Experimental Curves of Entropy and Susceptibility versus Temperature for Copper Nuclear Spins Down to the Ordered State

M. T. Huiku, T. A. Jyrkkiö, and M. T. Loponen[(a)]
Low Temperature Laboratory, Helsinki University of Technology, SF-02150 Espoo 15, Finland
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The entropy and susceptibility of copper nuclear spins below 1 μK have been measured as a function of temperature both in the paramagnetic and in the antiferromagnetic states. The critical temperature is 63 ± 10 nK, about 30% of the mean-field estimate. The results are in agreement with calculations based on the spin-wave spectrum of the dipolar and the Ruderman-Kittel interactions in the fcc lattice of copper.

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The magnetic phase transition of nuclear spins in metallic copper was recently observed at low entropies by demagnetizing highly polarized spins adiabatically.[1] In the ordered state, at the beginning of the warm-up, the susceptibility $\chi'(0)$ increased with time. The effect was largest at zero field, about 5%. With growing external field B_e, the initial increase in $\chi'(0)$ first decreased, until at 0.09 mT, $\chi'(0)$ was approximately constant in the ordered state. In higher fields the change in $\chi'(0)$ first grew to about 2%, and then vanished when the paramagnetic behavior set in at 0.22 mT.

The ordering is assumed to take place into the antiferromagnetic $(\pi/\alpha)(1,0,0)$ state.[2] There are several theoretical studies about the thermodynamics of copper nuclear spins,[2-6] based on the combined dipolar and Ruderman-Kittel (RK) indirect-exchange[7] Hamiltonian. To compare these calculations with experimental data, we have measured the spin temperatures as a function of entropy and susceptibility. For the first time such a measurement has now been extended down to the ordered state of nuclear spins. The heat pulses δQ were applied to the nuclear spins directly by NMR absorption. For the excitation field $B_{exc}\cos(2\pi ft)$, $\delta Q = \pi f B_{exc}^2 \chi''(f)\delta t/\mu_0$. $\chi''(f)$ is the absorptive part of the susceptibility and δt the pulse length. The absolute temperatures were derived from the second law of thermodynamics,

$$T = \delta Q/\delta S. \tag{1}$$

An experiment of this kind was performed several years ago,[8,9] but the accuracy was low as a result of the short spin-lattice relaxation time. The earlier measurements were also limited to the paramagnetic state.

In the new experiments our sample consisted of eight high-conductivity copper foils, 0.125 mm thick. To avoid eddy-current shielding, f had to be set as low as 50 Hz. The reduction of the heating power could be compensated for by increasing B_{exc}, but the direct measurement of $\chi''(f)$ became impossible. Instead, $\chi''(f)$ was related to $\chi'(0)$ by use of previously measured copper NMR spectra.[9] Extrapolation by $\chi''(f) \propto f$ below 0.5 kHz was justified since the widths of the spectra were about 5 kHz. The deviations from $\chi''(50\text{ Hz}) \propto \chi'(0)$ were not more than 20%. Another small correction, corresponding to a demagnetizing factor $D = 0.08$, was needed because $\chi'(0)$ was usually measured perpendicular to B_{exc}.

Polarization p was determined from the transverse susceptibility $\chi'(0)$, measured at 1 mT:

$$\chi'(0) = [(\mu_0 p M_s/B_{eff})^{-1} - (L - D + R)]^{-1}. \tag{2}$$

Here

$$B_{eff} = \{[B_e + \mu_0(L+R)pM_s]^2 + (1-p^2)B_0^2\}^{1/2}$$

is the effective local field, M_s is the saturation magnetization, the Lorentz factor $L = \frac{1}{3}$, and $D = 0.15$.[10] For copper the RK exchange parameter $R = -0.42$.[9,11] $(1-p^2)^{1/2}B_0$ is the random internal field,[12] and $B_0 = 0.36$ mT, calculated from the dipolar and RK interactions. Equation (2) also provided the calibration for $\chi'(0)$. The entropy S could then be determined from p, by use of the equations of the paramagnetic state which are valid for $B_e \gg B_0$.[13]

Above the transition B_e could be swept between zero and 1 mT adiabatically. To determine T, $\chi'(0)$ was first measured at 1 mT. Then B_e was swept to zero and $\chi'(0)$ was recorded for a short time both before and after a heat pulse δQ. Finally, $\chi'(0)$ was again measured at 1 mT.

This procedure could not be applied in the ordered state, because the field sweep from 1 mT to zero caused an extra increase of entropy.[1,9] Therefore, the relation between S and $\chi'(0)$ was found from a series of demagnetizations. The polarized nuclei were first demagnetized always with the same procedure, and the increase of $\chi'(0)$ at zero field was recorded. The field was then swept back to 1 mT for determining p and thus the entropy. By varying the time spent in the ordered state, and thereby the value of $\chi'(0)$, the relation between S and $\chi'(0)$ was found. The heat pulses δQ were applied during separate demagnetizations while following $\chi'(0)$; the temperature was calculated from $T=[\delta Q/\delta\chi'(0)]/[dS/d\chi'(0)]$.

