LETTERS TO THE EDITORS

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Nuclear Magnetic Resonance Spectra from a Crystal rotated at High Speed

HINDERED molecular rotation in solids reduces the width of their observed nuclear magnetic resonance spectra, with a consequent decrease in the measured second moments[1]. By contrast, on general theoretical grounds it has been shown[2] that the second moments of dipolar-broadened spectra should remain invariant and should not be reduced by such motion. In a recent explanation[3] of this apparent discrepancy the nuclear magnetic interaction was divided into two parts, namely, a steady mean interaction and a fluctuating part. The steady mean interaction is less than the interaction in a static crystal devoid of hindered rotation and generates an observed spectrum narrower than that of the static crystal. The fluctuating part of the interaction generates side-spectra set at integral multiples of the frequency of molecular rotation on either side of the central narrowed spectrum. Since the molecules do not rotate uniformly, but are re-oriented with an irregular motion, these side-spectra are dispersed over a band of frequencies with an intensity too weak to be observed. It was shown, however[3], that when these weak side-spectra are included the second moment does indeed remain invariant even though the second moment of the central portion, which is all that is observed experimentally, becomes smaller.

Since this explanation requires the existence of side-spectra which are too weak in intensity normally to be seen, it seemed desirable to devise an experiment which would render them observable. If all the molecules in a solid were to rotate with the same uniform frequency, the side-spectra would then be centred at well-defined frequencies and should, under suitable conditions, have sufficient intensity to be observed. The most convenient way in which to achieve this situation is to take a crystal within which there is no appreciable motion of the nuclei and to rotate it uniformly. In this way all nuclei in the crystal rotate with the same uniform frequency with respect to their neighbours. Since the accepted criterion[1] for spectral narrowing is a rotation-rate at least comparable with the width of the spectrum, it was clear that a high speed of rotation would be necessary.

Using an air-driven rotor, a single crystal of sodium chloride was spun at speeds up to 50,000 revolutions per minute about the [001] direction in a magnetic field of 6,000 gauss directed normally to the axis of rotation. With this geometry it may readily be shown[3] that side-spectra should occur only at even multiples of the rotation frequency ν_r on either side of the narrowed central spectrum. Examples of the sodium-23 resonance derivative spectra recorded with a modified Pound–Watkins spectrometer are shown in Fig. 1. The first-order side-spectra are clearly seen at the highest rotation-rates and occur, as predicted, at a separation of $2\nu_r$ from the centre of the spectrum. The central portion is approximately halved in width as the theory requires for this case. There is good general agreement between the shape of the derivatives recorded and those calculated, at all rates of rotation. In particular, at the highest

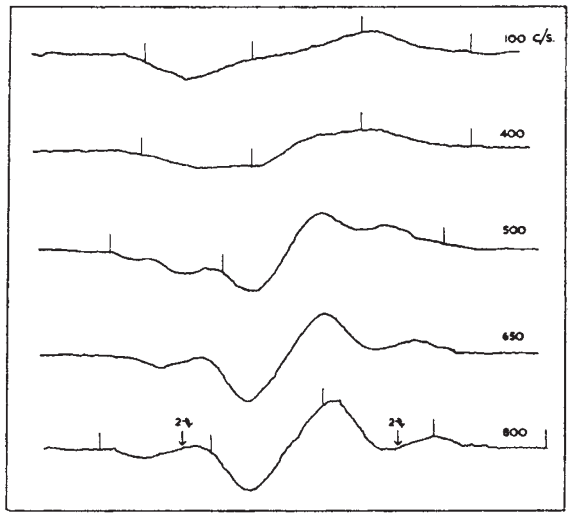

Fig. 1. Sodium-23 nuclear magnetic resonance derivative spectra of a single crystal of sodium chloride rotated at the rates indicated. The markers on the recordings are 1,660 c./s. apart

rate of rotation (800 c./s.), where the first side-spectra are well resolved, their intensity relative to that of the central portion is in satisfactory agreement with theory. At 800 c./s. the expected relative intensity of the second side-spectra at $\pm 4\nu_r$ is less than 1 per cent, and they have not been observed.

The second moments of spectra recorded at different rotation-rates are given in Table 1 ; the rotation-rates were measured photoelectrically.

Table 1

ν_r (c./s.)	Second moment (gauss²)	ν_r (c./s.)	Second moment (gauss²)
100	0·57	500	0·55
200	0·54	700	0·56
400	0·57	800	0·59

The mean theoretical value of the second moment for the static crystal with the magnetic field in the (001) plane has been found from Van Vleck's formula[4] to be 0·55 gauss². This value is in satisfactory agreement with the results in Table 1 and verifies the invariance of the second moment.

This experiment shows in a direct manner that the relative rotation of nuclei in solids does cause a narrowing of the nuclear magnetic resonance spectrum. Moreover, in addition to demonstrating the presence of side-spectra and verifying the invariance of the second moment within the limits of the experimental uncertainty, the experiment also shows directly that for spectral narrowing the necessary rate of nuclear motion is of the order of the spectral width. (The r.m.s. line-width 0·74 gauss is equivalent to 833 c./s.)

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