Nuclear Magnetic Resonance Spectra in Solids: Invariance of the Second Moment under Molecular Reorientation

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Résumé. — La réorientation gênée des molécules d'un solide entraîne un amincissement des raies d'absorbtion et une réduction apparente du second moment. Nous montrons ici qu'une telle réorientation fait apparaître de faibles satellites latéraux et que, en tenant compte de ces satellites le second moment reste constant. La théorie a été vérifiée dans le cas particulier de la rotation uniforme en faisant tourner un monocristal de chlorure de sodium à une vitesse correspondant à la largeur de raie du réseau rigide. Le second moment est resté invariant et on a observé les bandes latérales prévues.

In absence of quadrupole effects the nuclear magnetic resonance spectra of non-metallic crystals have widths which generally originate in the nuclear magnetic dipolar interactions. It has long been accepted that hindered rotation in such solids causes a narrowing of the spectrum and is accompanied by a reduction in its second moment. In fact quite early in the history of the application of nuclear magnetic resonance techniques to solid state studies modifications were made [1] to Van Vleck's celebrated second-moment formula [2] which were apparently adequate in taking into account the averaging by molecular motion of the dipolar interactions. In order that the spectrum should be narrowed and that the mean interaction should determine its width, the frequency of molecular reorientation must exceed the spectral width.

Recently, however, Pake [3] has pointed out that the second moment should not be reduced by molecular motion. The terms in the nuclear Hamiltonian which describe the nuclear motion do not influence the second moment though they do increase the fourth moment; this implies a narrowing of the central part of the spectrum together with a strengthening of

its skirts.   In this respect nuclear motion has a similar effect on the nuclear magnetic resonance line to that produced by exchange in the case of electron paramagnetic resonance.

A theoretical treatment [4] shows that hindered rotation does cause the spectrum to develop wide skirts of low intensity.   When these are
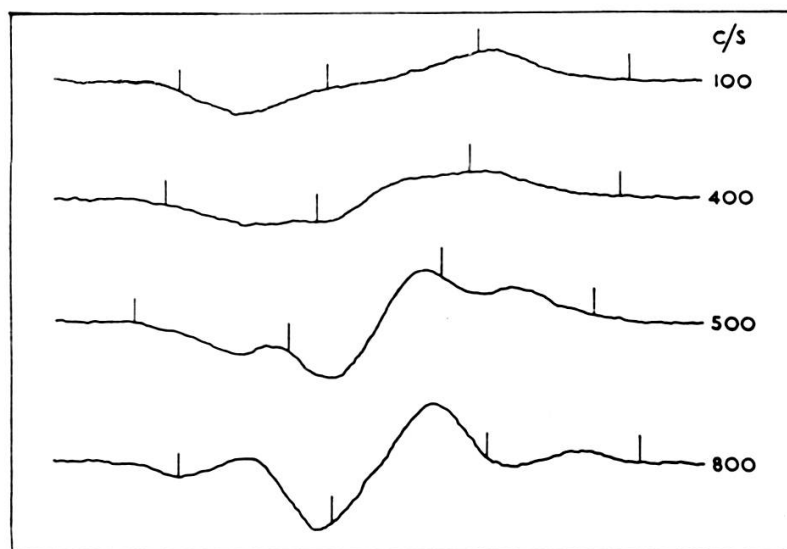

Fig. 1.

Recorded derivative spectra for the ^{23}Na resonance in a single crystal of sodium chloride rotated about [001] in a field of 6162 gauss perpendicular to the axis of rotation.   The rates of rotation are indicated with each trace.   The interval between markers on the traces is 1660 c/s.

included in the spectrum the second moment does indeed remain invariant. In practice however when the reorientation rate greatly exceeds the static line-width the skirts are too weak to be detected and then the second moment of the *observable* part of the spectrum has just the reduced value derived earlier by Gutowsky and Pake [1].

