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# Some Nuclear Magnetic Resonance Studies with Solids

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## *Summary*

An account is given in the first part of the paper of the anisotropy of spin-lattice relaxation time in some alkali halides. In particular the  $^{19}\text{F}$  relaxation time in lithium fluoride is described, and it is shown by using crystals enriched in  $^6\text{Li}$  that the anisotropy of the fluorine relaxation time largely originates in the anisotropy of the dipolar interactions of the  $^7\text{Li}$  nuclei.

The second part of the paper summarises experiments on the nuclear magnetic resonance spectrum of solid specimens rotated at high speed. It is shown that for high speeds of rotation the shape of the central part of the spectrum is a replica of that for the static specimen with the field along the axis used for rotation, but scaled down by a factor  $\left| \frac{1}{2} (3 \cos^2 \alpha - 1) \right|$ ;  $\alpha$  is the angle between the axis and the direction of the applied magnetic field. A new effect of cross-relaxation induced by rotation was found when a specimen of solid phosphorus pentachloride was rotated at a rate equal to the difference between the two resonance lines of its  $^{31}\text{P}$  spectrum; the theory of this effect is briefly discussed.

In this lecture I intend to mention two pieces of work which we have been doing recently in Bangor. The first is concerned with the anisotropy of spin-lattice relaxation time in single crystals; the second is concerned with experiments on crystals rotated at high speed.

## 1. ANISOTROPY OF SPIN-LATTICE RELAXATION TIME IN CRYSTALS

It is worth pointing out that the nuclear spin-lattice relaxation time  $T_1$  is not an isotropic characteristic of a crystal, even a cubic crystal. Unlike the situation in liquids the environment of a nucleus in a crystal is not effectively isotropic, and consequently the relaxation time can be expected to depend on the orientation of the crystal in the applied magnetic field. One consequence of this is that relaxation in a polycrystalline specimen proceeds at rates which differ from one crystallite to another. The measured relaxation time for the whole specimen is then some average over the

assembly of crystallites, and if the anisotropy is large the return to equilibrium may differ significantly from exponential form. This complex relaxation behaviour is quite distinct from that which may arise from having different nuclear sites in a unit cell, or from relaxation of nuclei having  $I$  greater than  $\frac{1}{2}$  which in general is described by  $2I$  relaxation times (Andrew and Tunstall, 1961).

The nature of the angular dependence of relaxation time depends on the manner in which the nucleus interacts with its environment. Consequently an investigation of the anisotropy of  $T_1$  can be of service in determining the nature of the mechanism responsible for relaxation, and can shed light on its detailed features. We have examined the angular dependence of  $T_1$  for a number of alkali halide crystals (Andrew, Swanson and Williams, 1961), the most interesting of which is lithium fluoride.

At room temperature, using a good single crystal of lithium fluoride containing the natural abundance (7.4%) of  $^6\text{Li}$ , we found that  $T_1$  for the  $^{19}\text{F}$  nuclei varied from a maximum of 340 sec with the field along [100] to a minimum of 180 sec along [111]. Along [110] the value was 210 sec.

The relaxation mechanism for fluorine nuclei must be magnetic, and the spin-diffusion process of Bloembergen (1949) provides a satisfactory detailed mechanism. With such long relaxation times it is clear that the concentration of impurity centres is small (probably of order  $3 \times 10^{14} \text{ cm}^{-3}$ ), and consequently the diffusion of energy is the time-determining part of the mechanism rather than the disposal of the energy via the paramagnetic centres to the lattice.

