Novel Low Temperature Cross Relaxation in Nuclear Quadrupole Resonance

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We have observed a new cross relaxation mechanism in the presence of a pure nuclear quadrupole splitting. This process involves two simultaneous nuclear spin flips and dramatically changes the form of the magnetization recovery curves at low temperature. We present a model which combines this mechanism with spin-lattice relaxation. The addition of cross relaxation allows us to explain nonmonotonic features that were previously not understood in the recovery curves of Sc nuclei in a variety of samples.

Quadrupolar systems are well suited for use in the ultralow temperature regime. Their potential as absolute thermometers in the submillikelvin regime has been recently demonstrated [1]. In addition, because of their large heat capacity at the Schottky anomaly, they may be useful as nuclear refrigerants [2]. Factors which influence and limit nuclear spin equilibration are therefore important to understand. We report the observation of a novel dipolar cross relaxation mechanism in nuclear spin systems with pure quadrupole splittings. The result of cross relaxation in Sc (nuclear spin $I = \frac{7}{2}$) is the coupling of the $\pm \frac{1}{2} \rightarrow \pm \frac{5}{2}$ transition to the $\pm \frac{5}{2} \rightarrow \pm \frac{7}{2}$ transition which has the same energy difference. In nuclear magnetic resonance, the energy differences between sets of levels with $\Delta m_I = 1$ are equal [3]. Mutual nuclear spin flips which conserve both energy and angular momentum allow spins to come into equilibrium at a unique spin temperature [4] which is not necessarily equal to the lattice temperature. The total ΔM for the nuclear spin system does not have to be zero. In LiF, for example, a cross relaxation process involving two Li spin flips and one F spin flip has been observed [5] at low field where the difference in Zeeman energy between the adjacent levels of Li is nearly one-half of the difference in adjacent levels in F. In this case the extra unit of angular momentum is absorbed by a rigid rotation of the whole crystal [6]. The behavior of the quadrupolar system differs from that of LiF because the $\pm \frac{5}{2}$ level is involved in both transitions; therefore different analytical techniques must be applied. In addition, the $\pm \frac{3}{2}$ states are present and do not participate in this cross relaxation process.

Pure nuclear quadrupole splittings result from the interaction of the nuclear electric quadrupole moment with the static electric field gradient present in the lattice [7]. The energy level diagram for such a system with $I = \frac{7}{2}$, with axial symmetry, and at zero field is shown in Fig. 1. The origin of the new cross relaxation effect is the exact energy equality between the lowest transition and the sum of the two higher transitions.

At very low temperatures ($T < 10$ mK), where the spin-lattice relaxation time T_1 is long, the effect of the cross relaxation on the nuclear magnetization recovery is dramatic: the recovery curves are unexpectedly and no-

ticeably nonmonotonic. We have observed similar curves in the two highest frequency transitions in Sc nuclei in three different systems [8]: polycrystalline Sc metal ($\nu_Q = 130$ kHz) [9], single crystal Sc metal ($\nu_Q = 130$ kHz), and a polycrystalline alloy $Sc_{0.5}Y_{0.5}$ ($\nu_Q = 194$ kHz) [10]. In this paper we model the new cross relaxation and reproduce the interesting features observed in the data. This model also successfully accounts for differences between the observed behavior in these three systems and has important implications on the measured relaxation times at low temperature.

For a system with $I = \frac{7}{2}$ the recovery curve should be a sum of three exponentials when only magnetic coupling to the conduction electrons is considered [11]. The time constants in the exponentials are well-defined fractions of T_1, the Korringa time [12]. Equation (1) describes the time dependence of the nuclear magnetization M as it recovers to its equilibrium value, M_{eq}, following an rf pulse at the frequency of one of the transitions:

$$-u \propto M_{eq} - M(t) = A \exp\left(-\frac{3t}{T_1}\right)$$
$$+ B \exp\left(-\frac{10t}{T_1}\right) + C \exp\left(-\frac{21t}{T_1}\right).$$

(1)

Here A, B, and C are constants determined by the initial
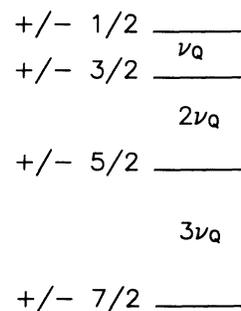

FIG. 1. The energy levels of a spin $\frac{7}{2}$ nucleus are shown in the presence of nuclear quadrupole splitting; ν_Q is a characteristic frequency for the system.

conditions. One can also express u in terms of population differences, where p_n is the population of the nth level and p_n^{eq} is the equilibrium population in that level. For the lowest transition of Fig. 1

$$u \equiv u_{7/2} = (p_{7/2} - p_{7/2}^{eq}) - (p_{5/2} - p_{5/2}^{eq}) . \qquad (2)$$

Although a model based on this equation has successfully been used to explain relaxation in quadrupolar systems at higher temperatures [13], it cannot reproduce the oscillation that we observe during the short time recovery [1]. We will show that the addition of cross relaxation terms allows us to explain the unusual shape of these recovery curves.

