A more refined calculation has been carried out by Eagles[14] which shows (i) that the simple model discussed before is a very good approximation and (ii) that the coupling constant including all polar modes of TiO_2 is $\langle A\rangle = 1.77\sqrt{m^*}$. This gives $\langle A\rangle = 3.4$ and $m^* \sim 3m_0$ in very good agreement with our first determination.

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Torsional Spectroscopy by NMR in the Rotating Frame

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Nuclear-spin Zeeman states prepared at a low temperature in the rotating frame were matched to the torsional ground-state splittings of NH_4 and CH_3 groups in solid lattices at a higher temperature. A resonant transfer of order was observed to occur instantaneously. Measurements yield a part of the torsional spectrum and the torsional relaxation time. From the torsional relaxation, the torsional lifetime broadening of a NH_4 ground state in ammonium iodide at 10 K was found to be ~ 1 Hz.

Because a nuclear-spin Zeeman system and a torsional system of atomic groups (such as CH_3 or NH_4) embodied in a solid lattice are coupled strongly[1-7] by the magnetic dipolar interaction which contains both spin and space operators, it is possible to induce a double resonance by adjusting the rf field H_1. In resonance, any experimentally prepared difference of population distributions between the two systems vanishes in a time which is orders of magnitudes shorter than either the spin-lattice or torsional-phonon relaxation time. For this reason the concept of a semiequilibrium of the Zeeman plus torsional system is applicable. In other words, it is possible to resonantly cool (or heat up) the torsional system by a cold (hot) Zeeman system without interference from the lattice. With this double resonance method it is possible to determine a part of the torsional spectrum and its specific heat. In addition, the torsional relaxation time, a quantity which has not been measured before, can be detected without any disturbance from the Zeeman system.

The experiment begins by establishing a nuclear Zeeman system in the rotating frame by the spin-locking pulse sequence. With this sequence the equilibrium nuclear magnetization $\vec{M}_0$ in high field is turned 90° off the high-field direction and an rf field $\vec{H}_1$ is established parallel to $\vec{M}_0$. After spin locking, the nuclear Zeeman levels population is characterized by a spin temperature of the order of 10^{-2} K while the lattice (and torsional) temperature is ~ 10 K. When Zeeman and torsional energies are brought in resonance (by varying H_1) the considerably different populations are equalized in a time which is shorter than the spin-spin lattice relaxation time T_2 and orders of magnitudes shorter than torsional (T_{1T}) or spin-lattice relaxation time. In other words, after the semiequilibrium in the rotating frame is established the resulting magnetization is considerably smaller than the high-field value M_0. This loss of spin polarization, which is the result of the resonant heating of nuclear spins by the torsional system, is maximum when the two systems are perfectly matched. Thus the loss of magnet-

ization as a function of H_1 gives directly the part of the torsional spectrum which is in contact with spins. As the semiequilibrium is established the torsional temperature falls to $\sim 2\times10^{-2}$ K in an environment with a lattice temperature of ~ 10 K. This torsional polarization vanishes with a relaxation time T_{1T}. In the solid studied, T_{1T} was found to be at least one order of magnitude shorter than the "nonresonant" Zeeman spin-lattice relaxation time T_{1X}.

After the establishment of the Zeeman-torsional semiequilibrium the cold Zeeman system is removed. Following is a pause in which no rf is present. Next, Zeeman levels in the rotating frame are brought back for a short time by re-establishing the rf field H_1. This second rf pulse is applied without a preceding 90° pulse; thus Zeeman levels have an effective spin-temperature of $\sim 10^4$ K. This "sensing" rf pulse is left on so long that a semiequilibrium between Zeeman and torsional energies is established. However, in this instance the energy flow is in the reverse direction: The torsional system is cooler than the spins, and thus it produces a spin polarization. If the time between the cold spin-locking rf sequence and the hot sensing rf pulse is varied, information on relaxation of the torsional order to the lattice is obtained.

The proton magnetization was spin locked along rf fields from 2 to 36 G (Fig. 1). In the ammonium halide NH_4I, with a known NH_4 torsional splitting[8] of ~ 10 G, the evolution towards a state of semiequilibrium was observed as a function of the proton Zeeman splitting $\hbar\gamma H_1$. Results at 10 K are shown in Figs. 1(a) and 1(b). If the field H_1 is such that the Zeeman splitting closely matches a torsional splitting the two systems exchange energy rapidly. For H_1 between 12 and 36 G the semiequilibrium was established in a time of the order 100 μsec, Fig. 1(a). At smaller fields it took longer to achieve semiequilibrium. Note that spin and torsional states are in contact only for the duration of the field pulse. Once the semiequilibrium is established, an effective torsional specific heat may be derived from the M_x vs H_1 curve, Fig. 1(b), in complete analogy with the experiment in which the dipolar specific heat in the rotating frame is obtained. This experiment involves measurement of M_x following a 4-msec spin-locking pulse of variable strength [Fig. 1(b)]. Near 36 G the magnetization does not depend on H_1. It reaches half the amplitude when $H_1=H_T$ [Fig. 1(b)], with $M_x=M_0H_1^2/(H_1^2+H_T^2)$. From Fig. 1(b) we derive

