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Coupling of the Larmor precession to the correlated motion of pairs of nuclear spins in noble metals

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The coupling of the Larmor line to pairs of nuclear spins being flipped by one photon is studied for the nuclear-spin system in the noble metals. The coupling parameter has been evaluated using the spherical model. The separation of the NMR frequencies of the Larmor line and the double-spin-flip line is calculated. The anticrossing feature in the Larmor-line frequency due to the coupling of the two modes is calculated in order to determine if the strength of the Ruderman-Kittel exchange interaction can be measured in Ag and Au.

INTRODUCTION

Spin absorption corresponding to a single photon flipping two nuclear spins was first observed indirectly by Anderson[1] using a field-cycling technique. The advent of a superconducting-quantum-interference-device NMR has made it possible to directly observe the double-spin-flip mode at low temperatures and high nuclear-spin polarizations.[2,3] The coupling of the single-spin-flip (Larmor) and double-spin-flip modes and their anticrossing behavior have been used to measure the strength of the Ruderman-Kittel (RK) interaction in copper[2] at micro-Kelvin temperatures. The double-spin-flip mode was not observed in silver at nano-Kelvin temperatures.[4,5] To predict if the coupling of the two modes can be used to determine the strength of the RK interaction in Au, and to understand why the double-spin-flip mode was unobserved in Ag, we have calculated the intensity of the double-spin-flip mode and the anticrossing behavior for all three metals.

INTENSITY OF THE NMR LINES

The resonance frequency and the intensity of the two modes are determined from a study of their coupled equations of motion. The Larmor mode corresponds to the operator $S^+=\sum_j(s_j^x+is_j^y)$, which is the operator of interest in NMR, and describes a single spin being flipped by one photon. Double-spin flips correspond to the operator $s_i^+s_j^+$, which describes two spins flipped by one photon.

The equations of motion for the single- and double-spin-flip operators are derived from Liouville's equation. The nuclear-spin interaction has the form

$$H=-\frac{1}{2}\sum_{i,j}J_{ij}\mathbf{s}\cdot\mathbf{s}_j+\frac{1}{2}\frac{\mu_0\hbar^2\gamma^2}{4\pi}\times\sum_{i,j}\left\{\frac{\mathbf{s}_i\cdot\mathbf{s}_j-3\left[\mathbf{s}_i\cdot\mathbf{r}_{ij}\right]\left[\mathbf{s}_j\cdot\mathbf{r}_{ij}\right]}{r_{ij}^3}\right\}, \quad (1)$$

where $\mathbf{r}_{ij}$ is the lattice vector from spin i to spin j, and γ is the nuclear gyromagnetic ratio. There is no quadrupole interaction due to the cubic symmetry of the noble metals. The terms that are neglected after evaluating the commutators in Liouville's equation correspond to higher-order spin flips and cross terms involving the spin polarization and more than one ladder operator. The equations of motion without the rf excitation field have the form[2,6]

$$\dot{S}^+=-i(\omega_0+\tfrac{1}{2}\mu_0\hbar\gamma^2\rho sp)S^++iX \quad (2)$$

and

$$\dot{X}=-2i[\omega_0+(\tfrac{1}{3}+R)\mu_0\hbar\gamma^2\rho sp]X-iAS^+, \quad (3)$$

where

$$X=\left[\frac{\mu_0\hbar\gamma^2}{4\pi}\right]\sum_{i,j}\frac{\sin\theta_{ij}\cos\theta_{ij}e^{-i\phi_{ij}}}{r_{ij}^3}s_i^+\cdot s_j^+ . \quad (4)$$

The angles θ and ϕ are the spherical coordinates of the lattice vector $\mathbf{r}_{ij}$, and s is the spin quantum number $s=\frac{3}{2}$ for Cu and Au and $s=\frac{1}{2}$ for Ag. The demagnetizing field in Eq. (2) is for a cylindrical sample, whose axis is parallel to the z axis. The factor p is the spin polarization, ρ is the number density of the nuclear spins in the sample, and $\omega_0=\gamma B$ the Larmor frequency. The exchange parameter R is given by

$$R=\frac{\sum_j J_{ij}}{\mu_0\hbar^2\gamma^2\rho} \quad (5)$$

and measures the relative strength of the RK and dipolar interactions.

The equation of motion [Eq. (2)] for the Larmor mode is unmodified by the presence of the RK interaction. This is due to the RK interaction commuting with the single-spin-flip operator. The coupling of the Larmor mode to the double-spin-flip mode arises due to terms in the dipolar interaction that do not commute with the single-spin-flip operator. The RK interaction plays no role in the coupling. The parameter R enters only in the

equation of motion for the double-spin-flip operator, and produces a shift in the resonance frequency. This shift is the experimental quantity of interest.

