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Sensitivity of Nuclear Magnetic Double Resonance*

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The dynamics of the nuclear magnetic double-resonance process for Na nuclei in a (2,0,0) position relative to a substitutional Ag^+ impurity in NaCl has been studied for several Ag concentrations. The purpose was to determine experimentally the factors which limit the double-resonance sensitivity. For Ag concentrations below 0.03 mole %, the magnetization of unperturbed Na nuclei decayed exponentially with rates proportional to the impurity concentration when a rf field at the resonance frequency of the quadrupole-shifted transitions was applied. Using a method of intermittent search-field irradiation, evidence was found that the finite spin diffusion rate caused a double-resonance energy transfer rate under continuous search-field irradiation about 30% less than the transfer rate which would be observed if the spin diffusion were infinitely fast. A theoretical explanation of the results is given using a perturbation approach based on the concept of spin diffusion. In addition, we have studied the Na spin-lattice relaxation in the completely demagnetized state as a function of impurity concentration, and found a rapid initial decrease of spin order. This was caused by cross relaxation within the nuclear spin system.

I. INTRODUCTION

THE idea of nuclear magnetic double resonance (DNMR) was proposed several years ago by Hartmann and Hahn (HH)[1] as a method to detect very weak nuclear magnetic resonances in solids. Modifications in the experimental technique have been given.[2] In recent years a number of experiments have been described in which this method was used to study nuclear magnetic resonances of rare nuclei in solids.[3–8] Special interest has been paid to the investigation of electric-field gradients around impurities by studying the quadrupole splittings of the nuclear-magnetic-resonance signals.[5–8] Redfield[9] introduced a field-cycling technique to study the pure electric quadrupole resonance in impure copper, a technique which has been used thereafter to study the quadrupole splitting around impurities in a variety of metallic[10–12] and nonmetallic[13] solids.

The double-resonance scheme involves two spin systems, one abundant and the other dilute, say I and S, respectively. The I system is prepared in a very ordered state (i.e., low spin temperature). Then if the S nuclei are maintained in a disordered state or at high spin temperature and if there is a coupling between the two spin systems, energy will be transferred from the S system to the I system. Success or failure of a DNMR experiment depends entirely on the rate of communication or temperature exchange between the two systems. The purpose of this research is to investigate the dynamics of this process, using a physical system previously studied[6]: silver-ion impurities in sodium chloride. This system is advantageous because of the presence of an abundant spin system (I spins or Na^{23} nuclei) with a large nuclear magnetic moment and a spin-lattice relaxation time of several minutes at liquid nitrogen temperature. In addition the silver substitutional ion is nearly the same size as the sodium ion it replaces, so the lattice distortion and electric-field gradients are small enough to avoid difficulty with second-order quadrupole effects.

In the experiments to be described, the S spins were Na^{23} nuclei which experienced a quadrupole perturbation because of the electric-field gradient near a silver impurity. Of the Na^{23} neighbors near such an impurity, only the (2,0,0) neighbors were detected. We assume that the other sites have a smaller quadrupole splitting. It is not obvious that the (1,1,0) neighbors experience a smaller perturbation than the (2,0,0) neighbors. However, experimental results by Hartland,[5] Nelson and Ohlsen,[7] and a theoretical calculation by Dick[14] in other alkali halide systems indicate that the (1,1,0) neighbor to an impurity can have a smaller quadrupole splitting than the (2,0,0) even though the (1,1,0) neighbor is closer to the impurity.

The quadrupole shifted transitions of the (2,0,0) neighbors can be observed down to concentrations of about 10^{-3} mole % of silver, so that the concentration dependence of the double-resonance sensitivity can be studied over a range of several orders of magnitude.

In Sec. II the experimental procedure is outlined. Section III gives the experimental results. In Sec. IV

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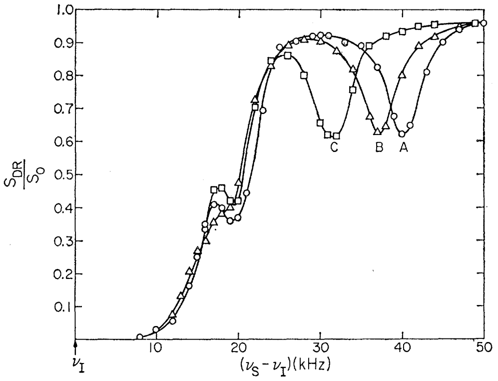

FIG. 1. Nuclear double-resonance spectra for a NaCl single crystal containing 0.1 mole % Ag^+ impurities. The angle between the [100] direction and the external magnetic field was 0°, 10°, and 20° for A, B, and C, respectively.

we attempt a theoretical analysis based on the concept of spin diffusion as introduced by Bloembergen.[15]

II. EXPERIMENTAL PROCEDURE

The experimental procedure was a combination of the methods used by HH,[1] and Lurie and Slichter (LS)[2], which have been described in detail in their papers. Therefore we will give only a short review of the experimental procedure.

In a nuclear double-resonance experiment we have to prepare the abundant I and the rate S spins at different spin temperatures. In order to do so we use the field-pulse method of LS for an adiabatic demagnetization of the I spins in their rotating frame.[16] In this process the Na magnetization M_I is made parallel to the rotating rf field H_{1I} by pulsing the static magnetic field H_0 away from its resonance value H_{00} by an amount h, turning H_{1I} on suddenly, and then gradually decreasing h to zero. Following this adiabatic demagnetization in the I spin rotating reference frame H_{1I} is turned off in a time slow compared to the precession period in the rotating frame. The I spins are then at a very low temperature, Θ_{I0}.

We now give a simple but approximate theory, which we refine in Sec. IV B. Let us turn on H_{1S}, at angular frequency ω_S, nonadiabatically, i.e., in a time short compared to the spin-spin relaxation time, T_2. This brings the S spins to a high spin temperature—if exactly at resonance to an infinite temperature. After a certain cross relaxation time, which will be a minimum for $\sqrt{3}\gamma_S H_{1S}=\gamma_I H_L$,[1] both spin systems will reach common spin temperature,

$$\Theta_{I1}=(1+\epsilon)\Theta_{I0}, \tag{2.1}$$

where ϵ is the ratio of the respective heat capacities and will be calculated in Sec. III C. If we now shift the phase of H_{1S} nonadiabatically by 180°, the S spins end up at $-\Theta_{I1}$, and after the cross-relaxation the common temperature is

$$\Theta_{I2}=(1+2\epsilon)\Theta_{I1}\approx(1+3\epsilon)\Theta_{I0}. \tag{2.2}$$

After n phase shifts we have

$$\Theta_{In}\approx(1+2\epsilon)^n\Theta_{I0}\approx e^{2n\epsilon}\Theta_{I0}. \tag{2.3}$$

This equation describes Hahn's basic idea: Though ϵ will be small if the S spins are rare, n may be large so that Θ_{In} may be made much larger than Θ_{I0}.

After a heating time T_h, H_{1S} is turned off and H_{1I} is turned on adiabatically, restoring the remaining order in the I spin system as magnetization along the rotating field, then suddenly switched off. The I-spin free-induction decay (FID) amplitude, which is proportional to the I-spin magnetization, is measured with a digital boxcar integrator. A similar device has been described elsewhere.[17] In order to improve the signal-to-noise ratio we averaged in critical cases over several experiments taking advantage of the infinite holding time of the digital readout.

The phase modulation of H_{1S} was achieved using a balanced modulator[6] which was driven by a trapezoidal audio voltage, the rise time of which could be adjusted to give a phase switching time which was short compared to T_2 but not instantaneous. To avoid unnecessary sidebands we usually used a "phase switching time" of about 100 μsec, with 1000 phase reversals per second.

All our experiments were done at liquid nitrogen temperature, where the spin-lattice relaxation times in the laboratory frame, T_1, and the rotating frame, $T_{1\rho}$, are

$$T_1=250\pm20\text{ sec},$$
$$T_{1\rho}=105\pm10\text{ sec},$$

respectively. Since the spin system has to return to thermal equilibrium after the free-induction decay, we had to wait after each FID for several minutes before performing another double-resonance experiment. Therefore, it took several hours to obtain an entire double-resonance spectrum. Consequently, good long time stability of the static magnetic field, H_{00}, was required. To obtain field regulation a commercial marginal-oscillator field control was used. However, the marginal-oscillator frequency, which controlled the magnetic field, was itself unstable. We therefore mixed it in a balanced mixer with the output of a crystal oscillator at the desired frequency. The output of the balanced mixer was amplified and fed to a varactor in parallel to the proton probe. In this way it was possible to phase lock the frequency of the marginal oscillator to the crystal frequency and therefore to achieve a long-time magnetic-field stability determined by the crystal.

