Cross-Relaxation in the NMR of Solids

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Received July 30, 1995

Cross-relaxation between different nuclear spin species can result in unusual temperature and frequency dependences of the measured relaxation rates, $T_1^{-1}$, raising the possibility of misinterpretation of the data. In the cases considered, quadrupolar broadening of one spin species results in spectral overlap with a second species. Early experiments of Woessner and Gutowsky on $^{35}$Cl-$^1$H cross-relaxation are summarized, together with the recently studied cases of metal-hydrides, Li$_3$NbO$_2$, and laser-polarized solid Xe. Two experiments are described that unambiguously test the existence of cross-relaxation, one using high-frequency field modulation and the other employing slow sample rotation.

I. Introduction

Cross-relaxation is an indirect longitudinal relaxation pathway. In a two-spin (or more) system, the spins I may relax directly to the lattice, or they may cross-relax: the spins I may exchange energy with the spin S and the spins S may subsequently relax to the lattice temperature, as represented in Fig. 1. When cross-relaxation is a significant relaxation path for the I spins, unusual temperature and frequency dependences of $T_1^{-1}$ can occur. Thus, to avoid mis-interpretation of relaxation data, the conditions under which cross-relaxation is important should be understood, whether or not one is purposefully studying cross-relaxation.

The first requirement for cross-relaxation is spin-spin coupling between the spins I and S, for the transfer of spin energy. In a solid, this interaction is almost always present as dipole-dipole coupling. Second, the direct relaxation of the spins I to the lattice must not be so rapid that the direct relaxation dominates. Thus, the likeliest candidate systems in which to observe cross-relaxation are those with very weak direct I-spin relaxation and very strong S-spin relaxation: $T_1^{-1} \ll T_1^{-1}$.

The third and crucial requirement for the observation of cross-relaxation is spectral overlap: the absorption lines of I and S must overlap, to allow the transfer of spin energy. Quite approximately, the mismatch in the frequencies of the I and S resonance lines must be smaller than the I-S spin-spin interaction strength (in frequency units). Most nuclear spins have very different magnetogyracic ratios $\gamma_i$; thus in most systems, there is no spectral overlap and no cross-relaxation. Hence, cross-relaxation is a feature of relatively few (but quite interesting) spin systems.

![Figure 1: The flow of energy during spin-lattice relaxation. Cross-relaxation is the transfer of energy from the spins I to the spins S, with subsequent relaxation of the spins S to the lattice. The direct relaxation of the spins I is a competing process.](image-url)
the $^7$Li and $^{19}$F spins in LiF "mix" (come to a common spin temperature) at a rate which increases rapidly as the external field is decreased \cite{6}. Here we will only consider high-field (> 1000 Gauss) cross-relaxation, since most NMR relaxation measurements are performed at high fields. In all four examples discussed below, overlap of the I and S resonances results from quadrupole broadening of the S spins. The term "cross-relaxation" also refers to the coupled relaxation of two spin species in a liquid \cite{1,3}. The fluctuating I – S interaction generates the Overhauser and nuclear Overhauser and related "cross-relaxation" effects \cite{6}, but these are not the subject of this work.

II. Chlorine-proton cross relaxation

In a classic paper, Woessner and Gutowsky described \cite{5} cross-relaxation between protons and $^{35}$Cl and $^{37}$Cl in polycrystalline para-dichlorobenzene (C$_6$H$_4$Cl$_2$). In fields of order 7000 Gauss (30 MHz proton), the proton $T_1$ was approximately six hours! By comparison, the $^{35}$Cl $T_1$ was near 0.02 second, reflecting the strong quadrupole interaction of the I = 3/2 chlorine isotopes (in C$_6$H$_4$Cl$_2$ the pure quadrupole frequencies $\nu_0$ are about 34 and 27 MHz for $^{35}$Cl and $^{37}$Cl, respectively). Even though the chlorine and proton nuclei are in dipolar interaction, spin energy is not exchanged; evidently, the chlorine and proton resonances do not overlap.

The frequencies of the transitions of the chlorine nuclei are determined by the electric field gradient (EFG) tensor and the external magnetic field ($H_0$) and their relative orientation \cite{5}. Very approximately, the chlorine transition frequencies will lie between $\nu_0 - \nu_Q$ and $\nu_0 + \nu_Q$. Here $\nu_Q$ is the chlorine pure Zeeman resonance frequency, $\gamma H_0/2\pi$; the $\nu_Q > \nu_0$ limit applies and the spin frequencies are calculated more accurately in Ref. [5]. For a 7000 Gauss field, the $^{35}$Cl transitions are in the 29-42 MHz interval; the $^{37}$Cl lines are between 23-32 MHz.

