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Nuclear magnetism in metals: Thermodynamics and magnetic resonance

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Nuclear spins in metals can undergo phase transition into an ordered state. They have been studied for the thermodynamic properties over a wide temperature range including the transition temperature. The metallic nuclear spins interact via the Ruderman-Kittel (RK) exchange interaction in addition to the usual dipolar interaction. The oscillatory nature of this interaction gives rise to spin-density waves as the ground-state spin arrangement. The thermodynamics is then strongly affected by the fluctuations. Using a spherical model we calculate entropy, susceptibility, and the internal energy for systems with varying RK exchange constant. The results can be compared with experiments on copper, and the agreement is satisfactory. The spherical-model technique yields a substantial reduction in the transition temperature from the mean-field value. The nuclear-spin dynamics has been considered in the disordered as well as in the ordered phase. At low external fields, the spins absorb radiation at the Larmor frequency ω_L as well as the second harmonic ω_{2L}. We study the interference between these two absorption frequencies. We derive a set of equations that generalize the usual Bloch equations and can be used to extract the strength of the RK coupling constant.

I. INTRODUCTION

The system we consider consists of conduction electrons with spin $\frac{1}{2}$ and nuclei with nonzero spin. If the conduction electrons remain paramagnetic until the lowest temperatures T then at some low T, the localized nuclear spin, described by a Curie law susceptibility, are expected to condense into a spin-ordered state. The nuclear-spin interaction is of order 0.1 μK and we expect the transition temperature to be similar. The ordered state then becomes the lowest energy many-body state known so far.[1]

In dielectrics, the nuclei interact only via the classical dipolar interaction. The resulting effects have been studied carefully and in detail by Abragam, Goldman, and co-workers.[2,3] They have studied, mostly within the mean-field approximation, the spin arrangement and the thermodynamic properties. In a metal, the nuclei also interact via the conduction electrons, the well-known indirect exchange Ruderman-Kittel (RK) interaction.[4] This interaction is oscillatory, long range, and has magnitude usually comparable to that of the dipolar interaction. The two interactions compete and the resulting state turns out to be a spin-density wave (SDW) state, as shown by Kjäldman and Kurkijärvi.[5]

For copper the mean-field prediction for the transition temperature T_c is 0.2 μK. The experiments[6] have reached temperatures of order 0.1 μK and seen no conclusive evidence of a phase transition. We propose this reduction in T_c as an effect of SDW fluctuations. The fluctiations also explain the observed temperature dependence of the susceptibility χ, the entropy S, and the internal energy E. Briefly,[6] the observed χ follows a Curie-Weiss law for $T > 0.25$ μK but gets steadily smaller at low temperatures. The observed S decreases by 40% over the temperature range 1.0 to 0.1 μK. The observed E decreases even more rapidly over the same temperature range.

The nature of the ground-state spin arrangement[5] is a question separate from the thermodynamic properties. If the Hamiltonian H is written in a quadratic form (at external magnetic field $H=0$)

$$H=-\frac{1}{2}\sum_{ij\mu\nu} S_\mu^i G_{\mu\nu}^{ij} S_\nu^j \quad , \tag{1}$$

where ij refer to the lattice sites and μ, ν refer to the components of spin vector $\vec{S}$, the eigenvalue equation (in k space)

$$G_{\mu\nu}(k)\phi_\nu(k)=\lambda(k)\phi_\mu(k) \tag{2}$$

contains most of the necessary information. The largest eigenvalue $\lambda(k)$ describes the energy of the ground state with spin arrangement given by the corresponding eigenfunction. Such an analysis has been carried out by Kjäldman and Kurkijärvi (KK) who studied the eigenvalue $\lambda(k)$ as a function of the exchange-coupling constant. The function G includes the dipolar as well as the exchange interaction with the ratio of the coupling constants expressed as $\eta = J_{\rm ex}a^3/\gamma^2\hbar^2$ where γ is the gyromagnetic ratio and a is the lattice constant for copper.

For $\eta = 0$, KK find a ferromagnetic state. As η increases, the system breaks up into patterns of large wavelength because of the competitition between the two interactions. For $0 < \eta < 1$, the maximum eigenvalue $\lambda(k_0)$ decreases (the energy increases). For $\eta > 1$, the system is dominated by the exchange interaction, the ground state consists of commensurate spin-density waves (SDW) and $\lambda(k_0)$ increases with η. For copper ($\eta = 2.8$), the ground-state spin arrangements consists of antiferromagnetic orientation in x-y planes with spins in successive planes oriented at an angle. The arrangement, shown in Fig. 1 is described by

$$\langle I_i\rangle = (0,\alpha_1,\alpha_2)\cos(\vec{k}\cdot\vec{r}_i) + (\alpha_3,0,0)\cos(\vec{k}'\cdot\vec{r}_i)\ , \tag{3}$$
$$\vec{k} = \frac{\pi}{a}(1,0,0),\quad \vec{k}' = \frac{\pi}{a}(0,1,0)\ .$$

The condensation of two spin-density waves in the language of critical phenomena, makes copper an $n = 4$ system.

The calculations presented here have been done using the spherical model.[7] The method was invented as a technique which brought about many of the features of Onsager's exact solution of 2D (two-dimensional) Ising model and yet was managable in higher dimensions. Later on it was shown to be exact for a large coordination number[8] or a large number of components of the order parameter.[9] In as much as the interactions, both exchange and dipolar are long range and the number of ordering sublattices is $n = 4$, we expect the spherical model to provide a considerably improved description compared to the mean-field theory. To our knowledge, this is the first application of the spherical model to a real system. The calculations have been done without any adjustable parameters and are in satisfactory agreement with the experiments, elucidating the role played by fluctuations. Our calculations here are limited to the disordered state.