The coupling parameter A is given by

$$A = 18\left[\frac{\mu_0}{4\pi}\right]^2 \hbar^2\gamma^4 \sum_l \frac{\sin\theta_{lj}\cos\theta_{lj}e^{-i\phi_{lj}}}{r_{lj}^3} \times \sum_k \frac{\sin\theta_{kl}\cos\theta_{kl}e^{-i\phi_{kl}}}{r_{kl}^3}\langle s_l^z \cdot s_k^z\rangle \ . \tag{6}$$

We defer the calculation of A to the next section. The response of $\langle S^+\rangle$ to the rf excitation field $B_1 e^{-i\omega t}$ is found to be[2]

$$\langle S^+\rangle = \frac{\langle S^z\rangle \gamma B_1 e^{-i\omega t}}{A+(\omega_+-\omega_1)^2}\left\{\frac{A}{\omega_+-\omega}+\frac{(\omega_--\omega_2)^2}{\omega_--\omega}\right\}, \tag{7}$$

where

$$\omega_\pm = \tfrac{1}{2}[(\omega_1+\omega_2)\pm\sqrt{(\omega_1-\omega_2)^2+4A}\,] \tag{8}$$

with the uncoupled frequencies of the Larmor mode and the double-spin-flip mode

$$\omega_1 = \omega_0 + \tfrac{1}{2}\mu_0\hbar\gamma^2\rho sp \tag{9}$$

and

$$\omega_2 = 2\omega_0 + 2(R+\tfrac{1}{3})\mu_0\hbar\gamma^2\rho sp \ . \tag{10}$$

The resonance frequencies $\omega_\pm$ are shown in Fig. 1 for gold and Fig. 2 for silver. The inset in Fig. 1 is an enlarged view near the anticrossing of the two modes in Au. For fields above the anticrossing point, the frequency ω_+ corresponds to the double-spin-flip mode, while for fields below the anticrossing point the frequency ω_- corresponds to the double-spin-flip mode.

The ratio of the double-spin-flip mode intensity to that of the Larmor mode is given by

$$\xi = \frac{A}{(\omega_--\omega_2)^2} \tag{11}$$

from Eq. (4) for fields greater than the anticrossing field, while for fields smaller than the anticrossing field the ratio is given by the inverse of ξ, which reflects the change of identity of $\omega_\pm$ as described above. The intensity ratios for the noble metals are shown in Fig. 3.

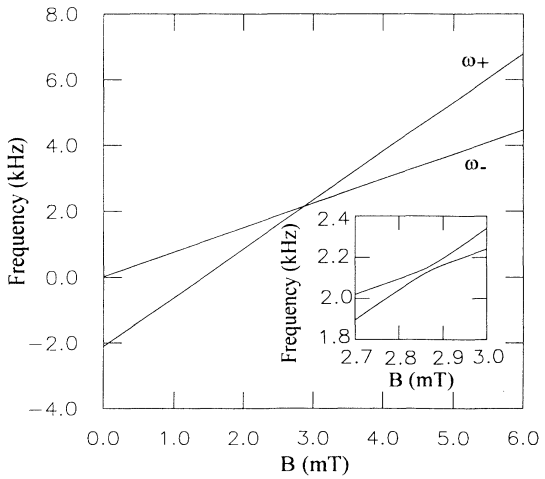

FIG. 1. Field dependence of $\omega_\pm$ for gold. The inset is an enlarged view of the anticrossing region.

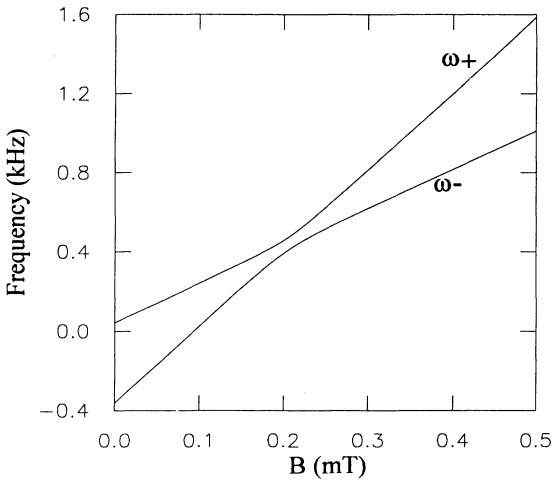

FIG. 2. Field dependence of $\omega_\pm$ for silver.

SPHERICAL MODEL

In order to evaluate the A parameter for Figs. 1–3 the correlation function in Eq. (6) has been calculated using the spherical model.[7,8] The partition function over three-dimensional spins

$$Z = \int ds_1 \cdots ds_N \exp\left[-\frac{H}{k_B T}\right] \tag{12}$$

is modified in the spherical model by putting a constraint on the measure. The constraint is of the form

$$\delta\left[\sum_i s_i^2 - Ns(s+1)\right],$$

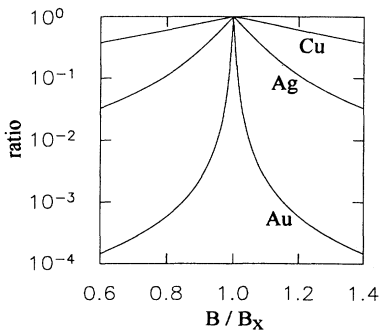

FIG. 3. Ratio of the line intensities of the double spin-flip mode to that of the Larmor mode for copper, silver, and gold. The magnetic field has been normalized by the anticrossing field B_x.

