

QUADRUPOLE EFFECTS IN NUCLEAR MAGNETIC RESONANCE IN  $\text{NaNO}_3\text{-AgNO}_3$   
MIXED CRYSTALS

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A study has been made of the intensity of satellites in  $\text{NaNO}_3\text{-AgNO}_3$  mixed crystals as a function of the  $\text{AgNO}_3$  content. The critical sphere model has been shown to be applicable, and the sphere radius has been determined and found equal to 13 Å.

At present there exist several publications<sup>1,2</sup> dealing with quadrupole effects in nuclear magnetic resonance (NMR) in crystals containing impurities. All this work deals with cubic crystals.

In a perfect cubic crystal the energy of the quadrupole interaction of the nucleus with the electric field of the crystalline lattice is equal to zero, since in virtue of the high symmetry of the crystal the gradient of the electric field at the nucleus is equal to zero. This leads to the result that in a cubic crystal the system of the energy levels of the nucleus in a magnetic field remains equidistant, i.e., the frequencies of all the possible N.M.R. transitions coincide. As a result of this coincidence only one "total" absorption line is observed in a cubic crystal. In the presence of an impurity the cubic symmetry of the lattice near the impurity atom or ion is destroyed and this leads to gradients different from zero. The interaction of nuclei with such gradients leads to a displacement of the nuclear energy levels and, correspondingly, to a displacement in the transition frequency. Since the magnitude of the gradient is different for nuclei situated at different distances from the impurity the frequency shift will also be different, and this in turn leads to a broadening of the absorption line. According to Pound's theory,<sup>3</sup> in the first approximation a broadening of the satellites occurs (the  $m \rightarrow m - 1$  transitions for  $m \neq \frac{1}{2}$ , where  $m$  is the magnetic quantum number), and in the second approximation a broadening of the central line ( $m = \frac{1}{2} \rightarrow m = -\frac{1}{2}$ ) takes place.

Experiments with cubic crystals have shown that at low impurity concentrations the intensity of the absorption line diminishes with increasing concentration of the impurity, attaining a value corresponding to the intensity of the central line. This effect is explained in the cited publications with the aid of the so-called critical-sphere model. Ac-

ording to this model the frequency shift is so great for nuclei situated at a distance from the impurity which is smaller than the radius of the critical sphere that these nuclei cease making a contribution to the absorption line, whereas nuclei situated at greater distances contribute only to the initial line. It might appear natural to suppose that the nuclei can have intermediate positions which must lead to a broadening of the line. But such broadening is not observed in cubic crystals. However, experiments with cubic crystals do not yield complete certainty that the satellites are not broadened, since in such crystals we cannot observe the satellites independently of the central line. More definite information on the behavior of the satellites can be obtained from a study of crystals of symmetry lower than cubic. In such crystals the gradient of the electric field in the lattice is different from zero, and the absorption line is split into components, i.e., into a central line and satellites. The amount of splitting is given for the case when the gradient is sufficiently small and has cylindrical symmetry by the following formula:<sup>3</sup>

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

where  $I$  is the nuclear spin,  $eq$  is the component of the gradient along the symmetry axis,  $\varphi$  is the angle between the axis of symmetry and the magnetic field, and  $Q$  is the nuclear quadrupole moment.

Thus, by carrying out investigations on a non-cubic crystal, we are able to make separate observations of the behavior of the satellites. We have utilized  $\text{NaNO}_3$  for such a crystal. These crystals belong to the rhombohedral system, and the  $\text{Na}^{23}$  NMR spectrum in them consists of three lines: a central line and two symmetrically situated satellites. In accordance with (1), the magni-

tude of the splitting depends on the orientation of the crystal in the magnetic field. The experimental curves fall smoothly on the curve:<sup>3</sup>

$$\Delta\nu = 83,5(3 \cos^2\varphi - 1) \text{ kc/sec} \quad (2)$$

where  $\varphi$  is the angle between the third order axis and the magnetic field.

