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Nuclear Magnetism in Silver at Positive and Negative Absolute Temperatures in the Low Nanokelvin Range

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We have investigated the susceptibility and entropy in the thermally isolated system of silver nuclei down to 0.8 nK and, at negative temperatures, up to -4.3 nK. Low-frequency SQUID-NMR techniques were employed to measure the dynamic susceptibility. Curie-Weiss behavior was observed for the static susceptibility at both $T>0$ and $T<0$; for Θ we deduce -4.4 ± 1.0 nK. Our results show directly that antiferromagnetic nuclear alignment at positive temperatures transforms into ferromagnetic orientation at $T<0$ in the nuclear-spin system of silver, dominated by the exchange interaction.

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Nuclear magnetism provides a wide spectrum of interesting phenomena as the experimental temperatures are extended downwards into the nK and even the pK range. In pure metals, nuclear magnetism has been studied in copper,[1-3] thallium,[4] and silver.[5] In copper and thallium, the experiments probe the behavior of a system in which the exchange energy is on the order of the dipolar energy or the Zeeman energy, respectively. In both cases, nuclear ordering is expected at low enough temperatures; in copper, ordering into several antiferromagnetic phases has been seen below 60 nK. In silver the exchange interaction dominates and, therefore, this metal provides a good model for a spin-$\frac{1}{2}$ Heisenberg system on an fcc lattice. We have measured the magnetic susceptibility of silver nuclei down to the record-low temperature of 800 pK.

Nuclear magnetism may be investigated at negative absolute temperatures in insulators,[6] and also in metals provided that the spin-lattice relaxation time is long enough.[5] At $T<0$, the isolated nuclear-spin system tries to maximize its energy at constant entropy. We present here the first measurements on an exchange-dominated nuclear-spin system at negative temperatures. Our results display a clear ferromagnetic behavior which is a convincing demonstration of theoretical concepts when $T<0$.[7]

Natural silver has two species: 51.8% of ^{107}Ag and 48.2% of ^{109}Ag; both have spin $S=\frac{1}{2}$. These isotopes also have slightly different magnetic moments, $-0.113\mu_n$ and $-0.130\mu_n$, respectively; here μ_n is the nuclear magneton. The difference may, to a large extent, be neglected in small magnetic fields which are the main concern in this paper. Therefore, the Hamiltonian of the spin system $\{S_i\}$ in silver is a sum of the dipolar and the indirect Ruderman-Kittle (RK) exchange interaction[8] contributions, in addition to the Zeeman energy, viz.,

$$\mathcal{H}=\mathcal{H}_{\rm dip}+\mathcal{H}_{\rm ex}+\mathcal{H}_Z$$
$$=(\mu_0/8\pi)\hbar^2\gamma^2\sum_{ij}\mathbf{S}_i\cdot\mathbf{A}_{ij}\cdot\mathbf{S}_j-\hbar\gamma\mathbf{B}\cdot\sum_i\mathbf{S}_i\,, \qquad (1)$$

where $\mathbf{B}$ is the external field, γ is the average gyromagnetic ratio, μ_0 is the permeability, and the spin-spin interaction matrix, contributing to $\mathcal{H}_{\rm dip}$ and $\mathcal{H}_{\rm ex}$, is

$$A_{ij}^{\mu\nu}=r_{ij}^{-3}\{[\delta_{\mu\nu}-3(r_{ij})_\mu(r_{ij})_\nu]+\eta f(2k_Fr_{ij})\delta_{\mu\nu}\}\,.$$

The parameter η describes the relative magnitudes of the exchange and dipolar interactions; f is the form function of the RK interaction which, in the case of a spherical Fermi surface, is $f(x)=\cos(x)-\sin(x)/x$. In silver, which has an fcc lattice, the RK interaction is thus antiferromagnetic. The magnitude of η may be estimated from the NMR experiment by Pointrenaud and Winter,[9] using a linewidth analysis which yields $\eta=2.9$. The RK interaction may also be written in terms of the exchange coefficients $J_{ij}=(\mu_0/4\pi)\hbar^2\gamma^2\eta f(2k_Fr_{ij})/r_{ij}^3$ directly.

Monte Carlo calculations predict nuclear ordering in silver into a simple type-I antiferromagnetic state at 0.5 nK.[10] However, the tendency to antiferromagnetism may be observed well above T_c by looking for a Curie-Weiss type of behavior, $\chi=C/(T-\Theta)$, where $c=2.0$ nK is the Curie constant and $\Theta=S(S+1)\sum_j J_{ij}/3k_B\cong-4$ nK for a spherical specimen.[11]

Our sample[5] consists of 78 silver foils with dimensions 25 μm$\times$4.5 mm$\times$40 mm along the x, y, and z axes, respectively. The nominal purity of the material is +99.99%. The foils were selectively oxidized at 750 °C for 20 h in 1×10^{-4} Torr of dry air to neutralize the magnetic impurities which might shorten the spin-lattice relaxation time τ_1 at small magnetic fields. The heat treatment and oxidization increased the residual-resistivity ratio of the sample from 100 to 900. The foils were electrically insulated by a 7-μm layer of SiC powder to reduce eddy-current heating during demagnetization.

