Evidence for Nuclear Antiferromagnetism in Copper

G. J. Ehnholm, J. P. Ekström, J. F. Jacquinot,[a] M. T. Loponen, O. V. Lounasmaa, and J. K. Soini
Low Temperature Laboratory, Helsinki University of Technology, SF-02150 Espoo 15, Finland
(Received 26 March 1979)

We have studied, in a two-stage nuclear demagnetization cryostat, the NMR properties of copper nuclei in magnetic fields from 0 to 15 mT and at polarizations up to 0.9. In zero field the spin entropy decreases less rapidly with temperature than expected for an interacting paramagnet with a constant local field; at 50 nK the entropy is still 45% of $R \ln 4$. The temperature dependence of magnetic susceptibility points to nuclear antiferromagnetism in copper.

In order to investigate nuclear cooperative phenomena, i.e., nuclear ferromagnetism and antiferromagnetism, it is necessary to cool the nuclear spin system to a temperature below 1 μK. This is because the magnetic dipole-dipole interaction between nuclei is extremely weak due to the smallness of the nuclear dipole moments. Solid ^{3}He is an exception because of the strong quantum mechanical exchange force. Spontaneous ordering occurs when the interaction energy is an appreciable fraction of the thermal energy kT.

We have constructed a cryostat, with two nuclear demagnetization stages operating in series, in which the spins of copper nuclei have been cooled to 50 nK (5×10^{-8} K). This is the lowest temperature ever produced. The second law of thermodynamics was employed directly to measure the temperature. Our experimental information about the nuclear spin system of copper, in fields from 0 to 15 mT, was obtained by means of superconducting quantum interference device (SQUID) NMR measurements. The magnetic susceptibility data point to nuclear antiferromagnetism.

Investigations of spontaneous nuclear ordering have previously been done on three insulators by Abragam and Goldman and their collaborators.[1] Their experimental method is dynamic polarization with the help of some electronic magnetic impurities, followed by adiabatic demagnetization in the rotating frame. Antiferromagnetism in LiH was recently confirmed by neutron diffraction studies.[2]

The brute-force cascade nuclear cooling technique used by us has several advantages: There is no need to add electronic impurities to the specimen, our method is applicable to a number of metals, we work in the laboratory frame, and we are able to measure the absolute temperature directly.

Our apparatus and experimental procedure will be explained elsewhere[3]; only a few details will be given here. For a general description of the nuclear cooling method, pioneered by Kurti *et al.*,[4] we refer to Lounasmaa.[5]

The second nuclear stage, which also is our specimen, was made of 2000 copper wires,[6] 0.04 mm in diameter and insulated by oxidation. The first nuclear stage, also made of copper, cools this sample, in a field of 7.3 T, to 0.4 mK, corresponding to an equilibrium nuclear spin polarization $p > 0.99$. There was no heat switch between the two nuclear stages; demagnetization of the specimen thus had to be carried out in a time short in comparison with the spin-lattice relaxation time τ_1 to avoid losses of polarization due to relaxation. At the conduction-electron temperature $T_e = 0.4$ mK, τ_1 for copper is about 50 min in external fields $B_{\text{ext}} > 10$ mT and about 12 min in $B_{\text{ext}} = 0$.

The observed T_e after demagnetization corresponds to a heat leak $\dot{Q}_2 \cong 1$ nW to the conduction electrons of the specimen. $\dot{Q}_2$ is much larger than the cooling power of the nuclei in the small second stage. As a result it is better to have no heat switch between the two nuclear stages: Most of $\dot{Q}_2$ is then absorbed by the nuclei in the large first stage.

The NMR spectra, after demagnetization, were measured by employing a continuous-wave frequency sweep. The static field B_{ext} was applied in the vertical direction parallel to the copper wires. For excitation and pickup of the NMR signal, two saddle-shaped coaxial coils, with their axes in the horizontal plane, were used. The reason for this geometry is that the familiar crossed-coil arrangement works only when the macroscopic response of the spin system rotates; this happens when the spins can precess around an external field. For $B_{\text{ext}} = 0$ there is no preferred direction and the spin system vibrates linearly along the axis of excitation; this response can be detected by a coaxial pickup coil. The induced ac current was monitored by a

SQUID, which was used without any feedback to obtain a fast response.[7] We were thus able to measure the nuclear susceptibility $\chi'(\nu) - i\chi''(\nu)$ from 1 to 200 kHz.

Goldman[8] has shown that polarization of the nuclear spin system in high fields can be obtained from the expression

$$p = A\int_0^\infty \chi''(\nu)\,d\nu, \tag{1}$$

which relates the NMR absorption spectrum to p; it is then possible to calculate magnetization and entropy as well. We found experimentally that this integral is independent of magnetic field at constant polarization, as long as $B_{\rm ext} > 0.3$ mT.