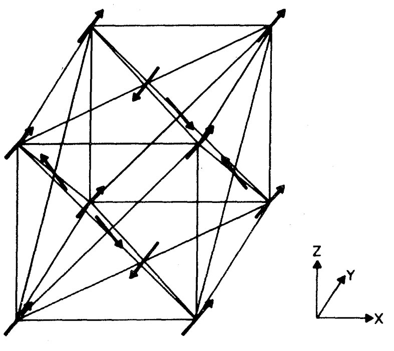

FIG. 1. The mean-field-theory prediction for the ground-state arrangement, as calculated by Kjäldman and Kurkijärvi. The spin in $z = 0$ plane are in a relative antiferromagnetic orientation. In the plane $z = a$, they are at an angle $2\cos^{-1}(\alpha_3)$ with $z = 0$ spins. In the absence of any anisotropy energy, the overall orientation is arbitrary.

We present a brief introduction to the spherical model in Sec. II A followed by a discussion of the eigenvalues and density of states in Sec. II B. The latter constitute the building blocks of this model and we discuss them in some detail for various values of the exchange constant. Such an analysis brings out, in terms of the parameters of the spherical model, the physical processes involved in the precursor fluctuations of the condensed state. We also study the density of states for CaF_2 for comparison. This system contains no exchange interaction but its Hamiltonian consists of only those terms in the dipolar interaction that conserve the z component of the total spin. In Sec. III, we present the thermodynamic properties. We present the results for the disordered phase, compare them with the experiments and offer speculations about the sources of remaining discrepancy. We also discuss the effects to be expected on the ordered state.

In Sec. IV we consider the equations for the spin dynamics. The dipolar interaction causes spin precession at $\omega_L = \gamma H_0$ as well as $\omega_{2L} = 2\omega_L$, $\omega_{3L} = 3\omega_L$, etc.[10] Usually, the intensity of the harmonic absorption is weak and unobservable. In nuclear spins of copper (a) the Larmor frequency ω_L is shifted due to demagnetization and (b) the exchange interaction causes negative shift of comparable amount in ω_{2L}. This results[11] in a level crossing at a magnetic field of 7 G, where the absorption intensities of the two lines are equal. From microscopic considerations, we can derive a set of generalized Bloch equations that describe coupling between ω_L and ω_{2L} lines (a misnomer, since after the shifts are accounted for, the frequencies are not multiples; we continue to use the label however) in terms of a parameter that is calculated from first principles. These equations have been used in Ref. 11 to analyze the experimental data. Section V consists of a concluding discussion.

II. SPHERICAL MODEL

A. Method

Copper nuclei occupy sites on an fcc lattice and interact via a Hamiltonian given in Eq. (1). The function $G_{ij}^{\mu\nu}$ is given by

$$G_{ij}^{\mu\nu} = -\frac{1}{2r_{ij}^3}\left\{[1+\eta f(2k_F r_{ij})]\delta_{\mu\nu} - \frac{3(r_{ij})_\mu (r_{ij})_\nu}{(r_{ij})^2}\right\} , \tag{4}$$

where

$$f(x) = \cos x - \frac{\sin x}{x}, \quad \vec{r}_{ij} = \vec{r}_i - \vec{r}_j . \tag{5}$$

The Fermi wave vector is denoted by k_F and r_{ij} are the lattice vectors. The Hamiltonian H is written in the units of $\hbar = \gamma = 1$. The greek subscripts refer to the spin indices. The RK interaction function $f(x)$ has been assumed to be free-electron form. Its strength η is a variable in our calculations. For copper $\eta = 2.8$.

The partition function Z contains the thermodynamic information $(\beta = 1/k_B T)$

$$Z(T) = \int D[S(r)]\exp(-\beta H) , \tag{6}$$

where $D[S(r)]$ represents the functional integration over the hypercube in the space of functions $S(r)$. In spherical approximation, the cube is replaced by the surface of a sphere of radius $[NS(S+1)]^{1/2}$ where N is the total number of spins. The Hamiltonian H can be written in a quadratic form by suitable rotation. The condition on the radius of the hypersphere, expressed as a delta function is rewritten in an integral representation. The integrals are mostly Gaussian and can be done easily. The measure of the functional integral, usually taken to be a $3N$-dimensional unit volume, is fixed so as to yield the correct high-temperature limit of the entropy. These are all the standard procedures in spherical approximation. The final results for the free energy F (in zero magnetic field), the internal energy E, the entropy $\mathcal{S}$, and the spin susceptibility χ can be written as

$$\begin{aligned} -\beta F &= \ln Z \\ &= \ln(2S+1) + \beta S(S+1)(t_0 - t_0^\infty) - I , \end{aligned} \tag{7}$$

$$\mathcal{S} = -\frac{\partial F}{\partial T} = k_B[\ln(2S+1) - I] , \tag{8}$$

$$\beta E = \beta F + \mathcal{S}/k_B = \tfrac{3}{2}(1 - t_0/t_0^\infty) , \tag{9}$$