The experiments were performed in our cascade nuclear demagnetization cryostat.[1] The sample itself forms the second nuclear stage in an initial field of $B_z=7.35$ T. Demagnetization of the specimen to zero field was performed in 20–30 min. Two coaxial Mumetal cylinders were used as magnetic shields around the silver foils to

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exclude the −4- to 2-mT remanent field of the main demagnetization solenoid. Inside the shields, three small coils were located for NMR measurements: The steady field B_y was produced by a 60-mm-high saddle-shaped coil, and the rf-excitation field B_z^{rf} by a 38-mm-long solenoid; for pickup, an astatically wound 6-mm-diam solenoid along the z axis was used. The remanent field on the sample, due to flux trapped onto these coils, was on the order of 10 μT but could be compensated to zero within ± 2 μT. Warm-up of the nuclear-spin system after demagnetization was slow because of the long τ_1 in silver, about 10 h at the 200-μK conduction-electron temperature.

After demagnetization of the main solenoid the sample was left in a $B_y = 120$ μT static field. The population inversion of the nuclear energy levels, for obtaining negative temperatures, was achieved by inverting this field rapidly. The coil has a time constant of $L/R = 10$ msec, which is somewhat large since the spin-spin relaxation time in silver is also $\tau_2 = 10$ msec. Nevertheless, flipping the 120-μT field by a mechanical switch yielded a population-inversion efficiency of 50%; this is about a factor of 5 better than in previous attempts.[5] The highest initial polarizations in the present experiments were 72% at $T > 0$ and 40% at $T < 0$.

NMR spectra were measured using an rf-SQUID amplifier at 4.2 K. The flux transformer had its low-frequency cutoff around 100 Hz which, below 130 Hz, was compensated by an increased excitation amplitude up to $B_z^{rf} = 60$ nT. The output of the SQUID control box was monitored with a two-phase lock-in amplifier. Its gain and phase were calibrated after each experiment to allow for a proper separation of the absorption and dispersion signals.

One of the serious problems in studying an isolated spin system is the determination of temperature. This can be accomplished by using the second law of thermodynamics $T = \Delta Q/\Delta S$ directly. Here ΔQ is the heat pulse applied to the system and ΔS is the ensuing entropy change. At negative temperatures, $\Delta Q < 0$ when entropy increases, showing that energy is removed from the system. This is also evident for heating with NMR excitation: $\Delta Q = \pi f \chi''(B_z^{rf})^2 \Delta t/\mu_0$, where the absorptive part of the susceptibility $\chi'' < 0$ when $T < 0$ (see Fig. 1); Δt is the duration of the rf-excitation pulse and f is its frequency.

The entropy was calculated directly from polarization using the relevant equation for the paramagnetic state.[12] Polarization $p = A\int \chi'' df$;[6] the proportionality constant A was obtained from $1/\chi'(0) = B/\mu_0 p M_{sat} + D_z - D_y$, where M_{sat} is the saturation magnetization, and D_y and D_z are the demagnetization factors along the directions of the static and the rf fields, respectively.[1] Both D_y and D_z are close to zero owing to the small thickness of the foils. Our calibration gave the same A at low and high temperatures, indicating that small inaccuracies in the demagnetization factors did not change the polarization

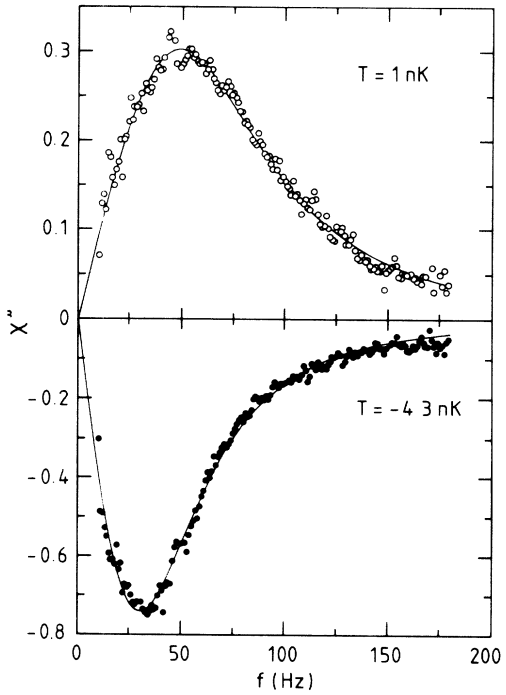

FIG. 1. NMR absorption χ'' (arbitrary units) measured by increasing the frequency f at the rate of 1 Hz/sec. Solid curves are fits of Lorentzian lines

$$\chi_L''(f) - \chi_L''(-f) = A/[1 + (f - f_0)^2/\Gamma^2] - A/[1 + (f + f_0)^2/\Gamma^2]$$

to the experimental data, with $A = 0.457$, $f_0 = 39.6$ Hz, and $\Gamma = 59.6$ Hz at $T = 1$ nK and $A = -0.911$, $f_0 = 19.8$ Hz, and $\Gamma = 43.8$ Hz at $T = -4.3$ nK, respectively. Note the different vertical scales.

