Thermometric NMR of Stable Nuclei by Low-Temperature Nuclear Orientation

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Nuclear magnetic resonance of the stable ^{55}Mn nuclei in antiferromagnetic $MnCl_2 \cdot 4H_2O$ has been detected by observation of the nuclear orientation of ^{54}Mn nuclei doped into the sample. The technique allows the detection of NMR under conditions in which NMR from oriented nuclei cannot be observed. Also the NMR linewidths of the concentrated ^{55}Mn spins and the dilute system of ^{54}Mn spins can be compared.

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We report in this Letter a novel method for detecting nuclear magnetic resonance (NMR) at low temperatures. A system of concentrated spins is resonated and warms the lattice by spin-lattice relaxation (SLR). This warming is detected by monitoring of the change in the γ-ray intensity emitted by a system of dilute radioactive nuclei which interact with the lattice also by SLR.

We note that some years ago NMR was successfully detected thermometrically,[1–3] but in these experiments the temperature rise of the lattice was monitored by a thermometer placed in thermal contact with the specimen. In the present experiments the radioactive nuclei constitute an "internal" thermometer. Also it is possible to compare the NMR linewidth of the concentrated spins with that of the dilute spins, the resonance of the latter spins being observed directly by the technique of nuclear magnetic resonance of oriented nuclei (NMRON).

The specimen investigated was an antiferromagnetic $MnCl_2 \cdot 4H_2O$ crystal into which were doped ^{54}Mn atoms with a few microcuries activity. Thus, the stable ^{55}Mn nuclear spins are the concentrated system, and the radioactive ^{54}Mn nuclear spins constitute the dilute system. Note that ^{54}Mn-$MnCl_2 \cdot 4H_2O$ has been the object of recent NMRON experiments[4,5]: Indeed, it is the first antiferromagnet investigated by this technique.[6] In a field $\mathbf{B}_0$ applied along the easy axis of the crystal, for $B_0 < B_{SF}$, the spin-flop field, the magnetization of one sublattice is parallel to $\mathbf{B}_0$ while that of the other is antiparallel. Calculating to second order the separation of adjacent levels for the lowest hyperfine structure multiplet yields for the two sublattices

$$\Delta E^{\mathrm{I}}_{M,M+1} = -\tfrac{5}{2}A + \frac{\frac{5}{2}A^2 M}{g\mu_{\mathrm{B}}(B_E + B_0) - 4D} + P(2M+1) - g_n\mu_N B_0, \tag{1a}$$

$$\Delta E^{\mathrm{II}}_{M,M+1} = -\tfrac{5}{2}A + \frac{\frac{5}{2}A^2 M}{g\mu_{\mathrm{B}}(B_E - B_0) - 4D} + P(2M+1) + g_n\mu_N B_0. \tag{1b}$$

These equations apply both to the ^{55}Mn spins ($I = \frac{5}{2}$) and the ^{54}Mn spins ($I = 3$). The exchange field B_E and the crystalline-field anisotropy constant D are the same for each nuclear species, whereas the isotropic hyperfine interaction strength A, the electric quadrupole interaction strength P ($P << A$), and the nuclear g factors are different. We calculate the hyperfine interaction parameters for ^{55}Mn from the ^{54}Mn data[4,5] and the ^{55}Mn nuclear data,[7] obtaining $A/h = -257.3$ MHz and $P/h = 0.3$ MHz.

At temperature T, the 835-keV γ-ray intensity emitted in the decay of ^{54}Mn along the alignment axis (normalized to the "warm" count at 1 K) is

$$W = 1 - 0.495 g_2 B_2 - 0.447 g_4 B_4. \tag{2}$$

Here g_2 and g_4 are solid-angle correction factors equal to 0.960 and 0.865, respectively, for the 3-in.×3-in. NaI detector used in the experiment and B_2 and B_4 are orientation parameters.[8] Thus the γ-ray intensity is temperature dependent, and indeed this property of oriented nuclei is the basis of the nuclear orientation thermometer.[9]

Also of considerable importance in our experiment are the SLR times for ^{54}Mn and ^{55}Mn, $T_1(54)$ and $T_1(55)$. The former can be deduced from the NMRON measurement of the recovery of the ^{54}Mn spins to equilibrium with the lattice at temperature T_L. In $B_0 = 0$, direct spin-magnon processes are not allowed because of the $k = 0$ energy gap $\hbar\omega_0$ due to anisotropy. The SLR results from higher-mode Raman processes so that $T_1(54)$ is very long. For example, we measure $T_1(54) \simeq 10^6$ s at $T_L = 50$ mK in ^{54}Mn-$MnCl_2 \cdot 4H_2O$.[10] However, on application of B_0 the energy gap for one magnon branch is reduced and $T_1(54)$ becomes very short when B_0 is close to the spin-flop field B_{SF}.[5] The value of $T_1(55)$ is $T_1(54) \times [A(55)/A(54)]^2$ so that $T_1(55) \sim T_1(54) \sim T_1$.