$$\underline{\chi}^{-1} = 2[t_0 - \underline{\lambda}(q=0)] , \tag{10}$$

$$I = \frac{1}{2N}\sum_{q\mu}\ln[(t_0 - \lambda_q^\mu)/t_0^\infty] . \tag{11}$$

Here t_0, a function that represents the temperature dependence of the Curie constant, is a solution of the equation

$$\beta S(S+1) = \frac{1}{2N}\sum_{q\mu}\frac{1}{t_0 - \lambda_q^\mu} \tag{12}$$

and approaches $t_0^\infty = 3k_B T/2S(S+1)$ in the high-temperature limit. The Gaussian approximation corresponds to $t_0 = t_0^\infty$ at all temperatures. It yields the Curie-Weiss law for the susceptibility and $E = 0$. In mean-field theory the phase transition takes place at $t_0^\infty = \lambda_q^\mu$, the result obtained in Ref. 5.

Equation (12) states that the local susceptibility $\chi(r=0)$ must not diverge at $T = T_c$ but should be given by $S(S+1)/k_B T$. It is easy to prove the inequality, $\beta S(S+1)$ can be shown to be greater than or equal to the right-hand side using Bogoliubov's inequality[12]; however the exact equality is an approximation. Yet this limitation on the unphyiscal divergence of the fluctuations brings out (a) the fluctuation caused lowering of the transition temperature. That in turn comes from the (b) decrease in the temperature-dependent effective Curie constant. Finally (c) all the thermodynamic quantities Eqs. (7) to (10) appear with temperature dependence in satisfactory agreement with the experiments.

B. Energy eigenvalues and density of states

The exchange part of the operator G_{ij} is diagonal in spin space. Diagonalization in real space can be done by Fourier transform, notwithstanding the shape-dependent demagnetization effects. We are then left with the final diagonalization of the spin dipolar term in the spin space. This must be done explicitly.

Our calculations, from this stage onwards, have been done numerically. The dipolar term has been Fourier transformed by Cohen and Keffer[13] for 512 discrete values in the first Brillouin zone. We use those values. The Fourier summation of the exchange contribution has been done explicitly. Finally, the eigenvalue matrix in spin space is diagonalized for each point in k space. In Ref. 5 only the largest eigenvalue was studied, here we study carefully the entire eigenvalue spectrum.

The most useful function for our calculation is the density of states function $N(\lambda)$[14]

$$N(\lambda) = \frac{1}{N}\sum_{q\mu}\delta(\lambda - \lambda_q^\mu) , \tag{13}$$

such that all summations in Eqs. (7) and (12) can be replaced by energy integrations with the density of states $N(\lambda)$. One can indeed perform analytic calculations by choosing appropriate approximate forms for $N(\lambda)$. In Eq. (12), since the integrand is the product of a simple pole at t_0 and $N(\lambda)$, at moderate temperatures when $t_0 >> \lambda_{\max} = \max(\lambda_q^\mu)$, it is finite only in close vicinity of $\lambda_{\max}$. It may be sufficient to Taylor expand $N(\lambda)$ about $\lambda = \lambda_{\max}$. In Eq. (11), the integrand contains a logarithmic function which is slowly convergent and low eigenvalue fluctuations become important. The transition temperature T_c is particularly sensitive to the form of $N(\lambda)$ near $\lambda_{\max}$. The transition takes place[15] when $t_0 = \lambda_{\max}$. If $N(\lambda_{\max})$ is nonzero, the integral in Eq. (12) is divergent and T_c goes to zero. To yield a finite T_c, the density of states must approach zero at the upper band edge as $N(\lambda) \sim (\lambda - \lambda_{\max})^{\delta}$; $\delta > 0$. Hence in a numerical calculation where a finite set of points are used in a sum, special care must be taken in the calculation of T_c.

We show the numerical results for the density of states in Figs. 2. In Figs. 2(a) and 2(b), we show a collage of $N(\lambda)$ for $\eta = 0, 1, 2, \ldots, 5$. These correspond to the Hamiltonian in Eq. (4) and have been collected from the discrete eigenvalue spectrum in the first Brillouin zone. We will discuss later the method used to calculate T_c, here we only describe the histograms. As η increases, the maximum eigenvalue moves around, decreasing for $\eta < 1$ and increasing afterwards. The bandwidth $(\lambda_{\max} - \lambda_{\min})$ is large for $\eta = 0$; it decreases rapidly as η is switched on. For large η, the bandwidth is controlled by RK

