NUCLEAR QUADRUPOLE RESONANCE

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1. INTRODUCTION

Nuclear quadrupole resonance (henceforth abbreviated NQR) is one of the fields of radio-spectroscopy whose extensive development began only after the war. It is very closely related to nuclear magnetic resonance (NMR) from the point of view of the nature of the phenomenon and of the methods of observation. In this review we shall not dwell on a detailed description of NMR, but shall refer the reader to the excellent book by A. Lösche,[135] which contains very detailed information on this subject. In spite of the fact that the phenomenon of NQR was discovered by Dehmelt and Krüger more than nine years ago[69,79] there have appeared no papers in world literature bringing together the accumulated theoretical and experimental materials. The short reviews by Dehmelt[79,80] and by Orville-Thomas[139] are devoted only to special aspects of the problem. Moreover, the latter review, written by a nonspecialist, contains a number of errors, particularly in the description of experimental methods of observing the phenomenon. In this connection we have set ourselves the aim of systematizing the accumulated materials and also of giving a survey of the investigations which are being carried on at present in the Soviet Union in the field of NQR.

The essence of the phenomenon of NQR consists of the following. The nuclear quadrupole moment is a certain quantity that characterizes the deviation of the nuclear shape from a spherical one. A large number of nuclei of the periodic system have quadrupole moments. An orientation of nuclear spins in a definite direction takes place in crystals, as a result of the interaction of the nuclear quadrupole with the electric field of the electronic shells of the molecules. If a field of frequency equal to the frequency of transitions between levels is applied perpendicular to the above direction, absorption of radio-frequency power can be observed. At the present time NQR has a wide range of applications. It is utilized for the study of crystal structure, for the determination of nuclear quadrupole moments, for the investigation of the types of covalent bonds and of the degree of hybridization, for the determination

of the nonequivalence of position of resonating nuclei in the crystal lattice, and for the determination of the average values of the frequencies of rotational oscillations, of the moments of inertia of molecular groups, of the existence of rotation of these groups, etc. In addition to purely chemical and structural application, NQR is also utilized in low-temperature techniques. Within the last few years this method has made it possible to produce a secondary temperature standard.[22] One of the technical applications of NQR was proposed by the author,[101] viz., the stabilization of weak magnetic fields by the size of the signal.

The existence of a quadrupole moment in the case of odd-odd nuclei was discovered in early experiments with molecular beams. Later the molecular beam method was used to measure the magnitudes of the quadrupole couplings in some of the simplest compounds. In NMR it also turned out to be possible to observe the splitting of lines due to quadrupole interactions.[104,115,134] All these investigations, however, enabled one to observe the quadrupole splitting as a small effect superimposed on a large background, and therefore the accuracy of determining the quadrupole couplings was not great. In connection with this the need arose of observing transitions directly between quadrupole energy levels without applying an external magnetic field (therefore NQR is often referred to as pure quadrupole resonance). The pure quadrupole spectrum of 1,2-dichloroethane was observed by Dehmelt and Krüger in 1950. We should also note the unsuccessful attempt by Pound[140] who, because of an inappropriate choice of the object of his investigation, was forced at approximately the same time to report a negative result. The papers of the German scientists laid the foundation for the development of this new field of radiospectroscopy.

As already noted, the existence of quadrupole energy levels in crystals is associated with the interaction of the quadrupole moment of a given kind of a nucleus with the static electric field of the crystalline lattice. It follows from general considerations that in the nondegenerate ground state the nucleus cannot have an electric multipole moment of odd order. Consequently dipole mo-

ments have not been observed in nuclei, while quadrupole moments may be possessed by nuclei with spins greater than one-half. The quadrupole moment may be expressed in terms of the eccentricity of the ellipsoid. A nucleus prolate along the direction of the spin has a positive quadrupole moment, while an oblate nucleus has a negative quadrupole moment. Usually the scalar quadrupole moment is defined by

$$eQ = \langle \varrho \, (3z^2 - r^2) \rangle_{av}, \qquad (1)$$

where ρ is the charge density in the nucleus, while z and r are the coordinates of an element of charge. The averaging in this expression is carried out over all nuclei in the state m = J, where m is the magnetic quantum number.

In evaluating the quadrupole energy levels it is customary to distinguish two cases. The simplest one is the case of axial symmetry of the electric field gradient.[69,79,140] The energy of interaction of nuclear and electronic charges can be written classically in the form:

$$W_Q = \int \varrho V \, d\tau, \qquad (2)$$

where V is the potential due to the electronic shell at the nuclear site. On expanding the potential into a Taylor series we can obtain after several transformations:

$$W_Q = \frac{eQq_{zz}}{4J(2J-1)} [3m^2 - J(J+1)], \qquad (3)$$

where eQq_{zz} is the magnitude of the quadrupole coupling, J is the nuclear spin, and m is the magnetic quantum number. Expression (3) holds only for the case $q_{xx} = q_{yy}$, where q_{xx}, q_{yy}, q_{zz} are the components of the electric field gradient of the crystal. Wang[171] has calculated the quadrupole energy levels in the case of an axially symmetric electric field on the basis of quantum considerations. The relation which he obtained agreed with the classical expression.

In crystals the average field gradient is constant in time, and is approximately the same for all the nuclei of the sample; we can therefore observe a spectrum corresponding to transitions of a given kind of nuclei between their quadrupole energy levels. In principle NQR can also be observed in liquids[152] in the case of anisotropic motion (liquid crystals), however, apparently the NQR line will in this case be too broad, so that it is difficult to observe it against the background of amplifier noise.

