Nuclear magnetism in a metal

P. Kumar*
Low Temperature Laboratory, Helsinki University of Technology, SF-02150 Espoo 15, Finland

J. Kurkijärvi
Department of Technical Physics, Helsinki University of Technology, SF-02150 Espoo 15, Finland

A. S. Oja
Low Temperature Laboratory, Helsinki University of Technology, SF-02150 Espoo 15, Finland
(Received 17 May 1985)

We discuss the ordered-state properties of an assembly of nuclear spins, interacting via a classical dipolar and conduction-electron-mediated exchange interaction. The ground-state spin arrangement can be found by using a continuum model which casts light on the considerable degeneracy of the ground state. We have studied the effect of a magnetic field and have derived a set of equations for spin dynamics. We also discuss the implications of these results in specific examples such as Pt, Tl, Na, and Cu.

I. INTRODUCTION

Nuclear magnetism has become a subject of considerable activity in recent years.[1] The reasons for this are twofold: on the one hand, the quest for lower temperatures seems to have settled on adiabatic demagnetization of nuclear spins[2] as the best procedure. The only residual entropy in a system at ultralow temperatures that can be extracted by mechanical means (i.e., magnetic field) to produce even lower temperatures, belongs to nuclear spins. This approach is limited by the appearance of nuclear magnetic order and the accompanying reduction in entropy. The second reason for interest in nuclear magnetism is the simplicity and uniqueness of the nuclear-spin-spin interaction itself. In a dielectric, as extensively studied by Abragam and co-workers[1] at Saclay, the nuclear spins interact via the long-range classical dipole-dipole interaction. In the more familiar form of magnetism with electronic moment, there is a strong total-spin-conserving exchange interaction in addition to the total-spin-nonconserving dipolar interaction. The former dominates the local molecular fields, while the dipolar interaction determines the various relaxation times. Nuclear spins in a metal bridge these two regimes.

This paper is about nuclear magnetism in metals. In a metal the conduction electrons mediate another form of spin-spin interaction. Because of the hyperfine coupling, a nuclear spin polarizes the conduction electrons, which is then sensed by the neighboring nuclear spins. This indirect exchange interaction [Ruderman and Kittel[3] (RK)] has been widely studied in the literature in the context of rare-earth compounds.[4] It depends on the band structure of the conduction electrons and, in the case of nuclear-spin interaction, on the hyperfine coupling constant. The same features also determine the Knight shift[5] and the nuclear-spin-lattice relaxation[5] time T_1. One would then expect a simple correlation between these quantities. Such a correlation indeed exists qualitatively.[5] Since both the dipolar and the RK interactions vary as r^{-3} at large distances, it is possible to define[6] a parameter η that measures the relative importance of the RK interaction. Copper, which has one of the largest[7] T_1T ($=1.2$ sK), corresponds to $\eta=0.7$. Thallium, on the other hand, has one of the shortest[8] T_1T ($=2.7\times10^{-3}$ sK) and, therefore, $\eta\simeq80$, implying a basically exchange-dominated system. Platinum has an intermediate value[9] for T_1 ($T_1T=3\times10^{-2}$ sK) and $\eta=50$, and is still essentially an exchange-dominated nuclear-spin system. Copper admits a direct determination of η based on experiments[10] on nuclear spins alone. The values quoted for platinum and thallium have been estimated on the basis of a rather imprecise expected increase of η proportional to T_1. We thus have a class of magnets where the ratio of spin-conserving and spin-nonconserving forces varies over a wide range.

The class of metals where nuclear magnetism can be studied is not large. Most metals become either electronic magnets or superconductors upon cooling and access to the nuclear-spin system is lost. However, when nuclear spins are accessible, they become a prototype clean system to study complex phenomena. Platinum is an interesting example. Only one isotope, ^{195}Pt, with the natural abundance of 34% has a nuclear spin, all others are nonmagnetic. By varying the isotope composition, it should be possible to dilute only the magnetic moments without affecting anything else. Effects associated with percolation and/or a spin glass with long-range interactions could then be studied.

The Hamiltonian of nuclear spins in a metal is given by

$$H=\frac{1}{2}\sum_{\substack{ij\\ \mu\nu}} S_i^{\mu}G_{ij}^{\mu\nu}S_j^{\nu}\ , \tag{1}$$

where

$$G_{ij}^{\mu\nu}=(\hbar)^2\sum_{ij}\frac{\gamma_i\gamma_j}{|\mathbf{r}_{ij}|^3}\{[1+\eta f(2k_F|\mathbf{r}_{ij}|)]\delta_{\mu\nu}-3(\hat{\mathbf{r}}_{ij})_\mu(\hat{\mathbf{r}}_{ij})_\nu\}\ . \tag{2}$$

Here S_i^μ is the μth component of the spin at site i with γ_i as the gyromagnetic ratio, and the previously mentioned quantity η measures the relative strength of the RK interaction. The varying γ_i allows for different isotopes. Furthermore, $f(x)$ is the range function that depends on the band structure of the conduction electrons and $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$ is the lattice vector between nuclear spins. The kernel of the interaction is anisotropic in spin space. The function $f(x)$ for a spherical Fermi surface[3,5] is given by

$$f(x)=\cos(x)-\sin(x)/x \tag{3}$$

with[5]

$$\eta=\frac{4\pi}{9}\gamma_e^2\hbar^2\rho_f|U_{k_F}(0)|^4\ , \tag{4}$$

where γ_e is the electron gyromagnetic ratio, ρ_f the density of states at the Fermi surface, and $U_{k_F}(0)$ the wave-function amplitude at the nuclear site.