For a single crystallite in the ~7000 Gauss field, the comparatively narrow (~ 40 kHz) proton NMR line is unlikely to overlap any of the chlorine transitions (distributed over many MHz). Thus, in a powder sample, cross-relaxation will occur in only a tiny fraction of the crystallites (the lucky few with spectral overlap); this fast relaxing fraction was indeed observed \cite{6}. The bulk of the proton magnetization relaxes with the intrinsic, slow proton $T_1$ (hours).

However, cross-relaxation can be enhanced by rotating the sample. Sample rotation will modulate the chlorine frequencies within the above-indicated frequency ranges, because the Cl frequencies depend on the relative orientations of $H_0$ and the EFG. Thus, crystallites which initially have no overlap are brought into proton-chlorine spectral overlap two or more times per revolution of the sample. Indeed, Woessner and Gutowsky found that the apparent proton $T_1$ was as short as 2.5 s for 0.5 Hz sample rotation (provided by fingers on the glass tube) and a proton frequency of 30-36 MHz. For a proton frequency below 23 MHz (near the lowest predicted $^{37}$Cl frequency), the cross-relaxation abruptly disappeared, yielding only long $T_1$ values independent of sample rotation. Thus, the cross-relaxation is enabled by the sample rotation.

An interesting observation is that the proton magnetization recovers to nearly 100% for any proton frequency between 23.5 and 41 MHz; i.e., all the protons experience cross-relaxation. This is surprising because one expects that a fraction of the crystallites will not undergo significant Cl-frequency variation. Specifically, those crystallites with the chlorine EFG tensor’s unique axis (the asymmetry $\eta$ is approximately zero) nearly parallel to the rotation axis will only have small variations of the relative orientation of the EFG tensor and the magnetic field $H_0$. Thus, cross-relaxation is expected to occur in such crystallites only when the proton frequency is near the pure NQR frequencies of $^{35}$Cl or $^{37}$Cl. However, there are two differently-oriented EFG tensors in each crystallite, corresponding to the two molecules per unit cell (the two chlorines on each benzene are symmetry related) \cite{6}. Evidently, the combination of two chlorine EFG tensors nearly completely covers the frequency ranges (23-32 and 29-42 MHz); it is not possible for both EFG’s to be near the special orientation. We note that proton spin diffusion should transport the magnetization only ~0.2 micron in the time of a typical $T_1$ (~ 10 s). This should not be sufficient to transport magnetization between different crystallites.
III. Cross-relaxation in metal hydrides

Metal-hydrides are solid solutions or compounds of H atoms with metals; in some systems, up to 3 H atoms can be absorbed per metal atom (e.g., YH₃)⁷. These systems find application in storage of H₂ for transportation, in advanced electrochemical cells and in thermally-driven pumps and heat pumps with no moving parts⁸. Reflecting the high diffusivity of H in metal-hydrides, a relaxation peak⁹ occurs when the H jump rate matches the resonance frequency; typically the peak is at 220-750 K, depending on the system and measurement frequency¹⁰,¹¹. Below 100 K, in most systems only the conduction electrons retain their mobility, so the proton relaxation rate T⁻¹ is due to interaction with conduction electrons. The rate follows the Korringa relation⁴,¹² with T⁻¹ ∝ T with no frequency dependence.

However, the Iowa State group found several metal-hydrides for which T⁻¹ was not linear in temperature and was not independent of frequency (or field H₀ equivalently)¹³,¹⁴. These systems¹³ include NbH₀.₂₁ Nb₀.₅ V₀.₅ H₀.₂₃ and TaH₀.₃₂. Similar effects occur¹⁴,¹⁵ in Zr₂PdH₆ (both amorphous and polycrystalline, x ≈ 2.4) and LuH₁₈. For NbH₀.₂₁ at 20 K, the proton T⁻¹ increases¹³ by a remarkable factor of 500 as the proton frequency is decreased from 90 MHz to 4.45 MHz. In addition, the temperature dependence of T⁻¹ at, say, 5 MHz is substantially weaker than linear in T. The proton T⁻¹ of TaH₀.₃₂ shows two large, broad peaks at 70 and 120 MHz (proton frequency)¹³. These temperature and frequency dependences cannot be explained by relaxation by conduction electrons or hydrogen motion.