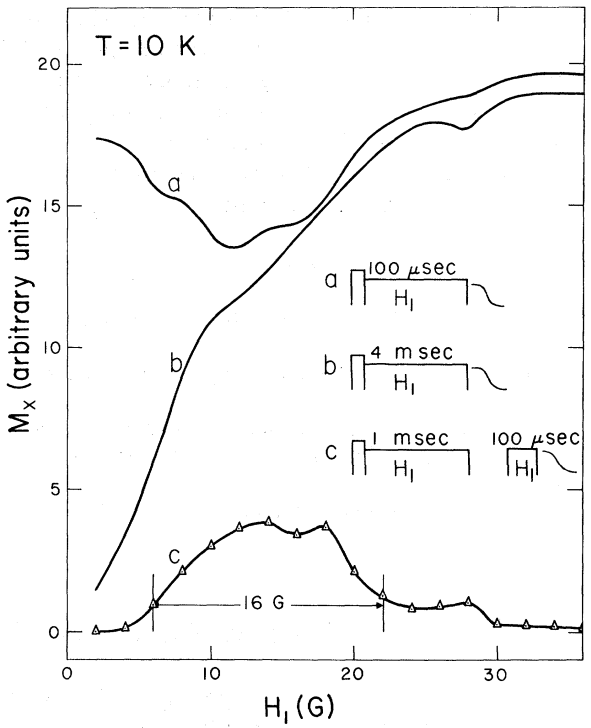

FIG. 1. M_x vs H_1. M_0 is 19.8 units. Curves *a* and *b* were arrived at by measurements at 1-G interval. Accuracy is ± 5%. The delay between the spin-locking pulse and the SPOTS pulse sequence *c* was 2 ms while $T_{1T}=1.35$ sec. The material is NH_4I.

$H_T=13.0\pm0.5$ G.

The nuclear polarization loss was evaluated for all possible torsional ground-state splittings.[9] For simplicity we present here only two cases. In the first, the triply degenerate F level is split by ω_T into a doubly degenerate and nondegenerate level. In the second, the degeneracy of the F level is completely removed, with equal splittings ω_T between adjacent levels. For these configurations specific heats were calculated as follows. The specific heat is defined as $C_T=\partial E_T/\partial\beta$, where β is the inverse temperature. We get for the first case $C_T{}^F=\frac{1}{8}\hbar^2N\omega_T{}^2$, where N is the number of NH_4 torsional groups. For the second case we get $\frac{3}{8}\hbar^2N\omega_T{}^2$. The specific heat of the Zeeman system is $C_Z=\hbar^2\omega_1{}^2(2N_A+\frac{2}{3}N_F)=N\hbar^2\omega_1{}^2$, where N_A is the number of NH_4 torsional oscillators in the ground state (A), and N_F the number in the F state. There are sixteen spin states of which $N_A=\frac{5}{16}N$ and $N_F=\frac{9}{16}N$, and the nonmagnetic states are $N_E=\frac{2}{16}N$.

In semiequilibrium between Zeeman and torsional states, the combined system reaches a

common inverse temperature β, given by

$$\beta(C_Z + C_T^F) = \beta_0 C_Z + \beta_L C_T^F.$$

The initial Zeeman inverse temperature β_0 is the one achieved by spin locking $\vec{M}_0$ along $\vec{H}_1$: $\beta_0 = \beta_L H_0/H_1$. The torsional system is initially in equilibrium with the lattice; thus it has the lattice inverse temperature β_L. As a result of the matching of the cold spin system with a hotter torsional reservoir, the spin polarization instantaneously diminishes: $M_x = M_0\beta/\beta_0$. The time constant for this fast change is near $\omega_T = \omega_1$ of the order of a μsec or less. Using the semi-equilibrium condition, we get

$$M_x = M_0\left[\frac{C_Z}{C_Z + C_T^F} + \frac{H_1}{H_0}\frac{C_T^F}{(C_Z + C_T^F)}\right].$$

Since C_T^F is of the same order as C_Z and H_1/H_0 is 10^{-3}, the second term is negligible, and thus

$$M_x = M_0 C_Z/(C_Z + C_T^F).$$

If $\omega_T = \omega_1$, the magnetization loss $(M_0 - M_x)/M_0$ for the partial removal of the F degeneracy equals 11%, and for the complete removal of F degeneracy, 27%. The measured loss has a maximum of (32 ± 4)% near 12 G. Good agreement indicates that the triply degenerate F state is split into three F levels spaced apart by $\sim 6\times 10^4$ Hz. In Fig. 2 the case with partially removed degeneracy is shown under the condition of one and two accidental Zeeman degeneracies.