An experimental determination of η usually involves the product $\eta g(q)$, where $g(q)$ represents the Fourier transform of $f(x)$. Frequently, $\eta g(q=0)$ is measured. Copper has been the most widely studied system of nuclear spins. The constant η has been determined[10] in two different experiments. At high fields, the two isotopes of copper, ^{63}Cu and ^{65}Cu (abundance ratio 7:3) have different Larmor frequencies due to the differing gyromagnetic ratios. The ratio of the absorption intensities at high polarization is different from the abundance ratio and can be understood in terms of the exchange enhancement of the exciting (transverse) fields. An analysis of the intensity ratio for two isotopes delivers $\eta g(0)$. Assuming the free-electron value for $g(0)$, this yields $\eta=0.7$. In the second experiment, at low fields and high polarizations, extra absorption was seen at roughly twice the Larmor frequency. There is a shift in that frequency which involves the exchange interaction via the coherent precession of two spins in the mode. An analysis of the results yields $\eta=0.7$. Thermodynamic quantities[11] such as magnetic susceptibility, entropy, and energy depend on the moments of the eigenvalue spectrum of the Hamiltonian kernel in Eq. (1). At this level, the agreement between a free-electron spherical Fermi surface and experiments becomes qualitative. Evidently, the nonspherical features of the Fermi surface play an important role. We will discuss this further later.

This paper is an analysis of the ground-state properties of a system described by the Hamiltonian of Eq. (1). To be specific, we have assumed a fcc lattice structure in the discussion of the ground-state spin arrangement of Sec. II. In Sec. III we study consequences of the presence of a magnetic field. Section IV consists of a discussion of spin dynamics. Finally, Sec. V includes a summary of conclusions with a brief discussion of the expected properties in four examples: copper, sodium, platinum, and thallium.

II. GROUND STATE

The ground-state spin arrangement can be obtained using mean-field approximation (MFA). Numerical results for the fcc lattice that include both the spin arrangement and the transition temperature as a function of η have been reported by Kjäldman and Kurkijärvi.[6]

The classical ground state of spins in a continuum can be found exactly. This helps in understanding the numerical results. Not only are many of the continuum results unaffected by the introduction of a discrete lattice, but it is often possible to estimate the nature of lattice effects. Unless otherwise specified, spins are treated as classical vectors. The kernel of the Hamiltonian of Eq. (1) is an operator in both spin and real spaces. Knowledge of the eigenfunctions of

$$\sum_{j\nu}G_{ij}^{\mu\nu}\phi_j^\nu=\lambda\phi_i^\mu \tag{5}$$

allows us to write

$$E=\tfrac{1}{2}\sum_{\mathbf{k},n}\lambda_n(\mathbf{k})|a_n(\mathbf{k})|^2\ , \tag{6}$$

$$\mathbf{S}(\mathbf{k})=\sum_n a_n(\mathbf{k})\boldsymbol{\phi}_n(\mathbf{k})\ , \tag{7}$$

where $\mathbf{S}(\mathbf{k})$ and $\boldsymbol{\phi}(\mathbf{k})$ are the Fourier transforms of $\mathbf{S}_i$ and $\boldsymbol{\phi}_i$, respectively. From Eq. (6) it is evident that the lowest energy state corresponds to the minimum of the eigenvalue $\lambda_n(\mathbf{k})$ as a function of $\mathbf{k}$, and the corresponding $\boldsymbol{\phi}_n(\mathbf{k})$ describes the arrangement of spins in a continuum. Fourier transformation diagonalizes Eq. (5) in real space and the spin space diagonalization is straightforward with the results

$$\lambda_1(\mathbf{k})=\frac{8\pi}{3}+\eta g(\mathbf{k}),\quad \hat{\boldsymbol{\phi}}_1(\mathbf{k})=\hat{\mathbf{k}}\ , \tag{8a}$$

$$\lambda_2(\mathbf{k})=\lambda_3(\mathbf{k}),\quad \hat{\boldsymbol{\phi}}_2(\mathbf{k})=\hat{\mathbf{d}}\quad(\hat{\mathbf{k}}\cdot\hat{\mathbf{d}}=0)\ , \tag{8b}$$

$$\lambda_3(\mathbf{k})=-\frac{4\pi}{3}+\eta g(\mathbf{k}),\quad \hat{\boldsymbol{\phi}}_3(\mathbf{k})=\hat{\mathbf{k}}\times\hat{\mathbf{d}}\ , \tag{8c}$$

and

$$g(k)=\bar{g}(k)-\sum_{\mathrm{BZ}}\bar{g}(k)\ ,$$
$$\bar{g}(k)=1+\frac{4k_F^2-k^2}{4kk_F}\ln\left|\frac{k+2k_F}{k-2k_F}\right|\ . \tag{8d}$$