Expression (3) enables us to estimate the quadrupole resonance frequency, after taking into ac-

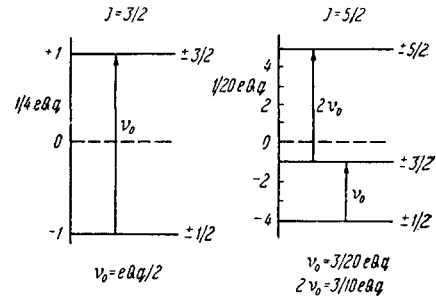count the fact that the selection rule has the form $\Delta m = \pm 1$.

FIG. 1. Nuclear quadrupole energy levels for two values of the spin in the case of axial symmetry of the electric field gradient.

Figure 1 shows the quadrupole energy levels for spins $\frac{3}{2}$ and $\frac{5}{2}$, and also the corresponding transitions. In the case of spin $\frac{5}{2}$ two transition frequencies are observed.

References 24, 125, and 171 considered the case when the assumption of axial symmetry of the electric field gradient does not hold. Usually in order to describe the degree of deviation of the gradient from axial symmetry the following asymmetry parameter is introduced

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}}. \qquad (4)$$

In such a case we have

$$\left.\begin{aligned}
q_{xx} &= \left(-\frac{1}{2} + \frac{\eta}{2}\right) q_{zz}, \\
q_{yy} &= \left(-\frac{1}{2} - \frac{\eta}{2}\right) q_{zz}.
\end{aligned}\right\} \qquad (5)$$

The quadrupole interaction energy can then be written in the form of the following Hamiltonian:

$$H = \frac{eQq_{zz}}{4J(2J-1)} \left[(3I_z^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2) \right], \qquad (6)$$

where I is the nuclear spin operator, $I_\pm = I_x + iI_y$. On taking into account the fact that the asymmetry parameter is usually considerably smaller than unity, one can treat the second term in the Hamiltonian as a perturbation. The problem of calculating the quadrupole energy levels in such a case is equivalent to the problem of the asymmetric top in rotational spectra.[171] Since the unperturbed operator is two-fold degenerate, a secular equation has to be set up. In the general case for half-integral spin the secular equation of 2J+1 degree may be broken up into two identical equations of $J + \frac{1}{2}$ degree. For $J = \frac{3}{2}$ closed formulas can be obtained

$$W_{m=\pm\frac{1}{2}} = -\frac{1}{4}eQq_{zz}\left(1+\frac{1}{3}\eta^2\right)^{1/2},$$

$$W_{m=\pm\frac{3}{2}} = \frac{1}{4}eQq_{zz}\left(1+\frac{1}{3}\eta^2\right)^{1/2}. \qquad (7)$$

For $J = \frac{5}{2}$ we have

$$W_{m=\pm\frac{1}{2}} = -\frac{1}{5}eQq_{zz}\left(1+\frac{4}{9}\eta^2-\frac{172}{729}\eta^4+\frac{15322}{59049}\eta^6\right),$$

$$W_{m=\pm\frac{3}{2}} = -\frac{1}{20}eQq_{zz}\left(1-\frac{3}{2}\eta^2-\frac{23}{24}\eta^4-\frac{449}{432}\eta^6\right),$$

$$W_{m=\pm\frac{5}{2}} = \frac{1}{4}eQq_{zz}\left(1+\frac{1}{18}\eta^2+\frac{17}{5832}\eta^4-\frac{143}{944784}\eta^6\right). \qquad (8)$$

Similarly for spin $J = \frac{7}{2}$ we can approximately obtain

$$W_{m=\pm\frac{1}{2}} = -\frac{5}{28}eQq_{zz}\left(1+\frac{5}{6}\eta^2-\frac{311}{216}\eta^4\right),$$

$$W_{m=\pm\frac{3}{2}} = -\frac{3}{28}eQq_{zz}\left(1-\frac{31}{30}\eta^2+\frac{21967}{9000}\eta^4\right),$$

$$W_{m=\pm\frac{5}{2}} = \frac{1}{28}eQq_{zz}\left(1+\frac{5}{6}\eta^2+\frac{25}{216}\eta^4\right),$$

$$W_{m=\pm\frac{7}{2}} = \frac{7}{28}eQq_{zz}\left(1+\frac{1}{30}\eta^2+\frac{29}{27000}\eta^4\right). \qquad (9)$$

These formulas enable us to calculate the absorption frequency from known values of the quadrupole coupling and the asymmetry parameter. But the evaluation of the magnitude of the quadrupole coupling is associated with calculations involving many-electron systems; therefore, the experimental measurement of this quantity is of considerable theoretical and practical interest.

Recently Lurcat[136] has succeeded in obtaining,

on the basis of quantum mechanical equations for the average values, the macroscopic equations of motion for the average values of the components of the quadrupole moment tensor, similar to Bloch's equations in the case of magnetic resonance.[27,97] The solution of the macroscopic equations of quadrupole resonance enables one to elucidate a number of interesting features of this phenomenon.

2. EXPERIMENTAL METHODS OF OBSERVING NUCLEAR QUADRUPOLE RESONANCE

Since the absorption coefficients in nuclear quadrupole resonance are small, and the signals may be easily lost in amplifier noise, stringent demands from the point of view of sensitivity are imposed on the apparatus utilized for the observation of this phenomenon. The most intense NQR signals are considerably weaker than the NMR signals from protons in water. In addition to high sensitivity the spectrograph must have a wide range of frequency variation, and must give small distortion of line shape. The last requirement is less strict since the study of line shape in NQR is of secondary importance.