The calibration of $B_{\rm exc}$ was done[14] by fitting the experimental data with the $1/T$ expansion[4] of $\Delta s = 1 - S/\mathcal{R}\ln 4$ between 1 and 5 μK. The accuracy of our measurements was still good enough at these relatively high temperatures, and the main contribution to Δs, $\gtrsim 75\%$, came from the leading T^{-2} term.

The resulting $\Delta s = 1 - S/\mathcal{R}\ln 4$ vs T data are plotted in Fig. 1, on both logarithmic and semilogarithmic scales. The straight line describes the leading T^{-2} term of Δs. HTE denotes the fifth-degree $1/T$ expansion.[4] PA is the Padé approximant [0, 2]; it agrees with our data very well in the paramagnetic region. Also shown is the spherical model result (SM),[3] which predicts somewhat too high temperatures below 200 nK.

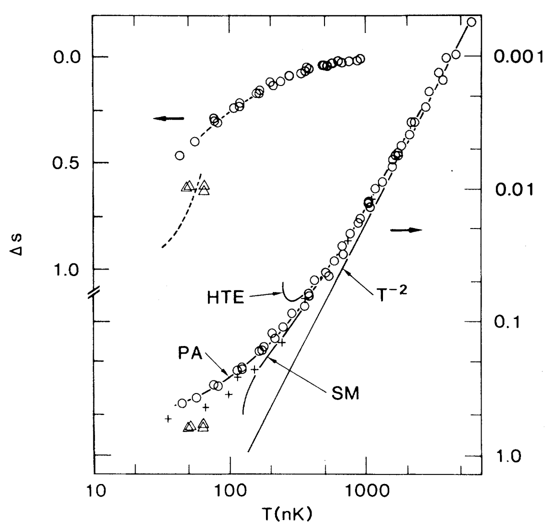

FIG. 1. Reduction of the entropy, $\Delta s = 1 - S/\mathcal{R}\ln 4$, shown as a function of temperature T at zero field on logarithmic (right) and semilogarithmic (left) scales. Open circles are for the paramagnetic phase, triangles for the ordered phase, and crosses for the old data. The dashed line shows the qualitative behavior of Δs around the transition region. The theoretical curves denoted by T^{-2}, SM, PA, and HTE are explained in the text.

However, this is in exact accordance with the linked-cluster expansion (LCE) analysis,[6] which shows that the discrepancy originates from the quantum spin effects neglected in the SM.

Also shown in Fig. 1 are the results of the previous S vs T measurements.[8,9] The earlier temperatures have been rescaled to fit our new data around 1 μK. At low temperatures the old points fall below the new data, probably because of the too low entropy assumed in the earlier analysis.

In the ordered state our measurements were restricted to a narrow entropy range around $0.4\mathcal{R}\ln 4$ by the nonadiabaticity during demagnetization and by the fact that close to the transition $d\chi'(0)/dt \cong 0$. Further, the accuracy of the S vs $\chi'(0)$ measurement was reduced by the smallness of the change in $\chi'(0)$. Since this effect becomes even smaller for $B_e \neq 0$,[1] we had to limit our measurements to zero field.

The temperatures measured in the ordered state range from 51 to 67 nK. Under the assumption $S \propto T^n$ with $n = \frac{3}{2} - 3$, the critical temperature for the antiferromagnetic first-order transition can be estimated to be $T_c = 63 \pm 10$ nK, which is only about 30% of the mean-field (MF) critical temperature $T_{\rm MF}$. This is in rough agreement with the SM and LCE calculations. Similar results have been predicted for antiferromagnetic systems also in other fcc lattices.[15] The experimental value of the integral $\int_0^{\ln 4} T\, dS/\mathcal{R}$ then becomes 180 ± 10 nK, whereas the theoretical result is $\frac{9}{10}T_{\rm MF} = 210$ nK. The agreement is reasonable, to say the least, and supports our temperature measurements.

The inverse susceptibility $\chi_0'(0)^{-1}$ vs T at $B_e = 0$ is shown in Fig. 2. The Curie-Weiss Θ and the shape dependence were eliminated from the measured values of $\chi'(0)^{-1}$ by use of the equation

$$\chi_0'(0)^{-1} = \chi'(0)^{-1} + (L - D + R) = \chi'(0)^{-1} + \lambda_z \qquad (3)$$

with[10] $D = 0.08$. According to the MF theory $\chi_0'(0)^{-1} = T/C$, where the Curie constant $C = 562$ nK for copper, until it becomes equal to the maximum eigenvalue of the spin-wave spectrum, $\lambda_{\max}$, at $T_{\rm MF} = \lambda_{\max} C$.[2] However, deviations from the Curie law are clear below 500 nK.