Here $\bar{g}(k)$ is the Fourier transform of $f(x)$.[3,4] The equation relating $g(k)$ to $\bar{g}(k)$ accounts for the absence of self-interaction. The lower eigenvalue $\lambda_2(\mathbf{k})$ is doubly degenerate in spin space. Apart from the constraint that it should be orthogonal to $\hat{\mathbf{k}}$, the unit vector $\hat{\mathbf{d}}$ is arbitrary. The eigenvectors $\hat{\boldsymbol{\phi}}_i(\mathbf{k})$ constitute an orthogonal triad in the spin space. Since $\mathbf{k}$ is a continuous vector and $g(k)$ is a monotonically decreasing function of k, the wave vector corresponding to the minimum of $\lambda_2(\mathbf{k})$ is at infinity in a continuum. The cutoff maximum of $\mathbf{k}$ is imposed by the lattice. Detailed lattice calculations[6,12] show that the lowest eigenvalue lies at the high symmetry points $\mathbf{k}_0^j$ at the zone boundary in the $\langle 1,0,0\rangle$ directions: $\mathbf{k}_0^j=(2\pi/a)\hat{\mathbf{k}}^j$, $j=1,2,3$, where a is the lattice constant.

The ground state thus has a threefold degeneracy in $\mathbf{k}$ space and a twofold degeneracy in spin space.

The most general ground state can be written as a linear combination,

$$\mathbf{S}(\mathbf{r}_i)=\sum_j \mathbf{d}_j \exp(i\mathbf{k}_0^j\cdot\mathbf{r}_i)\ , \tag{9}$$

subject to the condition that $\mathbf{d}_j\cdot\mathbf{k}_0^j=0$. If we further require that $|\mathbf{S}(\mathbf{r}_i)|^2$ be independent of $\mathbf{r}_i$, the $\mathbf{d}$'s must satisfy $\mathbf{d}_i\cdot\mathbf{d}_j=|\mathbf{d}_i|^2\delta_{ij}$. It is then possible to write three possible degenerate ground states, classified according to the number of $\mathbf{k}$ vectors involved (see Fig. 1).

(1) The $1-\mathbf{k}$ state, the usual collinear antiferromagnetic referred to as type I [Fig. 1(a)]:

$$\mathbf{S}(\mathbf{r}_i)=\mathbf{d}_1\exp(i\mathbf{k}_0^1\cdot\mathbf{r}_i)\ . \tag{10}$$

The ferromagnetic planes with spins alternate as $\pm\mathbf{d}_1$ perpendicular to $\mathbf{k}_0^1$.

(2) The $2-\mathbf{k}$ state, shown in Fig. 1(b), is a four sublattice state, consisting of antiferromagnetic planes:

$$S(\mathbf{r}_i)=\mathbf{d}_1\exp(i\mathbf{k}_0^1\cdot\mathbf{r}_i)+\mathbf{d}_2\exp(i\mathbf{k}_0^2\cdot\mathbf{r}_i)\ . \tag{11}$$

In the above, $\mathbf{k}_0^1$ and $\mathbf{k}_0^2$ are a pair of energy minimum wave vectors. The relative orientation of the staggered magnetization between successive planes $(=|d_1|^2-|d_2|^2)$ in the direction $\hat{\mathbf{k}}_3$ is arbitrary

(3) The $3-\mathbf{k}$ state. This state too is a four sublattice antiferromagnetic state:

$$\mathbf{S}(\mathbf{r}_i)=\mathbf{d}_1\exp(i\mathbf{k}_0^1\cdot\mathbf{r}_i)+\mathbf{d}_2\exp(i\mathbf{k}_0^2\cdot\mathbf{r}_i)+\mathbf{d}_3\exp(i\mathbf{k}_0^3\cdot\mathbf{r}_i)\ . \tag{12}$$

The only restriction here is that the sum of the four sublattice magnetizations be zero. As shown in Fig. 1(c), this state has the highest degeneracy of the possible ground states.

All three of these states have been discussed by Kjäldman.[13] We will call these states KK states. Belobrov *et al.*[14] have studied the dipolar Hamiltonian in two dimensions numerically and report a state which can be interpreted as a $2-\mathbf{k}$ state.

The extensive degeneracy of the ground state within MFA must be lifted by additional unknown terms in the Hamiltonian of Eq. (1). No simple general principles argument appear to lift this degeneracy. The only symmetry-breaking field in the problem is the magnetic field.