The transition probability for mutual spin exchange between a fluorine nucleus and its  $n^{\text{th}}$  neighbour is proportional to

$$g_{\text{max}}(\nu)(3 \cos^2 \theta_n - 1)^2 r_n^{-6}, \quad (1)$$

where  $r_n$  is the internuclear distance,  $\theta_n$  is the angle between the internuclear vector and the applied field and  $g_{\text{max}}(\nu)$  is the normalized resonance lineshape function. Expression (1) contains the origin of the angular dependence of  $T_1$ , which enters in two ways. The factor  $g_{\text{max}}(\nu)$  reflects the angular variation of the resonance linewidth and in physical terms expresses the smaller chance that the  $n^{\text{th}}$  neighbour will have the closely similar energy necessary for spin exchange when dipolar broadening is large. The second factor expresses the angular variation of the dipolar coupling between the two nuclei.

Contributions such as (1) to the spin diffusion coefficient are summed over all neighbours in the lithium fluoride lattice and it is found that the ratios of  $T_1$  for  $^{19}\text{F}$  nuclei along [100], [110] and [111] should be 1: 0.62: 0.49, in good agreement with experimental ratios 1: 0.62: 0.53. The agreement provides good support for the spin-diffusion mechanism.

The major contribution to the anisotropy arises from the first term in (1), namely from the angular dependence of the dipolar breadth, and this in turn originates mainly in the interaction of the  $^7\text{Li}$  nuclei; if the lithium nuclei had no magnetic moment, the fluorine dipolar breadth would be much more nearly isotropic. To test this point we carried out experiments with a crystal in which the lithium in the form of  $^6\text{Li}$  had the enriched proportion of 90.4%; the nuclear magnetic moment of  $^6\text{Li}$  is very much smaller than that of  $^7\text{Li}$ . The anisotropy of  $T_1$  was greatly reduced, the ratio of values with the field along [111] and [100] being reduced from 1.88 to 1.22, in good accord with theory.

The  $^7\text{Li}$  nuclei in lithium fluoride also show an anisotropy of  $T_1$  of the same order as the  $^{19}\text{F}$  nuclei, showing that their dominant relaxation mechanism is also magnetic and is not quadrupolar. The quadrupolar relaxation mechanism of van Kranendonk (1954) would predict an isotropic relaxation time in this cubic crystal.

## 2. NUCLEAR MAGNETIC RESONANCE IN RAPIDLY ROTATING CRYSTALS

We are all familiar with the fact that nuclear motion causes a narrowing of the dipolar breadth of nuclear magnetic resonance spectra. The reorientation and migration of molecules in liquids and some solids provide immediate and well-known examples. We can point to the fact that every term in the truncated dipolar Hamiltonian contains the angular factor  $(3 \cos^2 \theta_{ij} - 1)$ , where  $\theta_{ij}$  is the angle between the vector joining nuclei  $i$  and  $j$  and the applied field. When there is a relative motion of the nuclei,  $\theta_{ij}$  is a function of time; the mean dipolar interaction of a nucleus with all its neighbours is smaller than in the static situation, and the resonance line becomes narrower.

If the motion is effectively isotropic the mean value is small and the resonance line can be very narrow when the rate of motion greatly exceeds the linewidth. If the motion has a restricted character, for example when molecules such as benzene molecules rotate about a well-defined axis in the

solid state, the limiting linewidth is narrower than in absence of motion, but does not tend to zero.

Suppose now we consider a crystal within which the nuclei are at rest, apart from vibrational motion, and we uniformly rotate the entire crystal about a defined axis. Provided this axis is not parallel to the applied field each nucleus is again moving relative to its magnetic environment and the  $\theta_{ij}$  are once more functions of time. Again we may expect line-narrowing if the rate of rotation exceeds the linewidth. However, there is one important difference between this macroscopic rotation and the molecular reorientation with which we were already familiar, namely that the rotation is now coherent. All internuclear vectors in the crystal rotate uniformly and in phase, in contrast with the microscopic molecular motion in liquids which is random in character; as we shall see, this difference alters the form of the observed spectrum.