The Iowa State group proposed that the unusual relaxation at low temperatures was not due to a subtle motion but to cross-relaxation between protons and metal nuclei¹³. The metal nuclei in all of the unusually relaxing systems have large quadrupolar moments. It was proposed that static quadrupole interactions spread the ¹⁸¹Ta resonances (in TaH₀.₃₂, to take a specific case) over a broad range (nearly 0 to 140 MHz). A continuous distribution of frequencies (a consequence of unspecified structural disorder) was assumed. Thus, at any proton frequency in the 0-140 MHz interval, the protons could cross-relax to a few tantalum spins. The straightforward test of the model, isotopic substitution of the metal nuclei, is exorbitant in cost and has not been attempted to our knowledge.

A crucial feature of the above model is that only a very small fraction of ¹⁸¹Ta overlap the proton resonance at a given field. The proton linewidth is ∼ 30 kHz and the 7 transitions of Am = ±1 of ¹⁸¹Ta (S = 7/2) are spread over 140 MHz. Thus the probability of overlap is 30 x 10⁻³ x 7/(140 x 10⁻³), or about 1 in 1000! Because only 1 tantalum spin in 1000 is effective in relaxation, each tantalum must “carry the relaxation burden” of ∼ 320 protons (recall 0.32 H per Ta). Thus for cross-relaxation to be effective, the intrinsic relaxation rate of the ¹⁸¹Ta nuclei must be very fast indeed.

Here we are involving spin heat capacity arguments; see Eq. (1) in ref. [16]. This is perfectly reasonable; the large positive charge of Ta attracts a large conduction electron density at the nucleus, yielding a large Knight shift and Korringa relaxation rate⁴.

A first test of the cross-relaxation hypothesis was performed using large-amplitude, high-frequency field modulation¹⁷. As shown in Fig. 2(c), the Zeeman field is modulated during the waiting interval of a traditional saturate-wait-inspect T₁ measurement. The modulation is removed during all rf pulses and observation of the nuclear signal. The modulation causes the proton frequency to sweep through the frequency of ¹⁸¹Ta nuclei with which the protons could not otherwise communicate (Fig. 2(b)). The Ta frequencies are nearly constant, because of their much smaller γ. The modulation needs to exceed the proton linewidth to be effective. In TaH₀.₄₅ at 12.8 K, modulation amplitudes of 0.5 to 1.0 MHz peak-to-peak (250 Gauss, p - p) at 40 kHz cause a substantial increase (∼ double) in the proton T⁻¹₁. Sample heating by the modulation was ruled out experimentally. The only known relaxation mechanism which is sensitive to such field modulation is cross-relaxation.

The field modulation experiments required ∼ 60 W of audio-frequency power to the modulation coil located inside the dewar. The heat generated precluded longer modulation bursts than ∼ 1 s. Thus, we turned to a superior experiment, slow sample rotation, à la Woessner and Gutowsky⁶. As shown in Fig. 2(b), sample rotation causes the ¹⁸¹Ta frequencies to vary, while the proton frequency (I = 1/2) is constant. As emphasized in Fig. 2(b), the field modulation and sample rotation
experiments are complementary, in terms of which nuclei are swept in frequency and which stay put.

**Figure 2.** (a) The proton-metal cross-relaxation model. (b) Proton resonance overlapping the continuous distribution of metal nuclear frequencies. Both ac field modulation and sample rotation cause the proton or metal nuclear frequencies to sweep through the other, increasing the spectral overlap during a cycle of modulation or rotation. (c) Saturate-wait-inspect NMR pulse sequence used for ac field modulation experiments.

The proton $T_1^{-1}$ for TaH$_{0.45}$ at five rotation rates is presented in Fig. 3, as a function of temperature$^{[16]}$. At 4.2 K, the relaxation rate is enhanced by a factor of 40 with 5 Hz rotation (rotation axis perpendicular to $H_0$). Again, such an effect can only indicate cross-relaxation. The dependence of $T_1^{-1}$ upon the rotation rate has been examined and is in accord with the simple concepts of spin heat capacity.

One aspect of cross-relaxation in the metal-hydrides warrants further emphasis. The metal-hydrides are known to form ordered phases (e.g., TaH$_{0.5}$) by hydrogen phase-segregation at low temperatures$^{[7]}$. Thus, one expects the sample to be ordered with a finite number of Ta nuclei per unit cell and a finite number of $^{181}$Ta resonances per crystallite. On this basis, one would expect that spectral overlap and cross-relaxation would occur in very few crystallites (e.g., 1 in 1000) in non-rotating samples, similar to the case of para-dichlorobenzene$^{[6]}$. But this is not so: the entire proton magnetization of the non-rotating sample follows a single exponential recovery. Thus, substantial disorder must be present in the metal-hydrides at low temperatures. We note that single exponential recovery is predicted$^{[18]}$ for relaxation to dilute, randomly distributed relaxation centers, whether spin-diffusion is the bottleneck or not.