III. MAGNETIC FIELD EFFECTS

A number of general results about the effect of a magnetic field on the ordered state can be found by studying the ground state at $T=0$. The Hamiltonian in Eq. (1) must now be supplemented by the Zeeman energy; within the MFA it shall be minimized subject to the constraint

$$\langle\mathbf{S}_i\rangle=\mathbf{B}_i/|\mathbf{B}_i|\ , \tag{13}$$

where the length of the spin vector has been normalized to one. As before, $\langle\mathbf{S}_i\rangle$ and $\mathbf{B}_i$ are the average spin and local magnetic fields. We use a generalization of the Luttinger-Tisza[1,15] method, i.e., we minimize the energy subject to the weaker constraints

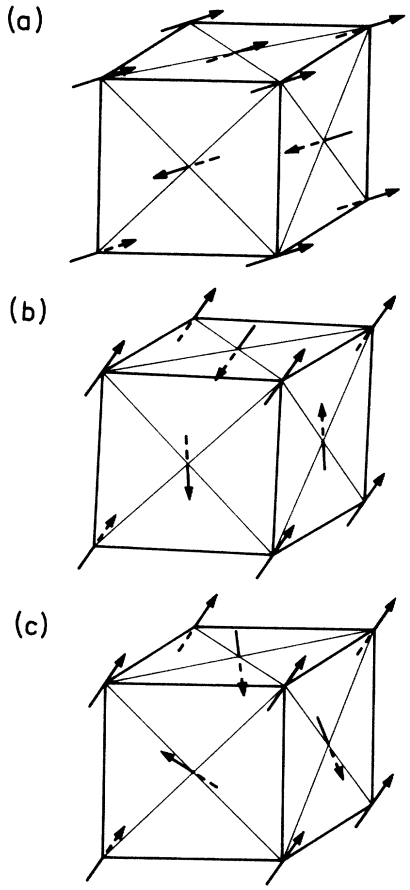

FIG. 1. Three possible ordered states are (a) $1-\mathbf{k}$, (b) $2-\mathbf{k}$, and (c) $3-\mathbf{k}$. The $1-\mathbf{k}$ state is the usual collinear type-I antiferromagnet. The $2-\mathbf{k}$ and $3-\mathbf{k}$ states are four sublattice states. In the $2-\mathbf{k}$ states, the spins in a plane are arranged antiferromagnetically. However, there is no correlation between the staggered magnetization between successive planes. In the $3-\mathbf{k}$ state, each plane has a finite moment. However, successive planes have moments oriented antiparallel to each other. The dashed line parts of the arrows present the part which is inside the conventional primitive cell.

$$\sum_i |\langle\mathbf{S}_i\rangle|^2=N \tag{14}$$

and

$$\sum_i(\langle S_i^\mu\rangle-B_i^\mu/|\mathbf{B}_i|)=0\ , \tag{15}$$

which are incorporated using Lagrangian multipliers. If the solution so obtained also satisfies Eq. (13), the stronger constraint, it is the solution we are looking for. The effective energy can then be written as

$$\langle H_{\rm MF}\rangle=-\tfrac{1}{2}\sum_i\mathbf{B}_i\cdot\langle\mathbf{S}_i\rangle-\tfrac{1}{2}\mathbf{B}_0\cdot\sum_i\langle\mathbf{S}_i\rangle-\frac{\lambda}{4}\left[\sum_i|\langle\mathbf{S}_i\rangle|^2-N\right]-\tfrac{1}{2}\mu\cdot\left[\sum_i(\mathbf{S}_i-\mathbf{B}_i/|\mathbf{B}_i|)\right]\ , \tag{16}$$

whose minimum is described by

$$\frac{\delta\langle H_{\rm MF}\rangle}{\delta\langle \mathbf{S}_i\rangle}=-\tfrac{1}{2}\mathbf{B}_i-\tfrac{1}{2}\mathbf{B}_0-\frac{\lambda}{2}\langle \mathbf{S}_i\rangle-\tfrac{1}{2}\mu=0\ . \tag{17}$$

In Eq. (16), the standard method of splitting up the Zeeman energy in two pieces has been used such that,

$$\mathbf{B}_i=\mathbf{B}_0-\sum_j \underline{G}_{ij}\cdot\langle \mathbf{S}_j\rangle \tag{18}$$

and λ and μ are the Lagrangian parameters. Since Eq. (17) must be valid for all sites i, it follows that

$$\mathbf{B}_0+\mu=0\ , \tag{19a}$$

$$\mathbf{B}_i+\lambda\mathbf{S}_i=0 \tag{19b}$$

with $\lambda<0$, the strong constraint Eq. (13) is then automatically satisfied. The energy can be written as

$$E=\frac{\langle H_{\rm MF}\rangle}{N}=\tfrac{1}{2}\lambda-\tfrac{1}{2}\mathbf{B}_0\cdot\langle \mathbf{S}(\mathbf{k}=0)\rangle\ , \tag{20}$$

where $\mathbf{S}(\mathbf{k})$ is the Fourier transform of $\langle \mathbf{S}_i\rangle$. Substituting Eq. (18) into Eq. (19b) and using $\sum_j \underline{G}_{ij}=\lambda(0)\underline{I}$, where I is a unit matrix, for a spherical sample,

$$\mathbf{d}_0=\langle \mathbf{S}(\mathbf{k}=0)\rangle=\mathbf{B}_0/[\lambda(0)-\lambda] \tag{21}$$

and

$$E=\tfrac{1}{2}\lambda-\tfrac{1}{2}\,|\,\mathbf{B}_0\,|^2/[\lambda(0)-\lambda]\ . \tag{22}$$

