SECOND-ORDER QUADRUPOLE EFFECTS IN SODIUM NITRATE

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A shift of the central nuclear magnetic resonance line of Na^{23}, due to second-order effects, was observed in sodium nitrate single crystals. The sign and the magnitude of the shift agree with theoretical values.

NUCLEAR magnetic resonance of Na^{23} in sodium nitrate crystals was first investigated by Pound.[1] Pound observed a spectrum consisting of three lines, a central line and two symmetrically situated satellites. Such a spectrum is due to the quadrupole interaction of the Na^{23} nuclei with the electric field gradient in the crystalline lattice.

Assuming the quadrupole interaction energy of the nuclei to be sufficiently small compared with their energy of interaction with the external magnetic field, and therefore employing first-order perturbation theory, Pound showed that the magnitude of the splitting is given by the following formula

$$\Delta\nu = \frac{3(2m-1)}{8I(2I-1)}\frac{e^2qQ}{h}(3\cos^2\varphi - 1), \qquad (1)$$

where I is the nuclear spin (equal to $\frac{3}{2}$ in the case of Na^{23}), Q is its quadrupole moment, m is the magnetic quantum number, eq is the component of the gradient along the symmetry axis, and φ is the angle between the symmetry axis and the magnetic field.

According to Pound's experimental data the coefficient e^2qQ/h is equal to 334 kc/sec.

As may be seen from (1), in the first approximation a shift of the satellite frequencies occurs (the $m \rightarrow m-1$ transitions for $m \neq \frac{1}{2}$), while the central line ($m = \frac{1}{2} \rightarrow m = -\frac{1}{2}$) remains undisplaced. However, as will be shown below, the energy of the quadrupole interaction of the Na^{23} nuclei in sodium nitrate is not sufficiently small to enable us to limit ourselves to only the first approximation of perturbation theory, i.e., to consider that there is no shift of the central line.

Second-order perturbation theory yields (cf., for example, reference 2) a shift of the central line which in the case of the Na^{23} nuclei is given by

$$\Delta\nu_c = \frac{3}{64\nu_0}\left(\frac{e^2qQ}{h}\right)^2(1 - 9\cos^2\varphi)(1 - \cos^2\varphi). \qquad (2)$$

The shift increases as the operating frequency ν_0 is diminished. For the frequency $\nu_0 = 5.2$ Mc/sec which corresponds to a field of 4600 oe, and for the value of e^2qQ/h quoted previously, the shift lies in the range from +1.0 to -1.8 kc/sec. Such a shift of the central line can be easily observed experimentally.

In order to obtain this shift experimentally, we have recorded by means of the apparatus described previously[3] nuclear resonance signals from Na^{23} in a single crystal of $NaNO_3$ and in a saturated aqueous solution of NaCl. The absorption line of Na^{23} in solution was used as the reference point with respect to which the position of the absorption line of Na^{23} in sodium nitrate was measured.

Experiment showed that in accordance with (2), the two lines coincide for $\varphi = 0°$, i.e., $\Delta\nu_c = 0$, while the biggest shifts, which differ in sign, occur for $\varphi = 42$ and 90°. Within the limits of experimental error, the magnitudes of the shifts correspond to the theoretical expression (2).

The dependence of the shift of the central line on the orientation of the single crystal must lead to a broadening of this line in a powdered sample, since such samples contain small crystals of random orientation. Indeed, experiment shows that in powdered sodium nitrate the absorption line is broadened by a factor of approximately 1.5 while retaining its full intensity.

Moreover, it can be seen from (1) and (2) that for no orientation of the single crystal is it possible to obtain complete coincidence of the satellites and the central line, and this is also confirmed by experiment.

[1] R. V. Pound, Phys. Rev. 79, 685 (1950).

[2] M. H. Cohen and F. Reif, Solid State Physics 5, 321 (1957).

[3] V. V. Lemanov, Приборы и техника эксперимента (Instrum. and Meas. Techniques), in press.

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