NUCLEAR MAGNETIC RESONANCE IN ELASTICALLY DEFORMED ROCK SALT

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The effect of elastic deformation on the nuclear magnetic resonance absorption line of Na^{23} was studied in rock salt crystals. Components of the tensor relating the elastic deformation of the lattice to the gradient of the nuclear electric field were determined and found to be $S_{11} = \pm 2 \times 10^{15}$ and $S_{44} = \mp 0.5_5 \times 10^{15}$ cgs esu.

THE investigation of quadrupole effects in nuclear magnetic resonance (NMR) makes it possible to obtain an amount of information on defects in solids. The defects create additional gradients of the electric field in the crystalline lattice, and the interaction of the nuclei with these gradients leads to a change in the NMR absorption lines. Excitation of additional gradients is brought about on the one hand by lattice distortions, i.e., by local changes in the symmetry of the lattice close to the defect, and on the other by the electric fields, which the defects create in those cases where they possess a charge.

In order for it to be possible to estimate the amount of lattice distortion near the defects by the results of NMR studies, a knowledge of the connection between the elastic deformations of the lattice and the nuclear electric field gradient is obviously necessary. This connection can be found from NMR experiments in elastically deformed crystals, and has recently been determined by Shulman et al.[1] for In^{115} in InSb.

Let us consider what is the effect of elastic deformation on the NMR absorption line. Elastic deformation changes the symmetry of the crystal; consequently, the electric field gradient in the lattice also changes. In a cubic crystal, such as NaCl, the field gradient is equal to zero by virtue of the high symmetry; in this case, the NMR line, consisting of the central line and satellites, is observed as a single "total" absorption line.

Elastic deformation, lowering the symmetry of the cubic crystal, leads to the generation of a field gradient which produces a splitting of the absorption line into its components. In principle, for sufficiently large elastic deformations in the cubic crystal, complete splitting of the components is possible. In reality, however, the gradients obtained in practically attainable elastic deformations are very small and lead not to a splitting of the components of the line, but only to its broadening.

Shulman et al.,[1] introduce the tensor C, which relates the nuclear electric field gradient with the elastic stresses in the lattice, and investigate its properties. It is of great interest to consider the tensor S which relates the tensor of the nuclear field gradient φ with the elastic deformations in the lattice δ. This tensor can be introduced by analogy with the tensor C in the following way:

$$\varphi_{\mu\nu} = \sum_{\varkappa,\lambda} S_{\mu\nu,\varkappa\lambda}\, \delta_{\varkappa\lambda} \qquad (\varkappa, \lambda, \mu, \nu = x, y, z) \tag{1}$$

For cubic crystals, there are only two independent components of the tensor S, which in the universally adopted notation are written as S_{11} and S_{44}. These components, as will be shown below, can be determined by measurement of the broadening of the NMR absorption line in an elastically deformed crystal. As objects of investigation in the present work, we used specimens of rock salt with dimensions of approximately $8 \times 8 \times 20$ mm, cut along the [001], [110] and [111] directions.

The specimens were placed in the coil of an NMR oscillator circuit[2] and were elastically deformed by linear compression along the specified direction; the axis of compression in this case was perpendicular to the direction of the magnetic field. The maximum loading on the specimens amounted to 66 kg/cm^2. For each specimen, the derived absorption lines of Na^{23} were recorded for different loadings and angles of rotation of the specimen around the compression axis relative to the magnetic field.

The effect of elastic deformation on the absorption line was weak, as expected. In elastically deformed specimens, only a reversible decrease in the maximum of the derived absorption line was observed, without a noteworthy change in its width, within the limits of experimental error. The largest decrease amounted to about 20 percent.

For the determination of the components of the tensor S, it is necessary to connect this decrease with the frequency shift of the satellites. If we assume that the elastic deformation produces only a shift of the satellites without change in their shape, then, by making use of the property of additivity of the second moment of the line, we can write

$$\Delta\nu^2 = \Delta\nu_0^2 + 0.6\Delta\nu_c^2,$$

where $\Delta\nu_0^2$ and $\Delta\nu^2$ are the second moments of the absorption line in the undeformed and deformed specimens, respectively; $\Delta\nu_c$ is the frequency shift of the satellites, and the coefficient 0.6 takes into account the relative intensity of the satellites.