The Lagrangian multipliers λ satisfies the eigenvalue Eq. (5). It is not immediately clear whether the ground-state wave vector in the presence of a finite field in an arbitrary direction with respect to the crystalline axes of a fcc lattice is the same as the zero-field wave vector $\mathbf{k}_0^j$. Suppose that an alternative state characterized by λ' (where $0>\lambda'>\lambda_{kk}$; λ_{kk} being the eigenvalue of the KK state) has a lower energy for $B_0>B_c$. Then B_c would have to satisfy

$$B_c^2=[\lambda(0)-\lambda_{kk}][\lambda(0)-\lambda']\ . \tag{23}$$

The magnetization for this state would be

$$|\,\mathbf{d}_0'\,|=\left[\frac{\lambda(0)-\lambda_{kk}}{\lambda(0)-\lambda'}\right]^{1/2}>1\ , \tag{24}$$

and it would violate the condition $|\,\langle \mathbf{S}(\mathbf{k}=0)\rangle\,|\leqq 1$. A simple substitution is sufficient to demonstrate that the solution

$$\langle \mathbf{S}_i\rangle=\mathbf{d}_0+\sum_{j=1}^{3}\mathbf{d}_j\exp(i\mathbf{k}_0^j\cdot\mathbf{r}_i) \tag{25}$$

satisfies the strong constraint Eq. (13). The conditions on the $\mathbf{d}$'s then are

$$|\,\mathbf{d}_0\,|^2+\sum_{j=1}^{3}|\,\mathbf{d}_j\,|^2=1 \tag{26}$$

and

$$\begin{aligned}&\mathbf{d}_0\cdot\mathbf{d}_1+\mathbf{d}_2\cdot\mathbf{d}_3=0\ ,\\ &\mathbf{d}_0\cdot\mathbf{d}_2+\mathbf{d}_1\cdot\mathbf{d}_3=0\ ,\\ &\mathbf{d}_0\cdot\mathbf{d}_3+\mathbf{d}_1\cdot\mathbf{d}_2=0\ .\end{aligned} \tag{27}$$

The four equations along with the constraint $\mathbf{d}_j\cdot\hat{\mathbf{k}}_j=0$ are sufficient to determine coefficients of Eq. (25). In sum then, Eq. (25) along with Eq. (21) are finite-field solutions. At the field $B_c=\lambda(0)-\lambda_{kk}$, there is a continuous transition to a polarized paramagnetic state. These results seem to be anticipated already by Luttinger and Tisza.[15]

The effect of finite temperature is to scale the vectors $\mathbf{d}_j$ $(j=1,2,3)$ so that

$$|\,\mathbf{d}_0\,|^2+\sum_{j=1}^{3}|\,\mathbf{d}_j\,|^2=p^2\ , \tag{28}$$

where p is the polarization, determined[16] (B_S is the Brillouin function for spin S) by

$$p(T)=B_S[\alpha p/(T/T_c)],\quad \alpha=3S/(S+1) \tag{29}$$

and

$$k_B T_c=-\tfrac{1}{3}S(S+1)(\hbar\gamma)^2\rho\lambda_{kk}\ , \tag{30}$$

where ρ is the number density. The susceptibility $\underline{\chi}(B_0,T)$ is independent of temperature and field and is isotropic for a spherical sample

$$\underline{\chi}(\mathbf{B}_0,T)=[\lambda(0)-\lambda_{kk}]^{-1}\underline{I}\ . \tag{31}$$

The critical field $B_c(T)$ is given by

$$B_c(T)=[\lambda(0)-\lambda_{kk}]p(T)\ . \tag{32}$$

IV. SPIN DYNAMICS

It would be nice to be able to perform an analysis of the NMR response of the ordered nuclear spins in the spirit of the adiabatic analysis used by Leggett[17] in his theory of ^{3}He spin dynamics. The result would be useful in determining experimentally the kind of order the nuclei maintain in as much as the NMR frequencies depend on the spin arrangement.[18] This works for the strongly exchange-dominated systems. Only when the RK interaction is much stronger than the dipolar interaction, does one have the strong interaction which maintains the quasiconserved components of the order parameter. This is, for example, the case in Pt. Application of the spin-dynamics discussion below to copper is questionable.