scale. A small field $B_y = 191$ μT was chosen for the polarization measurements because the identity of the spins with different magnetic moments is then largely lost, resulting in a single exchange-narrowed NMR line which can be integrated with good precision. This field is also sufficiently far above the intrinsic local field of 35 μT, which is obtained from $B_{loc} = \{B_{dip}^2 + S(S+1)\sum_j J_{ij}^2/2\hbar^2\gamma^2\}^{1/2}$,[13] using $B_{dip} = 16.7$ μT for the internal dipolar field and $\sum_j J_{ij}^2/h^2 = 8430$ Hz^2.[9]

The excitation field B_z^{rf}, involved in ΔQ, is not known exactly owing to changes in the field distribution caused by the Mumetal shields. Therefore, the high-T expansion for entropy per molar volume $(n/V)R\ln 2 - C(B_{loc}/T)^2/2\mu_0$ was employed to anchor the temperature scale.

The calibration runs for polarization were made around 1 mK where thermal gradients between the silver sample and the copper refrigerant could be neglected. The temperature was measured using pulsed NMR on Pt wires; the system was calibrated against the T_c of a Be piece supplied by the NBS. The accuracy of the polarization calibration is estimated to be 5%. At negative temperatures the same calibration was used.

The measured NMR absorption χ'' in zero field is displayed in Fig. 1 at $T = 1$ and -4.3 nK. The absorp-

tion at $T<0$ is negative indicating that, instead of absorbing, the spin system is releasing energy. Both resonance curves are close to Lorentzian shape as shown in the figure where the data have been fitted by an absorption line with the negative-frequency side included, $\chi''(f) = \chi_L''(f) - \chi_L''(-f)$, using the Lorentzian shape for χ_L''. These successful fits imply that the Kramers-Kronig relations are valid and, therefore, that the static susceptibility $\chi'(0)$ can be obtained by integrating χ''/f over frequency.

The 30-Hz peak frequency of the NMR spectrum at $T<0$ is clearly less than that at $T>0$. Excluding the lowest temperatures, this may be qualitatively understood in terms of an equation[14] relating the susceptibility of the noninteracting system χ_{bare} to the interacting, ideally measured, susceptibility $\chi(f) = \chi_{\text{bare}}(f)/[1 - R\chi_{\text{bare}}(f)]$; here the interaction parameter $R = \sum_j J_{ij}/\mu_0\hbar^2\gamma^2\rho \cong -2$ and ρ denotes the number density of the silver atoms.

The entropy as a function of $|T|$ is shown in Fig. 2 down to 0.8 nK. The high-temperature expansion fits the data above 5 nK but clear deviations from a $1/T^2$ law are observed below. Results at negative temperatures are included. With our accuracy the data at $T>0$ and at $T<0$ coincide, and we are not able to say anything about the expected asymmetry in the odd higher-order $1/T$ terms.

The absolute value of $1/\chi'(0)$ is displayed in Fig. 3. The static susceptibility was obtained by integrating χ''/f from 30 to 180 Hz; the extrapolation to zero frequency was performed using similar fits as those shown in Fig. 1. Clearly, the susceptibility at $T<0$ is much larger than that at $T>0$. This is a consequence of the fact that the system tries to maximize its energy at constant entropy when $T<0$. Since the exchange coefficient $J<0$, the maximum-energy state has a ferromagnetic alignment of spins and the susceptibility is large.

The data display an antiferromagnetic Curie-Weiss law $\chi = C/(T - \Theta_A)$, with $\Theta_A = -4.8$ nK at positive temperatures. At $T<0$, we obtain a ferromagnetic law $\chi = C/(|T| - \Theta_F)$, with $\Theta_F = +2.8$ nK. These values for Θ_A and Θ_F were found by least-squares fittings of $\chi^{-1} = T/C + \Delta$ to all our experimental points by varying Δ.

Both sets of data in Fig. 3 follow the Curie-Weiss law to the lowest temperatures to an amazing extent. In fact, the susceptibility displays no saturation that is expected to be present close to an antiferromagnetic transition temperature at $T>0$.[1] No changes were observed in the NMR line shapes that could be assigned to actual antiferromagnetic or ferromagnetic ordering at $T>0$ or $T<0$, respectively (cf. Ref. 1). Apparently the required temperature for transitions was not yet reached.