**IV. Cross-relaxation in Li$_x$NbO$_2$**

Li$_x$NbO$_2$ is a lithium deficient ($x \leq 1$) semiconductor and ionic conductor that has been examined for its potential as a lithium battery electrode$^{[19]}$. Line-narrowing of the 12 kHz wide $^7$Li resonance occurs just above room temperature$^{[20]}$. With such a relatively slow motion, it is surprising then that the room-temperature $^7$Li $T_1$ is only 1.5 s at 10 MHz and shows a strong field dependence (faster than $H_0^2$), increasing by a factor of 10 between $^7$Li frequencies of 10 and 25 MHz$^{[20]}$. As in many cross-relaxing systems, the $^7$Li $T_1$ becomes frequency independent at high frequencies (above 50 MHz).

The only candidate nucleus for $^7$Li cross-relaxation is $^{93}$Nb, with 100% abundance, $S = 9/2$, and a large quadrupole moment. At the high field of 8.4 T (where any cross-relaxation is absent), the $^{93}$Nb $T_1$ (measured at 1/e point of recovery, saturating central transition

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**Figure 3.** Proton relaxation rate $R_1$ for TaH$_{0.45}$ at 53.14 MHz as a function of temperature for several sample rotation frequencies. Notice the factor of 40 increase in $R_1$ at 4.2 K with only 5 Hz rotation.
only with a long comb of effective 90° pulses) is about 0.01 s at room temperature. This is much faster than the 1.5 s $^7$Li $T_1$ measured at room temperature and 10 MHz. $^7$Li cross-relaxation to $^{93}$Nb is certainly a possibility.

Slow sample rotation experiments were performed initially at room temperature and 12.2 MHz ($^7$Li frequency)\(^{[20]}\). Rotation at 10 Hz caused an increase of the $^7$Li relaxation rate of only a factor of 1.75, somewhat less than expected. But at 142 K, the same experiment (Fig. 4) resulted in a seven-fold increase in the $^7$Li $T_1^{-1}$.

![Figure 4](image)

Figure 4. The effect of slow sample spinning on the $^7$Li $T_1^{-1}$ of Li$_x$NbO$_2$ at low temperature where the Li atoms are stationary. $T_1^{-1} = 0.040$ s$^{-1}$ when the sample is not rotating. Sample rotation causes the $^{93}$Nb transition frequencies to vary periodically, sweeping through the $^7$Li line and enhancing cross relaxation.

This and other experiments show that the motion of Li vacancies near and above room temperature causes a time-dependent EFG at each $^{93}$Nb nucleus. As a result, the $^{95}$Nb transition frequencies vary as Li vacancies move in their vicinity. This “warbling” of the $^{93}$Nb causes the $^7$Li and $^{93}$Nb to have spectral overlap in every crystallite for $^7$Li frequencies below $\sim$ 33 MHz, provided the temperature is near or above room temperature. Because the $^{93}$Nb frequencies are modulated so effectively by the motions of Li vacancies, sample rotation causes only a comparatively small additional increase in the $^7$Li relaxation rate.

At 142 K, Li motion is essentially absent. Thus, the $^{93}$Nb frequencies are static in non-rotating samples. Evidently, there is little $^7$Li-$^{93}$Nb spectral overlap in most crystallites, as evidenced by the much weaker field dependence of $^7$Li $T_1$ at 142 K than at room temperature, for non-rotating samples. Thus, at 142 K, it is not surprising that sample rotation causes a large increase in the extent of spectral overlap and cross-relaxation, as evident in Fig. 4.

Thus, the unusual frequency dependence of the room-temperature $^7$Li $T_1$ arises from the warbling of $^{93}$Nb frequencies, enabling efficient cross-relaxation. The Li motion is crucial to this $^7$Li relaxation process, but in a very different way from BPP relaxation\(^{[9]}\). In the BPP case, motion causes fluctuations of the I-spin Hamiltonian; only fluctuations at the frequency of one of the transitions are effective in relaxation. In Li$_x$NbO$_2$ on the other hand, Li motion causes the Nb frequencies to sweep through the $^7$Li resonance. There is no requirement that the Li motion be at or near a specific frequency, only that the motion be fast enough to enable the Li-Nb cross-relaxation. In particular, the $^7$Li $T_1$ at room temperature and below 33 MHz is entirely due to Li motion via cross-relaxation, even though the Li motion rate is only, $\sim 10^4$ s$^{-1}$ (the $^7$Li line is not even motionally narrowed).