The three materials were studied during separate runs of the nuclear demagnetization apparatus. The cryostat and spectrometer, as well as the mounting techniques, are described in Ref. [1]. Each sample is a single foil of metal, $10 \text{ mm} \times 30 \text{ mm} \times 0.5 \text{ mm}$ in size. The recovery curve is measured by applying a train of rf pulses at the frequency of one transition and monitoring the magnetization at various times after this saturation. The delay times range from hundreds of μsec to hundreds of sec. The single crystal sample is uniform enough to allow the observation of free induction decays; only spin echoes are used in both polycrystalline samples.

The qualitative behavior of the recovery of all three samples is similar: an initial fast relaxation is followed by a sharp minimum, a slow increase, and finally a broader maximum before the magnetization recovers to its equilibrium value. The position of the first minimum is independent of temperature and transition, and occurs at the same delay time for both of the pure Sc samples, although the depth of the minimum is greater for the polycrystalline sample. It is shifted to a longer delay time in the Sc-Y sample, but remains independent of both transition and temperature.

It is clear that Eq. (1) cannot completely describe this behavior since the relaxation time T_1 is inversely proportional to temperature through the Korringa law [12]. The dipolar interaction, however, is independent of temperature and we will show that the presence of the cross relaxation process can explain the behavior described in the previous paragraph. We model the cross relaxation as follows. Following the procedure introduced in Ref. [14], the rate of change of the population in state n is given by

$$\frac{dp_n}{dt} = \sum_{m,r,s} (p_m q_s W_{ms,nr} - p_n q_r W_{nr,ms}) , \qquad (3)$$

where p_n or q_s is the population in the nth or the sth state and $W_{nr,ms}$ is the probability per unit time of a transition of two nuclear spins in states n and r to states m and s. To calculate the rate of change in the population of the $m_I = \pm \frac{5}{2}$ state we let $m = \frac{7}{2}$, $s = \frac{1}{2}$, and $n = r = \frac{5}{2}$. For the purpose of this calculation we consider only those transitions that conserve energy. From detailed balance it follows that $W_{nr,ms} = W_{ms,nr} \equiv W$. In addition, we as-

sign the spin temperatures Θ_1 to the transition $\frac{7}{2} \rightarrow \frac{5}{2}$ and Θ_2 to the $\frac{5}{2} \rightarrow \frac{1}{2}$ transition. In the high-temperature limit (valid since $h\nu_Q/k_B$ for Sc is 6μK), for an energy difference of ϵ

$$\Theta_1 = \frac{(\epsilon/k_B) p_{7/2}}{p_{7/2} - p_{5/2}} , \qquad (4)$$

$$\Theta_2 = \frac{(\epsilon/k_B) p_{5/2}}{p_{5/2} - p_{1/2}} . \qquad (5)$$

After some manipulation we find

$$\frac{dp_{5/2}}{dt} = [p_{5/2}]^2 [e^{(\Theta_1 - \Theta_2)/T} - 1] W . \qquad (6)$$

The condition of mutual spin flips is guaranteed by imposing the conditions

$$dp_{1/2} = dp_{7/2} = -dp_{5/2}/2 . \qquad (7)$$

From Eq. (2), u can be calculated for each of the three transitions. We have numerically simulated the relaxation by combining this process with that of Eq. (1) in an effort to model the simultaneous interaction of the nuclear spins with the electronic bath and with each other. The initial conditions, the values of p_n after the train of pulses, must be entered into the simulation to accurately model the decay. Because of the complexity of the effects of the pulse train and the cross relaxation that operates during this time, we left the initial condition as free parameters in the fitting program. We make the following observations about the initial conditions. To insure adequate saturation of a given line the pulses in the comb were made very short. The length is such that there are appreciable frequency components at the position of neighboring transitions. In addition, the skin depth of the rf is on the order of the thickness of the samples at the frequencies of interest, therefore lower frequency pulses are more effective at exciting spins inside the sample than higher frequency pulses. The values for the initial conditions are subject to the constraint of saturation of the transition of interest (equal population) and small variations in the other populations consistent with the fact that they are also being disturbed by the saturating comb. Any perturbation of the spin population enables both the cross relaxation and Korringa processes. Even transitions involving the $\frac{3}{2}$ state ($2\nu_Q$ or ν_Q) can initiate the cross relaxation by changing the populations in the $\frac{5}{2}$ or the $\frac{1}{2}$ state.