In order to study the effect of impurities on the  $\text{Na}^{23}$  spectrum in  $\text{NaNO}_3$ , we have studied  $\text{NaNO}_3$ — $\text{AgNO}_3$  mixed crystals in which an  $\text{Ag}^+$  ion replaces a  $\text{Na}^+$  ion.

$\text{NaNO}_3$  crystals and mixed crystals, weighing from 100 to 250 g, were grown in a crucible furnace by Steber's method<sup>4</sup> from chemically pure substances. Cylindrical samples of 1.2 cm diameter and from 1.42 to 2.7 cm high were cut from these crystals by means of a wet thread and were then polished on damp cloth.

The absorption spectra were studied (with apparatus described elsewhere<sup>5</sup>) under the following conditions: intensity of the magnetic field 4400 oe, modulation amplitude 0.7 oe, and synchronous-detector time constant 10 sec. The voltage in the oscillator circuit was set at 0.15 v in order to obtain the best signal-noise ratio. Such a voltage leads to some saturation of the central line,<sup>3</sup> but experiment has shown that a decrease in the voltage does not alter the results obtained, and leads only to a slight increase in the intensity of the central line.

The single crystals of  $\text{NaNO}_3$  and  $\text{NaNO}_3$ — $\text{AgNO}_3$  grown by us had a sufficiently pronounced mosaic structure. In the investigation of the absorption spectra in these crystals it was found that the widths of the satellites depended on the orientation. For  $\varphi = 0$  and  $90^\circ$  the satellites and the central line have a width of the order of 2 or 2.5 kc/sec, which approximately corresponds to the dipole-dipole width;<sup>3</sup> at intermediate angles the satellites become broader, but their intensity remains constant independently of the orientation. This effect can be explained by the mosaic struc-

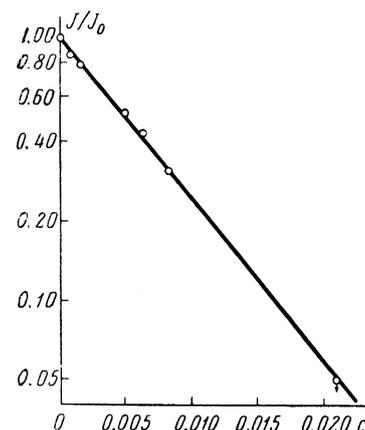


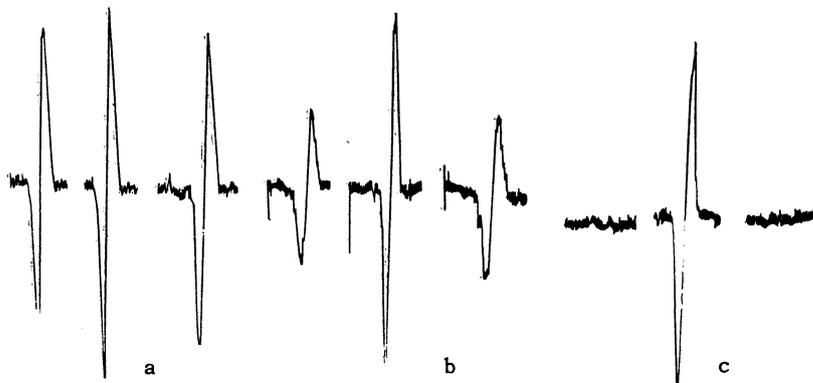
FIG. 2. Dependence of the relative intensity of the satellites on the concentration of  $\text{AgNO}_3$ .

ture referred to previously. Indeed, as can be seen from (2), the "disorientation" of individual regions of the sample even within  $5^\circ$  can lead to considerable broadening for  $\varphi = 45^\circ$  without producing any noticeable broadening of the satellites for  $\varphi = 0$  and  $90^\circ$ .