When Dr. Eades, Mr. Bradbury and I started our first rotation experiments four years ago (Andrew, Bradbury and Eades 1958, 1959) our interest was particularly stimulated by the discussion at that time about the invariance of the second moment of a dipolar-broadened spectrum. It had been pointed out by Anderson (1954) that despite motional narrowing of observed resonance lines, the second moment should remain constant. At first sight this appeared to run counter to observation, particularly in the case of solids. The answer to this apparent discrepancy is found when we examine the truncated dipolar Hamiltonian  $\mathcal{H}_1$  which is now time-dependent; we may divide it into two parts

$$\mathcal{H}_1 = \overline{\mathcal{H}_1} + \mathcal{H}'_1(t). \quad (2)$$

The first part  $\overline{\mathcal{H}_1}$  is the mean value, which gives rise to a smaller secular breadth, while the second, time-dependent, part  $\mathcal{H}'_1(t)$ , whose mean is zero, generates side spectra running out to frequencies of order  $\tau^{-1}$  on either side of the central resonance ( $\tau$  is the correlation time of the motion). Now if  $\tau$  is short ( $\ll T_2$ ), these side-spectra are thinly spread over a wide range and escape observation, and the measured second moment is that arising from  $\overline{\mathcal{H}_1}$  only.

Now it is always unsatisfactory to postulate something which is escaping observation and we sought to observe these side spectra. By macroscopic rotation of a crystal the time-dependent term has a regular periodicity and should give side spectra which are not spread thinly over a wide band; since the perturbation  $\mathcal{H}'_1(t)$  now has a regular periodicity, the side-spectra

should be lumped up at multiples of the rotation rate on either side of the central line. By observation of these side spectra the invariance of the second moment could be tested.

The truncated dipolar Hamiltonian is

$$\mathcal{H}_1 = \sum_{ij} (\vec{\mu}_i \cdot \vec{\mu}_j - 3\mu_{iz}\mu_{jz}) \frac{1}{2} (3 \cos^2 \theta_{ij} - 1) r_{ij}^{-3}, \quad (3)$$

in which the summation is carried out over all nuclear pairs in the specimen. When a crystalline specimen is rotated with angular velocity  $\omega_r$  about an axis inclined at angle  $\alpha$  to the direction of the applied magnetic field, each angular factor in (3) may be expanded as

$$3 \cos^2 \theta_{ij}(t) - 1 = \frac{1}{2} (3 \cos^2 \alpha - 1) (3 \cos^2 \gamma_{ij} - 1) + \frac{3}{2} \sin 2\alpha \sin 2\gamma_{ij} \cos(\omega_r t + \varphi_{ij}) + \frac{3}{2} \sin^2 \alpha \sin^2 \gamma_{ij} \cos 2(\omega_r t + \varphi_{ij}). \quad (4)$$

$\gamma_{ij}$  is the angle between the internuclear vector  $r_{ij}$  and the axis of rotation. Thus, using (3) and (4), we may divide  $\mathcal{H}_1$  into the two parts of equation (2) as follows:

$$\overline{\mathcal{H}}_1 = \frac{1}{2} (3 \cos^2 \alpha - 1) \sum_{ij} (\vec{\mu}_i \cdot \vec{\mu}_j - 3\mu_{iz}\mu_{jz}) \frac{1}{2} (3 \cos^2 \gamma_{ij} - 1) r_{ij}^{-3}, \quad (5)$$

$$\begin{aligned} \mathcal{H}'_1(t) &= \frac{3}{4} \sin 2\alpha \sum_{ij} (\vec{\mu}_i \cdot \vec{\mu}_j - 3\mu_{iz}\mu_{jz}) \sin 2\gamma_{ij} \cos(\omega_r t + \varphi_{ij}) r_{ij}^{-3} \\ &+ \frac{3}{4} \sin^2 \alpha \sum_{ij} (\vec{\mu}_i \cdot \vec{\mu}_j - 3\mu_{iz}\mu_{jz}) \sin^2 \gamma_{ij} \cos 2(\omega_r t + \varphi_{ij}) r_{ij}^{-3}. \end{aligned} \quad (6)$$

The time-dependent part (6) in general generates side-spectra at integral multiples of  $\omega_r$  on either side of the central resonance. For  $\alpha = 90^\circ$  however the first term in (6) is absent, and side spectra are generated by the second term only, at even multiples of  $\omega_r$ .

