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LETTER TO THE EDITOR

NMR 'diffraction' in solids?

P Mansfield and P K Grannell†

Department of Physics, University of Nottingham, University Park,
Nottingham, NG7 2RD

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Abstract. A new approach to the study of structure in solids by NMR is described. Multiple-pulse line-narrowing sequences and an applied magnetic field gradient are used. The theoretical analysis highlights the analogy with x-ray diffraction. Experimental results from a model one-dimensional lattice are presented.

In this letter, we wish to introduce a new method for the determination of spatial structures in solids which relies on NMR 'diffraction' effects.

The study of internuclear spacings in solids by NMR has traditionally relied upon the dipole-dipole interaction and its effect on lineshape and second moment in order to estimate intramolecular distances. Although all information on the unit cell is contained in the dipolar lattice sums, there is no direct way of obtaining the lattice structure from the free-induction decay (FID) or from the lineshape of a solid. In general, one needs a model of the structure being determined, so that the theoretical predictions for the second moment or for the lineshape may be compared with results obtained experimentally. This all comes about because a particular lattice site is not uniquely determined magnetically and hence is not uniquely identifiable in the frequency spectrum.

Identification of lattice sites in the frequency spectrum may be obtained by applying a linear magnetic field gradient to the sample. The usual effect of this is to produce a FID which reflects the bulk shape of the solid, assumed to be a continuous distribution of spins (Carr and Purcell 1954).

Of course, in a solid, the spins are actually distributed in a discrete manner at atomic sites. One reason that this discrete nature is not apparent in the observed FID signals is the large dipole-dipole broadening in solids. In mobile liquids, however, this broadening can be very small, so why do we not observe diffraction effects there? There are two reasons: the first is that temporal coherence of the signals from all sites is partially destroyed by random motions, though perhaps one could observe a partially coherent diffraction effect, as for example in a random solid, were it not for the second more important effect of self-diffusion in the applied field gradient.

In solids, the self-diffusion may be made arbitrarily small by lowering the sample temperature, but of course, the spin-spin interactions remain. By employing one of the recently developed multiple-pulse sequences (Waugh *et al* 1968, Mansfield *et al* 1973,) or a suitable modification described below, the dipolar and chemical shift interactions

† ICI Postdoctoral Research Fellow.

may be artificially reduced to a very high degree, while at the same time leaving the spin-field gradient interaction only slightly reduced in value. This can be achieved by applying a modified compensated reflection symmetry cycle, designed to remove dipolar and chemical shift terms, while at the same time appropriately reversing the linear field gradient direction. Such a sequence is, in the pulse-timing representation,

$$P_{-y} - \{\tau(+)-P_x - \tau(+)-P_y - 2\tau(+)-P_y - \tau(+)-P_x - 2\tau(-) \\ - P_x - \tau(+)-P_y - 2\tau(-)-P_y - \tau(+)-P_x - \tau(+)\}_N$$

where $\tau(\pm)$ indicates the sense of the field gradient applied during the delay τ .

For a set of non-interacting spins in a tetragonal lattice with unit-cell dimensions a, b, c , the displacement vector $r_{lmn}(k)$ from the origin to the k th spin site in the l, m, n th unit cell (l, m, n integers) is given by

$$r_{lmn}(k) = (l + u_k)\mathbf{a} + (m + v_k)\mathbf{b} + (n + w_k)\mathbf{c} \quad (1)$$

where $\mathbf{a} = a\mathbf{i}$ etc, and u_k, v_k, w_k are fractions of the primitive-cell dimensions.

For a semi-discrete spin distribution in a uniform field gradient \mathbf{G} , in which the spins are distributed with a density $\rho(\mathbf{r})$ over a range $\Delta x, \Delta y, \Delta z$ from the position $\mathbf{r} = r_{lmn}(k) + \mathbf{r}'$, where \mathbf{r}' is a continuous variable, we obtain for the FID function of the system at resonance

$$S(\mathbf{p}) = \mathcal{R} \sum_{l,m,n,k} \int_{la+u_k}^{la+u_k+\Delta x} \int_{mb+v_k}^{mb+v_k+\Delta y} \int_{nc+w_k}^{nc+w_k+\Delta z} \rho(\mathbf{r}) \exp(i\mathbf{p}\cdot\mathbf{r}) d\mathbf{r}' \quad (2)$$

where $\mathbf{p} = \gamma\mathbf{G}t$ in which γ is the magnetogyric ratio and t the time.