To speed up the response of the magnet to regulation signals we wound small coils on the pole pieces to which we fed the fast components of the regulating signal. We

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thereby improved slow regulation response due to the large inductance of the main magnet coils. The two modifications greatly increased the stability of the magnetic field. In spite of these steps we feel that field fluctuations were one of the largest sources of noise, limiting the signal-to-noise ratio for the sodium FID signals to about 200.

Since the spin-lattice relaxation time was long, we could use heating times up to 100 sec. To correct for the influence of the spin-lattice relaxation in the demagnetized state, we always normalized our signals by dividing them by the FID amplitude observed using the same pulse sequence, but without an H_{1S} search field being applied.

Our crystals were grown from reagent grade NaCl doped with AgCl, both of which had been chlorine treated for 12 h to reduce the OH$^-$ impurity concentration. They were grown from the melt under argon gas atmosphere. Impurity concentrations in the crystals were: 0.001, 0.003, 0.007, 0.03, 0.11, 0.3, and 0.5%. These concentrations were determined using several independent methods: gravimetry, uv absorption spectroscopy,[18] flame, and absorption spectroscopy with visible light. There was significant inconsistency between the results for different methods. The limits of error for the absolute values of the concentrations given above are probably about ±50%, but we feel that the ratios of the concentrations are known more precisely, within ±20%. On the average the silver concentration in the crystal was about 40% of that in the melt for low concentrations.

III. EXPERIMENTAL RESULTS

A. Double-Resonance Spectrum

Double-resonance spectra, or graphs of I spin magnetization as a function of the search field frequency, ν_S, obtained using the procedure explained in Sec. II are shown in Fig. 1 for three orientations of the sample relative to H_{00}. The I spin resonance frequency, $\nu_I = 11.000$ MHz for $H_{00} = 9770$ G, is subtracted from the horizontal axis. The experimental parameters were: total heating time, $T_h = 2$ sec; H_{1S} (rotating component) $= 1.6$ G; and time between phase reversals, $t_p = 1.0$ msec. The large magnetization destruction for ν_S less than 16 kHz was caused by direct irradiation in the I spin resonance tail by H_{1S}. Plotting the resonance frequencies as a function of the sample orientation gave a rotation pattern consistent with that reported by Mallick and Schumacher[6] who assigned it to a Na nucleus in a (2,0,0) position relative to the impurity.

TABLE I. Destruction time constants under continuous search-field irradiation.

c (%)	τ (sec)
0.001	88 ±40
0.003	58 ±15
0.007	22.5±3
0.03	5.3±0.4
0.011	2.4±0.3
0.3	1.4±0.2
0.5	1.4±0.2

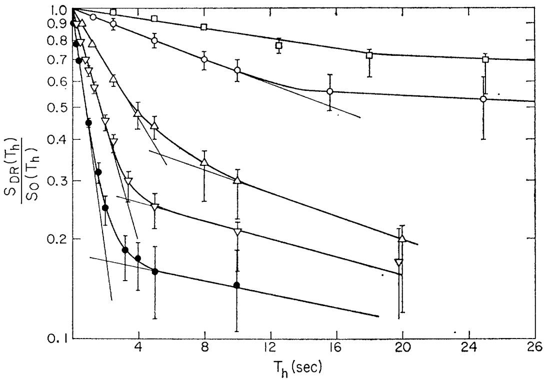

FIG. 2. I-spin magnetization remaining after search-field irradiation versus heating time for five impurity concentrations. From top to bottom c was 0.003, 0.007, 0.03, 0.11 and 0.5%. {$(\nu_S - \nu_I) = 40$ kHz, [100] parallel $\mathbf{H}_0$, $H_{1S} = 1.6$ G, continuous heating with time between phase reversals, $t_p = 1$ msec.}

Several very weak double-resonance lines, which could be observed in samples with very low Ag concentration, could not be identified as belonging to a specific impurity.

B. Time and Concentration Dependence of Double-Resonance Line

In this subsection we describe how the intensity of the double resonance line depended on the concentration of the impurities and the number of phase reversals of H_{1S} (or the heating time, T_h). For this study we chose the double resonance line at 40 kHz. This line was present when H_{00} was parallel to the [100] direction of the sample, and was chosen because the 40-kHz splitting was the largest observed. It resulted from an S spin at a (2,0,0) site relative to the silver impurity, and was well resolved from the quadrupole line at 20 kHz and from the tail of the I-spin resonance. We were able to detect this line with silver mole concentrations as low as 10 ppm obtaining a signal-to-noise ratio of about 2 without averaging.

Preliminary experiments had shown that the intensity of this line increased monotonically with increasing rf amplitude, H_{1S}. Therefore, we used $H_{1S} = 1.6$ G which was the maximum obtainable with our transmitter. Other parameters were also the same as in the previous section.

I-spin magnetization versus S-spin heating time for five silver impurity concentrations is plotted in Fig. 2. For short times the magnetization decayed exponentially, but for longer heating times the heating rate decreased. Since the dynamic range of the double-resonance line was not large, especially for very low concen-

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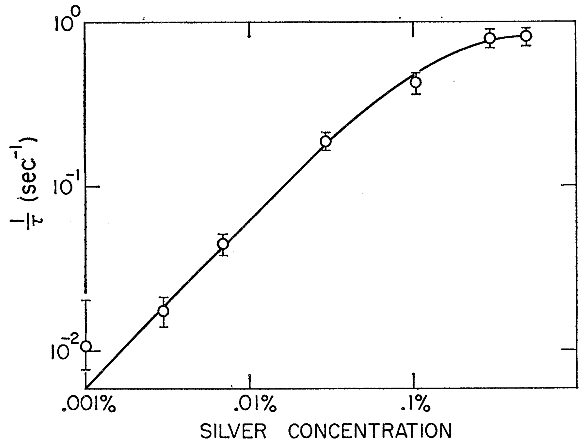

FIG. 3. Initial double-resonance destruction rate as a function of the Ag$^+$ concentration. Experimental conditions were the same as in Fig. 2. The precision of the concentration determination is discussed in the text.

trations, this decrease may have been an experimental error. It could also have been related to relaxation within various portions of the quadrupolar system which may have made our correction for spin-lattice relaxation during the heating time somewhat in error. We therefore focused our attention mainly on the initial times, during which the decay was exponential for all concentrations. In Table I the time constants τ of the initial decay are listed. The reciprocals of these initial time constants are graphed as a function of concentration in Fig. 3. Up to 0.03% the reciprocal time constants or destruction rates were proportional to concentration with a proportionality constant 600/sec. It seems reasonable that proportionality does not hold for larger concentrations since a significant fraction of the impurity atoms may be in adjacent pairs or groups. This would result in a smaller number of equivalent (2,0,0) neighbors per impurity ion which could contribute to the S-spin resonance.

We can calculate an upper bound for the destruction rate using a theory similar to that of LS. We are concerned with the quadrupole shifted transition $m=-\frac{1}{2} \leftrightarrow m=-\frac{3}{2}$. If the rf field is tuned to this transition, the energy levels of the two states in the rotating frame are easily calculated to be

$$E\pm=\pm\tfrac{1}{2}\sqrt{3}\gamma_S\hbar H_{1S}. \tag{3.1}$$

The total energy of the S-spin ensemble is, in the high-temperature approximation,

$$\bar{E}=-\tfrac{1}{2}Nc'\tfrac{3}{4}\gamma_S^2\hbar^2(H_{1S})^2/k\Theta, \tag{3.2}$$

where Θ is the ensemble spin temperature for these spins. c' is the concentration of equivalent nuclei which have quadrupole transitions satisfying the resonance condition with the rf field. In our case there are two equivalent (2,0,0) neighbors, so $c'=2c$, where c is the impurity concentration. However, since on the average two out of four states are connected by the rf field, only half of these nuclei are part of the S-spin system. $\bar{E}$ is the total energy given up by the S-spin ensemble if cooled from infinite temperature to temperature Θ. If this energy is used to heat the I spins from Θ_0 to Θ, energy conservation gives

$$\epsilon=(\Theta/\Theta_0)-1=\frac{Nc\frac{3}{4}\gamma_S^2(H_{1S})^2}{(5/4)N\gamma_I^2(H_L^2+H_{1I}^2)}, \tag{3.3}$$

where $(H_L^2)^{1/2}$ is the average local field at one nucleus due to its neighbors.[16] ϵ is the fractional change in magnetization of the I spins, as defined in Sec. II. In our experimental situation H_{1I} is zero, so

$$\epsilon=\tfrac{3}{5}c\gamma_S^2(H_{1S})^2/\gamma_I^2(H_L)^2. \tag{3.4}$$

If the total heating time is T_h, and the time between phase reversals is t_p, the fractional signal destruction is

$$M_f/M_i=e^{-T_h/\tau}, \tag{3.5}$$

with

$$1/\tau=2\epsilon/t_p=6000c\ \mathrm{sec}^{-1}. \tag{3.6}$$

This rate is ten times larger than observed experimentally. It could only be achieved if there were no limitation for the energy exchange process. In Sec. IV B we will discuss in detail how cross-relaxation time and spin diffusion determine the actual double-resonance destruction rate, which is smaller than the upper bound which we have estimated here.