To obtain the true susceptibility χ_S (susceptibility for a spherical sample), the measured data must be corrected for the dipolar interaction and for the shape of the sample: $\chi_S'(0)^{-1} = \chi'(0)^{-1} + L - D$, where $L = \frac{1}{3}$ is the Lorentz factor and D is the demagnetization coefficient. In our case $D = D_z \cong 0$. According to mean-field theory, $|\Theta_A|$ and $|\Theta_F|$ are equal and, by averaging, we obtain for the true Curie-Weiss temperature $\Theta = (|\Theta_A| + |\Theta_F|)/2 + LC = 4.4 \pm 1.0$ nK, where again $C = 2.0$ nK is the Curie constant.

Combining the value of $\sum_j J_{ij}^2/h^2 = 8430\ \text{Hz}^2$, obtained from the NMR experiments by Pointrenaud and Winter,[9] with our measured of $\sum_j J_{ij}/h = 3k_B\Theta/hS(S+1) = -370 \pm 80$ Hz, we may compare the magnitude of the nearest-neighbor interaction J_1 to that of the next-nearest neighbors J_2, provided that these are the most dominant terms. The maximum absolute value for J_2, compatible with the above constraints, is 4.3 Hz and the corresponding $J_1 = 26.3$ Hz. Then $|Z_2J_2/Z_1J_1| \leq 0.08$, where Z_1 and Z_2 are the coordination numbers for nearest and next-nearest neighbors, respectively. This means that the nearest-neighbor interaction strongly dominates in silver.

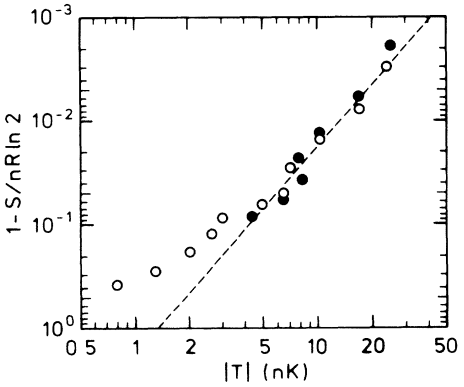

FIG. 2. Reduced entropy $1 - S/S_{\max}$ vs the absolute value of temperature for $T>0$ (○) and for $T<0$ (●). The dashed line displays the leading $1/T^2$ term of the high-temperature expansion.

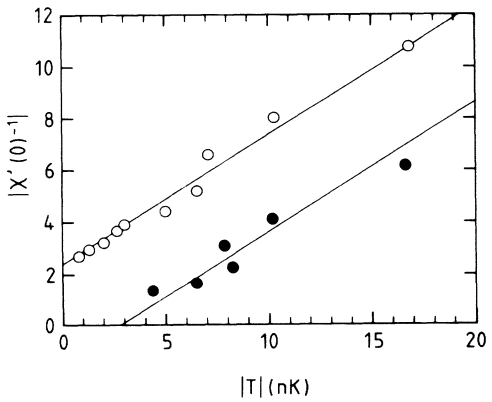

FIG. 3. The absolute value of the inverse static susceptibility $\chi'(0)^{-1}$ vs the absolute value of the temperature measured at $T>0$ (○) and at $T<0$ (●).

For an fcc lattice with nearest-neighbor dominance the molecular-field theory yields $\Theta/T_c = -3$ for antiferromagnetic ordering.[11] For silver we find that $\Theta/T_c \leq -5$, which indicates that fluctuations may be suppressing T_c in this metal.

Finally, we want to point out that the heat flow to the Ag nuclei is very small, indeed, during our experiments; this is because of the long spin-lattice relaxation in silver. Using polarization measurements as a thermometer, we obtained for the warm-up rate 3 nK/h at $T = 17.3$ nK, which yields a heat leak of 5×10^{-16} W/g. The usual relaxation due to τ_1 processes accounts for at least 80% of this value, which leaves an upper limit of 10^{-16} W/g for the energy input due to an unknown origin, e.g., cosmic rays or dark matter. Our value is smaller, by a factor of 50, than the sea-level cosmic-ray energy flux, absorbed presumably by the conduction electrons. Therefore, 10^{-16} W/g serves as an upper limit to any inelastic, coherent interactions of silver nuclei with dark matter that have been proposed recently.[15]

In conclusion, we have studied nuclear magnetism in silver, concentrating on the differences between negative and positive temperatures. We have measured the susceptibility and entropy down to the record-low spin temperature of 800 pK. The nearest-neighbor antiferromagnetic exchange interaction was seen to dominate in silver. At negative temperatures the susceptibility displays a ferromagnetic Curie-Weiss law; when $T > 0$, the behavior is antiferromagnetic.

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