Cross-Relaxation in the NMR of Solids

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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 mis interpretation of the data. In the cases considered, quadrupolar broadening of one spin specie results in spectral overlap with a second species. Early experiments of Woessner and Gutowsky on $^{35}Cl-^1H$ cross-relaxation are summarized, together with the recently studied cases of metal-hydrides, Li_xNbO_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, tlie 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: $T_{1,I}^{-1} \ll T_{1,S}^{-1}$.

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 $\mathrm{I}-\mathrm{S}$ spin-spin interaction strength (in frequency units). Most nuclear spins have very different magnetogyric ratios γ; 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.

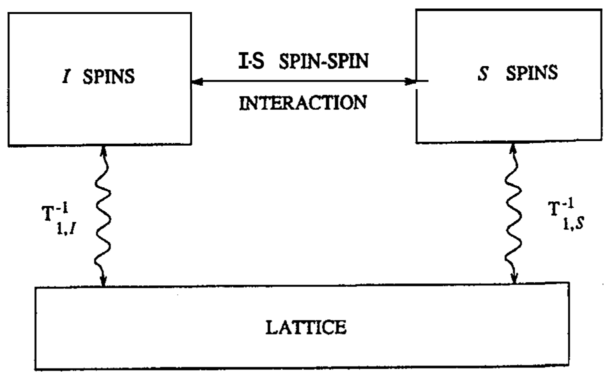

Figure 1. The flow of energy during spin-lattice relaxation. Cross-relaxation is the transfer of energy from the spins I to the spins S, with subsequent relaxation of the spins S to the lattice. The direct relaxation of the spins I is a competing process.

In low fields ($\lesssim$ 100 Gauss), where the dipolar fields become comparable to the external field, cross-relaxaton occurs readily[1]. Thus, Pershan found that

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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[2]. 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[1,3]. The fluctuating **I** – **S** interaction generates the Overhauser and nuclear Overhauser and related "cross-relaxation" effects[4], but these are not the subject of this work.

II. Chlorine-proton cross relaxation

In a classic paper, Woessner and Gutowsky described[5] cross-relaxation between protons and ^{35}Cl and ^{37}Cl in polycrystalline para-dichlorobenzene ($C_6H_4Cl_2$). 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 $\mathbf{I} = 3/2$ chlorine isotopes (in $C_6H_4Cl_2$ the pure quadrupole frequencies ν_Q 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*[4]. Very approximately, the chlorine transition frequencies will lie between $\nu_Q - \nu_0$ and $\nu_Q + \nu_0$. Here ν_0 is the chlorine pure Zeeman resonance frequency, $\gamma H_0/2\pi$; the $\nu_Q \gtrsim \nu_0$ 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 transitioris (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[5]. 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 η 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)[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-hyclrides 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., YH_3)[7]. These systerns find application in storage of H_2 for transportation, in advanced electrochemical cells and in thermally-driven pumps and heat pumps with no rnoving parts[8]. Reflecting tlie high diffusivity of H in metal-hydrides, a relaxation peak[9] occurs mhen tlie H jump rate matches tlie resonance frequency; typically the peak is at 220-750 K, depending on the system and measurement frequency[10,11]. Below 100 K, in most systems only the conduction electrons retain their mobility, so the proton relaxation rate T_1^{-1} is due to interaction with conduction electrons. Tlie rate follows the Korringa relation[4,12] with $T_1^{-1} \propto$ T with no frequency dependence.