For a set of point spins, as in a crystal lattice, equation (2) reduces to

$$S = \mathcal{R} \sum_{l,m,n} a_{lmn} \exp[2\pi i(le + mf + ng)] \sum_k f_k \exp[2\pi i(u_k e + v_k f + w_k g)] \quad (3)$$

where $e = \gamma t a G_x / 2\pi = a p_x / 2\pi$ etc, and $a_{lmn} = 0, 1$. The term involving the summation over k corresponds to signal contributions within the unit cell and is equivalent to the scattering factor S_k in electron or neutron scattering. In our case, the scattering cross section $f_k = 0, 1$. Unlike ordinary x-ray scattering, NMR scattering is in principle selective, since only resonant spins contribute to the signal, non-resonant spins having $f_k = 0$. This is an important point in the study of protons in solids which are effectively transparent to x-rays.

It is clear that the dimensionless quantities e, f, g correspond to the lattice Miller indices at appropriate times t .

The point-spin formula equation (3) shows that in a cubic lattice with \mathbf{G} along the [001] axis, observation of first-order diffraction requires $g = 1$. For protons with $c = 3 \text{ \AA}$ and $G_z = 10^8 \text{ G cm}^{-1}$ the diffraction peak would occur at 8 s from the time origin. Thus in order to observe this signal, an intrinsic narrowed linewidth of about 0.1 Hz is required. To date, the best line narrowing achieved in a single crystal of CaF_2 is about 20 Hz (Rhim *et al* 1973). Thus practical realization of NMR crystallography is some way off. In addition, the application of large field gradients degrades the line-narrowing efficiency in the present-day cycles, but this effect may be reduced by using samples of very small diameter so that the total static field variation over the sample is kept within reasonable limits.

At this point we may ask what field gradient would be necessary to observe first-order diffraction in a solid excited by a single 90° RF pulse? Again if we take $c = 3 \text{ \AA}$ and

insist that the diffraction peak be observed within about $2T_2 \sim 100 \mu\text{s}$, we find that $G_z = 10^8 \text{ G cm}^{-1}$.

NMR diffraction could be useful at the macroscopic level for microscopy in bio-physical systems with regular, or approximately regular, macroscopic structures; eg cell membranes and filamentary or fibrous structures. As an approximation to such a system we consider a uniform one-dimensional lattice of lattice constant c , which comprises $N + 1$ flat slabs of thickness Δz containing uniformly distributed spins. For this model, equation (2) gives for the normalized signal

$$S(p_z) = \mathcal{R} \left(\exp [i \frac{1}{2} p_z (\Delta z + cN)] \frac{\sin \beta}{\beta} \frac{\sin [\frac{1}{2} p_z c (N + 1)]}{(N + 1) \sin \frac{1}{2} p_z c} \right) \quad (4)$$

where $\beta = \gamma G_z t \Delta z / 2$. This result is similar to the classical diffraction grating formula. The $\sin \beta / \beta$ term represents the signal coming from one plate of thickness Δz , and corresponds to the results obtained by Carr and Purcell (1954) in the interference limit of a set of continuously distributed spins.

As a preliminary experimental test of our result, we have applied the $[[1, 3, 2; 1, \tilde{3}, 2]]$ multipulse line-narrowing sequence (Mansfield *et al* 1973) with $\tau = 6.4 \mu\text{s}$ to model

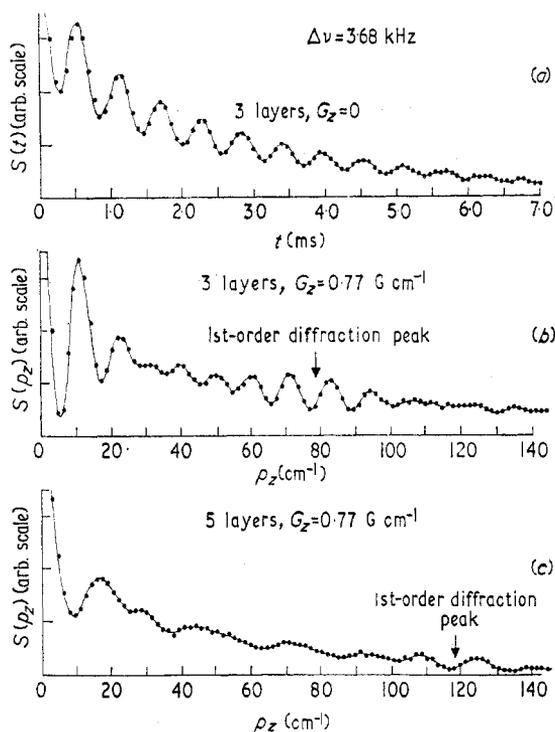


Figure 1. (a) The transient nuclear signal from protons in a three-layer sample of synthetic camphor $\text{C}_{10}\text{H}_{16}\text{O}$ in response to the $[[1, 3, 2; 1, \tilde{3}, 2]]$ multiple-pulse sequence, $\tau = 6.4 \mu\text{s}$, with zero applied field gradient. (b) The same as (a) but with an applied field gradient of 0.77 G cm^{-1} . A first-order diffraction peak is observed. (c) The transient nuclear signal from protons in a five-layer sample of synthetic camphor in response to the same pulse sequence and the same field gradient as in (b). The abscissae in (b) and (c) were calculated from the measured values of the field gradient and the scaling factor of the multiple-pulse sequence, which was 2.1.