C. Double Resonance with Intermittent Heating

The idea of the nuclear double-resonance experiment is based on the assumption that the energy absorbed by spins near impurities will be transmitted to the entire I-spin system, i.e., that the I-spin system is coupled strongly by spin spin interaction. If the S spins are brought to a high spin temperature they will couple strongly only to I spins nearby. Spin diffusion among the I spins has to distribute the energy within the I-spin system to reestablish a uniform I-spin temperature. In earlier works,[1,13] it was suggested that slow diffusion rates among the I spins may cause an inhomogeneous I-spin temperature and consequently reduce the double-resonance sensitivity. It was the purpose of the experiments described in this section to give experimental evidence for the build up of the inhomogeneous spin temperature.

To discuss these experiments we first want to describe the influence of slow spin diffusion in a conventional double-resonance experiment. Let us assume we turned on our heating field H_{1S} for a total time T_h during which we had n phase reversals. At the end of this period the I-spin temperature Θ_I is a function of the distance from the nucleus S, because of the slow I-spin diffusion rate. If we inspect the remaining order by remagnetizing the I spins, the amplitude of the free-induction decay signal will be proportional to the spatial average of the magnetization, which in turn is proportional to the spatial average of the inverse temperature before remagnetization,

$$M(t=T_h)=C_I H_{1I}\left(\frac{H_L^2}{(H_{1I})^2+H_L^2}\right)^{1/2} \times\int\frac{dv}{\Theta(r,\,t=T_h)},\tag{3.7}$$

where C_I is the I-spin Curie constant.

Now one might expect that leaving the I spins in the demagnetized state and giving them a chance to reach a uniform spin temperature during a delay time t_α before observing the free-induction decay might give some information about the degree of inhomogeneity of the spin temperature at the end of the search-field irradiation. However, a simple argument shows that this is not true: Apart from spin-lattice relaxation effects, for which we correct the experimental results, the internal energy of the I-spin system during the delay time is constant. Thus we have

$$-E=C_I H_L^2\int\frac{dv}{\Theta(r,\,t=T_h)} =C_I H_L^2\int\frac{dv}{\Theta(r,\,t=T_h+t_d)},\tag{3.8}$$

from which it follows that

$$M(t=T_h)=M(t=T_h+t_d).\tag{3.9}$$

Thus by waiting after the search-field irradiation before inspecting the FID signal we should not get information about the spatial distribution of the spin temperature. Figure 4 shows the experimental verification of this statement. The size of the remaining I-spin FID signal (after a heating time, $T_h=2.5$ sec, with 2500 phase reversals of H_{1S}) is plotted as a function of the delay time before inspection in a NaCl sample doped with 0.03% AgCl. In order to correct for spin-lattice relaxation these data have been normalized as described above. The figure shows that this ratio is essentially constant for t_d between 3 nsec and 90 sec.

How can one observe the buildup of a nonuniform I-spin temperature? Assuming that the S spins represent a continuous source of heat flowing into the I system, the I nuclei close to the impurity will rise to a higher than average spin temperature if the spin diffusion is not fast enough to communicate this heat flow to all the I nuclei. The S spins then can couple only to more distant I spins and consequently the double-resonance heating rate decreases. If the heat flow were interrupted the I-spin system would reach uniform spin temperature after a certain time. If then the heat source were turned on again, the full initial double-resonance rate would be observed. Consequently in order to observe the buildup of a nonuniform spin temperature we did not use continuous heating but rather groups of heating pulses which were separated by some interruption time t_i. We studied the double-resonance sensitivity as a function of this interruption time for a given number of pulses per group.

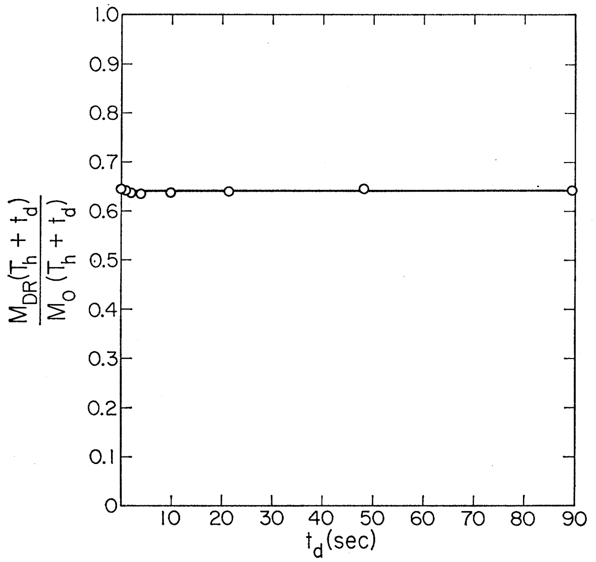

FIG. 4. Remaining I-spin magnetization after 2.5 sec of continuous heating as a function of the delay time t_d between the end of the heating time and the I-spin remagnetization. The data have been corrected for the effects of spin-lattice relaxation during the delay time.

Below are the results of an experiment which demonstrates this effect. In Fig. 5 the experimental values of D_{pp} (fractional destruction of the I-spin magnetization per phase reversal) are plotted as a function of the interruption time between heating bursts for 2, 4, and 20 phase reversals in each H_{1S} burst. The total number of pulses during the heating period was 1600, the time between phase reversals 1 msec, and H_{1S} 1.6 G. As expected for the diffusion limited case, the signal de-

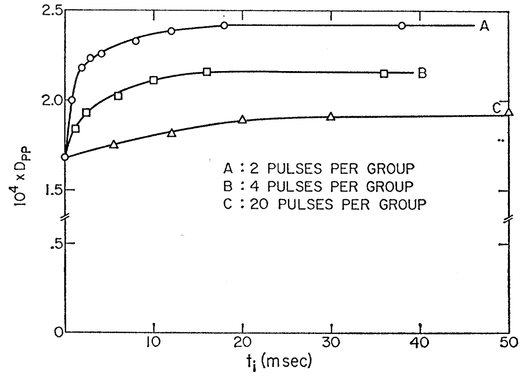

FIG. 5. Double-resonance efficiency with intermittent heating. The fractional destruction of I-spin magnetization per single phase reversal, D_{pp}, is plotted versus the interruption time t_i between the heating bursts. The total number of phase reversals was 1600, the time between phase reversals, $t_p=1$ msec, $\nu_S-\nu_I=40$ kHz, $H_{1S}=1.6$ G, [100] parallel to H_0, $c=0.03\%$.

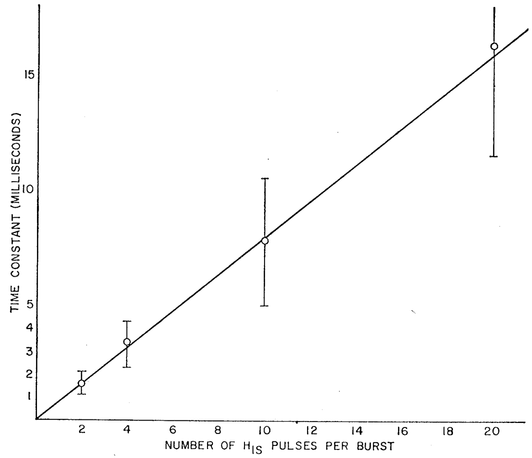

FIG. 6. "Recovery time constants" in an experiment with intermittent heating versus the number of pulses per burst. Experimental conditions are the same as in Fig. 5.

struction increased when the I-spin system was given time to carry away the heat transferred to I spins near S spins.