In practice regenerators and superregenerators are frequently used.[2,32,45,47,71,118,123,147] Figure 2 shows the block diagram of the radiospectroscope utilized by us.[99] The sample in the form of a powder or of a single crystal is placed in a coil in the circuit of an autodyne detector with frequency modulation. In sweeping through the resonance region one can observe the modulation of the rf voltage by the quadrupole resonance signal. After
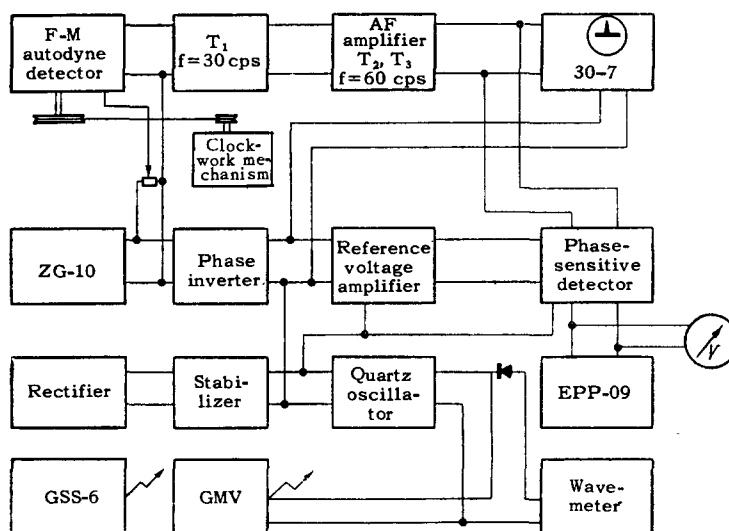
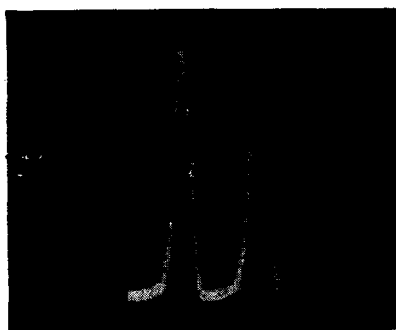FIG. 2. Block diagram of the apparatus for the observation of NQR.

FIG. 3. NQR signal in barium chlorate at room temperature. Two maxima appear because the vibrating condenser alters the oscillator frequency in such a way that the resonance condition is satisfied twice during each modulation period.

detection and low frequency amplification the NQR signal may be recorded on the chart of an automatic recorder, or may be directly observed on an oscilloscope screen. Figure 3 shows an oscillogram of the signal which we observed in barium chlorate at room temperature in the neighborhood of 29.6 Mcs. The sample was placed in the well-screened coil of an autodyne detector circuit, whose frequency was modulated by means of a vibrating condenser RV-1. For our autodyne detector we used a self-quenching superregenerator whose circuit is shown in Fig. 4.
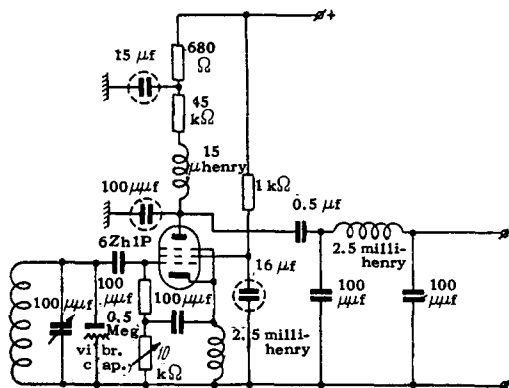

FIG. 4. Circuit diagram of a self-quenching superregenerator. With the values of the circuit components shown the quenching frequency will be of the order of 20 kcs. Taking into account the fact that the NQR signal frequency is 30 kcs, the quenching frequency can be easily filtered out by means of a filter in the tube plate circuit.

This circuit is a modification of the regenerative circuit due to Hopkins[113] whose parameters have been altered in such a way that a self-quenching mode can be obtained in which the circuit can be set by adjusting the coupling in the cathode circuit. We have achieved exceptionally high sensitivity by means of this circuit. On recording the signal on an automatic recorder we observed a multiplet structure of the NQR signals which is due to the
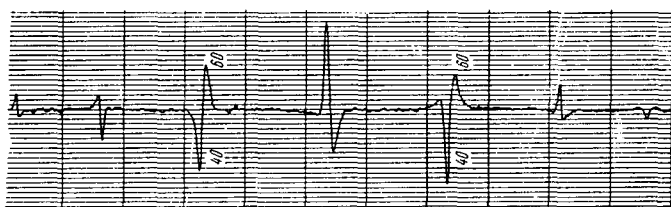

FIG. 5. NQR signals in potassium chlorate at room temperature. The multiplet signal structure is due to the superregenerator spectrum, the distance between signals being equal to the quenching frequency. The change in shape of the NQR signals is due to the superregenerator phase spectrum.

superregenerator spectrum (Fig. 5).

In a superregenerative spectrometer an ordinary oscillator is used, whose oscillations are periodically quenched by means of a quenching voltage. The use of a superregenerator with external quenching has been described in the foreign literature.[79,118] The duration of quenching is approximately ten times greater than the time constant for the decay of oscillations in the circuit, so that the oscillations drop to a millivolt or less before oscillation begins again. The best results in the case of superregeneration are obtained when the quenching frequency lies between 30 and 100 kcs. Semin and Fedin,[90,91] who have worked with Wang's regenerative circuit,[171] note that it is not sufficiently sensitive. We used Wang's circuit only when we required a good reproducibility of line shape.