At room temperature, the frequency dependence of the $^7$Li $T_1^{-1}$ shows that cross-relaxation occurs up to a Li frequency of $\sim$ 33 MHz. The strength of the Nb quadrupole interaction spreads the Nb Am = ±1 resonances over a maximum of ±4 MHz, while $\gamma_{Nb} \approx (2/3)\gamma_{Li}$. Hence one would expect that spectral overlap and cross-relaxation are non-existent for Li frequencies above about 12 MHz, far below the observed limit of $\sim$ 33 MHz. The reason cross-relaxation occurs at higher than expected frequencies is that the Nb quadrupole interaction strength is comparable to the Zeeman interaction, which allows the higher frequency $|\Delta m| > 1$ transitions.

V. Cross-relaxation in hyperpolarized xenon

It has been shown that circularly-polarized light may be used to produce highly nuclear-spin polarized (~35%) $^{129}$Xe and $^3$He (both I = 1/2) in the gas phase, using the optical absorption of dilute Rb vapor\(^{[21]}\). The polarized Xe may be frozen\(^{[22]}\) into a solid with $T_1 \sim 3$ weeks at 4.2 K and $H_0 \geq 1000$ G. This opens a route
to production, storage, and transport of 1-100 g quantities of polarized Xe for medical imaging applications\cite{23,24}.

A complicating factor in the storage is the requirement of a 1000 G or larger field. At smaller fields at 4.2 K, the $^{129}$Xe relaxation rate increases (5 times larger at 500 G)\cite{22}. Cross-relaxation between $^{129}$Xe and $^{131}$Xe ($S \geq 3/2$) has been proposed as the source of the relaxation\cite{22}. Only $^{131}$Xe at unusually defective sites (e.g., grain boundaries) have large enough static quadrupole interactions to create spectral overlap in fields of $\sim$ 500 G. Because of their quadrupole moment, the $^{131}$Xe will have a much larger intrinsic relaxation rate than the $^{129}$Xe, satisfying one of the requirements for cross-relaxation.

Experimentally, cross-relaxation has been confirmed in “mixing fields” of 100 G or less\cite{22}. The $^{131}$Xe polarization resulting from cross-relaxation from highly polarized $^{129}$Xe is proof of cross-relaxation in the low fields. In higher fields, the best evidence for cross-relaxation was obtained by studying a sample enriched in $^{129}$Xe relative to $^{131}$Xe; the $^{129}$Xe $T_1$ was increased by a factor of three compared to a natural abundance sample. The longest $T_1$ was obtained in a sample with Kr present: it is believed the Kr reduces the speed of condensation, producing larger grains of solid Xe. As a result, there are fewer $^{131}$Xe at grain boundaries, and these $^{131}$Xe are further away from the bulk of $^{129}$Xe, on average.

For medical imaging applications, $^{129}$Xe-$^{131}$Xe cross-relaxation is a nuisance to be avoided for low-loss storage of the polarized Xe.

VI. Conclusions

Cross-relaxation can occur in solids at high fields when spectral overlap is present between different spin species. A common situation is for quadrupole interaction to remove the frequency mismatch arising from unequal $\gamma$ values. Both large-amplitude field-modulation and slow-sample rotation can unambiguously identify cross-relaxation. Four systems with cross-relaxation have been described: partially chlorinated organics, certain metal-hydrides, Li$_2$NbO$_3$, and solid Xe. In the latter three, disorder plays an important role in the cross-relaxation. We suspect that disorder often makes cross-relaxation more effective than one would first expect.

Even if cross-relaxation is not the focus of an investigation of spin relaxation in a particular material, it may be essential to recognize the symptoms of cross-relaxation, to avoid mis-interpretation of the relaxation data.

Acknowledgments

The authors are grateful to E.-K. Jeong, P. A. Fedders, R. E. Norberg, D. R. Torgeson, R. G. Barnes, and R. C. Bowman, Jr. for their contributions to the research. MSC and DBB gratefully acknowledge support from NSF grant DMR-9403667. AFM acknowledges the support of the Pew Charitable Trust, through the Pew Midstates Mathematics and Science Consortium.

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