The proportionality constant A was determined by assuming that immediately after demagnetization the initial polarization $p_i = 0.9$. This value was obtained from measurements at 15 mT; in this relatively high field the NMR signal could be followed until the spin system had reached thermal equilibrium with conduction electrons. It was then possible to calculate p from the known $B_{\rm ext}$ and T_e; the latter was obtained by measuring τ_1 by relating it to temperature through Korringa's law $\tau_1 T_e = 1.19$ s K.[9] This procedure is valid because the conduction-electron temperature of the specimen is determined by the temperature of the first stage and by the heat leak $\dot{Q}_2$ entering directly to the second stage; T_e at the specimen is not affected by relaxation of the demagnetized nuclei. The 10% loss of polarization is estimated to be due to relaxation and eddy-current heating.

The static susceptibility is given by the Kramers-Krönig relation

$$\chi'(0) = \pi^{-1}\int_{-\infty}^{+\infty}(\chi''/\nu)\,d\nu, \tag{2}$$

where the principal value of the integral must be taken.

In Fig. 1 we have plotted $\chi'(0)$ as a function of $B_{\rm ext}$ at three different polarizations. All our experimental results have been corrected by the equation

$$\chi'(0) = \chi_{\rm exp}'(0)/[1 + (\tfrac{1}{3} - \tfrac{1}{2})\chi_{\rm exp}'(0)], \tag{3}$$

in order to take into account the Lorentz and demagnetization fields. Furthermore, the absolute values of $\chi'(0)$ were determined at 1 mT from the relation $\chi'(0) = \mu_0 M_z (B_z^2 + B_{\rm loc}^2)^{-1/2}$, where the magnetization M_z was calculated from p and $B_z = B_{\rm ext} + \mu_0 M_z/3$ is the external field with the Lorentz correction.

In the low-polarization limit our data in Fig. 1

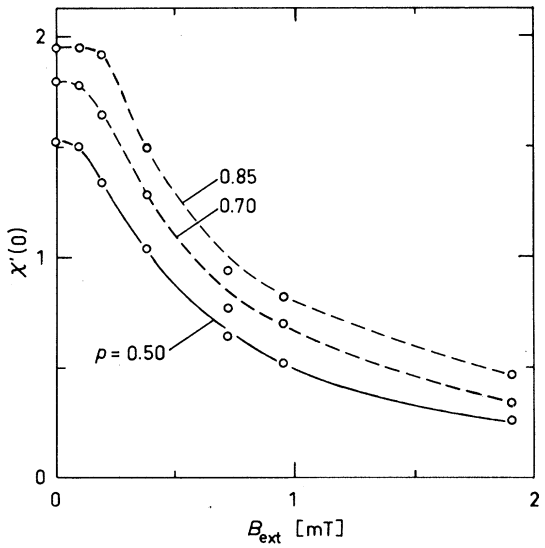

FIG. 1. The static magnetic susceptibility $\chi'(0)$ of copper nuclei as a function of the external magnetic field at various polarizations. At $p = 0.85$, $\chi'(0)$ shows a plateau at $B_{\rm ext} < 0.2$ mT. In the low-polarization limit, which in the figure has been extrapolated to $p = 0.5$, the experimental points can be fitted to Eq. (4) with $B_{\rm loc} = 0.34$ mT (shown by the dashed line).

can be fitted to the expression

$$\chi'(0) \propto (B_z^2 + B_{\rm loc}^2)^{-1/2}, \tag{4}$$

which yields for the local field $B_{\rm loc} = 0.34$ mT. At $p = 0.85$ this model is not valid and a plateau is observed at $B_{\rm ext} < 0.2$ mT.

The temperature of the copper nuclear spins in the second stage was measured after demagnetization by employing directly the second law of thermodynamics as applied to a system in thermal equilibrium, i.e., $T = dQ/dS$. At $B_{\rm ext} = 0$ the thermodynamic functions depend only on one independent variable and, by selecting $\chi'' = \chi''(7$ kHz), we obtain

$$T = (dQ/d\chi'')/(dS/d\chi''). \tag{5}$$

The nuclei were selectively heated by applying a small rf pulse of duration dt and amplitude $2B_1$ at the NMR peak absorption frequency of 7 kHz. Because $B_1 \simeq 100$ mT could be determined from the coil dimensions and from measurements at room temperature only with insufficient accuracy, its value was fixed by requiring that $B_{\rm loc} = 0.34$ mT in the high-entropy limit. Then $dQ = 4\pi\nu B_1^2 \chi''(\nu) dt/\mu_0$ and $d\chi''$ could be found by meas-