Figure 1 gives as an example some NMR spectra in  $\text{NaNO}_3$  and  $\text{NaNO}_3$ — $\text{AgNO}_3$  for  $\varphi = 90^\circ$ , which are derivatives of absorption lines. (For  $\varphi = 0^\circ$ , completely analogous spectra are obtained.) Figure 2 shows the dependence of the intensities of the satellites on the concentration of  $\text{Ag}^+$  on a semi-logarithmic scale. It is seen that a decrease in the intensity of the satellites becomes noticeable even at a concentration of 0.001, which corresponds to 1  $\text{Ag}^+$  ion for each 1000  $\text{Na}^+$  ions. At a concentration of 0.021 the satellites disappear completely while the central line still remains practically undistorted. The decrease in the intensity of the satellites is not accompanied by broadening. The width of the satellites measured between points of the maximum and minimum of the derivative of the absorption line remains the same in mixed crystals as in pure  $\text{NaNO}_3$ , and only a slight broadening of the wings of the line is observed.

Since the width and the shape of the satellites remain approximately the same, their intensity is

FIG. 1. NMR spectra in various crystals:  
a)  $\text{NaNO}_3$ , b)  $\text{NaNO}_3 + 0.5\% \text{AgNO}_3$ ,  
c)  $\text{NaNO}_3 + 2.1\% \text{AgNO}_3$ .



proportional to the maximum value of the derivative. Therefore in Fig. 2 the maximum values of the derivative have been adopted as a measure of the intensity of the satellites.

The lack of broadening of the satellites allows us in our case also to utilize the critical sphere model for the analysis of the results, i.e., to consider only two cases: either the  $\text{Ag}^+$  ion lies inside the critical sphere, so that for a  $\text{Na}^+$  nucleus lying at the center of this sphere the frequency shift is so great that the given nucleus ceases to make a contribution to the observed absorption line, or the  $\text{Ag}^+$  ion lies outside the critical sphere and then the  $\text{Na}^+$  nucleus at the center of the sphere makes a contribution to the initial unbroadened line. For a random distribution of the  $\text{Ag}^+$  ions, the intensity of the satellites must consequently be proportional to the probability that the impurity ion does not lie inside the critical sphere, i.e.,

$$J/J_0 = (1-c)^n, \quad (3)$$

where  $J_0$  and  $J$  are the intensities of the satellites in a pure and a mixed crystal,  $c$  is the molar concentration,  $n$  is the number of lattice points containing  $\text{Na}^+$  ions inside the critical sphere. Since  $c$  is small, we can rewrite (3) in the following form

$$\ln(J/J_0) = n \ln(1-c) \approx -nc.$$

As may be seen from Fig. 2 the dependence of  $J/J_0$  on  $c$  does indeed have the shape of a straight line on a semilogarithmic scale. From the slope

of this straight line we obtain  $n = 138$ , i.e., the critical sphere contains 138  $\text{Na}^+$  ions. This number of ions corresponds to a critical sphere radius approximately equal to 13 Å. (In the case of a non-cubic crystal we should really introduce a critical ellipsoid, but the absence of any angular dependence in the observed spectra gives some justification for using a spherical model.)

The results presented above show that in non-cubic crystals, too, an impurity leads only to a decrease in the intensity of the satellites without broadening. This fact, together with the fact that the experimental dependence of the intensity of the satellites on the concentration of the impurity has the form (3), supports the view that the critical sphere model is applicable. Nevertheless, the reasons for the absence of satellite broadening are not sufficiently clear, as has been noted previously, and this question requires further investigation.

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<sup>2</sup>Kawamura, Otsuka, and Ishiwatari, *J. Phys. Soc. Japan* **11**, 1064 (1956).

<sup>3</sup>R. V. Pound, *Phys. Rev.* **79**, 685 (1950).

<sup>4</sup>V. D. Kuznetsov, *Кристаллы и кристаллизация (Crystals and Crystallization)*, Gostekhizdat, 1953.

<sup>5</sup>V. V. Lemanov, *Приборы и техника эксперимента (Instrum. and Meas. Techniques)*, in press.

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