For the investigation of weak NQR lines one can utilize a system with a phase-sensitive detector. The use of a phase-sensitive detector, moreover, enables one to obtain good reproducibility of line shape. The influence of instrumental factors on the reproducibility of line shape in nuclear quadrupole resonance was investigated by us in reference 100. Let the absorption line be characterized by the form-factor $q(\nu)$, where $\nu = \nu' - \nu_0$, ν_0 is the frequency corresponding to the extremal value of $q(\nu)$. Since the frequency modulation of the source of radiation in the case of the observation of nuclear quadrupole resonance lines, and the magnetic modulation in the case of NMR observations are completely equivalent, it is possible to write without further analysis a formula similar to Andrew's formula,[5,6] which takes into account the distortion of the line due to the finite amplitude of frequency modulation:

$$S_2^* = S_2^0 + \frac{\nu_m^2}{4}, \qquad (10)$$

where S_2^* is the second moment of the absorption line observed experimentally, S_2^0 is the true second moment, and ν_m is the amplitude of frequency modulation. Formula (10) is obtained on the as-
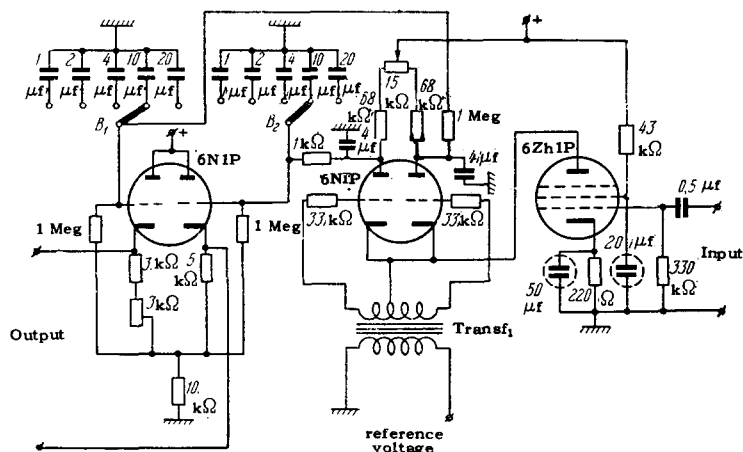
FIG. 6. Circuit diagram of the phase-sensitive detector.

sumption that the phase-sensitive detector is preceded by a narrow band amplifier which picks out the first harmonic of the signal, while the modulation amplitude is considerably smaller than the line width. The second moment of the absorption line is taken to mean the following integral characteristic of the line shape:

$$S_2 = \frac{\int_{-\infty}^{\infty} v^2 q(v)\,dv}{\int_{-\infty}^{\infty} q(v)\,dv}. \tag{11}$$

If the line shape is observed experimentally then its second moment may be calculated by the method of numerical integration.

If the second harmonic of the signal is selected, then the second derivative of the absorption line will be recorded. In this case it is possible to suppress strongly the parasitic amplitude modulation by means of a filter tuned to the first harmonic. However, it is necessary to double the frequency of the reference voltage supplied to the phase-sensitive detector. On expanding the form-factor into a Taylor series and on picking out the coefficient of the second harmonic we can obtain

$$S_2^* = S_2^0 + \frac{v_m^2}{6}. \tag{12}$$

Thus, when the second derivative is recorded, distortions due to the finite amplitude of modulation turn out to be even smaller than when the first derivative is recorded. If we pick out the third harmonic, then it is no longer necessary to utilize a frequency doubler for the reference voltage. In this case the distorting function has the form

$$S_2^* = S_2^0 + \frac{v_m^2}{8}. \tag{13}$$

We shall not dwell on a description of the principle of operation of the phase-sensitive detector,

well known in the literature, but shall restrict ourselves only to reproducing the widely known Schuster[149] circuit, which is shown in Fig. 6. The circuit utilizes the high plate resistance of a pentode to guarantee that the current in the output circuit should be independent of the action of the switching tube which switches the current in the output circuit into one of two load resistors in synchronism with the control voltage at the operating frequency.

An interesting method of observing the phenomenon of NQR was proposed by Pound and Watkins,[176] who used a magnetic field in the form of rectangular pulses. If a polycrystalline sample is used, then during the period of the pulse the NQR line is broadened and is not observed. The observation of the line is possible only in the interval between pulses. Thus, there arises an intensity modulation of the absorption line at a frequency corresponding to the frequency of the pulses of the magnetic field.
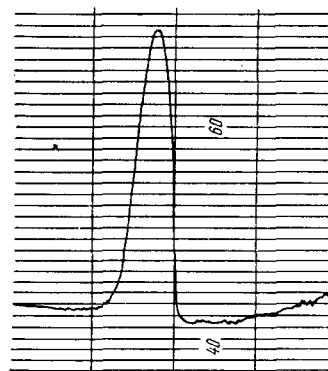
FIG. 7. NQR signal in potassium chlorate obtained by the Zeeman-modulation method. In this method the shape of the absorption line is recorded rather than its first derivative as in the case of frequency modulation.

Figure 7 shows a record of a NQR signal obtained by us by means of the Zeeman-modulation method. It should be noted that the use of a self-quenching superregenerator enables one to observe the NQR signal without any modulation directly on the os-

cilloscope screen. Thus, we observed the reso-
nance by means of the decrease in the superregen-
erator noise. When the oscillator frequency ap-
proaches the frequency of quadrupole resonance,
the noise decreases sharply. However, if a mag-
netic field is applied to the sample the noise in-
creases again.