The $\mathbf{d}$'s of Eq. (25) can be separated into equilibrium and nonequilibrium terms:

$$\mathbf{d}_j=\mathbf{d}_j^0+\mathbf{d}_j',\quad j=0,1,2,3 \tag{33}$$

where $\mathbf{d}_j^0$ are the coefficients of the equilibrium ground state and $\mathbf{d}_j'$ are small deviations. Since $\mathbf{d}_j$ is no more orthogonal to $\hat{\mathbf{k}}_j$, we can express the local field

$$\begin{aligned}\mathbf{B}_i=\mathbf{B}_0-\lambda(0)\mathbf{d}_0-\lambda_{kk}\sum_j\mathbf{d}_j\exp(i\mathbf{k}_0^j\cdot\mathbf{r}_i)\\ -(\lambda_1-\lambda_{kk})\sum_j(\mathbf{d}_j\cdot\hat{\mathbf{k}}_j)\hat{\mathbf{k}}_j\exp(i\mathbf{k}_0^j\cdot\mathbf{r}_i)\ ,\end{aligned} \tag{34}$$

where λ_1 is the larger eigenvalue as discussed in Eq. (8a). Defining $\lambda_D=\lambda_1-\lambda_{kk}$, we have basically an easy-plane anisotropy of the form $\lambda_D(\mathbf{d}_j\cdot\hat{\mathbf{k}}_j)^2$ in the total energy of the system, akin to the ^{3}He examples mentioned above. This energy comes from the dipolar interaction which does not conserve the total spin and, therefore, causes a shift in the Larmor frequency.

By substituting Eq. (34) into the Bloch equation, it is possible to derive, for small departures from equilibrium, the equations of spin dynamics

$$\frac{1}{\gamma}\dot{\mathbf{d}}_0'=\mathbf{d}_0'\times\mathbf{B}_0-\lambda_D\sum_{j=1}^{3}(\mathbf{d}_j^0\times\hat{\mathbf{k}}_j)(\mathbf{d}_j'\cdot\hat{\mathbf{k}}_j)\ , \tag{35a}$$

$$\begin{aligned}\frac{1}{\gamma}\dot{\mathbf{d}}_1'=\frac{1}{\chi}\mathbf{d}_0'\times\mathbf{d}_1^0-\lambda_D[&(\mathbf{d}_0^0\times\hat{\mathbf{k}}_1)(\mathbf{d}_1'\cdot\hat{\mathbf{k}}_1)\\&-(\mathbf{d}_2^0\times\hat{\mathbf{k}}_3)(\mathbf{d}_3'\cdot\hat{\mathbf{k}}_3)\\&-(\mathbf{d}_3^0\times\hat{\mathbf{k}}_2)(\mathbf{d}_2'\cdot\hat{\mathbf{k}}_2)]\ .\end{aligned} \tag{35b}$$

Here the magnetic field $\mathbf{B}_0$ includes the demagnetization corrections. Equations for $\mathbf{d}_2$ and $\mathbf{d}_3$ can be obtained from Eq. (35b) by cyclic permutation of indices 1,2,3. Here χ is the static susceptibility, Eq. (31). The four equations constitute a complete description of the classical spin dynamics in the ground state of exchange-dominated nuclear spins.

The relationship between these equations and the Leggett equations[17,18] is best seen if we limit ourselves to a $1-\mathbf{k}$ state (without linearization)

$$\frac{1}{\gamma}\dot{\mathbf{d}}_0=\mathbf{d}_0\times\mathbf{B}_0-\lambda_D(\mathbf{d}_1\times\hat{\mathbf{k}}_1)(\hat{\mathbf{k}}_1\cdot\mathbf{d}_1)\ , \tag{36a}$$

$$\frac{1}{\gamma}\dot{\mathbf{d}}_1=\mathbf{d}_1\times(\mathbf{B}_0-\mathbf{d}_0/\chi)-\lambda_D(\mathbf{d}_0\times\hat{\mathbf{k}}_1)(\hat{\mathbf{k}}_1\cdot\mathbf{d}_1)\ . \tag{36b}$$

The important difference lies in the presence of the last term in Eq. (36b).

The solution of Eqs. (35) is considerably facilitated by the observation that only three (out of nine) components of $\mathbf{d}_i$, $i=1,2,3$ are relevant. These are the components of $\mathbf{d}_i$ parallel to $\hat{\mathbf{k}}_i$ since

$$\frac{1}{\gamma}(\dot{\mathbf{d}}_i')_i=\frac{1}{\chi}(\mathbf{d}_0'\times\mathbf{d}_i^0)_i,\quad i=1,2,3\ . \tag{37}$$