The experimental curves can be fitted by single exponentials, the time constants of which reflect the approach of the I-spin system to a uniform temperature. Figure 5 shows that there is a slower recovery of heating efficiency for longer bursts. This is illustrated in Fig. 6 by a graph of the "recovery time constant" as a function of the number of phase reversals in each H_{1S} burst. Within the rather large limits of error the time constants were proportional to the number of pulses per group. This shows that a longer heating burst created a larger hot region and it then took a longer time to recover to a uniform spin temperature.

D. Ag^{109} Double Resonance

So far we have been concerned with the double resonance of sodium nuclei which had a nuclear magnetic resonance shifted by electric-field gradients in the neighborhood of an impurity. However, we were also able to observe the double resonance of the silver impurity itself, specifically the Ag^{109} nuclei.

Figure 7 shows an example of this line for impurity concentrations, $c=0.107\%$ and $c=0.5\%$. The heating time necessary to detect this line was 100 sec, H_{1S} was adjusted to 7.2 G, and H_{1I} was not turned off during the heating time in order to match the Hahn condition, $\gamma_S H_{1S}=\gamma_I H_{1I}$. With H_{1I} off during the heating period we were not able to detect the double resonance.

For the same impurity concentrations, the intensity of this double-resonance line was about 500 times lower than that of the (2,0,0) Na neighbors. A rough estimate of the relative intensities predicts a ratio of about 800 when the 48.7% natural abundance of Ag^{109}, the lower silver heat capacity, and the smaller dipole coupling of the S-spin ensemble to the I spins is taken into account. The latter two effects are caused by the smaller gyromagnetic ratio of the Ag^{109} nuclei and the fact that Ag^{109} has a spin $S=\frac{1}{2}$. Since experimental and theoretical ratios are approximately equal, we have no indication that the silver nuclei are more effectively isolated from the I-spin system by a "diffusion bottleneck" than are the (2,0,0) neighbors. A more thorough investigation of this topic did not appear promising since the intensity of the silver double-resonance line was so low.

IV. DOUBLE-RESONANCE PROCESS

A. Basic Equations

Since the double-resonance process has been described in detail in the basic papers by HH and LS we want to point out here only the modifications which result from the inclusion of the quadrupole interaction. We adopt in the following the notation of LS. The unperturbed abundant Na nuclei will be called the I-spin system, the rare quadrupole affected Na nuclei the S-spin system. The Hamiltonian in the laboratory frame thus is made up by the respective Zeeman energies, $\mathcal{H}_{ZI}$ and $\mathcal{H}_{ZS}$, the dipolar coupling within the spin systems, $\mathcal{H}_{dII}$ and $\mathcal{H}_{dSS}$, respectively, and the dipolar coupling between the I and S systems, $\mathcal{H}_{dIS}$. In addition to these terms we must include the quadrupole coupling acting on the S spins, $\mathcal{H}_Q$. Since the quadrupole interaction in our particular case is axially symmetric as a result of the lattice symmetry, we will consider only an axially symmetric Hamiltonian which may be written, to first order, as

$$\mathcal{H}_Q=E_Q(3\cos^2\Theta-1)(3S_z^2-S^2)\,, \tag{4.1}$$

where E_Q contains the field gradient and the quadrupole moment, and θ is the angle between the axis of the quadrupole interaction and the magnetic field.

For the Zeeman part we will pretend that we have applied rotating instead of linear polarized fields. We have then

$$\begin{aligned}\mathcal{H}_{ZI}(t)=-\gamma_I\hbar[I_zH_0+I_x(H_{1I}\cos\Omega_It+H_{1S}\cos\Omega_St)\\+I_y(H_{1I}\sin\Omega_It+H_{1S}\sin\Omega_St)]\,,\end{aligned} \tag{4.2}$$

and a similar equation for the S system, where the spin operators are understood as summations over all the respective nuclei.

In order to use the concepts of statistical mechanics and in particular of spin temperature we will transform our Hamiltonian to a representation where the time dependence of $\mathcal{H}_Z(t)$ is removed, as usual. Special care must be applied however in considering the quadrupole part. Leppelmeier and Hahn[19] have shown that for the pure quadrupole case with a linearly polarized rf field of frequency Ω_Q applied, the appropriate unitary transformation is given by

$$T_Q=\exp[\tfrac{1}{6}i\Omega_Qt(3S_z^2-S^2)]\,. \tag{4.3}$$

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[19] G. W. Leppelmeier and E. L. Hahn, Phys. Rev. **142**, 179 (1966).

They point out that this transformation corresponds to a transformation into two rotating frames precessing in opposite directions, one sense of rotation belonging to the $m_s=+\frac{3}{2}\leftrightarrow+\frac{1}{2}$ transition, the opposite to the $m_s=-\frac{3}{2}\leftrightarrow-\frac{1}{2}$ transition. Each of the two circularly polarized components of the linearly polarized rf field now couples that pair of spin levels, which has the corresponding direction of rotation.

In the high-field case, however, one of the circularly polarized components is strongly distinguished by the sense of the precession of the nuclei in the magnetic field. Therefore it is legitimate to consider only the corresponding rotating component of the linear field and simply to apply the transformation commonly used in the pure magnetic double-resonance case,

$$T=\exp[i\Omega_I I_z t]\exp[i\Omega_S S_z t]. \tag{4.4}$$

Standard evaluation gives for the transformed Hamiltonian[20]

$$\begin{aligned}\mathcal{H}&=T\mathcal{H}T^{-1}-i\hbar T\frac{\partial T^{-1}}{\partial t}\\ &=-\gamma_I\hbar[(H_0+\Omega_I/\gamma_I)I_z+H_{1I}I_x]\\ &\qquad-\gamma_S\hbar[(H_0+\Omega_S/\gamma_S)S_z+H_{1S}S_x]\\ &\qquad+E_{QS}(3\cos^2\theta_S-1)(3S_z^2-S^2)\\ &\qquad+E_{QI}(3\cos^2\theta_I-1)(3I_z^2-I^2)\\ &\qquad+\mathcal{H}_{dII}^0+\mathcal{H}_{dSS}^0+\mathcal{H}_{dIS}^0\\ &\qquad\quad+\text{time-dependent terms we ignore.}\end{aligned} \tag{4.5}$$

$\mathcal{H}_{dII}^0$, $\mathcal{H}_{dSS}^0$, and $\mathcal{H}_{dIS}^0$ are the so-called secular, or time-independent, parts of the dipolar interaction. They are given explicitly in Ref. 2.

In the Hamiltonian (4.5) we have included a quadrupole part for the I spins, although they were defined as unperturbed nuclei. The reason is that nuclei in the $m=\pm\frac{1}{2}$ levels belong to the I system as long as second-order quadrupole effects are unimportant. To first order, the energy difference between these levels in the laboratory frame is equal to that of the unperturbed nuclei. This is different in the rotating frame and as an illustration let us consider the energy levels in the rotating frame for a series of spins I with increasing quadrupole interaction. We will neglect the dipolar interaction and will restrict ourselves to a spin $\frac{3}{2}$. Furthermore we will assume that only one rf field, H_{1I}, is applied and that the quadrupole interaction is small enough to give no shift for the $m=\frac{1}{2}\leftrightarrow m=-\frac{1}{2}$ transition in the laboratory frame. Solution of the Schrödinger equation in the rotating frame, with Ω_I at the resonance frequency of the unperturbed $m=\frac{1}{2}\leftrightarrow m=-\frac{1}{2}$ transition gives the energy levels in the rotating frame

$$\begin{aligned}\epsilon_{1,2}&=[-1\pm(4+x^2+2x)^{1/2}]\tfrac{1}{2}\gamma\hbar H_{1I},\\ \epsilon_{3,4}&=[1\pm(4+x^2-2x)^{1/2}]\tfrac{1}{2}\gamma\hbar H_{1I},\end{aligned} \tag{4.6}$$

