NMR Spectrum of ^{23}Na and ^{127}I in Single Crystals of $NaIO_4$

Alarich Weiss

Institut für Physikalische Chemie der Universität Münster,
D-44 Münster, Germany

and

Wolf Weyrich

Eduard-Zintl-Institut für Anorganische und Physikalische
Chemie der Technischen Hochschule Darmstadt,
D-61 Darmstadt, Germany

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In the course of investigations on the quadrupole coupling in ABX_4 compounds[1], measurements of the ^{23}Na and ^{127}I nuclear magnetic resonance spectrum in single crystals of $NaIO_4$ have been carried out.

The single crystals have been grown from saturated aqueous solutions at 45 °C by slow evaporation of the water. Most of the crystals produced by this method were fairly imperfect. This could be seen by the deviations from optical flatness of the crystal surfaces, these deviations having magnitudes of up to one degree. But it was possible to obtain a few perfect specimens of a size of about 1 cm³.

With such a crystal the ^{23}Na- and ^{127}I-NMR spectrum has been investigated as a function of the angle ϑ between the magnetic field H_0 and the [001]-axis, the crystal being rotated about the [010]-axis. In agreement with the crystal structure of $NaIO_4$[2] (space group $C_{4h}^6 - I4_1/a$, point symmetry of Na: $\bar{4}$, point symmetry of I : $\bar{4}$) the following results have been obtained by a least-squares fit of the experimental curve with the function

$$e^2 q\, Q (3 \cos^2 \vartheta - 1 + \eta \sin^2 \vartheta)/2\, h$$

(magnetic field $H_0 = 9.34$ kOe corresponding to $\nu_{\text{Larmor}} = 10.516$ and 7.955 MHz for ^{23}Na and ^{127}I, respectively; temperature 23 ± 2 °C):

^{23}Na: Quadrupole coupling constant $e^2 q\, Q/h = 49.03 \pm 0.23$ kHz, asymmetry parameter $\eta = 0.012 \pm 0.009 \approx 0$. The quadrupole splitting $\Delta\nu = \nu' - \nu''$ of the satellites is shown in Fig. 1 and can be readily explained by first-order perturbation theory[3]. No significant deviation from the Larmour frequency could be detected for the central line, the experimental error being about 1 kHz.

^{127}I: The angular dependence of the central-line frequency investigated in the range of ϑ between 158° and 182° (see Fig. 2) proves the quadrupole coupling constant of the iodine to be very large. The well-known second-order perturbation theory[3] is completely insufficient for explanation of the results.

Both for ^{23}Na and ^{127}I, a very strong angular dependence of the signal intensities has been observed. Within a range of about 3° the signal-to-noise ratio increases by a factor estimated to be from 3 to 5, dropping sharply and symmetrically in both directions to the "normal" value. For ^{23}Na the sharp intensity maximum occurs when the [100]-axis is parallel to H_0 ($\vartheta = 90°$ and 270°). In the same 3° range the higher-frequency satellite has a larger and the lower-frequency satellite a smaller intensity compared with the central line. In contrast to that for ^{127}I such a maximum is observed when the [001]-axis is parallel to H_0 ($\vartheta = 0°$ and 180°.)

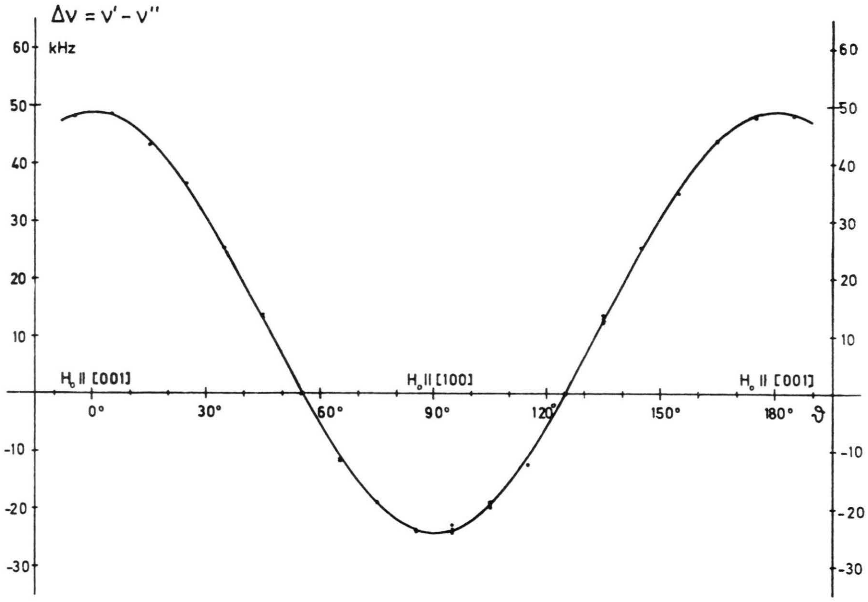

Fig. 1. Angular dependence of the quadrupole splitting $\Delta\nu$ of ^{23}Na in $NaIO_4$. $\Delta\nu$ = frequency difference $\nu' - \nu''$ between the two satellites $m = 3/2 \rightarrow 1/2$ and $m = -1/2 \rightarrow -3/2$; ϑ = angle between the [001]-axis and the magnetic field H_0, the rotation being about the [010]-axis.