The resonance frequencies are identical to the ones found for solid ^{3}He by Osheroff, Cross, and Fisher.[18] For a $1-\mathbf{k}$ state with $\hat{\mathbf{k}}_1=\hat{\mathbf{x}}$, $\mathbf{d}_1^0=|\,\mathbf{d}_1^0\,|\,\hat{\mathbf{y}}$, and $\mathbf{B}=B_0(\sin\theta\hat{\mathbf{x}}+\cos\theta\hat{\mathbf{z}})$,

$$\begin{aligned}\frac{\omega^2}{\gamma^2}=\tfrac{1}{2}\Bigg[&\left(B_0^2+\lambda_D\frac{|\,d_1^0\,|^2}{\chi}\right)\\&\pm[(B_0^2-\lambda_D\,|\,d_1^0\,|^2/\chi)^2\\&+4B_0^2\sin^2\theta\lambda_D\,|\,d_1^0\,|^2/\chi]^{1/2}\Bigg]\ .\end{aligned} \tag{38}$$

In solid ^{3}He, d_1^0 can be assumed independent of the magnetic field. The energy scale for its variation is determined by the exchange interaction, a much larger quantity. For nuclear spins in copper, d_1^0 varies with field according to Eqs. (20) and (24).

V. SUMMARY AND CONCLUSIONS

While the results of the present paper are mostly general, a certain preference has been given to monovalent metals with cubic lattice structure and exchange dominance. This preference is responsible for the absence of any discussion of ground states with wave vectors less than the zone boundary value.[6] If we assume a free-electron-like RK range function, a strong exchange brings the ground-state $\mathbf{k}$ vector to the zone boundary in the cubic symmetry directions. The physical properties of these states can be understood in the simple framework of a continuum model. We have further calculated the changes in the ground state brought about by a magnetic field and have derived equations for spin dynamics. The latter resemble the Leggett equations well known in the context of superfluid ^{3}He and magnetically ordered solid ^{3}He. The applicability of these results to specific examples is discussed below.

A. Strong exchange: platinum and thallium

Both platinum and thallium are strongly exchange dominated. As discussed in the Introduction, the estimated η for Pt and Tl are 50 and 80. The Tl lattice structure is hcp and gives rise to only twofold degeneracy of the $\mathbf{k}$ vectors in the basal plane. The ground state for Tl is, therefore, expected to be a $1-\mathbf{k}$ or a $2-\mathbf{k}$ (spiral) spin-density wave. It should be possible to determine η for Tl directly with an isotope-effect experiment. There are two isotopes ^{203}Tl and ^{205}Tl in the abundance ratio 3:7. The gyromagnetic ratios differ by 1%. Thallium is expected to have a $T_c=10\,\mu$K. An approximate estimate of T_c for an isotopically pure sample of ^{195}Pt is 1 μK. Both Pt and Tl have T_c's in the accessible range of electron temperatures and it should, therefore, be possible to cool the nuclear spins in a state of equilibrium with the lattice eliminating the problem of short spin-lattice times. Platinum is quite extraordinary since it affords an ideal opportunity to study the effects associated with dilute magnetism in an isotopically, i.e., "cleanly," doped system.

The exchange interaction in this class of systems is no longer as simple as the one described by Eqs. (1)–(4). More precisely, the non-s-wave character of conduction electrons in these high-Z materials gives rise to alternative media for nuclear-spin interaction. A detailed analysis of the nuclear-spin-lattice relaxation time in selected transition metals[19] shows that while such effects in copper can be small, although perhaps not entirely negligible, they are rather large in Pt and Tl. The Knight shift in Pt, known to be negative, has been understood as an effect of core polarization. We defer a detailed analysis of these effects until later.

B. Weak exchange: copper and sodium

Copper is by far the most widely studied nuclear-spin metal. Essentially the entire discussion above is motivated by the need to understand its properties in the spin-

ordered state. The ordering in copper occurs[20] at 60 nK, via a first-order phase transition,[21] into an antiferromagnetic state. The various thermodynamic and NMR properties in the paramagnetic phase have been analyzed[10,11,22] using the eigenvalue spectrum discussed in Sec. II. The agreement with experiments is good. In the ordered state, a phase diagram in the field-entropy plane has been suggested[23] with the aid of susceptibility measurements. According to this, the system undergoes a first-order phase transition at 60 nK in an antiferromagnetic (AF) phase at zero field. At fields B_0, $0.12 < B_0 < 0.17$ mT, another ordered state AF2 seems to appear. In fields with $B_0 > 0.17$ mT, the nuclear spins line up gradually with the external field leading to a polarized paramagnetic state at $B = 0.27$ mT. The low-field AF1 and the high-field AF3 states can be interpreted as being consistent with the states discussed in Sec. III. Although transitions within the mean-field approximation are continuous, the cubic symmetry of the system may lead to a fluctuation-induced first-order transition.

It is also possible that nonzone-boundary **k**-vector states appear in copper. On the fcc lattice, the ground state $\mathbf{k}_0$ is locked to the zone boundary for $\eta > \eta_c = 0.52$. It may be instructive to view the problem in terms of the Fourier components of the RK interaction. As discussed in the Introduction, experiments in the paramagnetic state largely determine either $\eta g(0)$ or some moment over the density of states. If the RK interaction does not have the free-electron range function, and "effective" η could be different for properties that depend on the ground state and, therefore, a specific nonzero $\mathbf{k}_0$. A preliminary investigation[24] shows that if the nearest-neighbor coupling is changed by as little as 15%, the effective η falls below η_c. Then the **k** vector of the ground state depends on both the external magnetic field and the temperature.