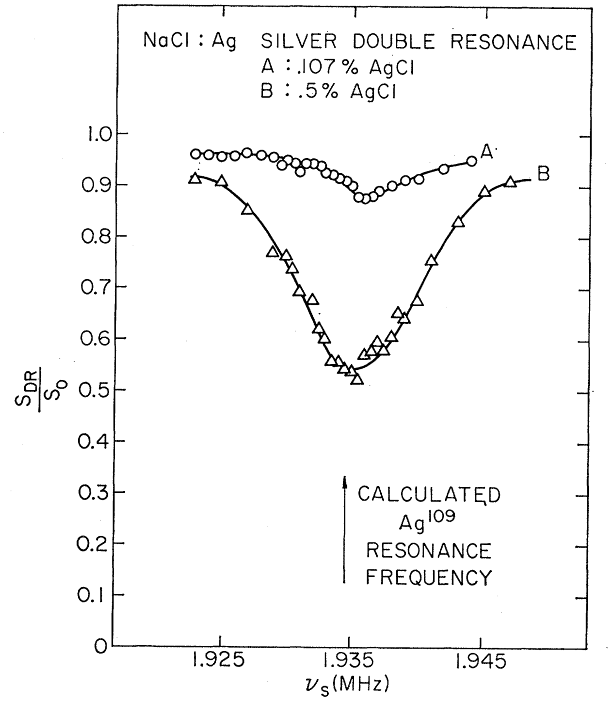

FIG. 7. Ag^{109} double-resonance spectrum for 0.11% $Ag^+(A)$ and 0.5% $Ag^+(B)$ in a NaCl single crystal. (Heating time, $T_h=100$ sec, $H_{1I}=1.3$ G, $H_{1S}=7.2$ G, time between phase reversals $t_p=1$ msec.)

with

$$x=\frac{3E_{QI}(3\cos^2\theta_I-1)}{\frac{1}{2}\gamma\hbar H_{1I}}. \tag{4.7}$$

In the laboratory frame for a first-order perturbation approximation, the energy levels of the states $m=+\frac{1}{2}$ and $m=-\frac{1}{2}$ remain equidistant. In contrast, there is no such pair of equidistant levels in the rotating frame for a set of nuclei experiencing slightly different electrical field gradients, as shown in Fig. 8. The success of a nuclear double resonance experiment depends on the possibility of spin diffusion within the surrounding I-spin system, and it has been shown that spin diffusion decreases rapidly if the energy levels of the nuclei involved are not equally spaced.[21,22] Now in our experiment the surrounding spins are nuclei which feel decreasing field gradients and therefore do not have equally spaced energy levels in the rotating frame. However, if H_{1I} is smaller or on the order of the linewidth, the difference in the level spacing may be made up by local field variations and no serious decrease in the spin-diffusion rate might be expected.

B. Spin Diffusion

In the experiments with intermittent heating, which were described in Sec. III C, the heating rate per pulse

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[20] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row Publishers, Inc., New York, 1963).

[21] P. S. Pershan, Phys. Rev. **117**, 109 (1960).

[22] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

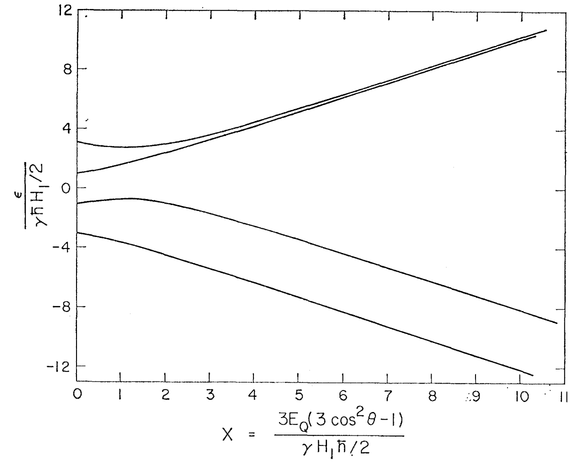

FIG. 8. Energy levels of a spin $\frac{3}{2}$ in a frame rotating at the unperturbed Larmor frequency versus the quadrupole shift of the transition $m=\frac{3}{2} \leftrightarrow m=\frac{1}{2}$, $|\nu_Q| = 6\, E_Q(3\cos^2\Theta - 1)$.

decreased a few milliseconds after the heating field was turned on. In other words, after a few pulses the S spins were no longer able to couple to the I spins so effectively as at the start.

In this subsection we discuss a simple phenomenological model, based on the concept of spin diffusion introduced by Bloembergen,[15] in terms of which we try to describe the dynamics of the nuclear double-resonance process. Similar models have been used previously for the calculation of nuclear double-resonance dynamics.[1,13] The idea of spin diffusion has been applied most successfully for the calculation of nuclear spin-lattice relaxation times in solids with paramagnetic impurities[23–26] for different limiting cases. DeGennes[23] studied the case in which coupling of the S spin (in his case a paramagnetic ion) to the lattice held its temperature at the lattice temperature. Furthermore, he assumed that the coupling of the S spins to the neighboring I spins was so strong that the neighbors were at the S-spin temperature. In our case we cannot assume that the I-S coupling is strong compared to the I-I coupling —it is in fact weak, a limiting case considered by Blumberg.[24] Below we present an analysis which differs from his. Our leading term is the same as his, but we find the correction arising from the I-I coupling.

During the nuclear double-resonance process, energy has to be exchanged between the I and the S spins. This energy exchange is made possible by the dipolar interaction between I and S spins. However, since this is a short range interaction, the S spins can exchange energy only with nearby neighbors. To make an efficient energy exchange possible, spin diffusion among the I spins must carry the energy to the entire I-spin system in an attempt to reestablish a spatially uniform I-spin temperature. If the spin diffusion is not fast enough, the I-spin temperature around the impurities will increase locally, thereby decreasing the coupling rate between the S-spin ensemble and the I-spin reservoir. We call this phenomenon the "diffusion bottleneck."

We assume that the S spins are homogeneously distributed over the lattice, each of them having a sphere of equal radius B around it which contains only unperturbed nuclei I.

The S spins communicate with the I spins through their mutual dipolar interaction. We approximate the resulting coupling rate by a simple radial function,[15]

$$g(r) = K/r^6, \tag{4.8}$$

neglecting the angular dependence of the interaction. r is the distance between the S spin at the origin and the I spin. Because of the r^{-6} dependence of the coupling rate, the S spins will effectively interact only with close neighbors. However the strong dipolar interaction between the I spins provides a path to transfer energy over longer distances. This has been analyzed by Bloembergen in terms of a diffusion concept, where

$$\frac{\partial\beta(r,t)}{\partial t} = D\nabla^2\beta(r,t) - g(r)[\beta(r,t) - \beta']. \tag{4.9}$$

$\beta(r,t)$ is the inverse I-spin temperature $(k\Theta)^{-1}$, β' the inverse S-spin temperature (which we will set equal to zero).[27]

The diffusion approach is valid only on a scale large compared to the lattice constant. Consequently we set $D=0$ in a small sphere of radius b around the S spin, where b is probably on the order of the nearest I-spin neighbor distance. The inner boundary condition then becomes

$$\left.\frac{\partial\beta(r,t)}{\partial r}\right|_{r=b} = 0. \tag{4.10}$$

The outer boundary condition is given by the fact that there is no net heat flow across this boundary, which is "equidistant" from impurities, and thus no gradient in temperature, so

$$\left.\frac{\partial\beta(r,t)}{\partial r}\right|_{r=B} = 0. \tag{4.11}$$

We will use for the solution of Eq. (4.9) a perturbation

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[23] P. G. de Gennes, J. Phys. Chem. Solids **7**, 345 (1958).

[24] W. E. Blumberg, Phys. Rev. **119**, 79 (1960).

[25] G. R. Khutsishvili, Proc. Inst. Phys. Acad. Sci. Georgia (USSR) **4**, 3 (1956).

[26] G. R. Khutsishvili, Usp. Fiz. Nauk **87**, 211 (1965) [English transl: Soviet Phys.—Usp. **8**, 743 (1966)].

[27] In actual fact, β' is not zero, but changes from positive to negative or from negative to positive each time H_{IS} changes phase. In between, β' relaxes towards the positive value of β of the nearby I spins. If this relaxation time is long compared to the time between phase reversals, the time average of β' is zero, and β' may be taken as zero in Eq. (4.9). Experimental evidence that this condition is satisfied is that the destruction per pulse, D_{pp}, shall be proportional to the duration of the pulse. In our case for a pulse length of 8 msec the proportionality factor was 83% as large as for the 1-msec pulse, showing that the assumption $\beta'=0$ was well satisfied for the 1-msec pulse length. This result is consistent with the theoretical value of T_X given in Eq. (4.53).

approximation. For values of r much beyond b, $g(r)$ is small enough to be considered a small perturbation for the diffusion equation,

$$\frac{\partial\beta^0(r,t)}{\partial t}=D\nabla^2\beta^0(r,t). \tag{4.12}$$

We will show later that this approach is justifiable for small concentrations.

