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Stochastic Theory of Nuclear Magnetic Resonance in Rotating Solids

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Abstract.

Dipolar broadening is described by a random function characterised by two parameters ω_1 and ω_2 which determine the widths of its Gaussian probability distribution and its Gaussian frequency spectrum. With this model, a general method for obtaining the spectrum of a rotating sample is given. When the axis of rotation is inclined at 54 degrees to the magnetic field, an approximate criterion for the spectrum to exhibit structure is

$$\exp - (3\pi^2 \omega_1^2 \omega_2^2 / 4 \omega_r^4) \sim \omega_r / 2\pi\omega_1$$

where ω_r is the rotational angular frequency. At high rotation frequencies the central line has the width

$$(2\pi)^{1/2} (2\omega_1^2 / 3\omega_2) \exp - (\omega_r^2 / 2\omega_2^2).$$

Théorie stochastique de la résonance magnétique dans les solides en rotation

Résumé.

L'élargissement dipolaire est décrit par une fonction aléatoire caractérisée par deux paramètres ω_1 et ω_2 qui déterminent les largeurs de sa probabilité de distribution gaussienne et de son spectre de fréquence gaussienne. A partir de ce modèle, nous donnons une méthode générale pour obtenir le spectre d'un échantillon tournant. Quand l'axe de rotation est incliné de 54,7 degrés sur le champ magnétique, pour que le spectre présente une structure, il faut vérifier sensiblement le critère suivant:

$$\exp. - (3\pi^2 \omega_1^2 \omega_2^2 / 4\omega_r^4) \sim \omega_r / 2\pi\omega_1$$

où ω_r est la fréquence angulaire de rotation. Pour des fréquences de rotation élevées, la raie centrale a pour largeur:

$$(2\pi)^{1/2} (2\omega_1^2 / 3\omega_2) \quad \exp. - (\omega_r^2 / 2\omega_2^2)$$

Introduction.

The existence of a local field at a particular nucleus in a stationary solid implies that the spin environment of the nucleus departs from spheri-

cal symmetry. If the sample rotates the asymmetry moves with the sample and now generates a time varying local field causing a frequency modulation of the Larmor precession. Simultaneously the environment is changing in a random way due to the effects of spin diffusion.

The stochastic theory of magnetic resonance [1, 2, 3] provides a natural framework in which to describe this situation. The spectrum shape function is the Fourier transform of the correlation function of the transverse magnetization.

$$I(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau}\, \emptyset(\tau)\, d\tau \tag{1}$$

Dipolar broadening is described by the random function $\Delta\omega(t)$ whose probability distribution and frequency spectrum determine $\varnothing(\tau)$.

$$\emptyset(\tau) = \left\langle \exp\left(i\int_{t}^{t+\tau} \Delta\omega(t')\, dt'\right) \right\rangle \tag{2}$$

If $\Delta\omega(t)$ has a Gaussian probability distribution of second moment ω_1^2 then $\emptyset(\tau)$ may be obtained in terms of the correlation function $\emptyset_{\Delta\omega}(\tau)$ of $\Delta\omega(t)$.

$$\emptyset(\tau) = \exp -\left(\omega_1^2 \int_0^{\tau} (\tau - x)\, \emptyset_{\Delta\omega}(x)\, dx\right) \tag{3}$$

$$\emptyset_{\Delta\omega}(\tau) = \frac{\left\langle \Delta\omega(t)\,.\,\Delta\omega(t+\tau) \right\rangle}{\left\langle \Delta\omega(t)\,.\,\Delta\omega(t) \right\rangle} \tag{4}$$

The spectrum in the absence of spin diffusion.

In this case the local field at nucleus j is in frequency units

$$\Delta\omega_j = \sum_k A_{jk}\, r_{jk}^{-3} (3\cos^2\theta_{jk} - 1) \tag{5}$$

where A_{jk} is a constant and $(\hat{r}_{jk}\,.\,\hat{z}) = \cos\theta_{jk}$, the caret indicating a unit vector. Choosing a vector $\hat{s}$ and defining angles $\alpha\,\gamma$ and φ by $(\hat{s}\,.\,\hat{z}) = \cos\alpha$, $(\hat{s}\,.\,\hat{y}) = 0$, $(\hat{r}_{jk}\,.\,\hat{s}) = \cos\gamma_{jk}$, $(\hat{r}_{jk}\times\hat{s}\,.\,\hat{y}) = \cos\varphi_{jk}\sin\gamma_{jk}$, then (5) may be written

$$\Delta\omega_j = \sum_k A_{jk}\, r_{jk}^{-3} \left\{ \frac{1}{2}(3\cos^2\alpha - 1)(3\cos^2\gamma_{jk} - 1) + \frac{3}{2}\sin^2\alpha\sin^2\gamma_{jk}\cos 2\varphi_{jk} + \frac{3}{2}\sin 2\alpha\sin 2\gamma_{jk}\cos\varphi_{jk} \right\} \tag{6}$$