Let us compare now the two modulation methods
from the point of view of reproducibility of line
shape. Let us take into account the distortions due
to the time constant of the phase-sensitive detec-
tor. The response of the integrating RC circuit to
a unit pulse has the form

$$U_0 = 1 - \exp\left(-\frac{t}{\tau}\right) \tag{14}$$

where $\tau = RC$. Let us now examine the response
of this circuit to a NQR signal in the case of fre-
quency modulation; in order to do this we shall ap-
ply the Duhamel formula

$$U_{out}(t) = q'(-\alpha)U_0(t) + \int_0^t q''(x-\alpha)U_0(t-x)\,dx. \tag{15}$$

Introducing the substitutions $\beta = x - \alpha$, $t' = t - \alpha$,
and $\psi = t' - \beta$ and integrating, we obtain

$$U_{out}(t') = q'(t') - q'(-\alpha)e^{-\frac{(t'+\alpha)}{\tau}} - \int_0^{t'+\alpha} q''(t'-\psi)e^{-\frac{\psi}{\tau}}\,d\psi. \tag{16}$$

We choose the origin for α at the center of the
line. On neglecting quantities of the second order
of smallness we rewrite (16) as

$$U_{out}(t') = q'(t') - \int_0^\infty q''(t'-\psi)e^{-\frac{\psi}{\tau}}\,d\psi. \tag{17}$$

From this, on taking into account the fact that inte-
grals of odd functions between symmetric limits
vanish, we obtain the following expression for the
second moment

$$S_2^* = S_2^0 + 2(v\tau)^2, \tag{18}$$

where S_2^* is the second moment of the line ob-
served experimentally, S_2^0 is the true second mo-
ment, τ is the detector time constant, v is the
speed of passage through the resonance region. It
can be easily shown that the output voltage after
the RC circuit in the case of Zeeman-modulation
is given by the following formula

$$U_{out}(t') = q(t') - \int_0^\infty q'(t'-\psi)e^{-\frac{\psi}{\tau}}\,d\psi. \tag{19}$$

After a number of simple transformations similar
to those carried out earlier, we obtain

$$S_2^* = S_2^0 + 2(v\tau)^2. \tag{20}$$

Thus, distortions due to the time constant of the
phase-sensitive detector are the same in the case
of both frequency and Zeeman modulation. Since
distortions determined by formulas (11) or (12)
and (13) are absent in the case of Zeeman modula-
tion, this method of observing the phenomenon is
more acceptable from the point of view of repro-
ducing the shape than the frequency-modulation
method. It should be noted that the resulting asym-
metry of the line leads to a shift of the origin.
Formulas (18) and (20) have been derived with re-
spect to the undisplaced origin, and consequently
this circumstance should be taken into account in
introducing corrections.

In addition to the advantage indicated above,
Zeeman modulation has also another significant
advantage. In utilizing frequency modulation we
are forced to make the modulation amplitude
smaller than the line width, and this leads to a
loss of intensity. But by using Zeeman modula-
tion we can obtain a better signal/noise ratio under
the same conditions.

3. THE SHAPE OF NUCLEAR QUADRUPOLE RESONANCE LINES AND RELAXATION PROCESSES

The investigation of the shape of NQR lines is
considerably more complicated than in the case of
NMR. Even taking into account the dipole-dipole
interaction between nuclei leads to great difficul-
ties, since the axes of the cones of precession are
oriented along the directions of the chemical bonds.
We can list the following causes for the broadening
of NQR lines:

1. Direct magnetic dipole-dipole interactions
between nuclei.

2. Broadening associated with the spin-lattice
relaxation time.

3. The existence of mechanical stresses in the
crystals.

4. Broadening due to the presence of paramag-
netic ions.

5. The presence of the earth's magnetic field in
the case of a polycrystalline sample.

Such an abundance of causes of broadening
makes it more difficult to investigate the shape of
NQR lines.

At the present time attempts are being made to
calculate the line shapes theoretically.[1,9,12] Often
it is useful to combine a rigorous calculation with
purely qualitative conclusions, since sometimes the
excessive awkwardness of theoretical calculations

complicates the analysis of results.

Abragam and Kambe[1] make the assumption that the resonating nuclei have spin 1 or $\frac{3}{2}$, while the gradient of the electric field possesses axial symmetry. The theory allows the calculation of only certain integral properties of the line shape (moments), which possess the property of additivity, i.e., broadening due to various causes leads to summation of the corresponding moments.

Broadening resulting from magnetic interaction between the resonating nuclei (A) is considered, and also broadening due to interactions with all the other nuclei in the sample (B). The Hamiltonian describing the interactions in the spin system can be given in the following form

$$H = q^2\beta^2 \sum_{j>k} r_{jk}^{-3} \{(J_j J_k) - 3r_{jk}^{-2}(J_j r_{jk})(J_k r_{jk})\}, \quad (21)$$

where r_{jk} is the distance between nuclei j and k, q is the gyromagnetic ratio, β is the nuclear magneton, J_j is the spin operator for the nucleus j, J_k is the spin operator for the nucleus k. The above Hamiltonian enables us to calculate the second moment due to the dipole-dipole interactions between the resonating nuclei.