The experimental arrangement was very similar to that for the NMRON measurements.[4] The ^{54}Mn-MnCl$_2\cdot$4H$_2$O sample was attached with Apiezon-N grease to a copper fin connected to the mixing chamber of a dilution refrigerator. The easy axis (close to the c axis) was vertical. The rf field was applied along the crystalline b axis through a plastic window on the 1-K shield surrounding the dilution unit.

The energy-flow diagram after resonating of the ^{55}Mn spins would be as represented in Fig. 1. The maximum energy put into the ^{55}Mn spins in the $\nu_{-5/2-3/2}$ resonance is the energy required to equalize the populations of the $M=-\frac{5}{2}$ and $M=-\frac{3}{2}$ sublevels which at $T=50$ mK is $E_{\mathrm{res}}^{\mathrm{sat}}=37$ μJ for the $n=1.5\times10^{-3}$-mole sample used in the experiment. The energy e_{res} flows out of the ^{55}Mn spin system into the lattice (magnons and phonons) with a time constant T_1. This energy then flows partially into the ^{54}Mn spin system, with time constant T_1, and partially into the copper fin through the Kapitza resistance with time constant τ_K. The conductance between the crystal and fin with area of contact A is $\dot{Q}/A\,\Delta T\simeq\alpha T_L^3$, where we have adopted a typical value $\alpha=10^2$ W/m^2 K^4.[11,12] We note that the dominant heat capacity at low temperatures in these systems is the ^{55}Mn nuclear heat capacity.[13] The lattice has relatively very small heat capacity as has the ^{54}Mn spin system because of its very small concentration. For the 10-μCi specimen used in the experiment, this concentration, defined by the fraction of manganese nuclei that are ^{54}Mn, is $c\sim10^{-8}$.

It is evident that no signal (change in ^{54}Mn γ-ray intensity) will be observed if $T_1 >> \tau_K$. In fact, in zero applied field at $T_L=50$ mK, on a sweep of the rf field over a frequency range including the resonance frequency for ^{55}Mn estimated from Eq. (2) to be $\nu_{-5/2-3/2}=631.1$ MHz, no signal was observed.

We then decided to apply a field $B_0=0.63$ T in which T_1 is much reduced [we measure $T_1=4000$ s (Ref. 10)]. A ^{54}Mn nuclear orientation run showed that the spin-flop transition took place in fields $0.69\leqslant B_0\leqslant0.73$ T so that in $B_0=0.63$ T there are two sets of resonance lines for ^{55}Mn, one for each sublattice, and we estimate from Eq. (3) $\nu^{\mathrm{I}}_{-5/2-3/2}=628.0$ MHz, $\nu^{\mathrm{I}}_{-3/2-1/2}=631.6$ MHz, $\nu^{\mathrm{II}}_{-5/2-3/2}=628.3$ MHz, and $\nu^{\mathrm{II}}_{-3/2-1/2}=637.1$ MHz. Figure 2 shows the result of a run in which the frequency was changed in 0.1-MHz steps with a counting time of 1000 s. The rf field was frequency modulated at 100 Hz with 0.11 MHz amplitude. The initial ^{54}Mn spin temperature was 46 mK (estimated from the γ-ray intensity) and the observed signal corresponds to $\Delta T_L\simeq20$ mK. The line profile is difficult to calculate exactly because the spins of the two sublattices have different relaxation rates and the linewidths may also be different. However, the signal between 625.5 and 630.5 MHz is consistent with two lines with HWHM $\Delta\nu$ of the order of 1 MHz centered at approximately 628 MHz and separated by a frequency smaller than $\Delta\nu$. The simple analysis to obtain $\Delta\nu$ for the single line if $B_0=0$ is given below. The magnitude of the maximum signal can be estimated by our assuming that the resonance is saturated and that the heat flow per second out of the ^{55}Mn spin system $\sim E_{\mathrm{res}}^{\mathrm{sat}}/T_1$ equals at equilibrium the heat flow from the lattice to the fin through the contact area $A=1$ cm^2. Then

$$\Delta T_{\max}(54)\lesssim\Delta T_L\simeq E_{\mathrm{res}}^{\mathrm{sat}}/T_1\alpha A T_L^3. \tag{3}$$