However, the Iowa State group founcl several metal-hydrides for which T_1^{-1} was not linear in temperature and was not independent of frequency (or field H_0 equivalently)[13,14]. These systems[13] include $NbH_{0.21}$ $Nb_{0.5}V_{0.5}H_{0.23}$ and $TaH_{0.32}$. Similar effects occur[14,15] in Zr_2PdH_x (both amorphous and polycrystalline, x $\sim$ 2.4) and $LuH_{0.15}$. For $NbH_{0.21}$ at 20 K, the proton T_1^{-1} increases[13] 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^{-1} at, say, 5 MHz is substantially weaker than linear in T. The proton T_1^{-1} of $TaH_{0.32}$ shows two large, broad pealts 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 tlie unusual relaxation at low temperatures was not due to a subtle motion but to cross-relaxation between protons and metal nuclei[13]. The metal nuclei in all of the unusually relaxing systems have large quadrupolar moments. It was proposed that static quadrupole interactions spread the ^{181}Ta resonances (in $TaH_{0.32}$, to take a specific case) over a broad range (nearly 0 to 140 MHz). A *contin- u o u ·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 attemptecl to our linowledge.

A crucial feature of the above model is that only a *very small fraction* of ''Ta overlap the proton resonance at a given field. The proton linewidth is $\sim$ 30 kHz and the 7 transitions of Am = ± 1 of ''Ta $(S = 7/2)$ are spread over 140 MHz. Thus tlie probability of overlap is 30 x 10^3 x 7/(140 x 10^6), or about 1 in 1000! Because only 1 tantalum spin in 1000 is effective in relaxation, each tantalum must "carry the relaxation burden" of $\sim$ 320 protons (recall 0.32 H per Ta). Thus foi cross-relaxation to be effective, the intrinsic relaxation rate of the ^{181}Ta nuclei must be very fast indeed. Here we are involting 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 rate[4].

A first test of the cross-relaxation hypothesis was performed using large-amplitude, high-frequency field modulation[17]. As shown in Fig. 2(c), the Zeeman field is modulated during the waiting interval of a traditional saturate-wait-inspect T_1 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 ^{181}Ta nuclei *wath whach 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 $TaH_{0.45}$ 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 ($\sim$ double) in the proton T_1^{-1}. Sample heating by the modulation was ruled out experimentally. The only known relaxation mechanism wliich is sensitive to such field modulation is cross-relaxation.

Tlie field modulation experiments required $\sim$ 60 W of audio-frequency power to the modulation coil located inside the dewar. The heat generated precluded longer modulation bursts than $\sim$ 1 s. Thus, we turned to a superior experiment, slow sample rotation, à la Woessner and Gutowsky[5]. As shown in Fig. 2(b), sample rotation causes the ^{181}Ta 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 whicli nuclei are swept in frequency and which stay put.

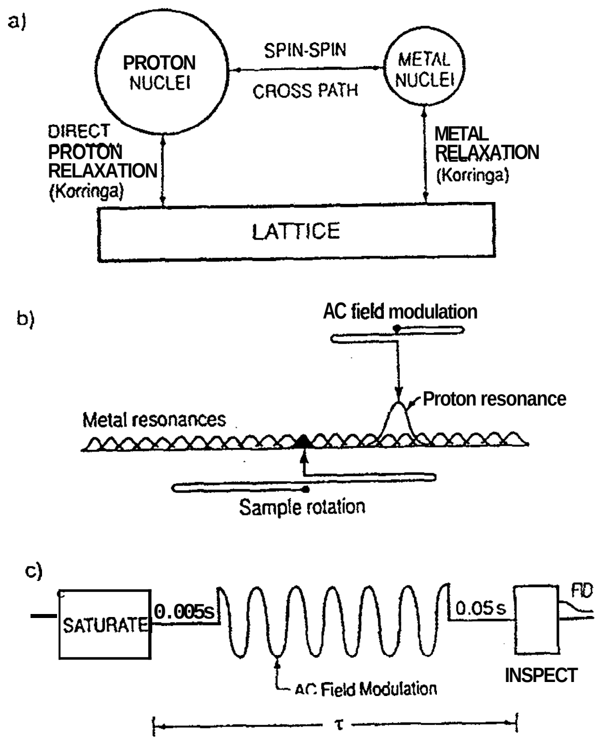

Figure 2. (a) The proton-metal cross-relaxation model. (b) Proton resonance overlapping the continuous distribution of metal nuclear frequencies. Both ac field modulation and sample rotation cause tlie proton or metal nuclear frequencies to sweep through tlie otlier, increasing tlie spectral overlap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