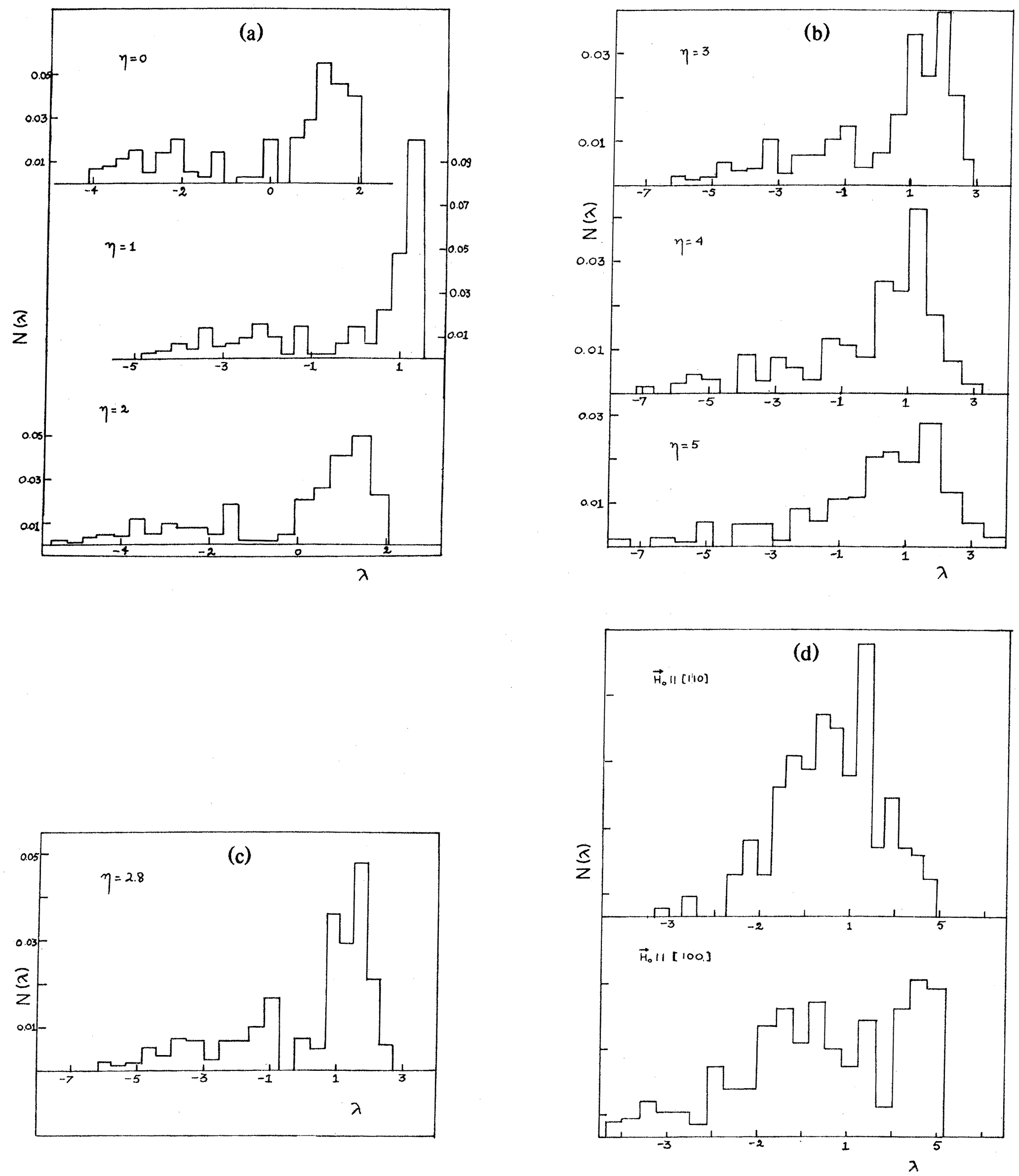

FIG. 2. (a),(b) Density of states $N(\lambda)$ of the fluctuations eigenvalues for $\eta = 0$, 1, 2, 3, 4, and 5. In these figures $N(\lambda)$ has been normalized to one. The histograms are calculated for 20 sections of the eigenvalue band. (c) Density of states $N(\lambda)$ for $\eta = 2.8$, the exchange coupling constant for copper nuclei. Here too $N(\lambda)$ has been normalized and the eigenvalue band divided in 20 sections. (d) Density of states $N(\lambda)$ for a truncated spin-dipolar Hamiltonian. The physical system is CaF_2. The upper curve shows the density of states for the external field $\vec{H}_0 \parallel [110]$ while the lower curve corresponds to $\vec{H}_0 \parallel [100]$.

interaction and is small compared to dipolar bandwidths. The interesting features are the forms of $N(\lambda)$ near the upper band edge. With the exception of $\eta = 1$, the histograms clearly show a positive δ and therefore a finite T_c. Even for $\eta = 1$ a finer histogram thickness reveals decrease in $N(\lambda)$ as λ approaches $\lambda_{\max}$. Figure 2(c) shows the density of states for copper ($\eta = 2.8$).

Figure 2(d) presents calculations for CaF_2, a system studied by Goldman *et al.*[3] in detail. The Hamiltonian for this system consists of only those terms that commute with the total spin. There is no RK interaction. Our calculations refer to the two magnetic field orientations with respect to the crytalline directions. For $\vec{H}_0 \parallel [100]$ direction, δ is quite small and this is reflected in a large change in T_c discussed later in Sec. III. For $\vec{H}_0 \parallel [110]$, the eigenvalue spectrum is more favorable for a phase transition again reflected in a relatively small decrease in T_c from its mean-field value. An important conclusion of these calculations is that, *in contrast to the mean-field theory predictions, the state* $\vec{H}_0 \parallel [110]$ *is more robust.*

III. THERMODYAMICS

The results are separated into several subsections.

A. T_c

The calculation of transition temperature T_c is strongly sensitive to numerical errors. In a discrete sum, the pole in Eq. (12) at $t_0 = \lambda_{\max}$ is divergent and $T_c = 0$. To study the temperature dependence more carefully, we calculated $\partial t_0 / \partial T$. Its temperature dependence consists of three different regions. At high temperatures it approaches $3k_B/2S(S+1)$, the Curie-Weiss value. At some intermediate temperatures, it drops rapidly but does not reach zero. Rather the actual decrease happens smoothly. If the last slow decrease is a result of numerical uncertainties, we can extrapolate the intermediate temperature $\partial t_0/\partial T$ to zero yielding a T_c. Another estimate of T_c can be obtained from the intersection of the low temperature $t_0(T)$ line with the intermediate temperature fall. The resulting T_c differs by a small amount, typically less than 10%.