In the case $J_A = \frac{3}{2}$ we have

$$\hbar^2 \langle(\Delta\nu)^2\rangle_{av} = \frac{1}{96} q_A^4 \beta^4 \sum_k r_{jk}^{-6} [207(1 - 3\gamma_{jk})^2 + 1512\gamma_{jk}^2$$

$$\times (1 - \gamma_{jk}^2) + 459(1 - \gamma_{jk}^2)^2 - 108(1 - 3\gamma_{jk}^2) \times (\alpha_{jk} - \beta_{jk})], \quad (22)$$

where α_{jk}, β_{jk}, γ_{jk} are the direction cosines of the lines r_{jk}.

In the case $J = 1$ we have

$$\hbar^2 \langle(\Delta\nu)^2\rangle_{av} = \frac{1}{4} \sum_k q^4 \beta^4 r_{jk}^{-6} \{5(1 - 3\gamma_{jk}^2)^2 + 9(1 - \gamma_{jk}^2)^2$$

$$- 2(1 - 3\gamma_{jk}^2)(\alpha_{jk}^2 - \beta_{jk}^2)\}. \quad (23)$$

In the case of a simple cubic lattice the above expressions assume a simpler form:

$$\begin{aligned} &\text{for } J = 1 \quad \hbar^2 \langle(\Delta\nu)^2\rangle_{av} = 28.4\beta^4 q^4 d^{-6}, \\ &\text{for } J = \frac{3}{2} \quad \hbar^2 \langle(\Delta\nu)^2\rangle_{av} = 60 q^4 \beta^4 d^{-6}, \end{aligned} \quad (24)$$

where d is the size of the elementary crystal cell.

The second moment due to the interactions with the nonresonating magnetic nuclei is calculated for the case of spin $J_B = \frac{1}{2}$:

$$\hbar^2 \langle(\Delta\nu)^2\rangle_{av} = \frac{1}{3} q_A^2 q_B^2 \beta^4 J_B (J_B + 1) \sum_k r_{jk} \times [(1 + FG)$$

$$\times (1 - 3\gamma_{jk}^2)^2 + 9(G + 2F)\gamma_{jk}^2 \times (1 - \gamma_{jk}^2) + 9FG(1 - \gamma_{jk})^2], \quad (25)$$

where $F = 0$ for $J_A = 1$ and $F = \frac{1}{2}$ for $J_A = \frac{3}{2}$.

If quadrupole coupling is absent, then $G = 1$; in the presence of quadrupole coupling $G = 0$ for integral spin, and $G = (\frac{3}{8})(2J_B + 1)/[J_B(J_B + 1)]$ in the case of half-integral spin.

The total width of NQR lines due to direct magnetic interactions between nuclei is obtained by summing the corresponding second moments. A study of line shapes enables one to draw conclusions with respect to the mobility of the nuclei and with respect to crystal structure. The effect of partial rotation on the width of a NQR line was noted in reference 8. If the ratio of the period of quadrupole precession to the lifetime of a given orientation is smaller than unity, then partial rotation does not alter the position of the line, but broadens it. Such broadening is approximately inversely proportional to the lifetime of the given orientation. For example, in $CHCl_3$ the NQR lines vanished at $-183°C$. This can be attributed to the onset of rotation, since on heating the intensity of the NQR line decreased, while broadening took place in such a way that the area under the curve remained practically unaltered. If the reduction in intensity was associated with the appearance of a new phase, then the width would have remained unaltered.

Usually the width of NQR lines is of order of several kilocycles, while the relative width is usually $10^{-2} - 10^{-5}$. The presence in the sample of protons, and also of paramagnetic ions, leads to a considerable broadening of the lines, and therefore it is desirable to use purified samples. Mechanical stresses in crystals give rise to a difference in the local quadrupole frequencies for different regions of the sample, which also leads to a considerable broadening of the NQR lines. It is very difficult to take this broadening into account.

The effect of external magnetic fields on the width of NQR lines was examined by us elsewhere.[101] When an external magnetic field is imposed on a single crystal sample the nuclear quadrupole energy levels are given in the first approximation by the following expression:

$$E_Q = \frac{eQq_{zz}}{4J(2J-1)} [3m^2 - J(J+1)] \pm \gamma\hbar m H_0 \cos\theta, \quad (26)$$

where θ is the angle between the direction of the quadrupole polarization and the external magnetic field and H_0 is the magnitude of the external magnetic field. From this expression it is seen that the magnetic field removes the $\pm m$- degeneracy and leads to a splitting of each level. The magnitude of this symmetric splitting is given by

$$\nu' = \pm \frac{\gamma}{4\pi} H_0 \cos\theta. \qquad (27)$$

When polycrystalline samples are used the probability that the splitting in a given small single crystal will fall within the frequency interval $(\nu', \nu' + d\nu')$ characterizes the spectral density of the distribution of splittings, and consequently also the shape of the absorption line when only this cause of broadening is taken into account. If we assume that in the case of a random distribution of directions of the quadrupole coupling the probability of finding its orientation lying within a certain solid angle is proportional to this angle, we obtain the following expression for the line intensity

$$\chi'' = \pm \frac{4\pi^2}{\gamma H_0}. \qquad (28)$$

Thus, we obtain a rectangular line shape the intensity of which is inversely proportional to the magnitude of the magnetic field, while its width is directly proportional to it; the area under the curve remains unaltered. This calculation enables us to introduce a correction for the earth's magnetic field.