Analysis of the readings showed that the shape of the absorption line, both in the initial and in the deformed specimens, is very close to Gaussian. For the Gaussian shape $\delta\nu^2 = 4\Delta\nu^2$, where $\delta\nu$ is the breadth of the line measured between the points of maximum and minimum of the derivative. Taking this into account, we have

$$\delta\nu^2 = \delta\nu_0^2 + 2.4\Delta\nu_c^2.$$

The intensity of the absorption line is proportional to $A\delta\nu^2$, where A is the maximum of the derivative, and the coefficient of proportionality is determined by the shape of the line.

Inasmuch as the intensity of the absorption line should not change in elastic deformation, and its shape remains Gaussian, as has already been noted, $A\delta\nu^2 = A_0\delta\nu_0^2$, and A and A_0 are the maxima of the derivatives of the absorption line in the deformed and undeformed crystals, respectively.

By use of the latter relation, we obtain the final formula for the frequency shift of the satellites:

$$\Delta\nu_c = \pm\delta\nu_0\sqrt{(A_0/A - 1)/2.4}. \qquad (2)$$

The dependence of the frequency shift of the satellites $\Delta\nu_c$, calculated by this formula, is shown in Fig. 1, from a loading for a specimen with the compression axis along the [001] direction. As expected, the frequency shift is proportional to the loading.

Figures 2 and 3 show the dependence of $\Delta\nu_c$ on the angle of rotation of the specimen α for a constant load. In the first case (Fig. 2) the compression axis is directed along [111], while the angle α is the angle between the direction of the magnetic field and the $[1\bar{1}0]$ direction. In the second case, (Fig. 3), the compression axis is directed along [110], while the angle α is the angle between the direction of the magnetic field and the [001] direction.

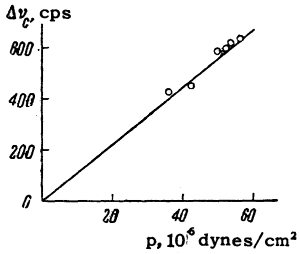

FIG. 1. Loading dependence of the frequency shift of the satellite for a specimen with the compression axis along the [001] direction.

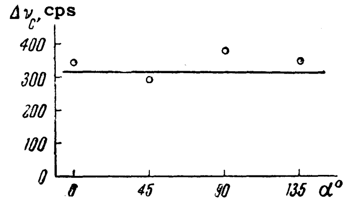

FIG. 2. Dependence of the frequency shift of the satellites on the angle between the direction of the magnetic field and the $[1\bar{1}0]$ direction for a specimen with compression axis along [111]. Loading is 65×10^6 dynes/cm².

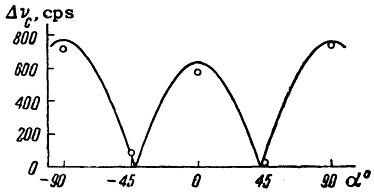

FIG. 3. Dependence of the frequency shift of the satellites on the angle between the direction of the magnetic field and the [001] direction for a specimen with the compression axis along [110]. Loading is 61×10^6 dynes/cm².

All the points in Figs. 1 — 3 represent the mean of 4 or 5 independent measurements.

As is seen from the drawings, for a deformation along [111] there is no angular dependence (the same holds for a specimen with the compression axis along [001]), while for a deformation along [110], a clear cut angular dependence is observed.

The formula for the frequency shift of the satellites can also be obtained by means of perturbation theory:[3]

$$\Delta\nu_c = 3eQ(2m - 1)\varphi_{HH}/4I(2I - 1)h,$$

where I — spin of the nucleus, Q — its quadrupole moment, m — magnetic quantum number, φ_{HH} — component of the nuclear gradient along the direction of the magnetic field. For Na^{23}, I = 3/2 and the formula for the frequency shift of the satellites has the form

$$\Delta\nu_c = \pm(eQ/2h)\varphi_{HH}. \qquad (3)$$

Use of Eqs. (2) and (3) makes it possible to obtain the components of the tensor of the gradient φ_{HH} in an elastically deformed crystal from the experimental results. Further, expressing φ_{HH}

in terms of the tensor S and the elastic strain tensor δ, we can determine the components of S in accord with (1).

It should be noted that inasmuch as for the cubic crystals only two independent components of the tensor S exist, it suffices for their determination to measure the effect of elastic deformation only for a specimen with the axis of compression along [110] for two different values of α. Nevertheless, with the aim of checking the results, we thought it desirable to carry out measurements for specimens with the compression axis along three different directions.