The results from such a calculation of T_c are shown in Fig. 3 as a function of η. The functional dependence is similar to the one obtained in mean-field theory by KK. As η increases, the ferromagnetism, preferred by spin dipolar interaction is weakened and T_c decreases. The symmetry of the ground state also changes. The ferromagnetic state breaks up into periodic domains of opposite spin orientation. For $\eta > 1$, the ground state becomes progressively antiferromagnetic and the transition temperature increases. For all η, the fluctuation reduced T_c is related to mean field T_c^0 by the expression (in μK) $T_c = 1.19\, T_c^0 - 0.16$. For copper, $\eta = 2.8$ and thus $T_c = 0.1$ μK, a result not inconsistent with the experiments. The lowest temperatures reached so far are in the range of 0.1 μK.

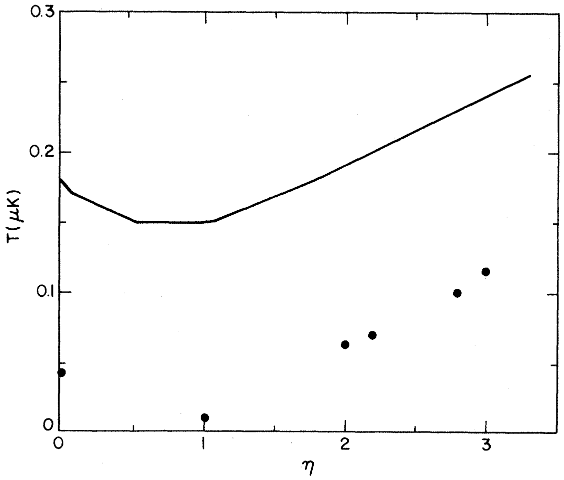

FIG. 3. The transition temperature T_c as a function of the exchange strength. The solid line shows the mean-field results. The points show the results of the spherical model calculation. The shift in T_c is a weak function of η.

One criticism of the spherical model has been the lack of a well-defined (even in principle) method to improve on this approximation and thus gauge its accuracy. The only possible test then is to study systems where T_c has been experimentally measured. Unfortunately in dielectrics where a transition to an ordered state has been seen,[2,16] the temperature has not been measured. We have however calculated T_c for CaF_2 for two different ground states[3] (static field $\vec{H}_0$ parallel to [001] or [110] axes) studied by Goldman *et al.*[3] For $\vec{H}_0 \parallel [001]$ we find $T_c = 0.17$ μK ($T_c^0 = 0.34$ μK^3) and for $\vec{H}_0 \parallel [110]$ we have $T_c = 0.2$ μK ($T_c^0 = 0.31$ μK^3). This could be an overestimate of the fluctuation effects. However yet another estimate of fluctuation effects can be found in Rushbrook and Wood's series expansion calculation for a nearest-neighbor exchange interaction (z being the coordination number)

$$\frac{T_c}{T_{cMF}} = \frac{5}{64}\left(1 - \frac{1}{Z}\right)\left(11 - \frac{1}{S(S+1)}\right) \tag{14}$$

approximately the same order of magnitude as our results.

B. Susceptibility

The fluctuations affect the susceptibility χ via the effective Curie constant C. In mean-field theory,

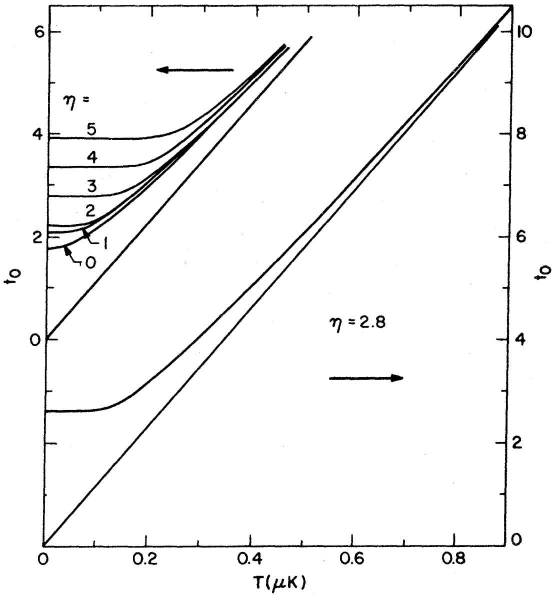

FIG. 4. The function $t_0(T)$ for several values of η. The susceptibility $\chi(T)$ is related to $t_0(T)$ so that $\underline{\chi}^{-1}(T)=2t_0(T)-\underline{\lambda}(q=0)$ and can be obtained by shifting the y axis by a constant $\lambda(q=0)$. Any departure from a linear temperature dependence in $t_0(T)$ can be interpreted as an effect of fluctuations on the Curie constant. $t_0(T)$ for copper ($\eta=2.8$) is shown separately over a wide temperature range.

