{f_2}^\dagger\rangle\rangle$ via Eq. (2.17):

$$n(E)=\Sigma_f\,(2\,\mathrm{Im}G_{ff}(E)/\langle S_f^z\rangle)=\Sigma_f\,\mathrm{Im}A_f(E).$$

For the assumed separation into bulk, nearest neighbors, and impurity sites, one obtains, neglecting impurity mutual interaction,

$$n(E)=N\{(1-7c)N_0(E)+6c\,\mathrm{Im}A_{\varrho}(E)+c\,\mathrm{Im}A_0(E)\},$$

c being the concentration of impurity atoms. Thus, the three contributions to the specific heat can be computed separately. In the text, we have taken nearest neighbors identical to host, giving

$$n=N\{N_0(E)+c[\mathrm{Im}A_0(E)-N_0(E)]\}.$$

Note that the concentration-dependent term is dominated by the impurity contribution in the neighborhood of a resonance in $\mathrm{Im}A_0(E)$. Further, if the resonance occurs at low energy, where N_0 is small, $Nc\,\mathrm{Im}A_0$ can dominate $n(E)$.

[7] G. W. Lehman and R. E. DeWames, Phys. Rev. 131, 1008 (1963). Also Yu. Kagan and Ya. Iosilevskii, Zh. Eksperim. i Teor. Fiz. 45, 819 (1963) [English transl.: Soviet Phys.—JETP 18, 562 (1964)].

[8] G. W. Lehman *et al.*, Bull. Am. Phys. Soc. 9, 251 (1964).

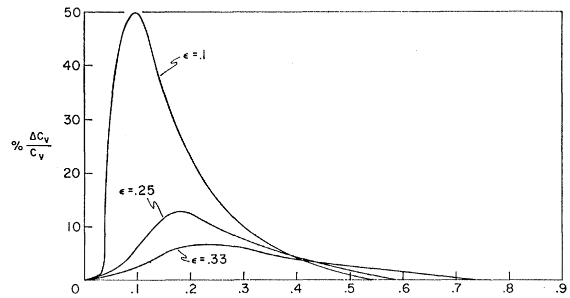

FIG. 6. The change in the specific heat due to a 1% spin-impurity concentration for various values of ϵ as a function of the reduced temperature $T=T/T_c$ (assuming additivity).

louin function for spin $\frac{1}{2}$, $\tanh(6J'\langle S_1^z\rangle)$ to the calculated values for $\langle S_0^z\rangle$ for $\epsilon=0.25$. The curves are obviously quite similar. A plot of the change in specific heat due to impurities divided by the host specific heat as a function of temperature is shown in Fig. 6 for several values of ϵ.

IV. DISCUSSION AND CONCLUSIONS

In the previous sections we have investigated the effect of an impurity spin on the spin-wave spectrum of an ideal simple cubic spin-$\frac{1}{2}$ Heisenberg ferromagnet. It was shown that for a weakened impurity-host exchange low-lying s-type virtual spin-wave states result which cause a large density of states to occur at low energies. These low-energy states are excited at low temperatures and lead to an accumulation of spin disorder at and near the impurity site. Consequently, the thermal average of the impurity spin decreases far more rapidly than that of the host. This effect is accompanied by a large increase in the spin wave specific heat. In detail, a set of three simultaneous integral equations were obtained by means of the two-time Green's function procedure which determines the thermal averages $\langle S_0^z\rangle$, $\langle S_1^z\rangle$ and $\langle S^z\rangle$ for the impurity, its N.N. (nearest neighbor) and the host spin. In obtaining these equations it was assumed that the perturbation was localized to the impurity and N.N. spins. Asymptotic solutions were obtained for temperatures near the Curie point. It was shown that the N.N. spins deviate from the unperturbed spins by about 16% for the strongest perturbation (i.e., $J'=0$) as $T\rightarrow T_c$. The impurity magnetization was shown to approach the Curie point according to $\frac{3}{2}\epsilon\sigma_1$ for small ϵ. Approximate solutions to the equations were obtained for small temperatures. In the limit as $T\rightarrow 0$ the impurity and N.N. spins approach the host behavior but for small but finite temperatures an exponential contribution due to the s-like virtual resonance appears. This latter term begins to dominate the impurity response in the temperature range where $T\sim\epsilon T_c$ for small ϵ and leads to a magnetization which follows the Brillouin function with an effective field equal to the N.N. exchange field. A concomitant anomaly in the spin-wave specific heat occurs which for $\epsilon\sim 0.1$ amounts to a 50% increase in bulk spin-wave specific heat. The magnetization of the impurity and the change in specific heat were calculated numerically as a function of temperature for several values of ϵ.