Time and radial dependence in the solutions of this differential equation can be separated, giving

$$\beta_n(r,t)=R_{k_n}(r)e^{-\mu_n t}, \tag{4.13}$$

where the $R_{k_n}(r)$ are the eigenfunctions of the unperturbed radial problem

$$D\nabla^2 R_{k_n}(r)=-\mu_n R_{k_n}(r). \tag{4.14}$$

The spherically symmetric solutions of this equation are well known and can be written as

$$R_{k_n}(r)=(1/r)\sin[k_n(r-b)+\Phi]. \tag{4.15}$$

The boundary condition at $r=b$ determines the phase constant,

$$\tan\Phi=k_n b$$

or

$$\Phi\approx k_n b,\quad k_n b\ll 1. \tag{4.16}$$

The values k_n are determined from the boundary condition $\tan(k_n B)=k_n B$. The solutions of this equation can be written in the form

$$k_n B=\alpha_n\pi, \tag{4.17}$$

where the α_n's have the limits

$$n\leq\alpha_n\leq n+\tfrac{1}{2}, \tag{4.18}$$

with $\alpha_0=0$. For higher n the α_n's converge fairly rapidly towards the value $n+\frac{1}{2}$. The eigenvalues μ_n are then given by

$$\mu_n=Dk_n{}^2=\alpha_n{}^2\pi^2 D/B^2. \tag{4.19}$$

If we normalize the functions by requiring that

$$4\pi\int_b^B |R_{k_n}(r)|^2 r^2 dr=1, \tag{4.20}$$

the approximately normalized solutions for the diffusion problem are

$$\beta_{k_0}(r,t)=(4\pi B^3/3)^{-1/2}=|k_0\rangle, \tag{4.21}$$

and for $n>0$

$$\begin{aligned}\beta_{k_n}(r,t)&=\frac{\sin k_n r}{(2\pi B)^{1/2}r}\exp\left(-\frac{D}{B^2}\alpha_n{}^2\pi^2 t\right)\\ &=|k_n\rangle\exp\left(-\frac{D}{B^2}\alpha_n{}^2\pi^2 t\right).\end{aligned} \tag{4.22}$$

Since, at $t=0$, we have uniform spin temperature,

$$\beta(r,\,t=0)=(H_0/H_L)\beta_{\text{lattice}}=\beta_i, \tag{4.23}$$

we have the initial condition

$$\beta(r,\,t=0)=(4\pi B^3/3)^{1/2}\beta_i|k_0\rangle. \tag{4.24}$$

Now we turn on the heating field so that the direct dipolar coupling term is no longer zero. However, we will treat it as a small perturbation to the diffusion equation, an approximation we justify below. The solutions of the entire differential equation can be separated as before,

$$\beta_{q_m}(r,t)=R_{q_m}(r)e^{-\lambda_m t}=|q_m\rangle e^{-\lambda_m t}, \tag{4.25}$$

where the λ_m are the eigenvalues of the radial part. Since the same boundary conditions hold and since the solutions $|k_n\rangle$ of the diffusion part alone form a complete set of orthonormal functions we can expand the functions $|q_m\rangle$ in terms of the $|k_n\rangle$:

$$|q_m\rangle=\sum_n |k_n\rangle\langle k_n|q_m\rangle. \tag{4.26}$$

Immediately after turning on H_{1S} there is still a uniform spin temperature and we can expand this initial distribution in terms of the q_m:

$$\beta(r,\,t=0)=(4\pi B^3/3)^{1/2}\beta_i\sum_m |q_m\rangle\langle q_m/k_0\rangle. \tag{4.27}$$

However this is no longer an equilibrium distribution because of the heating. The time evolution is given by

$$\begin{aligned}\beta(r,t)&=(4\pi B^3/3)^{1/2}\beta_i\sum_m |q_m\rangle\langle q_m|k_0\rangle e^{-\lambda_m t}\\ &=(4\pi B^3/3)^{1/2}\beta_i\sum_{m,n}|k_n\rangle\\ &\qquad\times\langle k_n|q_m\rangle\langle q_m|k_0\rangle e^{-\lambda_m t}.\end{aligned} \tag{4.28}$$

Experimentally we measure the spatial average of β, which we calculate as

$$\begin{aligned}\bar{\beta}(t)&=(4\pi B^3/3)^{-1/2}\langle k_0|\beta(r,t)\rangle\\ &=\beta_i\sum_m |\langle k_0|q_m\rangle|^2 e^{-\lambda_m t}.\end{aligned} \tag{4.29}$$

The spatial average of the magnetization thus decays with a series of rate constants λ_m each of which is weighted by the matrix element $|\langle k_0|q_m\rangle|^2$.

The rate constants λ_m may be computed by perturbation theory to be

$$\lambda_m=\mu_m+\langle k_m|g(r)|k_m\rangle+\sum_n\frac{\langle k_m|g(r)|k_n\rangle\langle k_n|g(r)|k_m\rangle}{\mu_m-\mu_n}. \tag{4.30}$$

If we define the fractional S-spin concentration to be c_S, we will show below that μ_m is proportional to $c_S{}^{2/3}$, whereas the next terms in (4.30) go as c_S. Therefore the first-, second-, and higher-order perturbation terms are small compared to the difference between the unperturbed values μ_m at low concentration.

On the other hand, as we also show, the ratio of the second order correction term to the first-order correction term is independent of concentration, but is proportional to T_D/T_x, where

$$1/T_x \equiv K/d^6, \qquad 1/T_D \equiv D/d^2, \tag{4.31}$$

d being the lattice constant. Thus, as D becomes infinite, the case of negligible diffusion barrier among the I spins, we can neglect the second-order terms. The relative size of the first- and second-order terms thus indicates the importance of the diffusion bottleneck.

Using Eqs. (4.19) and (4.30) we see that the exponentials λ_m for $m\neq 0$ decay rapidly compared to that term $m=0$, so that after a short time we are left with only a single exponential of rate λ_0.

Since $\mu_0=0$, we have

$$\lambda_0=\langle k_0|g(r)|k_0\rangle-\sum_n\frac{|\langle k_0|g(r)|k_n\rangle|^2}{\mu_n}. \tag{4.32}$$

Inserting explicit forms for $|k_0\rangle$ and $|k_n\rangle$ (in the limit $k_nb\ll 1$) enables us to evaluate the matrix elements. We find

$$\langle k_0|g(r)|k_0\rangle=K/B^3b^3. \tag{4.33}$$

The outer boundary B can be related to c_S, d, and the number of spins per unit cell n^* ($n^*=4$ for fcc NaCl), assuming b is equal to the nearest I spin distance $b=d/\sqrt{2}$

$$B^3=3d^3/4\pi n^*c_S. \tag{4.34}$$

Using Eqs. (4.31) and (4.34) we find

$$\langle k_0|g(r)|k_0\rangle=8\sqrt{2}n^*c_S/3T_x, \tag{4.35}$$

$$\langle k_0|g(r)|k_n\rangle=16\pi^2n^*\alpha_nc_S/3\sqrt{3}T_x, \quad k_nb\ll 1 \tag{4.36}$$

$$\mu_n=(4\pi n^*c_S/3)^{2/3}\alpha_n^2\pi^2/T_D. \tag{4.37}$$

Utilizing Eqs. (4.36) and (4.37) we see that

$$|\langle k_0|g(r)|k_n\rangle|^2/\mu_n$$

is proportional to $(c_S)^{4/3}$ but is independent of n since α_n^2 in the denominator is exactly canceled by α_n^2 in the numerator. If the terms were *strictly* independent of n, the summation in Eq. (4.32) would be infinite. In fact, however, the term is only independent of n for $k_nb\ll 1$. An evaluation of the matrix element without this restriction shows that the terms begin to drop significantly when

$$k_nb=\tfrac{1}{2}\pi. \tag{4.38}$$

Utilizing Eq. (4.18), we see that the number of terms N with k less than or equal to any value k_n is

$$N=k_nB/\pi, \tag{4.39}$$

so that

$$N=\frac{B}{2b}=\frac{1}{\sqrt{2}}\left(\frac{3}{4\pi n^*c_S}\right)^{1/3}. \tag{4.40}$$

Roughly, therefore,

$$\sum_n\frac{|\langle k_0|g(r)|k_n\rangle|^2}{\mu_n}=N\frac{|\langle k_0|g(r)|k_1\rangle|^2}{\mu_1}=\frac{64\pi}{9}\frac{T_D}{T_x^2}n^*c_S. \tag{4.41}$$

The second-order term can be evaluated more accurately by using the exact boundary condition at $r=b$ in computing the matrix elements, replacing the sum over k_n by an integral over k and doing the integration. The result is

$$\sum_n\frac{|\langle k_0|g(r)|k_n\rangle|^2}{\mu_n}=\frac{64\sqrt{2}\pi n^*c_S}{21}\frac{T_D}{T_x^2}. \tag{4.42}$$

This equation verifies our previous statement that the first order and second order terms are both proportional to c_S, but that their relative magnitudes go as T_D/T_x.