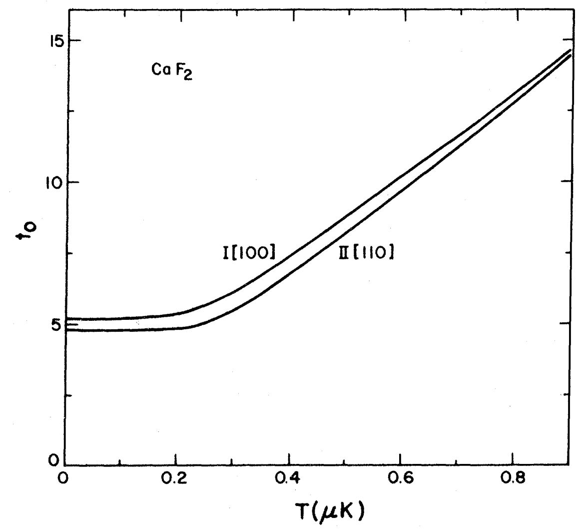

FIG. 5. The function $t_0(T)$ for CaF$_2$ for the two orientations of the magnetic field with respect to the crystalline axes. Curve I is calculated for field $\vec{H}_0$ parallel to [100] direction while curve II is calculated for $\vec{H}_0$ parallel to [100] direction. The temperature at which t_0 becomes a constant indicates the transition temperature. For I, $T_c=0.17$ μK and for II, $T_c=0.2$ μK. The mean-field values are, respectively, 0.34 and 0.31 μK (Ref. 3).

$\chi=C/(T+T_N)$ and one can identify $t_0^\infty=kT/2C$. Thus a departure from linear temperature dependence in t_0 can be interpreted as a temperature dependence of C due to the fluctuations. This effect can be isolated by subtracting the zero-temperature intercept in a χ^{-1} vs T plot. The resulting t_0 [see Eq. (12)] is shown in Fig. 4 for several values of η. We also show the calculated t_0 for $\eta=2.8$.

In Fig. 4, the antiferromagnetic states ($\eta>1$) have large deviations from the Curie-Weiss law, present over a wider range of temperatures. As η decreases, the effect of fluctuations decreases. In the $T_c-T_c^0$ relationship, the slope of the linear curve is larger than 1; signifying an increased effect on T_c for large η as well. The results for $\eta<1$ are less sensitive to the fluctuations.

Again, to compare with known systems, we calculate the susceptibility for CaF$_2$. The results are shown in Fig. 5 and refer to two possible orientations of the magnetic field with respect to the crystalline axes. The calculated susceptibility appears very close to the Curie-Weiss law indicating that the Curie constant is affected only weakly by the fluctuations due to the spin-flip terms of the Hamiltonian. The ground-state spin arrangement in the two cases is different resulting in different values of T_c.

C. Entropy and internal energy

The results for entropy and internal energy for copper are shown in Fig. 6. For comparison, we show the entropy calculation for $\eta=0$ and 2.8. The results are limited to the disordered region and are sensitive to η. The surprising result is the excess observed entropy for temperatures below 0.15 μK. One expects the spherical model to overestimate the fluctuations. Indeed all of the thermodynamic measure-

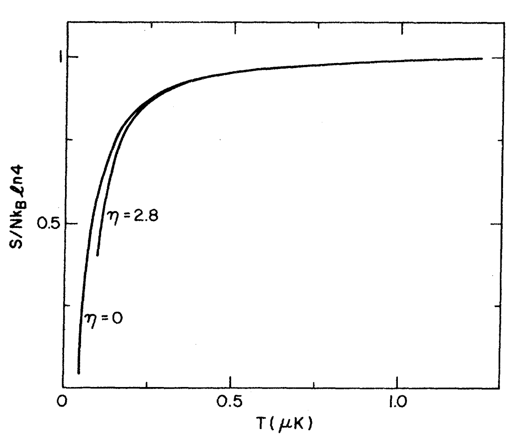

FIG. 6. The temperature-dependent entropy $\mathcal{S}(T)$ is shown for $\eta=0$ and $\eta=2.8$. The curves are drawn up to the transition temperature.

ments appear to have excess fluctuationlike effects at temperatures below 0.15 μK. We suspect the random magnetic field due to the spatial distribution of ^{65}Cu (concentration 30%, gyromagnetic ratio larger by 7%) as one possible source.[1]

D. High field effects

In the presence of an external magnetic field H_0, the parameter t_0 is determined from the equation [instead of Eq. (12)]

$$\beta S(S+1)=\frac{1}{2N}\sum_{q\mu}\frac{1}{t_0-\lambda_q^\mu}+\frac{\beta}{4}H_0^\mu[t_0\underline{1}-\underline{\lambda}_0]^{-1}_{\mu\nu}H_0^\nu \;, \tag{15}$$

where $\underline{\lambda}_0$ is the eigenvalue matrix for $q=0$. If the phase transition takes place at $t_0=\lambda_{\max}$ the shift in the transition temperature is given by

$$T_c(H)=T_c(0)(1-H^2/H_c^2) \;, \tag{16}$$

where $H_c=(\lambda_{\max}-\lambda_0)S(S+1)$ represents a critical field and depends on the orientation of the magnetic field. This calculation is valid only for nonferromagnetic states such that $\partial T_c/\partial H\leq 0$ and $\lambda_{\max}\neq\lambda_0$. In the latter cases ($\eta\neq 0$), the critical field is linearly dependent on ($\lambda_{\max}-\lambda_0$). For copper, it is about 3 G, in agreement with the experiments.