In NQR two relaxation times are introduced — transverse and longitudinal. The transverse relaxation time is a measure of the line width, while the longitudinal or spin-lattice relaxation time characterizes the rate of re-establishment of Boltzmann equilibrium in the system. In the case of NQR the dominant relaxation mechanism is the quadrupole interaction.[140,166] The electric fields in the crystals are large, and therefore the lattice vibrations give rise to time dependent parts in the electric field gradient. This circumstance allows us to expand the gradient into a Fourier integral and to determine the magnitude of the spectral density at the resonance frequency. The theory of quadrupole relaxation was developed by Bayer.[20] He obtained an expression which determines the principal contribution to the spin-lattice relaxation time:

$$T_{1|\Delta m_z|=2} = \frac{16}{3} \frac{(\pi\theta\nu_t)^2}{(h\nu_Q)^2 \tau_a} \times \frac{(e^x - 1)^2}{\frac{2(\cosh x - 1)}{1 + 4\pi^2\nu^2\tau_a^2(e^x - 1)^2} + \frac{2\cosh x - 1}{1 + 4\pi^2\nu^2\tau_a^2}} \qquad (29)$$

where T_1 is the spin-lattice relaxation time, ν_Q is the quadrupole resonance frequency at absolute zero temperature, τ_a is the mean lifetime of a vibrational quantum, θ is the moment of inertia, ν_t is the average frequency of rotational oscillations. From this expression it is seen that a measurement of the spin-lattice relaxation time allows in principle an estimate to be made of the mean lifetime of a quantum of rotational oscillations. We have measured T_1 in potassium chlor-

ate at room temperature.[98] For this measurement we utilized a method similar to the one used by us in NMR.[96] After analyzing the saturation curves we obtained $T_1 = 0.04$ sec. An estimate based on Bayer's theory leads to the following two values of τ_a: 0.5×10^{-11} sec or 7×10^{-6} sec. The second value appears to be too large; for comparison we note, for example, that an estimate of the mean lifetime of a quantum of translational oscillations (phonon) from the coefficients of thermal conductivity gives a value of the order of 10^{-11} sec at room temperature. The value $\tau_a = 0.5 \times 10^{-11}$ sec leads to an average natural width for the corresponding Raman scattering lines of the order of $2 - 6$ cm^{-1} (experimentally a width of 10 cm^{-1} is observed). A similar estimate made on the basis of data from the literature on the relaxation times[63,179] and the vibrational frequencies[124,180] for paradichlorobenzene yielded $\tau_a = 10^{-10}$ sec at room temperature and 9×10^{-11} sec at liquid-nitrogen temperature, which led to line widths for Raman scattering of the order of 0.3 cm^{-1}.

An interesting anomaly was found in urotropine[176] in which the spin-lattice relaxation time was observed to increase by a factor of 65 as the temperature was varied from 0°C down to -196°C.

In order to be able to calculate the intensity of a NQR line it is necessary to know the value of the corresponding transition probability:

$$W_{m \leftarrow m'} = \frac{8\pi^3}{3h^2} |(m|M|m')|^2 \varrho_\nu, \qquad (30)$$

where M is the operator for the magnetic moment and ρ_ν is the spectral density. The matrix elements of the magnetic moment are related to the matrix elements of the spin by the following simple expression:

$$|(m|M|m')|^2 = \left(\frac{\mu^2}{J^2}\right) |(m|J|m')|^2. \qquad (31)$$

On taking into account the fact that $J_X = J_y$, we obtain

$$|(m|M|m')|^2 = \frac{\mu^2}{2J^2}(J(J+1) - mm'). \qquad (32)$$

If the radiofrequency field is given in the form $H_1 = H_{10} \sin 2\pi\nu' t$, then $\int_0^\infty \rho_\nu \, d\nu = H_{10}^2/8\pi$. We assume that the spectral density is proportional to the form-factor

$$\varrho_\nu = \alpha q(\nu). \qquad (33)$$

On taking into account the normalization condition we obtain

$$\varrho_\nu = \left(\frac{H_{10}^2}{8\pi}\right) q(\nu). \qquad (34)$$

The knowledge of the transition probability enables us to calculate the imaginary part of the magnetic

susceptibility to which the signal amplitude is proportional:

$$\chi'' = \frac{2N_0\mu^2(J(J+1)-m(m\pm1))}{3kTJ^2(2J+1)}\frac{\nu}{\Delta\nu},$$ (35)

where N_0 is the number of resonating nuclei per cm^3, μ is the magnetic moment, ν is the resonance frequency, and $\Delta\nu$ is the line width. This expression holds in the absence of the saturation effect, which is observed at large amplitudes of the rf field. Since χ'' is proportional to the absorption coefficient, the intensities of the NQR signals are measured in cm^{-1}. Usually these intensities are of the order of 10^{-10} cm^{-1}. Thus, a study of the line shapes, of their intensities, and also a study of the relaxation processes are closely interconnected.

The greatest interest lies in the study of the widths of NQR lines due to different isotopes in the same compound. In reference 98 a study was made of the widths of NQR lines due to Cl^{35} and Cl^{37} in the chlorates of barium, sodium and potassium. The amplitude of the rf field was taken to be sufficiently small so as to avoid additional broadening, which exceeds by a factor of four the corresponding broadening in nuclear magnetic resonance. In the chlorates studied, the ratio of the line widths of the chlorine isotopes approximately agreed with the ratio of their magnetic moments, and this indicates that the line width in these compounds is determined primarily by the dipole-dipole interaction between the nuclei. It is possible to estimate the internuclear distances in such compounds by utilizing the formulas of Abragam and Kambe.[1] Similar investigations were carried out in reference 118 with bromates; it was shown that the line width in that case is also determined primarily by the magnetic dipole-dipole nuclear interactions, since $\Delta\nu(Br^{79})/\Delta\nu(Br^{81})$ = 0.94, while the ratio of their magnetic moments is 0.92. The contribution of the spin-lattice relaxation to the line width did not exceed 0.1 kcs at an average width of 4 kcs.