which forces the integration to be taken over the surface of a hypersphere. The δ function is then replaced by an integral representation that allows the partition function to be evaluated as the product of Gaussian integrals. In order to obtain physical results, an additional constraint on the measure is added, by fixing the high-temperature entropy to be that for free spins.[6] The correlation function takes the form

$$\langle s_k^z \cdot s_l^z \rangle = k_B T \sum_{\mathbf{q}} \frac{e^{i\mathbf{q}\cdot\mathbf{r}_{kl}}}{2(t-\lambda_{\mathbf{q}})} , \tag{13}$$

where the parameter t is determined by the self-consistency relation

$$s(s+1) = \frac{k_B T}{2N} \sum_{\mathbf{q}} \frac{1}{t-\lambda_{\mathbf{q}}} \tag{14}$$

and the $\lambda_{\mathbf{q}}$'s are the eigenvalues for the spin Hamiltonian equation (1), which are taken from published values.[8,9] In order to evaluate the expression for A, the term $e^{i\mathbf{q}\cdot\mathbf{r}_{kl}}$ is broken into $e^{i\mathbf{q}\cdot\mathbf{r}_k}$ and $e^{-i\mathbf{q}\cdot\mathbf{r}_l}$; the Fourier transform of the lattice sums is evaluated first,[8] and then the sum over $\mathbf{q}$ is taken. By changing the order of summation, the divergence in the dipolar sum of Eq. (6) is avoided.

RESULTS

The coupling parameter A is a weak function of temperature for all three metals, as shown in Fig. 4, which is consistent with the result found by Kjäldman, Kumar, and Loponen[6] for copper and follows from the form of Eq. (13). The value of A scales as $\lambda^4 s(s+1)\rho^2$ in the high-temperature limit.

The anticrossing field for the two modes is found by setting ω_1 equal to ω_2 and solving for the magnetic field B. The values of R that enter in ω_2 have been measured for Cu and Ag, are found to be -0.45 and -2.5, respectively.[2,4] We have taken the value of R for gold to be -29, based on scaling of the hyperfine interaction following Andrew and Hinshaw[10] and Viertiö and Oja.[11] This yields anticrossing fields of 0.62, 0.21, and 2.9 mT for Cu, Ag, and Au, respectively for a spin polarization $p=0.9$. The separation of the two modes at the anticrossing field gives A, while the shift of the double-spin-flip mode at zero field yields R.

The intensity of the double-spin-flip mode decays quickly away from the anticrossing region for Ag and Au. The experiment in Ag was unable to detect this mode in low fields where the two isotopic (^{107}Ag and ^{109}Ag) NMR lines have merged into one line. This was probably due to using too large a field step when scanning for the double-spin-flip mode. The coupling of the two modes should still be resolvable, by using smaller field steps about the anticrossing field. The situation in Au is difficult, since there is no experimentally determined value for R to precisely predict the value of the anticrossing field and the intensity of the second mode is such an extremely strong function of field; being 10% off the anticrossing field already yields a drop in signal intensity by 1000 (Fig. 3).

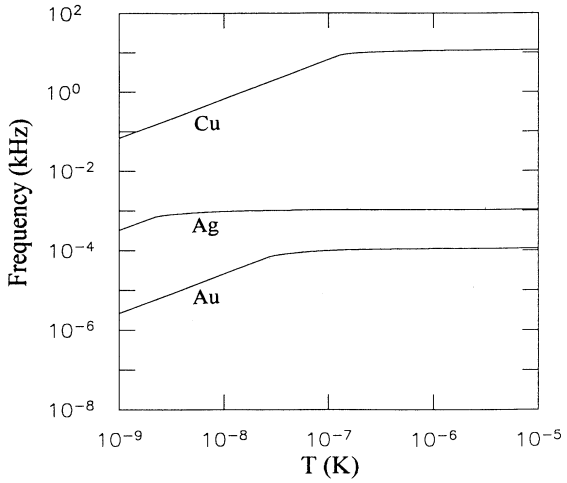

FIG. 4. Temperature dependence of the coupling parameter A for copper, silver, and gold.

It should still be possible to determine the value of R in Au if there is a detectable break in the Larmor mode frequency at the anticrossing field. The frequency separation of the two peaks at the anticrossing field is $2\sqrt{A} \cong 20$ Hz for $p=0.9$. We have estimated the linewidths of the Larmor and harmonic modes to be 0.8 and 50 Hz, respectively.[12,13] For a measurable change to occur in the frequency of the Larmor line at the anticrossing field, the linewidths of the two modes should not be too large compared to the frequency separation of the two peaks. This being the case for gold,[14] the determination of R is quite feasible.

ACKNOWLEDGMENTS

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[14] The sample should be well annealed to eliminate crystal defects that distort the local cubic symmetry and broaden the NMR line.