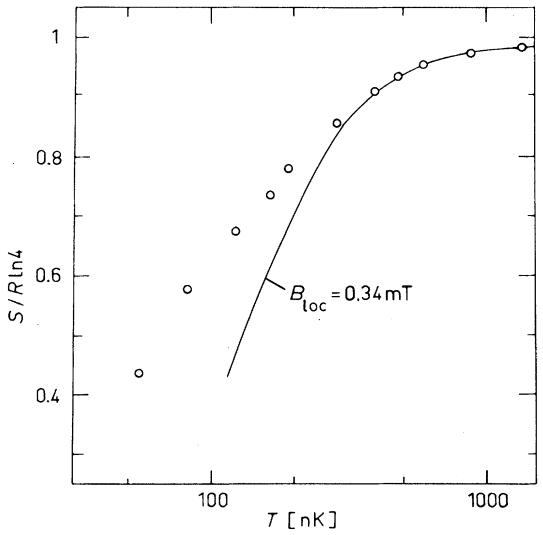

FIG. 2. The entropy vs temperature diagram of copper in $B_{ext} = 0$. For comparison we have also plotted the S vs T curve of a paramagnet with $B_{loc} = 0.34$ mT.

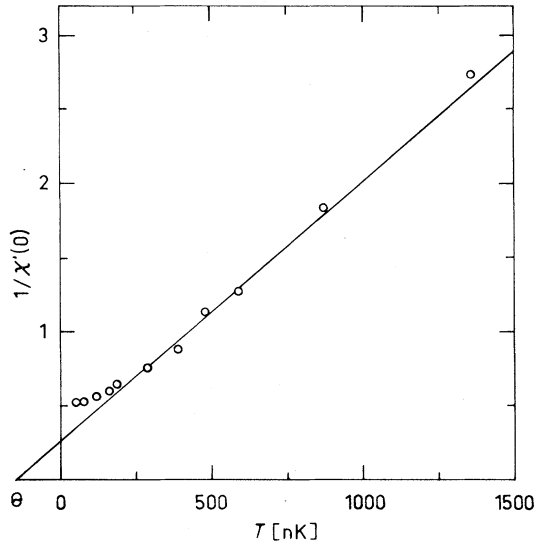

FIG. 3. The inverse static susceptibility of copper as a function of temperature. The straight line corresponds to equation $1/\chi'(0) = (T/C) + \Delta$, where the nuclear Curie constant of copper $C = 570$ nK and $\Delta = 0.26$.

uring χ'' at 7 kHz before and after each pulse. Eddy-current heating of conduction electrons by the rf pulse was found to be negligible.

We may further write

$$dS/d\chi'' = (dS/dp)(dp/d\chi''), \tag{6}$$

by noting that is is possible to sweep B_{ext} adiabatically from zero to 1 mT where p can be found from the measured NMR absorption line. The derivative dS/dp may then be obtained from the theory of the paramagnetic state. We thus have all the necessary information for calculating the absolute thermodynamic temperature by means of Eq. (5).

In Fig. 2 we show, as a function of temperature, the entropy of the nuclear spin system of copper in zero external field. The lowest temperature reached in our experiments was 50 nK. We notice from the figure that the temperatures measured by us are less than those calculated for an interacting paramagnet with the constant local field. For instance, at $S = 0.45R$ ln4 the measured temperature is 50 nK instead of 110 nK obtained with $B_{loc} = 0.34$ mT.

In Fig. 3 we have plotted the inverse susceptibility $1/\chi'(0)$ as a function of temperature. By analogy with electronic magnetism, the data indicate antiferromagnetism with the Weiss $\theta \simeq 150$ nK. By extrapolating our high-temperature data on $\chi'(0)$ to $T \to 0$ we calculate for the exchange interaction between nearest neighbors $J = -160$ Hz; the value measured at room temperature is $|J| = 230$ Hz for neighbors with unlike spins.[10]

The fact that our experimental data in Fig. 1 in low fields and high polarizations do not follow the paramagnetic behavior of Eq. (4) can perhaps be explained by assuming that the spin system is either approaching an ordered state or that there has already been an antiferromagnetic transition. In paramagnetic salts close to the Néel point a decrease in $\chi'(0)$ usually precedes the transition.[11]

On the other hand, no clear change in the entropy diagram or in the NMR data, indicating a transition to the ordered state, was found by us. This might be due to experimental inaccuracies. It is also possible that the nuclear spin system was not able to make the transition as a result of the rather rapid demagnetization or that the actual Néel temperature T_N is below 50 nK. In electronic antiferromagnets θ/T_N is frequently considerably larger than 1. According to theoretical calculations, a cooperative transition should occur in copper between 150 and 250 nK.[12,13] For $J = 0$ the ordered state should be ferromagnetic, whereas the experimental value, $J = -160$ Hz, although small compared with the dipolar interaction between nearest neighbors (~ 1060 Hz), changes the expected state to antiferromagnetic.