Results of the numerical simulations are shown plotted with the magnetization recovery data in Fig. 2 as a function of the logarithm of time. This plot emphasizes the early time behavior that is dominated by the cross relaxation. A simulation or fit to the $\frac{3}{2} \rightarrow \frac{5}{2}$ transition at $T = 1$ mK on the single crystal sample is shown in Fig. 2(a). Using the same values for the Korringa constant and for W we can obtain the simulation or fit of Fig. 2(b) to the same transition in the polycrystalline sample at the same temperature. We find a value of W of 8 sec^{-1}. It is pos-
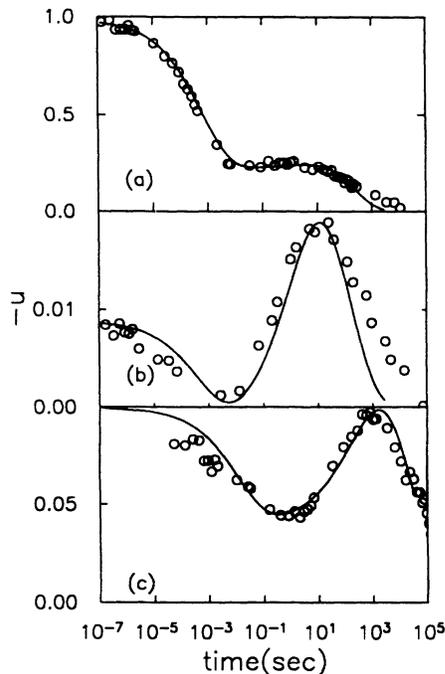
FIG. 2. The difference in magnetization, $-u \propto M_{eq} - M(t)$, is plotted as a function of the logarithm of time for the three different systems discussed in the text. (a) The recovery curve for the $\frac{3}{2} \rightarrow \frac{5}{2}$ transition in single crystal Sc at 1 mK. (b) The same transition and temperature for polycrystalline Sc. (c) The recovery of the $\frac{5}{2} \rightarrow \frac{7}{2}$ transition in ScY at 3 mK. The solid lines are the result of the numerical simulations.

sible to generate fits of equal quality to data taken from 0.1 up to 8 mK without changing either W or the Korringa constant. We can explain the difference in the single crystal and polycrystalline data by noting that the skin depth is larger for the polycrystalline sample. By suitably changing only the initial conditions the depth of the minimum changes; however, since the other parameters remain fixed, the position of the minimum is unaltered in agreement with the data (Fig. 2).

Figure 2(c) shows a simulation or fit to the $\frac{5}{2} \rightarrow \frac{7}{2}$ transition in the Sc-Y sample. For the Sc-Y sample the position of the minimum is shifted to longer times with respect to the minimum in the pure Sc. In a diluted system [15] the strength of the dipolar Hamiltonian is proportional to $x^{1/2}$, where x is the fraction of spins that are scandium nuclei. The effective Hamiltonian that is responsible for the cross relaxation is second order [16], and the cross relaxation time ($\propto 1/W$) varies as the square of this Hamiltonian [6]. In our experiment $x = 0.5$. We expect the value of W to decrease by a factor of 4, to 2 sec^{-1}. If we increase the value of the Korringa constant to reflect the longer magnetic relaxation time in the Sc-Y [10], the simulation or fit produces the solid line of Fig. 2(c).

This model successfully describes the behavior of the decay for delay times up to tens of seconds. In our previous analysis [1] we fit data using only Eq. (1). The

agreement is very good for times longer than 1 sec for the pure Sc. The value of the Korringa constant that we obtained was 90(9) msec K [1]. However, that model cannot reproduce the short time behavior. Our current simulations yield a Korringa constant of 25 msec K for the pure Sc. The agreement with the data at long times is not as good as in Ref. [1]. However, qualitatively, it is not surprising that the experimental value for the Korringa constant is shorter when cross relaxation effects are included. If the latter process is ignored, a larger Korringa constant will be required to fit a given data set for the following reason. Initial heating of the nuclear spin system will populate the upper states at the expense of the lower states. The return to thermal equilibrium at the lattice temperature by magnetic relaxation requires that the nuclei drop down through the different levels of Fig. 1. Cross relaxation opposes this process by pumping the nuclei into higher quadrupolar energy states because it couples state $\frac{5}{2}$ to state $\frac{1}{2}$. The implication is that the true relaxation time is shorter than that calculated by ignoring the cross relaxation process. An exact solution to this problem incorporating Eq. (1) and integrals of Eq. (6) for the different levels involved would yield the correct value for the Korringa constant.

In summary, we observed and identified a novel cross relaxation mechanism in a pure nuclear quadrupole split system. The origin of this new mechanism is the exact equality of the energy differences between two different sets of levels. This process will not be observable at high temperature where T_1 is short ($\ll 1$ sec) or in the presence of an appreciable magnetic field which makes the level spacings unequal. The results of a simple model which includes both this process and magnetic relaxation are in good agreement with data that we have taken on three different systems.

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