It has been shown, with use of the spherical model, that spin-wave fluctuations in copper decrease temperatures considerably from the mean-field values in the vicinity of the transition.[3] An even larger reduction results from the LCE calculation[6] with the quantum spin $I = \frac{3}{2}$. As shown in Fig. 2, the LCE result especially agrees with

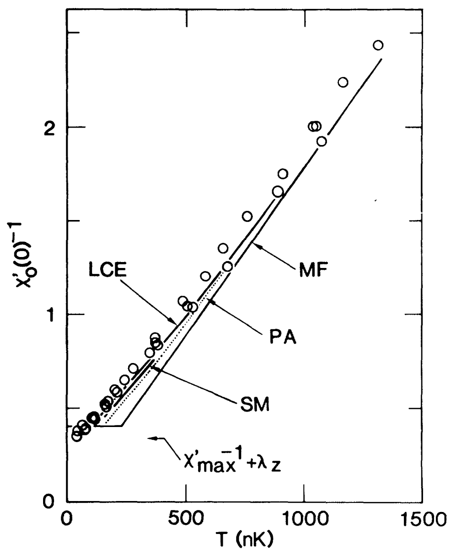

FIG. 2. Inverse susceptibility $\chi_0'(0)^{-1}$ as a function of temperature in the paramagnetic state at zero field. The lines denoted (from right to left) by MF, PA, SM, and LCE are explained in the text. $\chi_{max}'^{-1}+\lambda_z$ corresponds to the maximum susceptibility in the ordered state and the horizontal line shows λ_{max}.

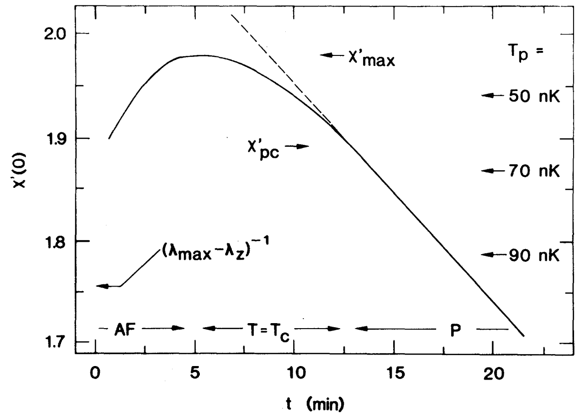

FIG. 3. The susceptibility $\chi'(0)$ in zero field after demagnetization as a function of time. The solid line illustrates the normal evolution of $\chi'(0)$ through the ordered phase. The dashed line shows $\chi'(0)$ in the metastable paramagnetic region. T_p indicates temperatures in the paramagnetic phase. χ_{max}' and χ_{pc}' are the values of $\chi'(0)$ at T_c for the ordered and paramagnetic phases, respectively. $(\lambda_{max}-\lambda_z)^{-1}$ is the theoretical maximum value of $\chi'(0)$.

our data. The Padé approximant [1,2] for the $1/T$ expansion[4] of $\chi_0'(0)$ also shows reduction of the temperature but not as strongly as the two other models.

In Fig. 3 we show $\chi'(0)$ vs t after demagnetization to zero field. The normal, curved behavior (solid line) and the metastable paramagnetic behavior (dashed line) of $\chi'(0)$ are both plotted. Also $(\lambda_{max}-\lambda_z)^{-1}$ and T_p, the temperature in the paramagnetic state, are indicated. The maximum susceptibility in the ordered state, χ_{max}', is 12% larger than $(\lambda_{max}-\lambda_z)^{-1}$. However, the curved behavior of $\chi'(0)$ deviates from the paramagnetic, exponentially relaxing line at a value smaller than χ_{max}'. The temperature at this point agrees well with $T_c = 63 \pm 10$ nK estimated from measurements in the ordered state.

We now have the following picture about the transition in the nuclear spin system of copper. In the region denoted AF the system is in the antiferromagnetic state, and T increases with time. When $T_c = 63$ nK is reached at $S \cong 0.46\mathcal{R}\ln 4$, the spin system starts moving gradually into the paramagnetic state. During the first-order transition $\chi'(0)$ decreases, since at T_c the susceptibility of the ordered state, χ_{max}', is larger than that of the paramagnetic state, χ_{pc}'. The remaining difference between χ_{pc}' and $(\lambda_{max}-\lambda_z)^{-1}$ is about 7%. Finally, in the region denoted by P above $S \cong 0.65\mathcal{R}\ln 4$, the system is completely paramagnetic, and the temperature starts rising again.

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[a] Present address: Neste Oy, Research Centre, SF-06850 Kulloo, Finland.

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[10]By comparing measurements of $\chi'(0)$ in various fields and geometries, it was concluded that D depends on B_e in the direction perpendicular to B_e, because the Mumetal shield surrounding the sample enhances magnetic fields, thereby partly canceling the opposite effect of the demagnetizing field. However, even a small field $B_e \cong 0.5$ mT decreases the μ of the shield enough to quench this effect. The B_e dependence of D explains the too small value of the Curie-Weiss Θ in Ref. 8 and the apparent direction dependence of $\chi'(0)$ reported by J. Soini, Physica (Utrecht) 108B, 1095 (1981).

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