Let us consider how the component of the tensor gradient φ_{HH} can be expressed for each case separately. It must be kept in mind that the tensor φ is a symmetric tensor of second rank and can be put into diagonal form if its principal axes are known.

1. Deformation along [001]. For such a deformation, the cubic crystal becomes tetragonal, and the principal axes of the tensor gradient are the cube axes from considerations of symmetry.

If the x, y, z axes are directed along [100], [010], and [001], then the tensor gradient is diagonal and its components are equal to

$$\varphi_{xx} = \varphi_{yy} = -\tfrac{1}{2}\varphi_{zz} = \tfrac{1}{2}S_{11}(s_{12} - s_{11})P,$$

where P is the stress and the elastic constants of the crystal are denoted by s.

The direction of the magnetic field lies in the xy plane and the component of the tensor gradient along this direction is equal to

$$\varphi_{HH} = \varphi_{xx}\sin^2\alpha + \varphi_{yy}\cos^2\alpha = \varphi_{xx} = \varphi_{yy}$$

(α — angle between the direction of the magnetic field and the [010] direction).

Thus φ_{HH}, and consequently the frequency shift of the satellites, in accord with (3), does not depend on α, which, as has been noted above, is the situation actually observed in experiment.

2. Deformation along [111]. The cubic crystal becomes trigonal. The tensor of the gradient along the principal axes xyz, which are [11$\bar{2}$], [1$\bar{1}$0] and [111], is diagonal and its components are:

$$\varphi_{xx} = \varphi_{yy} = -\tfrac{1}{2}\varphi_{zz} = -\tfrac{1}{3}S_{44}s_{44}P.$$

In this case $\varphi_{HH} = \varphi_{xx} = \varphi_{yy}$ also do not depend on α — the angle between the direction of the magnetic field and the [1$\bar{1}$0] direction. As is seen from Fig. 2, this is confirmed by experiment.

3. Deformation along [110]. The cubic crystal becomes orthorhombic with the three axes of second order [1$\bar{1}$0], [001], and [110]. The same axes are the principal axes of the tensor gradient. Denoting them by x, y, z, we have

$$\varphi_{xx} = \left[\tfrac{1}{4}S_{11}(s_{11} - s_{12}) - \tfrac{1}{2}S_{44}s_{44}\right]P,$$

$$\varphi_{yy} = -\tfrac{1}{2}S_{11}(s_{11} - s_{12})P,$$

$$\varphi_{zz} = \left[\tfrac{1}{4}S_{11}(s_{11} - s_{12}) + \tfrac{1}{2}S_{44}s_{44}\right]P.$$

It is easy to see that in this case φ_{HH} changes as a function of α with a period of 180°:

$$\varphi_{HH} = -\tfrac{1}{2}[\varphi_{zz} + (\varphi_{zz} + 2\varphi_{xx})\cos 2\alpha],$$

where α is the angle between the direction of the magnetic field and the [001] direction. Such a character of the dependence of $\Delta\nu_c$ on α is actually observed in experiment (Fig. 3).

Thus, in all three cases, the experimental results are identical with the predictions of the theory. This supplies a basis for assuming that decrease in the maximum of the derivative of the absorption line which was observed by experiment is actually connected with the shift in the frequency of the satellites brought about by elastic deformation.

Upon substitution of the expressions obtained for φ_{HH} in Eq. (3), the best correspondence with experimental results is obtained for $S_{11} = \pm 2 \times 10^{15}$ and $S_{44} = \mp 0.5_5 \times 10^{15}$ in cgs esu units.

The curves in Figs. 1 — 3 represent the theoretical dependences calculated by means of Eq. (3) for given values of the components of the tensor S.

Unfortunately, in view of the smallness of the observed effects, the results for S_{11} and S_{44} are not sufficiently accurate. According to our estimates, the random errors in these values amount to ± 15 percent. Moreover, it is evident that small systematic errors take place connected with the fact that the shape of the absorption line is not exactly Gaussian and probably changes slightly under elastic deformation.

In conclusion, the author thanks M. I. Kornfel'd for discussion of the results, O. M. Nilov for help in the measurements and V. V. Sokolov for carrying out mechanical tasks.

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