In this paper the effect of the impurity having a spin different from that of the host has not been calculated. It is clear, however, from WCI that an impurity spin larger than that of the host will have an effect similar to a decrease in ϵ resulting in a lower virtual state energy. This effect is also true for the Brillouin function (see, for example, Fig. 2 of Ref. 2). Thus the effects we have discussed here can be important for larger ϵ when the impurity spin is larger than that of the host.

We have considered only the simple cubic structure. The qualitative low-temperature features regarding the effect of the low-lying s-type states will be unaffected by the details of the structure. This is true because the results depend only upon the low-energy host spin-wave density of states being proportional to $\mathcal{E}^{1/2}$. This result, except for multiplicative factors, is the same for all cubic structures.

Recently Jaccarino *et al.*[3] reported the results of a nuclear-magnetic-resonance experiment on manganese in ferromagnetic iron. They observed that the NMR frequency of the Mn decreased with temperature much more rapidly than the magnetization of the bulk sample. A plot of the Brillouin function labeled ν/ν_0 given by Jaccarino *et al.* is shown in Fig. 7. The experimental data which cover the temperature range up to about $0.6T_c$ fall on the Brillouin curve. The curve M_h is for the magnetization of the host. (1.5% Mn in ferromagnetic Fe.) These results were interpreted as evidence for the existence of a low-lying virtual spin-wave state. With the assumption that the NMR frequency is proportional to the thermal average of the manganese electronic spin ($\langle S_0^z\rangle$ in our notation) and that the Mn-Fe exchange was substantially weaker than the host Fe-Fe exchange ($\epsilon<1$) they deduced that $\langle S_0^z\rangle$ should vary according to the Brillouin function with an effective field equal to the Mn-Fe exchange field which they assumed proportional to the bulk magnetization. By appropriate choice of ϵ and the Mn spin they were able to fit the experimental data quite well. A similar interpretation has been given for Fe in Ni by Howard *et al.*[9] The experimental data of Jaccarino *et al.*[2] is qualitatively similar to the numerical results we have obtained for ϵ between 0.25 and 0.35 for spin $\frac{1}{2}$. A numerical comparison cannot be made since our calculations are based on spin $\frac{1}{2}$, whereas the Brillouin function in Fig. 7 is for spin $\frac{3}{2}$. The results of our calculations are highly suggestive of the interpretation given by Jaccarino *et al.* for Mn in Fe; however, it should be noted that this model is in disagreement with

[9] D. G. Howard, B. D. Dunlap, and J. G. Dash, Phys. Rev. Letters 15, 628 (1965).

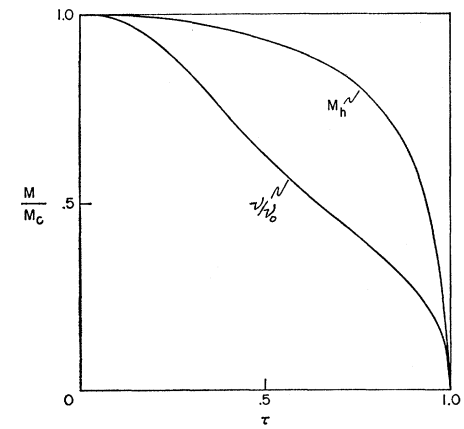

FIG. 7. A reproduction of a figure given by Jaccarino *et al.* (Ref. 3). The M_h curve is the bulk magnetization of a 1.5% Mn in Fe sample as a function of the reduced temperature $T=T/T_c$. The ν/ν_0 curve is a Brillouin function which best fitted the Jaccarino *et al.* NMR data.

the interpretation of the elastic neutron-scattering experiments by Collins and Low[10] which indicate that for Mn in Fe the Mn site has a negligible magnetic moment.