In conclusion we find that the nuclear spin sys-

tem of copper clearly favors antiferromagnetism but the question whether a transition occurs above 50 nK must be decided by future investigations.

We are greatly indebted to A. Abragam, M. Goldman, L. Kjäldman, P. Kumar, K. Kurkijärvi, N. Kurti, and P. Roubeau for fruitful discussions, comments, and criticism. This work was financially supported by the Academy of Finland.

[a]On leave of absence from Centre d'Etudes Nucléaires de Saclay, 91190 Gif-sur-Yvette, France.

[1]M. Goldman, Phys. Rep. 32C, 1 (1977); A. Abragam and M. Goldman, Rep. Prog. Phys. 41, 395 (1978).

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

[3]G. J. Ehnholm, J. P. Ekström, J. F. Jacquinot, M. T. Loponen, O. V. Lounasmaa, and J. K. Soini, to be published.

[4]N. Kurti, F. N. Robinson, F. Simon, and D. A. Spohr, Nature (London) 178, 450 (1956).

[5]O. V. Lounasmaa, *Experimental Principles and Methods Below 1 K* (Academic, New York, 1974), Chap. 6.

[6]Our copper wires are of grade *F* from Connolly Ltd., Liverpool, England. The manufacturer guarantees a purity of 99.999%; in our analysis the concentration of magnetic impurities was found to be 11 ppm.

[7]G. J. Ehnholm, J. P. Ekström, M. T. Loponen, and J. K. Soini, to be published.

[8]M. Goldman, J. Magn. Res. 17, 393 (1975).

[9]U. El-Hanany and D. Zamir, Phys. Rev. 183, 809 (1969).

[10]E. R. Andrew, J. L. Carolan, and P. J. Randall, Phys. Lett. 37A, 125 (1971).

[11]D. de Klerk, in *Encyclopedia of Physics*, edited by S. Flügge (Springer, Berlin, 1956), Vol. 15, p. 38.

[12]L. Kjäldman and J. Kurkijärvi, to be published.

[13]M. Goldman, private communication.

Enhancement of the Electron Spin Polarization in the Photoyield of Ni(111) in the Vacuum Ultraviolet

A. Bringer, M. Campagna, R. Feder, W. Gudat, E. Kisker, and E. Kulhmann
Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, West Germany
(Received 1 March 1979)

We have found that the spin polarization of the photoyield from single crystal Ni(111) at 16.8- and 21.2-eV photon energy is (8.0±3.5)% and (8.1±2)%, respectively, which is significantly larger than the bulk electron-spin polarization. The results of a theoretical model calculation are in good agreement with the experiment. We interpret this as direct evidence for spin-dependent electron-electron scattering in an itinerant strong ferromagnet.

Almost ten years after the first observation of electron spin polarization (ESP) in photoemission from Gd thin films in the photon energy range $h\nu \leq 5.5$ eV,[1] we report the first observation of ESP in photoemission from a ferromagnetic material (Ni) using photon energies in the near vacuum ultraviolet (vuv), namely, at 16.8 and 21.2 eV. We find that the ESP of the photoyield at these photon energies is positive (i.e., magnetic moment parallel to the magnetization) and significantly larger (~ 8.1% at 21.2 eV) than the bulk band contribution to the magnetization and giving a spin polarization $P=n_B/n \simeq 0.51/10 \simeq 5.1\%$ of bulk Ni at room temperature. These data are the encouraging results of initial steps of a major effort in our laboratory towards energy-resolved, photon-energy–dependent ESP measurements using tunable vuv radiation.

The results on Gd have been interpreted within the three-step model of the photoemission process and a direct correlation of the photoelectron-spin polarization with the spin polarization of the conduction electron has been suggested.[1] Later, De Wames and Vredevoe[2] pointed out that inelastic scattering from magnons during escape could significantly alter the initial ESP after photoexcitation. In subsequent experiments on Gd and Dy, Bänninger *et al.*[3] found evidence that effects of electron-magnon scattering were negligible. Since then most experimental results on ESP of photoelectrons have been interpreted without considering spin-flip processes,[4] especially because of the small photon-energy range used in the experiments done so far.

The first photoelectron-spin polarization data on single-crystal 3*d* ferromagnets were obtained