On the basis of Knight-shift measurements it is possible to estimate $\eta = 0.13$ for sodium.[25] The ground state for sodium is expected to correspond to a nonzone-boundary wave vector. Such a state must be highly sensitive to a magnetic field and it probably displays the usual commensurate lock-in transitions at varying values of temperature and magnetic field. Unfortunately, sodium has a rather low mean field T_c (60 nK) and is expected to get even lower due to fluctuations.[25] With the improvement in cooling techniques, however, it should be possible to explore the effects of competing interactions in sodium.

In conclusion, the properties of the ground state of a system described by the Hamiltonian of Eq. (1) are rich and diverse. Further experimental investigation of these systems would considerably help elucidate our understanding of this exotic type of magnetism.

ACKNOWLEDGMENTS

We acknowledge useful discussions with K. Andres, E. Dormann, B. Harmon, M. Steiner, N. Sullivan, G. Volovik, W. Wolf, and various members, past and present, of the Low Temperature Laboratory, in particular M. Huiku, M. Krusius, M. T. Loponen, M. Salomaa, and O. V. Lounasmaa. One of us (P.K.) is grateful for the hospitality of the Low Temperature Laboratory where this work was done. This work was partially supported by National Science Foundation Grant No. DMR 8006311.

*Permanent address: Department of Physics, University of Florida, Gainesville, FL 32611.

[1]A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder* (Clarendon, Oxford, 1982).

[2]K. Andres and O. V. Lounasmaa in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1982), Vol. VIII, p. 222.

[3]M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954). For a review, see C. Kittel, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 22, p. 1.

[4]T. Kasuya, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. II B, p. 215.

[5]C. P. Slichter, *Principles of Magnetic Resonance* (Springer, Berlin, 1978), contains an extensive discussion of these effects.

[6]L. H. Kjäldman and J. Kurkijärvi, Phys. Lett. **71A**, 454 (1979). The definition of η in this paper is somewhat eccentric in that it includes an additional factor that makes $\eta = 1$ for copper for the coupling constant obtained by the Knight measurements. To transfer their values of η to ours, multiply by 0.26.

[7]G. J. Ehnholm, J. P. Ekström, J. F. Jacquinot, M. T. Loponen, O. V. Lounasmaa, and J. K. Soini, J. Low Temp. Phys. **39**, 417 (1980).

[8]G. Eska and K. Andres (private communication).

[9]R. G. Gylling, Acta Polytech. Scand. **81**, 1 (1971).

[10]J. P. Ekström, J. F. Jacquinot, M. T. Loponen, J. K. Soini, and P. Kumar, Physica **98B**, 45 (1979).

[11]L. H. Kjäldman, P. Kumar, and M. T. Loponen, Phys. Rev. B **23**, 2051 (1981).

[12]A. S. Oja and M. M. Salomaa, J. Phys. C **17**, L187 (1984).

[13]L. H. Kjäldman, Diploma thesis, Helsinki University of Technology (1979).

[14]P. I. Belobrov, R. S. Gekht, and V. A. Ignatchenko, Zh. Eksp. Teor. Fiz. **84**, 1097 (1983) [Sov. Phys.—JETP **57**, 636 (1983)].

[15]J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946); **72**, 257 (1947).

[16]See, for example, D. C. Mattis, *The Theory of Magnetism* (Harper and Row, New York, 1965).

[17]A. J. Leggett, Ann. Phys. (N.Y.) **85**, 11 (1974).

[18]D. D. Osheroff, M. C. Cross, and D. S. Fisher, Phys. Rev. Lett. **44**, 792 (1980); M. C. Cross, Physica **109&110B**, 1796 (1982).

[19]T. Asada, K. Terakura, and T. Jarlborg, J. Phys. F **11**, 1847 (1981). For relativistic corrections to the contact interaction in Cu, see H. Ebert, H. Winter, and J. Voitländer, J. Phys. F **14**, 2433 (1984).

[20]M. T. Huiku and M. T. Loponen, Phys. Rev. Lett. **49**, 1288 (1982).

[21]M. T. Huiku, T. A. Jyrkkiö, and M. T. Loponen, Phys. Rev. Lett. **50**, 1516 (1983).

[22]P. Kumar, M. T. Loponen, and L. H. Kjäldman, Phys. Rev. Lett. **44**, 493 (1980).

[23]M. T. Huiku, T. A. Jyrkkiö, J. M. Kyynäräinen, A. S. Oja, and O. V. Lounasmaa, Phys. Rev. Lett. **53**, 1692 (1984).

[24]A. S. Oja and P. Kumar, Physica **126B&C**, 451 (1984).

[25]K. J. Niskanen, L. H. Kjäldman, and J. Kurkijärvi, J. Low Temp. Phys. **49**, 241 (1982).