If the sample rotates about $\hat{s}$ with an angular frequency ω_r then

$$\varphi_{jk} = \varphi^{o}_{jk} + \omega_r t \tag{7}$$

The function $\mathcal{O}_{\Delta\omega}^{(\tau)}$ is obtained by using (6) and (7) in (4), averaging over t and replacing terms in φ_{0jk} and γ_{jk} by their averages assuming an isotropic distribution of $\hat{r}_{jk}$.

$$\mathcal{O}_{\Delta\omega}(\tau) = \frac{1}{4}(3\cos^2\alpha - 1)^2 + \frac{3}{4}\sin^2 2\alpha \cos\omega_r\tau + \frac{3}{4}\sin^4\alpha\cos 2\omega_r\tau \tag{8}$$

The spectrum is now obtained by using (1) (3) and (8) and for a sufficiently large ω_r consists of a central line with resolved sidebands. The central line is approximately Gaussian with second moment $\omega_1^2\,(3\cos^2\alpha - 1)^2/4$, [4]. The total second moment is $(d^2\mathcal{O}(\tau)/d\tau^2)_{\tau=0}$ which is readily shown to be ω_1^2 and so invariant [5, 6, 7].

Interest centres on the value of α which makes the first term of (8) vanish. The spectrum would now be a set of δ functions spaced at frequency intervals of $\omega_r/2\pi$ with, in the limit of small ω_r the envelope $\exp(-\omega^2/2\omega_1^2)$ and in the limit of large ω_r, almost all the intensity in the central line. When the first term in (8) is small though, the spectrum is determined by spin diffusion.

Effect of spin diffusion.

An approximate description of the effect of spin diffusion can be given by introducing a decay factor into $\mathcal{O}_{\Delta\omega}(\tau)$. The simplest choice is an exponential decay, but as this leads to an infinite fourth moment, it will certainly fail to describe the wings of the spectrum adequately. It is more consistent with the assumption of a Gaussian probability distribution for $\Delta\omega(t)$ to assume that its frequency spectrum has a similar form, implicitly supposing that the properties of $\Delta\omega(t)$ reflect a large number of weak dipole-dipole interactions rather than a comparatively small number of near neighbour interactions. This is not unreasonable for a cubic crystal though it would not apply to a structure consisting of small rather isolated groups of nuclei, except to describe broadening due to interactions between different groups.

For $\cos^2\alpha = 1/3$,

$$\mathcal{O}_{\Delta\omega}(\tau) = \left(\frac{2}{3}\cos\omega_r\tau + \frac{1}{3}\cos 2\omega_r\tau\right)\exp -(\omega_2^2\,\tau^2/2) \tag{9}$$

For slow rotation the shape of the spectrum approaches that of the stationary sample and the discussion in the previous section corresponds to the limit of infinitely great rotation frequency. The second moment of the spectrum is still ω_1^2 and the fourth moment is $\omega_1^2 (3\omega_1^2 + \omega_2^2 + 2\omega_r^2)$.

A convenient experimental parameter whose variation can be predicted from the above assumptions is the ratio, at the centre of the spectrum of the second derivative to the intensity. This is the slope of the recorded first derivative divided by the area under one half of it. It is identical with the second moment of $\emptyset(\tau)$ as follows immediately from differentiating (1), and for $\omega_2 \ll \omega_r \ll \omega_1$ is approximately

$$\frac{1}{\omega_1^2} + \left(\frac{2\pi}{\omega_r}\right)^2 \exp - \left(3\pi^2 \omega_1^2 \omega_2^2 / 2\omega_r^4\right) + \ldots \qquad (10)$$

This gives as a rough criterion for the onset of line shape change $\exp(-3\pi^2\omega_1^2\omega_2^2/4\omega_r^4) \sim \omega_r/2\pi\omega_1$. In the limit of very rapid rotation the central line becomes Lorentzian with a width at half height $(2\pi)^{1/2} (2\omega_1^2/3\omega_2) \exp - (\omega^2/2\omega_2^2)$.

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DISCUSSION

M. Gorter. — Have I correctly understood that when the " magic angle " of 54,7 is chosen, the central lines are infinitely sharp, the zero width being increased by spin diffusion ? Does this agree with the data ?

The first statement would not appear to apply to all crystal structures and crystal orientations. What should be expected in the general case ?

Andrew. — Professor Gorter's first remark is correct, and the central line at angle 54° 44′ would only be infinitely narrow if the crystal were rotated infinitely fast. The situation is similar to that in a liquid for which the line becomes infinitely narrow only when the correlation frequency is infinite. The expression for the linewidth given by Mr. Clough is consistent with the experimental data.

The marked narrowing of the central line for rotation at angle 54° 44′ is quite general, and applies to both single crystals and powders. The residual width would have some dependence on crystal orientation, but in the example of cubic sodium chloride, this anisotropy should be small.

Clough. — The simplicity of the stochastic theory is obtained by ignoring the crystal structure and the spread in local field is described by the single parameter necessary to specify an isotropic Gaussian distribution. In a real crystal the distribution would be neither Gaussian nor isotropic but the results would be substantially the same.