One might expect that the Mn in Fe system would show an increase in the spin-wave specific heat if the present interpretation is correct. Unfortunately, even though the change in spin-wave specific heat may be large, the large lattice contribution would tend to mask the effect.

One might expect that a dilute solution of rare-earth ions in a transition ferromagnet would have a small ϵ since the f electrons are quite well shielded. The exchange would probably be indirect f-d exchange via the conduction electrons. If the rare-earth ion was a Mössbauer emitter one could get the local magnetization by a study of the Zeeman splitting of the line as a function of temperature. (This technique has been employed by Howard *et al.*[9] for Fe in Ni.) If one uses a Fe host then it may be possible simultaneously to study the nearest and next nearest-neighbor magnetization from the Fe^{57} Mössbauer line. The feasibility of such a study has already been established by Stearns and Wilson.[11]

APPENDIX A: NORMALIZATION OF THE DECOUPLED SPECTRAL FUNCTIONS

In Sec. IIIB it was remarked that neither decoupling the Green's function equations of motion nor truncating the perturbation matrix ΔM destroyed the intrinsic normalization of the reduced spectral intensity functions $\mathrm{Im}A_0(\mathcal{E})$ and $\mathrm{Im}A_1(\mathcal{E})$ defined by

$$\mathrm{Im}A_j(\mathcal{E})=\lim_{\epsilon\to0}-i[G_{jj}(\mathcal{E}+i\epsilon)-G_{jj}(\mathcal{E}-i\epsilon)]/\langle[b_j,b_j^\dagger]\rangle.$$

This result is most easily obtained from the analyticity and asymptotic properties of $G_{jj}(\mathcal{E})$. First, the discontinuity $\mathrm{Im}A_j$ vanishes for sufficiently large $|\mathcal{E}|$; this forces the real part of G_{jj} to be continuous across the real axis (by the symmetry principle). Further, for large arguments, each G_{jj} falls off at least as fast as $1/\mathcal{E}$; therefore, one may write the dispersion relation (for real $\mathcal{E}$)

$$\mathrm{Re}G_{jj}(\mathcal{E})=\frac{1}{\pi}\int_{+\infty}^{-\infty}\frac{d\mathcal{E}'\,\mathrm{Im}G_{jj}(\mathcal{E}')}{\mathcal{E}-\mathcal{E}'}$$

$$\equiv\frac{\langle[b_j,b_j^\dagger]\rangle}{2\pi}\int_{+\infty}^{-\infty}\frac{d\mathcal{E}'\,\mathrm{Im}A_j(\mathcal{E})}{\mathcal{E}-\mathcal{E}}.$$

Multiplying both sides above by $\mathcal{E}$ and letting $\mathcal{E}$ tend to infinity leads to the relation

$$\lim_{\mathcal{E}\to\infty}\frac{2\pi\mathcal{E}\,\mathrm{Re}G_{jj}(\mathcal{E})}{\langle[b_j,b_j^\dagger]\rangle}=\lim_{\mathcal{E}\to\infty}\int_{+\infty}^{-\infty}d\mathcal{E}\,\mathrm{Im}A_j(\mathcal{E}')$$

$$\times\sum_{n=0}^{\infty}(\mathcal{E}'/\mathcal{E})^n=\int_{+\infty}^{-\infty}d\mathcal{E}'\,\mathrm{Im}A_j(\mathcal{E}').$$