The signal estimated from Eq. (3) would equal the observed signal of 20 mK if it is assumed that the resonance is saturated and that $T_1\simeq500$ s at $T_L=70$ mK, a not unreasonable value since we have observed that T_1 increases by ~3 orders of magnitude on a change in T_L from 90 to 50 mK in $B_0=0$.[10]

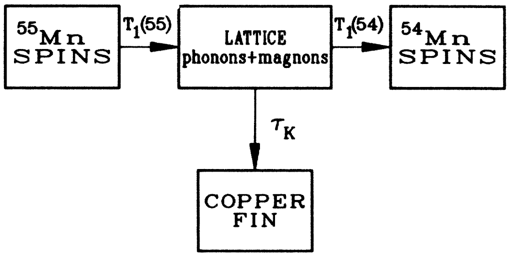

FIG. 1. Diagram illustrating energy flow from ^{55}Mn spins into the lattice, ^{54}Mn spins, and the copper fin.

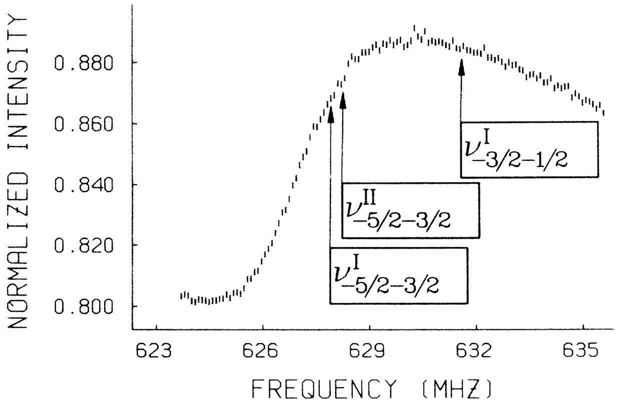

FIG. 2. The normalized ^{54}Mn γ-ray intensity vs frequency in $B_0=0.63$ T. The frequency step is 0.1 MHz and the modulation 0.11 MHz. The change in intensity resulting from the ^{55}Mn resonance is $\Delta T\simeq20$ mK. The line positions calculated from formula (1) are indicated.

In order to observe the single zero-field resonance we used a technique suggested by Allsop *et al.*[5] The rf field with frequency ν and modulated by 0.11 MHz was applied for a certain time (1000 s) while the γ-ray

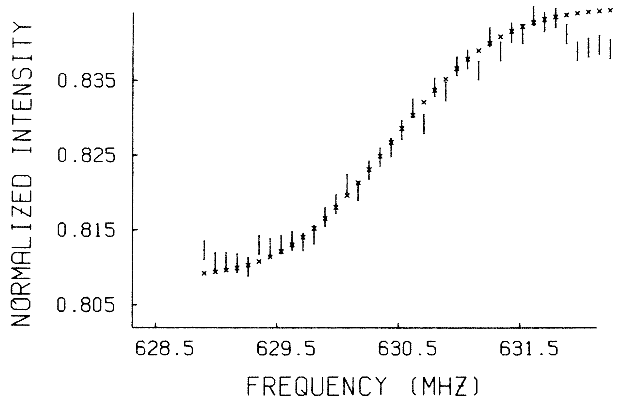

FIG. 3. The ^{54}Mn γ-ray intensity vs frequency in $B_0 = 0$. The frequency step is 0.1 MHz and the modulation is 0.11 MHz. In between steps, the Mn spins are brought into thermal contact with the lattice by application of $B_0 = 0.68$ T for 60 s. In this run $\Delta T \simeq 5$ mK. The points indicated by the crosses represent a theoretical plot for incremental temperature increase and no relaxation through a Gaussian line with $\Delta\nu = 0.7$ MHz.