The resultant decay rate λ_0 is therefore

$$\lambda_0=\frac{8\sqrt{2}\pi n^*c_S}{3T_x}-\frac{64\sqrt{2}\pi n^*c_S}{21}\frac{T_D}{T_x^2}. \tag{4.43}$$

The second term, being negative, reduces the destruction rate. It describes the bottleneck. Higher-order terms in the perturbation expansion can easily be shown to be proportional to c_S and progressively higher powers of T_D/T_x. The fact that the relative importance of the two terms in Eq. (4.43) is independent of concentration is physically reasonable since the bottleneck should occur close to $r=b$, and should not depend on the distance to the outer boundary $r=B$. A schematic diagram illustrating the perturbation theory is shown in Fig. 9.

A straightforward interpretation of Eq. (4.43) is to define two times T_{IS} and T_{II}, the decay times we would have if T_D or T_x are respectively taken to be zero. We assume the *total* decay time to be the sum of the two since it can never go faster than the slower of the two times. Then

$$\lambda_0=\frac{1}{T_{IS}+T_{II}}. \tag{4.44}$$

If $T_{IS}\gg T_{II}$ we can expand to get

$$\lambda_0=\frac{1}{T_{IS}}\left(1-\frac{T_{II}}{T_{IS}}\cdots\right). \tag{4.45}$$

Comparing this equation with Eq. (4.43) we get

$$\begin{aligned}\frac{1}{T_{IS}}&=\frac{8\sqrt{2}}{3}\frac{n^*c_S}{T_x},\\ \frac{1}{T_{II}}&=\frac{7\sqrt{2}}{3}\frac{n^*c_S}{T_D},\\ \lambda_0&=\frac{8\sqrt{2}\pi n^*c_S}{3}\frac{1}{T_x+(8/7)T_D},\end{aligned} \tag{4.46}$$

and

$$\frac{T_{II}}{T_{IS}}=\frac{8}{7}\frac{T_D}{T_x}. \tag{4.47}$$

We can therefore interpret Fig. 5 in simple terms. Assuming that no bottleneck has time to form for the two pulses, we have that curve A for long t_i corresponds to a decay rate of $1/T_{IS}$, but that when t_i is zero the decay rate is $1/(T_{IS}+T_{II})$.

We have derived an equation of the form of Eq. (4.45) by perturbation theory. It is tempting to believe that Eq. (4.44) is however more accurate than Eq. (4.45), and would in fact be the result of summing the second-, third-, and higher-order perturbations exactly. We shall assume Eq. (4.44) to be exact.

We get, therefore, from Fig. 5 that

$$\frac{T_{IS}+T_{II}}{T_{IS}}=\frac{2.4}{1.7} \tag{4.48}$$

or that

$$\frac{T_{II}}{T_{IS}}=0.4. \tag{4.49}$$

We can calculate T_x and T_D from first principles. We have to estimate the values of D and K. If the resonance condition in the rotating frame

$$\sqrt{3}\gamma_S H_{1S}=\gamma_I H_L \tag{4.50}$$

is matched we can calculate the probability W_{IS} for a mutual I-S spin flip flop transition in a manner similar to Bloembergen's calculation of the spin diffusion constant. A more detailed theory has been given by Khutsishvili[26] which yields, if extended to spin $\frac{3}{2}$,

$$W_{IS}=\frac{1}{8\sqrt{2}}\left(\frac{\mu_0}{4\pi}\right)^2 h^2\gamma^4(r_{IS})^{-6}T_2(1-3\cos^2\theta_{IS})^2$$
$$\times|\langle m_I m_S|I^+S^-+I^-S^+|m_I' m_S'\rangle|^2. \tag{4.51}$$

r_{IS} is the distance from an I nucleus to an S nucleus, θ_{IS} the angle between the line connecting them and the external magnetic field, H_0. If we assume a homogeneous distribution of I spins, and average over the angular function, we can approximate the dipolar coupling rate from an S spin to an I spin at a distance r by

$$g(r)=K/r^{-6}, \tag{4.52}$$

where numerical evaluation gives

$$1/T_x\equiv K/d^6\cong 14\ \text{sec.}^{-1}. \tag{4.53}$$

Similarly we estimated the diffusion constant,

$$1/T_D\equiv D/d^2\cong 180\ \text{sec}^{-1}, \tag{4.54}$$

giving

$$T_{II}/T_{IS}=0.09,$$

to be contrasted with the value of 0.4 determined from the intermittent pulse experiments.

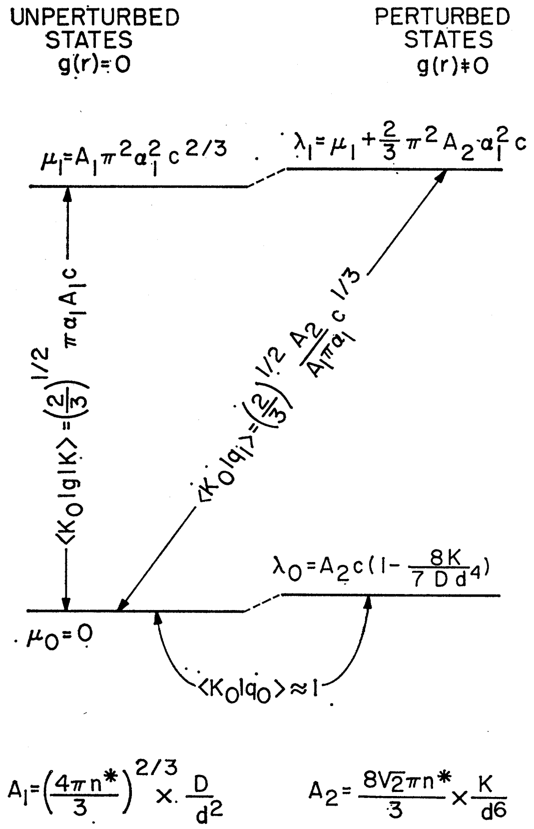

FIG. 9. Rate eigenvalues and matrix elements for a spherically symmetric diffusion problem.

As pointed out in Sec. III B, in our case c_s is equal to the impurity concentration, c. We get, therefore, that the theoretical value of T_{IS} is

$$1/T_{IS}\approx 670c\ \text{sec}^{-1}.$$

The experimental λ_0 is

$$(\lambda_0)_{\text{exp}}=600c\ \text{sec}^{-1}.$$

Using Eq. (4.48) this gives the experimental value of T_{IS} as

$$1/T_{IS}=840c\ \text{sec}^{-1}.$$

The fact that the theoretical T_{IS} is fairly close to this value suggests our estimate of D is too high, at least for the region near the impurity, perhaps because the model has simplified many of the details of the real situation. In fact, the agreement for T_{IS} is much better than one could reasonably expect, in view of the crude approximations we have made.

We do not know what causes the decrease in the double-resonance sensitivity at higher concentrations which was found experimentally. Our estimates tell us that perturbation theory is still valid. However, interactions between the impurities may become important, and there may be aggregation to pairs or groups of impurities, thereby reducing the number of active impurities.

Spin diffusion does not seriously limit the double resonance sensitivity in our case. Our leading term corresponding to $D=\infty$ is identical with that of Blumberg.[24] However, as we see it is possible to observe the small bottleneck and to account for it approximately by a simple theory.