IV. MAGNETIC RESONANCE

A. $T>T_c$

The spin dynamics at high fields is relatively simple. The spins precess with Larmor frequency ω_L determined by the external field. Among the spin-spin interactions, the exchange interaction has no effect because of the Larmor's theorem. The dipolar interaction is usually too weak. The various interactions do determine the damping processes.

At low fields, the Larmor precession acquires demagnetization shifts. In copper, these dipolar shifts correspond to maximum of approximately 6-G field or a 7-kHz frequency shift. The dipolar interaction also causes coherent precession of two spins at frequency $2\omega_L$. This motion is affected by the exchange interaction in addition to the dipolar interaction and because of their comparable magnitude, the shifts are found to almost cancel each other. (The η used in earlier sections is determined from the small negative shift of the second harmonic.)

The spin dynamics at low fields can be studied beginning with the Liouville's equation

$$-i\hbar\dot{S}=[H,S],\quad H=H_{\text{ex}}+H_d \;. \tag{17}$$

The Hamiltonian H is described in Eq. (4) and in the presence of an external field H_0, includes the Zeeman term $-\vec{S}\cdot\vec{H}_0$. The spin motion is best studied in terms of $S^\pm=S^x\pm iS^y$ which yields, on evaluating all the commutators

$$\begin{aligned}\dot{S}^+=&-i\omega_0S^+ + i\sum_{ij}\frac{3}{(r_{ij})^3}(1-3\cos^2\theta)S_i^zS_j^+ - i\sum_{ij}\frac{3}{(r_{ij})^3}\sin\theta\cos\theta e^{-i\psi}S_i^+S_j^+\\&-i\sum_{ij}\frac{1}{(r_{ij})^3}[3\sin\theta\cos\theta e^{i\psi}(S_i^-S_j^+-2S_i^zS_j^z)-\sin^2\theta e^{2i\psi}S_i^-S_j^z]\end{aligned} \tag{18}$$

Here $S=\sum_i S_i$ with S_i representing spins at site i. r_{ij} is a lattice vector with polar coordinates θ and ψ and ω_0 represents the unshifted Larmor frequency.

On taking averages, if $\langle S_i^zS_j^+\rangle$ is factored out as $\langle S_i^z\rangle\langle S_j^+\rangle$, a random-phase-type approximation, then the second term yields the demagnetization shifts, the magnitude of the shifts being proportional to the polarization. The next two terms, if treated this way, provide a shift proportional to the transverse magnetization, negligible since the transverse field is zero.

If, however these terms are viewed as operators with their own dynamics, the S^+S^+ term corresponds to correlated precession of two spins at $2\omega_0$ while S^-S^+ and S^zS^z terms correspond to correlated $\omega=0$ excitations. These excitations have negligible intensity at high fields (proportional to ω_0^{-2}). At low fields, especially in the frequency region of interest where the shifted ω_L and ω_{2L} are equal, the coupling to the second harmonic cannot be ignored. To consider them we write the equation of motion for

$$\begin{aligned}X=&\sum_{ij}(r_{ij})^{-3}\sin\theta\cos\theta e^{-i\psi}S_i^+S_j^+ \;,\\H_{\text{ex}}=&\tfrac{1}{2}\sum_{ij}A_{ij}\vec{S}_i\cdot\vec{S}_j \;,\\\dot{X}=&-2i\omega_0X+2\sum_{ki}A_{ki}S_k^z\sum_j(r_{ij})^{-3}\sin\theta\cos\theta e^{-i\psi}S_i^+S_j^+-12\sum_{kij}(r_{ik})^{-3}(r_{ij})^{-3}(1-3\cos^2\theta_{ik})(\sin\theta_{ij}\cos\theta_{ij}e^{-i\psi}ij)S_k^zS_i^+S_j^+\\&+18\sum_{kij}(r_{ik})^{-3}(r_{ij})^{-3}\sin\theta_{ij}\cos\theta_{ij}\sin\theta_{ik}\cos\theta_{ik}S_k^zS_i^zS_j^+ + \cdots \;.\end{aligned} \tag{19}$$

We have retained only those terms that (a) contain powers of S^z, the polarization and (b) couple to S^+ or (c) provide frequency shifts in X motion. The terms that have been ignored include $S^+S^+S^+$ that represent coupling to ω_{3L} absorption.

Assuming translational invariance (except in evaluation of the demagnetization shifts), the Eqs. (18) and (19) can be rewritten in a form suitable for data analysis

$$\dot{S}^+ = -i(\omega_0 + 2\pi\langle S^z\rangle\rho)S^+ + X \quad , \tag{20}$$

$$\dot{X} = -2i[\omega_0 + 4\pi(\tfrac{1}{3} + R)\langle S^z\rangle\rho]X - iAS^+ \quad , \tag{21}$$

$$A = 18\sum_{kl}(r_{lj})^{-3}\cos\theta_{lj}\sin\theta_{lj}e^{-i\psi lj} \times (\gamma_{kl})^{-3}\cos\theta_{kl}\sin\theta_{kl}e^{-i\psi kl}\langle S_k^z S_l^z\rangle \quad , \tag{22}$$

and $R = \sum_i A_{ij}$. In Ref. 11 this set of equations have been used to analyze the NMR results. The shift in ω_{2L} ($\Delta\omega_{2L} = -2$ kHz) has been used to determine R and used in the calculations of Sec. III. The quantity A had been treated as an adjustable parameter. Using spherical model, we can determine A and find it (a) weakly dependent on the polarization consistent with the assumption in Ref. 11 where the polarization dependence has been ignored and (b) $\sqrt{A}/2\pi = 2.15$ kHz at $T = 2.6$ K and $\sqrt{A}/2\pi = 2.12$ kHz at $T = 0.1$ μK. The experiments yield $\sqrt{A}/2\pi = 3.1$ kHz. The difference in view of the simple nature of Eqs. (18) and (19) is insignificant.