Since Zeeman levels can be removed virtually instantaneously by the removal of the field pulse, a direct measurement of the torsional relaxation time is also possible. The torsional system is first cooled by allowing contact with the very cold spin system, and then the Zeeman system is removed [Fig. 1(c)]. After this the torsional system relaxes independently until the application of the second field pulse. This pulse returns Zeeman levels, but this time at a very high temperature. Contact with the torsional system now cools the Zeeman system, producing spin polarization [Fig. 1(c)]. The resulting magnetization gives a signal (SPOTS) which is a measure of the torsional temperature. By increasing the spacing between the spin-locking pulse sequence and the "hot" rf pulse, Fig. 1(c), SPOTS intensity decreases exponentially with a time constant T_{1T}. The inverse of T_{1T} is given as a function of temperature in Fig. 3. It depends on temperature linearly up to 40 K which is a characteristic of a direct (one-phonon) process. At higher temperatures the torsional-phonon coupling becomes stronger and the torsional relaxation rate T_{1T}^{-1} increases rapidly with temperature; e.g., at 67 K it equals 700 sec^{-1}. The torsional relaxation time determines the lifetime broadening of the torsional ground state. At 10 K this equals 1 Hz, which is some thirteen orders of magnitude less than the splitting between the ground state and the first excited state.

It is expected that this form of double resonance, in which the nuclear-spin system couples strongly to a set of discrete lattice energy states of finite heat capacity, will occur whenever the splittings of the two can be made to coincide. Provided that the relaxation time of the second

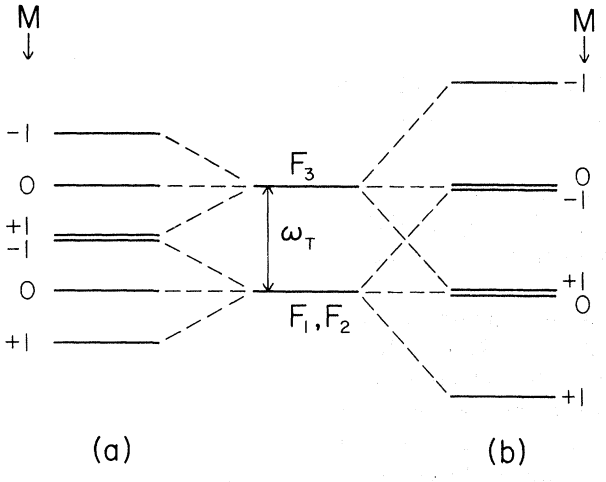

FIG. 2. Two possible Zeeman-torsional coupling schemes in the F manifold ($I=1$): (a) $\omega_1 = \omega_T/2$ and (b) $\omega_1 = \omega_T$. Note that the lower torsional state is doubly degenerate.

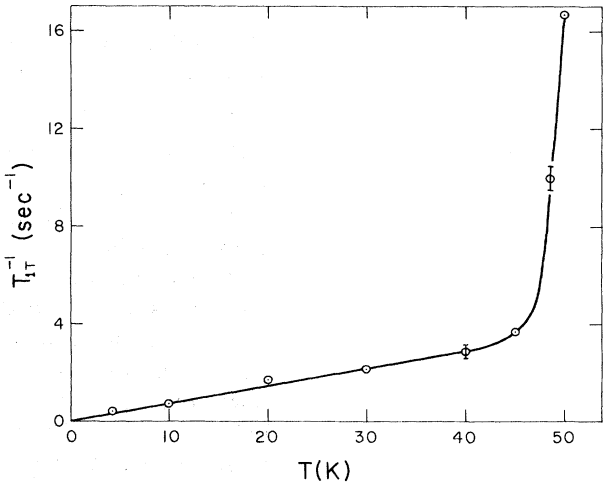

FIG. 3. NH_4 torsional relaxation rate plotted vs temperature for ammonium iodide.

system is not too short, its presence will be detectable by its effect on the spin polarization. If, however, the relaxation time is much less than the spin-lattice relaxation time, then the system merges with the rest of the lattice and is unobservable as a separate system. In addition to providing the energy splittings, which are obtained as in other spectroscopic techniques, the phenomenon allows for a determination of the heat capacity and relaxation time of the coupled energy reservoir. Torsional spectra and relaxation in $(NH_4)_2BeF_4$ and CH_3CD_2I with a theory of magnetization losses will be reported elsewhere.

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ERRATA

STRONG-SIGNAL THEORY OF A FREE-ELECTRON LASER. F. A. Hopf, P. Meystre, M. O. Scully, and W. H. Louisell [Phys. Rev. Lett. 37, 1342 (1976)].

In Fig. 1, the numbers on the horizontal axis should be multiplied by a factor of $\sqrt{2}/\pi^2$.

SUPERCONDUCTIVITY OF bcc BARIUM UNDER PRESSURE. C. Probst and J. Wittig [Phys. Rev. Lett. 39, 1161 (1977)].

On page 1162, column 2, the fourth line of the second paragraph should read, "... reported *decrease* of the melting temperature...," rather than "increase."

Starting on line four of the next paragraph, the sentences should read as follows: "Crystallographic phase transformations introduce only minor discontinuous changes of T_c whose directions, however, follow the general trend.[2] This simple behavior should have a rather general origin. Some final remarks....