Experiments with the  $^{23}\text{Na}$  resonance in sodium chloride rotated at speeds up to 2500 c/s clearly demonstrated the expected behaviour (Andrew, Bradbury and Eades 1958, 1959) \*. There were several points to be noted:

\* Experiments on rotating crystals were also performed independently by Lowe (1959).

1. First of all the side-spectra were for the first time demonstrated, the first three orders being observable in favourable cases.
2. The second moment of the entire spectrum including side spectra remained constant, independent of the rate of rotation. In the limit of very slow rates of rotation, the spectrum becomes equal to that of a static uniform distribution of crystals about the rotation axis.
3. The experiments provide a clear experimental demonstration of the correctness of the theoretical criterion for motional narrowing, namely that the rate of motion should be of the order of the linewidth.
4. It is observed that as the rate of rotation is increased the side-spectra move out from the central spectrum and become weaker. The intensity of the innermost sidebands falls as  $\omega_r^{-2}$  so that their contribution to the second moment remains constant. The higher order sidebands fall more rapidly in intensity and soon become too weak to observe.

We can make an interesting and exact calculation concerning the shape and second moment of the central line of the spectrum for any specimen. Let us compare two situations for any crystal: (a) the crystal is rotated about one particular crystalline direction, (b) the crystal is at rest, but oriented so that the applied magnetic field is parallel to the direction chosen for the axis of rotation in (a). It follows therefore that all the  $\theta_{ij}$  of (b) are identical with the  $\gamma_{ij}$  of (a). In experiment (a), when the rate of rotation is very rapid so that the sidebands are resolved from central line, the shape and second moment of the central line is determined by  $\overline{\mathcal{H}}_1$ , given by (5). In experiment (b) the shape and second moment of the resonance spectrum is determined by  $\mathcal{H}_1$ , given by (3), in which  $\theta_{ij}$  may be replaced by  $\gamma_{ij}$ . Hence we have

$$\mathcal{H}_1(a) = \frac{1}{2} (3 \cos^2 \alpha - 1) \mathcal{H}_1(b). \quad (7)$$

The lineshapes and second moments are therefore determined by the same perturbing Hamiltonian apart from a scale factor  $\frac{1}{2} (3 \cos^2 \alpha - 1)$ . Thus, although we may not be able to calculate the precise lineshape in either case, we can state that the spectra have the same shape in both experiments, the central spectrum in the rotating experiment being scaled down in width by a factor  $\left| \frac{1}{2} (3 \cos^2 \alpha - 1) \right|$ . The second moment of the central



line is just  $\frac{1}{4} (3 \cos^2 \alpha - 1)^2$  of that for the static crystal when it is oriented with the magnetic field along the axis used in the rotation experiment. In the case of polycrystalline specimens the orientation of the specimen is of no significance; the central line of the spectrum of the rotating specimen is always a replica of the spectrum for the static specimen, scaled down by the factor  $\left| \frac{1}{2} (3 \cos^2 \alpha - 1) \right|$ .

We have found that the central line does indeed behave in this manner, and in particular that the linewidth follows the angular variation  $\left| \frac{1}{2} (3 \cos^2 \alpha - 1) \right|$ . The angle  $\alpha = \cos^{-1} 3^{-\frac{1}{2}} = 54^\circ 44'$  is therefore of exceptional

interest since the width of the central line for this orientation should be very small. We have in fact observed that when a specimen is rotated at high speed about this special direction relative to the magnetic field the central line is very narrow, and if the speed of rotation is high enough to push the side-spectra well out and make them unobservably weak, this narrow central line is all that is observed.