B. $T < T_c$

The KK ground state can be used to calculate possible shifts in the ordered state. Since the ground state is antiferromagnetic the NMR frequency shift will be given by a geometric mean[17] of the anisotropy energy and the exchange energy. The KK ground state however is fully isotropic and the anisotropy energy is zero. As a result, the ordered state would not have substantial shifts in the resonance frequency (with the exception of demagnetization effects 5–6 kHz). Finally even if the ground state were anisotropic, since the exchange interaction is of comparable magnitude, the shift would remain in the 5–6 kHz region. For the same reason, there is no exchange narrowing in the system. The temperature dependence of the shift can be used to measure order parameter temperature dependence ($\Delta\omega \sim M^2$).

V. SUMMARY AND DISCUSSION

We have studied the static and dynamic properties of an assembly of spins interacting via spin dipolar interaction and an exchange interaction of variable magnitude. The calculations have been done using the spherical model. The ground state of these spins is expected to be a commensurate spin-density wave state.

Among the thermodynamic properties, the transition temperature to the ordered state T_c has been reduced due to the fluctuations from its mean-field value. The functional dependence of T_c on η remains qualitatively the same. The T_c decreases until $\eta = 1$ and then begins to increase again. The fluctuation contribution to the thermodynamic observables is found to be in agreement with experiments on copper nuclei. The strength of the exchange interaction in copper is obtained from independent NMR experiments. For copper these are the first principle calculations without any adjustable parameters.

The transition appears to be second order in the Ehrenfest sense. However the possibility of a first-order transition cannot be investigated within the present frame work; nor can we look at the possibility of an alternative ground state. Within the spherical model, the solutions of Eq. (2) are noninteracting. The interaction between them appears when we consider a restriction (in addition to the spherical approximation) on the fourth power of the spin vectors

$$Z = \int D[S(r)]\dot{\delta}\left(\sum_i S_i^2 - NS(S+1)\right) \times \delta\left(\sum_j S_j^4 - NS^2(S+1)^2\right)\exp(-\beta H) \quad . \tag{23}$$

The second delta function can be written in its integral representation. The upshot is the appearance of quartic terms like in a Ginzburg-Landau-Wilson functional with coefficients determined by saddle point methods. A detailed investigation of this problem remains beyond the scope of this paper.

In magnetic resonance, we present a microscopic derivation of equations that have been used to analyze the experimental data. The equations describe coupled correlated motion of the spins. The coupling constant $\sqrt{A}$, in the experiments, has been considered as a polarization independent fitting parameter. Using spherical model, we can calculate A and find it almost independent of the polarization and close to the fitted value. For the ordered state, we expect small temperature dependent shifts in the NMR frequency. Unlike an electronic antiferromagnet where a noncubic ground state can have large exchange-amplified NMR frequency shifts, copper spins have weak exchange interaction and even anisotropic ground states would give rise to shifts only of the order of 5 kHz.

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[1] A summary of results for copper has been reported in P. Kumar, M. T. Loponen, and L. H. Kjäldman, Phys. Rev. Lett. 44, 493 (1980).

[2] M. Goldman, Phys. Rep. 32, 1 (1977).

[3] M. Goldman, M. Chapellier, Vu Hoang Chau, and A. Abragam, Phys. Rev. B 10, 22 (1974).

[4] C. Kittel, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1968), Vol. 22.

[5] L. H. Kjäldman and J. Kurkijärvi, Phys Lett. 77A, 454 (1979).

[6] G. Ehnholm, J. P. Ekstrom, J. F. Jacquinot, M. T. Loponen, O. V. Lounasmaa, and J. K. Soini, Phys. Rev. Lett. 42, 1702 (1979); J. Low Temp. Phys. (in press).

[7] T. H. Berlin and M. Kac, Phys. Rev. 86, 821 (1952). For a recent review see G. S. Joyce, in *Phase Transition and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2.

[8] R. Brout, Phys. Rev. 122, 469 (1961).

[9] H. E. Stanley, Phys. Rev. 176, 18 (1968).

[10] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).

[11] J. P. Ekstrom, J. F. Jacquinot, M. T. Loponen, J. K. Soini, and P. Kumar, Physica (Utrecht) 98B, 45 (1979).

[12] N. D. Mermin and D. Wagner, Phys. Rev. Lett. 17, 1133 (1966).

[13] M. Cohen and F. Keffer, Phys. Rev. 99, 1128 (1955).

[14] M. Lax, J. Chem. Phys. 20, 1351 (1952).

[15] In spin-glasses with ferromagnetic interactions, the largest eigenvalue corresponds to a bound state — isolated from the band. Such a situation will be considered separately. See, however, J. Hertz, L. Fleishman, and P. W. Anderson, Phys. Rev. Lett. 43, 942 (1979).

[16] Y. Roinel, V. Bouffard, G. L. Bachella, M. Pinot, P. Meriel, P. Roubeau, O. Avenel, M. Goldman, and A. Abragam, Phys. Rev. Lett. 41, 1572 (1978).

[17] See, for example, S. Foner, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 1.