ACKNOWLEDGMENTS

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APPENDIX: SPIN-LATTICE RELAXATION IN DEMAGNETIZED STATE

At the beginning of each experiment we measured the spin-lattice relaxation time of the Na nuclei at 77°K. The spin lattice relaxation time in the laboratory frame, which was determined from the recovery of the magnetization after complete saturation, was independent of the impurity concentration $T_1=250\pm20$ sec. It was in all cases a single exponential relaxation within the experimental error.

The spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, was determined from the approach to thermal equilibrium of the I spins after a complete adiabatic demagnetization in the rotating frame, as measured by the size of the FID signal after adiabatic remagnetization. Figure 10 shows the results for different concentrations of silver impurities. After a few seconds the approach to thermal equilibrium for all samples was exponential with a time constant $T_{1\rho}=105\pm10$ sec. However, in the first few seconds the magnetization decreased rapidly and the size of this initial spike was larger for higher impurity concentrations.

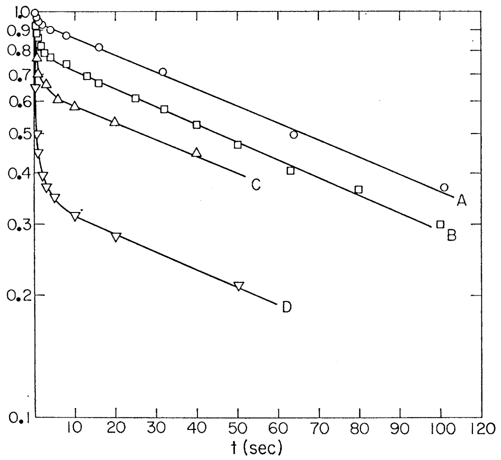

FIG. 10. Spin-lattice relaxation in the demagnetized state for NaCl with Ag^+ impurities. The magnetization of the sodium nuclei is plotted versus the time they have been in the demagnetized state. The impurity concentration was 0.03, 0.11, 0.3, and 0.5% for A, B, C, and D, respectively.

This result closely resembles the results obtained by Hebel,[28] who measured the spin-lattice relaxation at zero external field in aluminum with zinc impurities and by Fernelius,[10,11] who made further detailed studies of the cross-relaxation. We do not want to go through a detailed analysis here but will rather give a qualitative explanation. There are two groups of nuclei: Spins close to an impurity, which have quadrupole splittings greater than the rms dipolar splitting, will be called the Q system; spins which are sufficiently far from the impurity that the average dipolar interaction exceeds the quadrupole splitting will be called the dipolar system, D. They are represented by their spin Hamiltonians, $\mathcal{H}_Q$ and $\mathcal{H}_D$, respectively. (Note: Fernelius[10,11] showed that for zinc impurities in aluminum, part of the Q system should actually be added to the dipolar system, D. This part corresponds to nuclei with a small quadrupole coupling which exchange energy very rapidly with the dipolar system.)

If we perform the adiabatic demagnetization in the rotating frame, the dipolar system is brought to a very low temperature

$$\Theta_i=\Theta_{\mathrm{lattice}}H_L/H_0\approx5\times10^{-3}\,{}^\circ\mathrm{K}\,, \tag{A1}$$

for $H_L=0.68$ G, $H_0=10$ kG, $\Theta_{\mathrm{lattice}}=77$°K. The Q system remains at a higher temperature since it is not at resonance. As a crude approximation we assume that the Q system remains at the lattice temperature, so that its contribution to the total energy immediately after the adiabatic demagnetization is negligible. If the quadrupolar and the dipolar system can cross-relax at a rate fast compared to the spin-lattice relaxation, they will reach a common temperature Θ_f which can be calculated using the energy-conservation condition[29]

$$CH_L{}^2/\Theta_i=C(H_L{}^2+H_Q{}^2)\Theta_f\,, \tag{A2}$$

where we have used the abbreviations

$$H_L{}^2=\frac{1}{kC(2I+1)^N}\,\mathrm{Tr}\mathcal{H}_D{}^2 \tag{A3}$$

and

$$H_Q{}^2=\frac{1}{kC(2I+1)^N}\,\mathrm{Tr}\mathcal{H}_Q{}^2 \tag{A4}$$

($C=$ Curie constant, $k=$ Boltzmann constant). Curie's law then gives

$$M_i/M_f=\Theta_f/\Theta_i=1+H_Q{}^2/H_L{}^2\,. \tag{A5}$$

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[28] L. C. Hebel, Jr., Phys. Rev. **128**, 21 (1962).

[29] L. C. Hebel, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 409.

Thus, the ratio of the quadrupolar to the dipolar heat capacity is

$$H_Q^2/H_L^2=(M_i/M_f)-1. \tag{A6}$$

M_i is the magnetization before cross relaxation took place and M_f can be experimentally determined by extrapolating the exponential decay to $t=0$.

A plot of $(M_i/M_f)-1$ as a function of impurity concentration is shown in Fig. 11. For the two lowest concentrations, 0.003% and 0.007%, the heat-capacity ratio was independent of concentration. This indicated that crystalline strains and impurities other than silver contributed a quadrupolar heat capacity about 4% of the dipolar heat capacity. For concentrations from 0.03 to 0.5% the ratio was approximately proportional to the concentration,

$$H_Q^2/H_L^2\approx 200c. \tag{A7}$$

If we knew the field gradients at the individual lattice sites we could calculate H_Q^2,[11]

$$H_Q^2=(c/5)\sum_Q(2\pi\nu_{Qi}/\gamma)^2, \tag{A8}$$

where ν_{Qi} is the first-order quadrupole shift of the transition between the states $|m_i\rangle=|-\frac{1}{2}\rangle$ and $|m_i\rangle=|-\frac{3}{2}\rangle$ of the nucleus i. The sum must be extended over all nuclei i of the Q system which can cross-relax with the I spins. Thus our simple model results in a concentration dependence of the heat capacities which agrees with the experimental data.

ν_Q is known only for the six (2,0,0) neighbors of the silver impurity. We can therefore estimate their contribution to the quadrupolar heat capacity. The result is

$$H_Q^2(2,0,0)/H_L^2=1750c, \tag{A9}$$

which is much greater than the experimentally determined value. This indicates that the quadrupole shift of these nuclei is too large to allow cross-relaxation with the D spins in times shorter than the spin-lattice relaxation time.

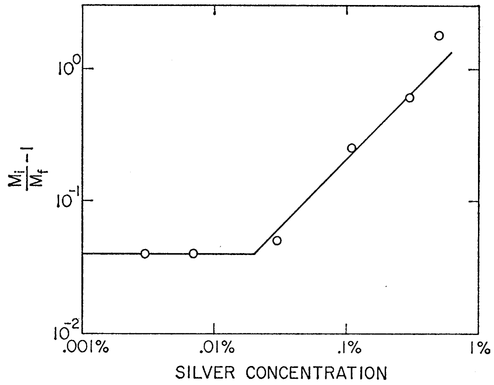

FIG. 11. Ratio of the initial magnetization, M_i, to the magnetization remaining after the quadrupole-dipole cross-relaxation, M_f. M_f is obtained from Fig. 10 by extrapolating the slowly relaxing component to $t=0$. The value of M_i/M_f-1 is interpreted as a measure of the ratio of the quadrupole heat capacity to the dipole heat capacity.

The number of Q spins which do cross-relax can be estimated as $N_Q\approx Ncn_0$, where N is the total number of spins, c the fractional impurity concentration, and n_0 the so-called wipeout number. That is the number of sodium nuclei per impurity for which the quadrupolar interaction is greater than the average dipolar interaction. Kornfel'd and Lemanov[30] have determined n_0 for Ag$^+$ in NaCl to be on the order of 100.

The experimental value for the heat-capacity ratio allows us to estimate the average quadrupole field h_Q^2 of the nuclei which are most effective in the cross-relaxation process

$$H_Q^2/H_L^2\approx n_0h_Q^2/H_L^2=200. \tag{A10}$$

Solving for ν_Q gives a result which suggests that the contribution to the cross-relaxation is greatest for Q nuclei whose quadrupole splitting is about three times the rms dipolar interaction.

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[30] M. I. Kornfel'd and V. V. Lemanov, Zh. Eksperim. i Teor. Fiz. **43**, 2021 (1962) [English transl.: Soviet Phys.—JETP **16**, 1427 (1963)].