One may now readily establish that

$$\int_{+\infty}^{\infty}d\mathcal{E}'A_j(\mathcal{E}')=1$$

simply by examining the asymptotic form of $\mathcal{E}G_{jj}(\mathcal{E})$ as obtained from the solution to the decoupled equations:

$$G_{00}(\mathcal{E})=\frac{\langle S_0^z\rangle}{2\pi}\frac{(\mathcal{G}_{00}-2\Delta M_{11}\mathcal{G}_{01})}{\det A}$$

$$G_{11}(\mathcal{E})=\frac{\langle S_1^z\rangle}{2\pi}\left\{\frac{\frac{1}{3}(\mathcal{E}-\Delta M_{00})\mathcal{G}_{01}}{\det A}+\frac{\frac{1}{2}[\mathcal{G}_{00}-\mathcal{G}_{03}]}{1-\Delta M_{11}[\mathcal{G}_{00}-\mathcal{G}_{03}]}\right.$$

$$\left.+\frac{\frac{1}{3}[\mathcal{G}_{00}+\mathcal{G}_{03}-2\mathcal{G}_{02}]}{1-\Delta M[\mathcal{G}_{00}+\mathcal{G}_{03}-2\mathcal{G}_{02}]}\right\}.$$

The behavior of $\mathcal{G}_{0j}$ for large $|\mathcal{E}|$ is easily derived from (2.18):

$$\mathcal{G}_{00}\cong\frac{1}{\mathcal{E}}+\frac{3}{2\mathcal{E}^3}+\cdots,$$

$$\mathcal{G}_{01}\cong\frac{1}{2\mathcal{E}^2}+\cdots,$$

$$\mathcal{G}_{02},\,\mathcal{G}_{03}\cong\frac{1}{4\mathcal{E}^3}+\cdots,$$

with the identity $\langle[b_j,b_j^\dagger]\rangle=\langle S_j^z\rangle$ one can now directly verify that

$$\lim_{\mathcal{E}\to\infty}\frac{2\pi\mathcal{E}}{\langle S_j^z\rangle}\mathrm{Re}G_{jj}(\mathcal{E})=1,$$

[10] M. F. Collins and G. G. Low, Proc. Phys. Soc. (London) **86**, 535 (1965).

[11] M. B. Stearns and S. S. Wilson, Phys. Rev. Letters **13**, 313 (1964).

which shows that the decoupling procedure preserves the requisite normalization.

APPENDIX B: APPROXIMATE MAGNETIZATION AND INTERNAL ENERGY AT LOW TEMPERATURES

When the impurity exchange is sufficiently weak ($\epsilon \ll 1$) it is possible to derive approximate expressions for the impurity magnetization and internal energy integrals in the region of temperature where the host magnetization decreases as $T^{3/2}$. Under these conditions the integrand

$$\frac{\mathrm{Im}A_0(\mathcal{E})}{\exp\beta(3-\mathcal{E})-1}=\frac{1}{\exp\beta(3-\mathcal{E})-1}\times\frac{\sigma_0\epsilon^2 N_0(\mathcal{E})}{[c+dR_0(\mathcal{E})]^2+[\pi d N_0(\mathcal{E})]^2}$$

is appreciable only for that range of $\mathcal{E}$ such that $0\leq 3-\mathcal{E}\lesssim 3\epsilon\sigma_1$, since $\mathrm{Im}A_0(\mathcal{E})$ approaches $\delta(\mathcal{E}-3+3\epsilon\sigma_1)$ for small ϵ and the temperature factor can counteract the vanishing of $\mathrm{Im}A_0$ only in the neighborhood of $\mathcal{E}=3$. This suggests immediately the replacement of $\mathrm{Im}A_0(\mathcal{E})$ by a function with the proper behavior at $\mathcal{E}\simeq 3$, plus a function which is sharply peaked about the resonance $\mathcal{E}=3-3\epsilon\sigma_1$, with width Γ equal to $\pi b N_0(3-3\epsilon\sigma_1)$. The simplest choice for such a function is

$$\mathrm{Im}A_0(\mathcal{E})\simeq N_0(\mathcal{E})+\frac{1}{\Gamma}[u(\mathcal{E}-3+3\epsilon\sigma_1+\tfrac{1}{2}\Gamma)-u(\mathcal{E}-3+3\epsilon\sigma_1-\tfrac{1}{2}\Gamma)],$$