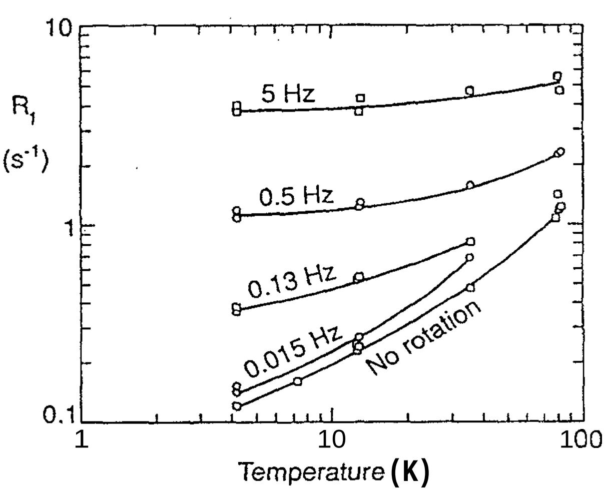

Figure 3. Proton relaxation rate R_1 for $TaH_{0.45}$ at **53.14** MHz as a function of ternperature for several sample rotation frequencies. Notice tlie factor of **40** increase in R_1 at **4.2** K with only **5** Hz rotation.

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[5]. 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_xNbO_2

Li_xNbO_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 tlie 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 only with a long comb of effective 90° pulses) is about 0.01 s at roorn temperature. This is mucli 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}.

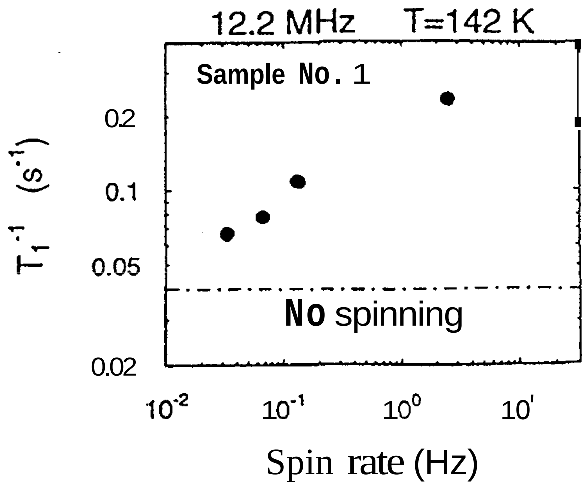

Figure 4. The effect of slow sample spinning on tlie ^{7}Li T_1^{-1} of Li_xNbO_2 at low temperature where the Li atoms are stationary. T_1^{-1} = 0.040 s^{-1} when the sample is not rotating. Sample rotation causes the ^{93}Nb transition frequencies to vary periodically, sweeping through the ^{7}Li line and enhancing cross relaxation.

This and other experiments show tliat tlie motion of Li vacancies near and above room temperature causes a time-dependent EFG at each ^{93}Nb nucleus. As a result, the ••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 tlie 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 tlie 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_xNbO_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 $= \pm 1$ 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 tlie 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 lias 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 medica1 inagnetic resonance imaging applications[23,24].

A complicating factor in the storage is tlie 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)[22]. Cross-relaxation between ^{129}Xe aiid ^{131}Xe ($S = 3/2$) has been proposed as tlie source of tlie relaxation[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 tlieir 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 lias been coiifirined in "mixing fields" of 100 G or less[22]. The ^{131}Xe polarization resulting from cross-relaxation from higlily 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 tlie 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 the ^{129}Xe, on average.

For medica1 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 wlien spectral overlap is present between different spin species. A common situation is for quadrupole interaction to remove the frequency mismatch arising from unequal γ 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_xNbO_2, 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

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