The formation of the spectrum can be appreciated by considering a crystal containing a static array of well-separated similarly-oriented identical nuclear pairs.   If the interaction between the nuclear pairs is neglected the spectrum consists of just two lines having angular frequency

$$\omega = \gamma_a \left[H_0 \pm \epsilon \, \mu_b \, r_{ab}^{-3} \, (3 \cos^2 \theta - 1) \right], \tag{1}$$

where γ_a is the magnetogyric ratio of the nuclei at resonance, μ_b is the magnetic moment of the nuclear neighbour in each pair, r_{ab} is the inter-

nuclear vector, θ is the angle between H_0 and r_{ab}, and $\in$ is $\frac{3}{2}$ if the two nuclei in each pair are identical and is unity if they are not identical. Classically equation (1) expresses the frequencies of precession of the nuclei in the resultant of the applied field H_0 and an effective local field given by the second term in the square bracket. If now all the nuclear pairs rotate with uniform angular velocity ω_r about axes normal to the pairs and making angles α with H_0 then $\cos \theta$ is given by $\sin \alpha \cos \omega_r t$ and expression (1) for the precession frequencies becomes

$$\omega = \omega_0 \mp \omega_1 \pm \omega_2 \cos 2\,\omega_r t \;, \qquad (2)$$

where $\qquad \omega_0 = \gamma_a H_0\;, \qquad \omega_1 = \frac{1}{2}\in \gamma_a \mu_b r_{ab}^{-3} (3\cos^2\alpha - 1)$

$$\qquad\qquad\qquad (3)$$

and $\qquad\qquad\qquad \omega_2 = \frac{3}{2}\in \gamma_a \mu_b r_{ab}^{-3} \sin^2\alpha \;\cdot$

The spectrum of this frequency-modulated precession consists of two central carrier frequencies $\omega_0 \pm \omega_1$ with side-frequencies spaced at integral multiples of $2\omega_r$ on either side, the nth side-band having intensity $J_n^2 (\omega_2/2\omega_r)$. The second moment ω_1^2 of the two carrier lines is just the reduced second moment given by Gutowsky and Pake [1], while the second moment of the entire spectrum is the same as for the static array [4]. The argument may be extended to more complicated situations. In practice the reorientation of molecules in crystals is not uniform and may be analysed into a wide spectrum of rotational frequencies. The sidebands do not therefore occur at definite frequencies $\pm 2n\omega_r$ on either side of the narrowed central portion, but instead are too thinly distributed over a range of frequencies to be observed.

In order to check the theory it is desirable to examine the spectrum of nuclei which all rotate uniformly with respect to their neighbours so that the side-spectra occur at definite frequencies and therefore with sufficient intensity to be observed. This situation can be achieved by studying the spectrum of nuclei in a crystal rotated at high speed. The ^{23}Na resonance was examined in a single crystal of sodium chloride spun at speeds up to 50,000 r.p.m. about the [001] direction. Examples of spectra recorded with a modified Pound-Watkins spectrometer are shown in the figure. The first sidebands are clearly seen at the highest rotation rate of 800 c/s and occur as expected at a separation $2\omega_r$ from the centre of the spectrum. The central portion is approximately halved in width as theory requires [1].

The second moments of the spectra recorded for different values of ω_r are given in the Table below; the rotation rates were measured photoelectrically. The mean value of the second moment for the static crystal with H_0 in the (001) plane is found by calculation from Van Vleck's formula to be 0.55

$\dfrac{\omega_r}{2\pi}$ in c/s	Second moment in gauss^2
100	0.57
200	0.56
400	0.57
500	0.60
700	0.55
800	0.57

gauss^2. This value is in satisfactory agreement with the results in the Table, and shows the invariance of the second moment under rotation. The experiment also demonstrates directly that molecular rotation in solids does lead to line-narrowing, and that the frequency of rotation required for this narrowing is of the order of the line-width (the r.m.s. line-width 0.74 gauss is equivalent to 833 c/s).

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3. PAKE, G. E., *Solid State Physics*, *2*, 1 (1956).
4. ANDREW, E. R. and R. A. NEWING, *Proc. Phys. Soc.* (in press).