In this manner we have removed dipolar broadening from a solid spectrum by macroscopic motion just as in a liquid it is removed by microscopic motion. In a liquid the lines are narrow because the isotropic mean of  $(3 \cos^2 \theta - 1)$  is very small; in our experiment with a solid we make use of the fact that the mean of  $(3 \cos^2 \theta - 1)$  for uniform rotation about the special axis inclined at  $54^\circ 44'$  to the magnetic field is similarly small.

The removal of dipolar broadening by specimen rotation opens up the possibility of examining fine structure of the kind obtained in the high-resolution spectra of liquids, but which in solids is normally overlaid by the strong dipolar broadening. It will become possible to measure chemical shifts in solid specimens with greater precision, to study their anisotropy, and to compare them with the corresponding shifts in the liquid state. An example of the use of this technique was provided by polycrystalline phosphorus pentachloride (Andrew, Bradbury, Eades and Jenks 1960), which yielded two sharp  $^{31}\text{P}$  resonance lines, whose separation was proportional to the strength of the magnetic field. The two lines were ascribed to the phosphorus nuclei in the  $\text{PCl}_6^-$  and  $\text{PCl}_4^+$  ions of which the crystal



is composed, and enabled a monotonic series of chemical shifts to be compiled for the tri-, tetra-, penta- and hexachlorides of phosphorus.

An interesting new effect was found with the phosphorus pentachloride spectrum. The  $PCl_4^+$  line saturated more readily than the  $PCl_6^-$  line, presumably on account of a larger relaxation time, and consequently it usually appeared less intense. However Mr. Bradbury noticed that when the spinning rate was just equal to the separation between the resonance lines the saturation properties of the two lines became almost identical and they now had the same intensity. The effect was also observed when the rate of rotation was a half of the separation between the lines. It was clear that there was now a means of rapidly exchanging energy between the two systems so that they had a common spin-lattice relaxation time; it is a case of cross-relaxation by rotation.

If, as in the case of phosphorus pentachloride, we have two different types of nuclei whose resonance spectra do not overlap, spin exchange between nuclei of the different types is negligible because their frequencies of precession are different, and the perturbation is not secular. However the parts of the dipolar Hamiltonian (3) concerned with spin exchange contains the angular factor  $(3 \cos^2 \theta_{ij} - 1)$ , which incidentally is the reason for its appearance in the earlier expression (1), and which is time-dependent when the crystal is rotated. As expansion of this factor in (6) shows, terms periodic in  $\omega_r$  and  $2\omega_r$  appear, so that there are now secular components in the spin-exchange Hamiltonian when the rate of rotation is equal to the difference in resonance frequencies, or to half that difference. Calculation shows that the spin-exchange transition probability is of order  $T_2^{-1}$ , and since  $T_2 \ll T_1$  there is now a means of energy exchange between the two types of nuclei.

Physically we may say that in the static crystal the rotating local field produced at one nucleus by a different neighbour is not rotating at the resonance frequency of the nucleus and cannot induce a transition. However when the crystal rotates at the difference frequency or half that frequency, the nucleus now moves through the rotating field of its neighbour at just the correct rate so that it experiences a component of the field at the right frequency to induce a transition. Further examination shows that the effect should also be observed when the rotation rate is any submultiple of the difference frequency.

## REFERENCES

- ANDERSON, P. W., *J. Phys. Soc. Japan*, **9**, 316, 1954.  
ANDREW, E. R., A. BRADBURY and R. G. EADES, *Nature*, **182**, 1659, 1958.  
——, A. BRADBURY and R. G. EADES, *Nature*, **183**, 1802, 1959.  
——, K. M. SWANSON and B. R. WILLIAMS, *Proc. Phys. Soc.*, **77**, 36, 1961.  
—— and D. P. TUNSTALL, *Proc. Phys. Soc.*, **78**, 1, 1961.  
BLOEMBERGEN, N., *Physica*, **15**, 386, 1949.  
LOWE, I. J., *Phys. Rev. Letters*, **2**, 285, 1959.  
VAN KRANENDONK, J., *Physica*, **20**, 781, 1954.
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