one-dimensional lattices comprising equally spaced plates of camphor. In these experiments, the field gradient is kept constant so that the chemical shift terms, which are rather small for protons, are retained in the average hamiltonian. However, the spatial resolution obtained is governed by much larger deviations from field gradient uniformity due to the coil design (Tanner 1965). The important point is not so much the resolution, which at present corresponds to 0.05 cm, but that temporal coherence of the first-order diffraction peak is restored due to removal of the dipole-dipole interaction in a solid.

Figure 1(a) shows the transient signal from a three-layer camphor sample with zero applied field gradient in response to the $[[1, 3, 2; 1, \bar{3}, 2]]$ multipulse sequence with $\tau = 6.4 \mu\text{s}$. The nuclear signal from camphor in the absence of artificial line narrowing decays with $T_2 \sim 44 \mu\text{s}$. Figure 1(b) shows the transient signal as for 1(a) but with an applied field gradient $G_z = 0.77 \text{ G cm}^{-1}$. Note the first-order diffraction peak. Figure 1(c) shows the narrowed transient signal from a five-layer camphor sample under the same conditions. A first-order diffraction peak is observed here also. All these data were recorded at room temperature, and off-resonance to facilitate Fourier transformation (Mansfield *et al* 1973).

We see from equation (2) that the inverse Fourier transform of $S(p)$ yields the spatial

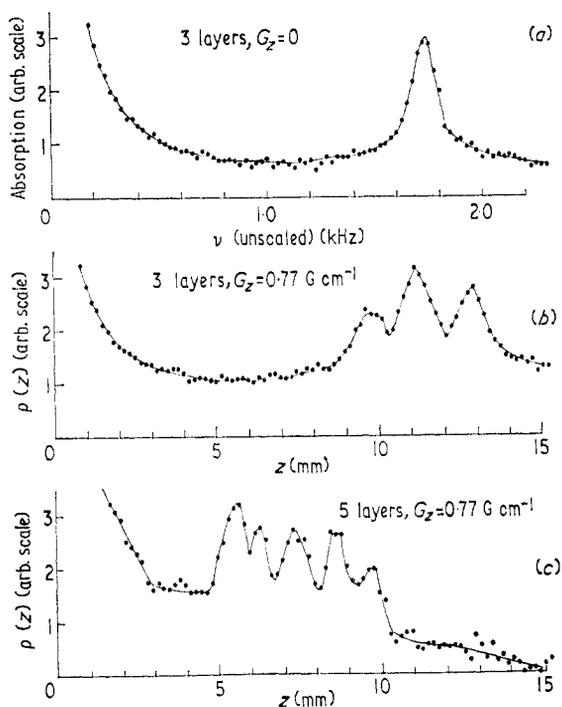


Figure 2. (a) The Fourier cosine transform of the transient response figure 1(a). A narrowed linewidth of 150 Hz is observed. (b) The Fourier cosine transform of the transient response figure 1(b). The three camphor layers are clearly resolved. (c) The Fourier cosine transform of the transient response figure 1(c). The five camphor layers are well resolved. The abscissae in (b) and (c) were calculated from the measured values of the field gradient and the scaling factor of the multiple-pulse sequence, which was 2.1. The peaks observed at the frequency origin arise from the damping and baseline shifts in the transient responses in figure 1.

transforming the data shown in figures 1(b) and 1(c) is presented in figures 2(b) and 2(c), and indicates clear resolution of the plate assemblies. The actual spacings of the plates agree with the spacings derived from figures 2(b) and 2(c) to within the 10% accuracy of our field gradient calibration.

These experiments are to our knowledge the first demonstration of NMR diffraction in a solid. We have obtained similar-looking results for layered liquid samples and liquid-like rubber samples in response to a single 90° pulse. However, these results are not as valuable for reasons stated earlier.

Although with improved field gradient coils the best spatial resolution that could be expected with current multipulse line-narrowing sequences is still only 10 μm, we believe that the practical realization of NMR diffraction and microscopy presents new and compelling reasons for continued effort to improve the line-narrowing efficiencies of these sequences.

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