intensity was counted. At the end of the count, the frequency was changed to a value far off resonance and a field $B_0 = 0.68$ T ($\lesssim B_{\rm SF}$) applied for a time t_c. In this field the relaxation times T_1 are relatively very short so that both sets of spins are in thermal contact. The field B_0 was then reduced to zero, the rf field was reset to a new frequency $\nu + 0.1$ MHz, and the γ rays were counted for another 1000 s. By this process the frequency range 629–633 MHz was covered. Again it is evident that in order to observe a signal the condition $T_1 \lesssim t_c \lesssim \tau_{\rm K}$ must be met. In fact, the choice of t_c is quite crucial because, whereas a good signal shown in Fig. 3 was observed for $t_c = 60$ s, no signal was observed for $t_c = 120$ s and only a very weak one ($\lesssim 1$ mK) for $t_c = 30$ s. We conclude that at $B_0 = 0.68$ T, $T_1(54) \sim T_1(55) \sim t_c \sim \tau_{\rm K} \sim 60$ s.

The signal in Fig. 3 corresponds to a temperature change $\Delta T \simeq 5$ mK from an initial spin temperature of 50 mK. We can estimate the signal for $t_c = 60$ s by assuming that in $B_0 = 0$, T_1 is very long and the spin-spin interaction allows the ^{55}Mn spins to reach a common spin temperature. Also the ^{55}Mn nuclear heat capacity is the dominant contribution so that when thermal contact is made with the lattice in $B_0 = 0.68$ T, the lattice is brought up to the spin temperature. This analysis yields $\Delta T_{\rm max} = 7$ mK.

The linewidth of the resonance is difficult to calculate from the signal because of the uncertainty in the time constants T_1 and $\tau_{\rm K}$. However, we can make a simple estimate by ignoring the relaxation effect and calculating the incremental temperature increase across the line. The result, on the assumption of a Gaussian profile with HWHM with $\Delta\nu = 0.7$ MHz, is also shown in Fig. 3. This is much larger than the width $\Delta\nu(54) = 35$ kHz observed for the ^{54}Mn spins by NMRON.[4] The ^{55}Mn spins interact strongly via the Suhl-Nakamura[14] interaction in which two nuclei couple by the virtual emission and reabsorption of a spin wave via the hyperfine interaction. For this indirect process we can estimate for ^{55}Mn $\Delta\nu_{\rm SN} \simeq 4$ MHz.[15] This broadening is homogeneous so that frequency modulation should be unnecessary to excite the ^{55}Mn resonances, and this we verified experimentally. For the ^{54}Mn spins $\Delta\nu'_{\rm SN} \sim c\Delta\nu_{\rm SN}$ so that with $c \sim 10^{-8}$ the broadening due to the Suhl-Nakamura interaction is completely negligible. The measured $\Delta\nu'$ is almost certainly a result of inhomogeneous broadening by impurities.

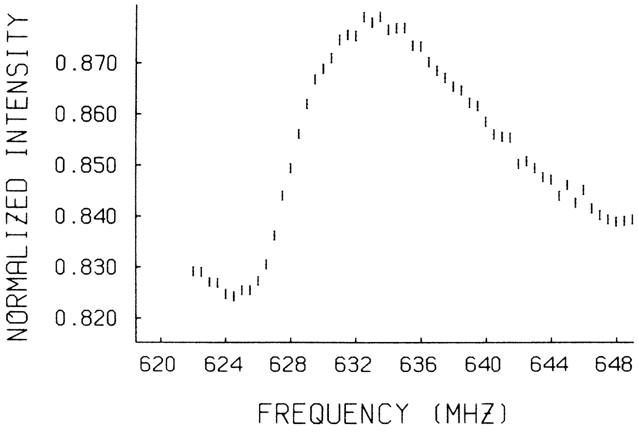

FIG. 4. The ^{54}Mn γ-ray intensity vs frequency in $B_0 = 0.72$ T. The NMRON of ^{54}Mn cannot be observed in this field because T_1 is too short.

Finally, we used this new technique to observe ^{55}Mn NMR in the field regime $B_0 \sim B_{\rm SF}$ in which previously no ^{54}Mn NMRON could be observed because T_1 is too short. Figure 4 shows the resonance observed in $B_0 = 0.72$ T which is in the spin-flop transition regime. It is interesting to note that the observed linewidth appears to be substantially larger than that observed below the spin-flop field although it is difficult (as was mentioned above) to calculate the linewidth exactly.

In conclusion, we have developed a new nuclear-orientation thermometric NMR technique and used it to develop ^{55}Mn resonances in $MnCl_2 \cdot 4H_2O$ in various (including zero) applied fields. This has allowed direct comparison of the ^{55}Mn and ^{54}Mn linewidths, the latter being obtained by NMRON.

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