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[3] See e.g. A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961, p. 232 et seq.

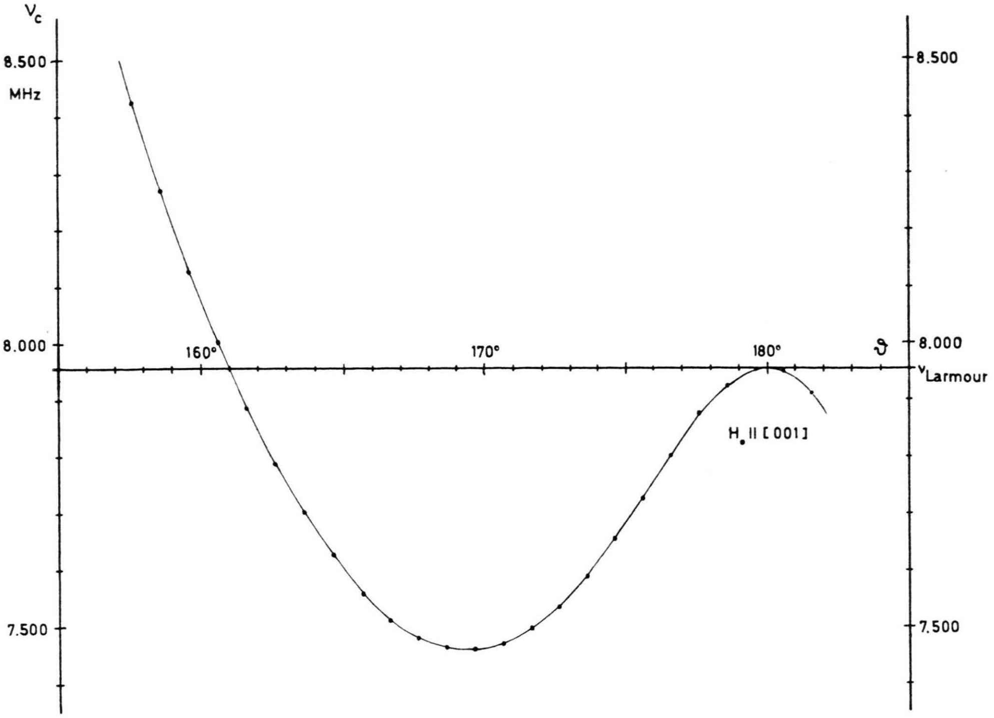

Fig. 2. Angular dependence of the frequency ν_c of the central resonance line $m = 1/2 \rightarrow -1/2$ of ^{127}I in $NaIO_4$. $H_0 = 9.34$ kOe. Orientation as in Fig. 1.

Since there is no correlation between these intensity effects and the angular dependence of the resonance frequencies (a similar maximum in intensity for the ^{23}Na lines should occur at $\vartheta = 0°$ and $180°$), the explanation by angular line broadening (mosaic structure) is not possible. This leads us to the supposition that our observation is due to relaxation effects. This observation proves also that one has sometimes to be careful in the interpretation of NMR spectra of powders where it is tacidly assumed that all crystal orientations have the same weight for the averaging.

The obtained value of $e^2 q\, Q/h$ for ^{23}Na in $NaIO_4$ is much smaller than the corresponding values in $NaBF_4$ (1008.4 ± 1.2 kHz[1]) and $NaClO_4$ (836 ± 20 kHz[4]), a fact which is certainly connected with η in $NaIO_4$ being zero ($NaBF_4$: $\eta = 0.095 \pm 0.003$ [1], $NaClO_4$: $\eta \lesssim 0.1$[4]). The value of $e^2 q\, Q/h$ for ^{127}I in $NaIO_4$ must be very large (it should be comparable to $e^2 q\, Q/h$ of Re in $KReO_4$ [5]), showing that the ionic charge distribution in the crystal produces only a minor part of the electrical field gradient at the ^{127}I-site. The greatest part must be produced by the distortion of the ideally tetrahedral arrangement of the I-O bonds by the surroundings in the crystal.

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