$u(x)$ being the unit step function. For the impurity magnetization near $T=0$ one may now write the approximate expression (taking $\sigma_0\simeq\sigma_1\simeq 1$)

$$\langle n_0\rangle\simeq\int_{-3}^{3}\frac{d\mathcal{E}\,N_0(\mathcal{E})}{\exp\beta(3-\mathcal{E})-1}+\frac{1}{\Gamma}\int_{3-3\epsilon-\frac{1}{2}\Gamma}^{3-3\epsilon+\frac{1}{2}\Gamma}d\mathcal{E}/[\exp\beta(3-\mathcal{E})-1].$$

The first term will be immediately recognized as $\langle n\rangle$ for the host, which for low temperatures is given by

$$\langle n\rangle\simeq(2\pi\beta)^{-3/2}\zeta(\tfrac{3}{2}),$$

$\zeta(x)$ being the Riemann zeta function. The second term can be evaluated approximately if either $\beta\epsilon\gtrsim 1$ or $\beta\epsilon\ll 1$, provided only that $\Gamma/6\epsilon\ll 1$. But

$$\Gamma=(3\epsilon)^{5/2}/\sqrt{2}\pi\ll\epsilon\quad\text{for}\quad\epsilon\lesssim 0.1,$$

so for ϵ in this range one readily derives the asymptotic forms:

$$(\beta\epsilon\gtrsim 1)\frac{1}{\Gamma}\int_{3-3\epsilon-\frac{1}{2}\Gamma}^{3-3\epsilon+\frac{1}{2}\Gamma}d\mathcal{E}/[\exp\beta(3-\mathcal{E})-1]\sim\left(\frac{2}{\Gamma\beta}\right)e^{-3\epsilon\beta}\sinh\left(\frac{\Gamma\beta}{2}\right)$$

$$(\beta\epsilon\ll 1)\frac{1}{\Gamma}\int_{3-3\epsilon-\frac{1}{2}\Gamma}^{3-3\epsilon+\frac{1}{2}\Gamma}d\mathcal{E}/[\exp\beta(3-\mathcal{E})-1]\sim\frac{1}{e^{3\beta\epsilon}-1}.$$

Thus, for the total spin deviation of the impurity one obtains

$$\langle n_0\rangle\simeq(2\pi\beta)^{-3/2}\zeta(\tfrac{3}{2})+(2/\Gamma\beta)e^{-3\epsilon\beta}\sinh(\tfrac{1}{2}\Gamma\beta),\quad(\beta\epsilon\gtrsim 1)$$
$$+(e^{3\epsilon\beta}-1)^{-1},\quad(\beta\epsilon\ll 1).$$

A similar set of expressions is obtained for the impurity internal energy if one recalls that

$$E_0=\int 4J\langle S^z\rangle(3-\mathcal{E})\,\mathrm{Im}A_0(\mathcal{E})d\mathcal{E}/\exp\beta(3-\mathcal{E})-1$$

with the above approximations, one obtains for low temperature and small ϵ

$$\frac{E_0}{4J}\simeq 3\pi(2\pi\beta)^{-5/2}\zeta(\tfrac{5}{2})$$
$$+3\epsilon\left(\frac{2}{\Gamma\beta}\right)e^{-3\epsilon\beta}\sinh\left(\frac{\Gamma\beta}{2}\right)+\frac{e^{-3\epsilon\beta}}{2\beta}\cosh\left(\frac{\Gamma\beta}{2}\right),\quad(\beta\epsilon\gtrsim 1)$$
$$+3\epsilon/(e^{3\epsilon\beta}-1),\quad(\beta\epsilon\ll 1).$$