4. TEMPERATURE AND PRESSURE DEPENDENCE OF THE QUADRUPOLE RESONANCE FREQUENCY

Both the shape and the position of the NQR lines depend on the nature of the crystalline fields; therefore the study of pure quadrupole spectra enables us to draw conclusions with respect to the structure of the crystal. When the temperature is varied both a shift of the line and a change in line width occur. The line broadening accompanying the change in temperature, as a rule, is a result of stresses and depends on the method of preparation and on the history of the sample. The NQR frequency is a function of the thermodynamic state of the solid. While the dependence on the pressure may in practice be frequently neglected, the dependence of the NQR frequency on the temperature is quite pronounced, being of the same order of magnitude as the changes in the vibrational frequencies of the crystalline lattice. The dependence of the frequency on the temperature was studied in 1,2-dichloroethane already in the early experiments on the observation of NQR.[69] Later the theory of the temperature dependence was developed by Bayer,[20] who took into account the rotational oscillations of nuclei which lead to the averaging of the electric field gradient. Bayer's theory was generalized and made more specific in references 126, 161, and 171, where other types of oscillations of the crystalline lattice were also taken into account. Thus, an investigation of the temperature dependence of the NQR frequencies enables us to draw conclusions with respect to the nature of the lattice oscillations. The frequencies of lattice oscillations may also be determined by observing the Raman spectra. However, in order to obtain such spectra, sufficiently homogeneous single crystals are usually required, while powdered samples may be used for the observation of NQR. The NQR method, of course, cannot compete with Raman spectra at low frequencies with respect to the amount of information that can be obtained, since it enables us to make an estimate only of the average value of the lattice frequencies. However, it is applicable also in those cases when the Raman-spectra method does not give any results (for intensely colored samples, or in the case when the lattice vibrational frequencies are inactive in spectra of this type).

As was noted earlier, the existence of lattice oscillations leads to averaging of the electric field gradient. If $\xi_i^0 \cos \omega_i t$ is the normal coordinate of the lattice, then the resonance frequency of the corresponding spin transition may be written in the following form

$$\nu = \nu_0\left[1 - \frac{3}{4}\sum_i(\xi_i^0)^2 A_i\right].$$ (36)

Here $A_i = \alpha_i - \frac{2}{3}\delta_{ij}$, where α_i and δ_{ij} are the coefficients in the following expressions:

$$\theta = \sum_i \alpha_i\xi_i + \ldots,$$

$$q = q_0(1 + \sum_i \beta_i\xi_i + \sum_{ij}\delta_{ij}\xi_i\xi_j + \ldots).$$ (37)

We set the energy of vibrational motion equal to the average energy of the corresponding harmonic

oscillator, i.e.,

$$\frac{1}{2}\omega_i^2(\xi_i^0)^2 = \hbar\omega_i\left(\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega_i}{kT}} - 1}\right). \qquad (38)$$

From this it follows that the relation between the NQR frequency and the temperature will be given by

$$\nu = \nu_0\left[1 - \frac{3}{2}\sum_{i=1}^{N}\frac{A_i}{\omega_i^2}\hbar\omega_i\left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega_i}{kT}\right) - 1}\right)\right], \qquad (39)$$

where ω_i is the characteristic frequency of the i-th lattice vibration, while

$$\nu_0 = \frac{eQq_0\frac{3}{2}(2m_z - 1)}{2J(2J - 1)}.$$

This formula takes into account the Debye waves and the intermolecular oscillations. In the case of the Debye waves the term in the sum (39) is of the form

$$-\frac{3}{2}\left(\frac{\overline{A}}{\langle m_a c^2\rangle_{av}}\right)9kT\left(\frac{T^3}{T_D}\right)\int_0^{\frac{T_D}{T}}\left(\frac{1}{2} + \frac{1}{e^x - 1}\right)x^3\,dx, \qquad (40)$$

where $\overline{A}$ is a constant, m_a and c are the atomic mass and the speed of propagation of acoustic waves in the crystal, and T_D is the characteristic Debye temperature.

If the experiments are carried out at not too low temperatures, one may divide the lattice vibrations into low-frequency and high-frequency ones, depending on whether their frequency is greater than or less than $\omega_M = kT_M/\hbar$, where T_M is the lowest temperature used in the experiment. For temperatures higher than the Debye temperature, the acoustic Debye waves can be classed among the low-frequency ones. Then (39) can be rewritten as

$$\nu = \nu_0\left\{1 - \frac{3}{2}kT\sum_1^{M}\frac{A_i}{\omega_i^2} - \frac{\hbar^2}{8kT}\sum_1^{M}A_i + \Omega(T)\right\}, \qquad (41)$$

where

$$\Omega(T) = -\frac{3}{2}\sum_{i=M+1}^{N}\frac{A_i}{\omega_i^2}\hbar\omega_i\left(\frac{1}{2} + \frac{1}{e^x - 1}\right); \qquad (42)$$

$\Omega(T)$ represents the contribution of the high frequency oscillations to ν. Because of the presence of the factor $1/\omega_i$ the high frequency terms of this sum contribute considerably less than the low frequency ones, and can therefore be frequently neglected. If we assume that $\Omega(T) = 0$, then we can write (41) in the following form

$$\nu = \left(a + b'T + \frac{c'}{T}\right) = a\left(1 + bT + \frac{c}{T}\right), \qquad (43)$$

where

$$a = \nu_0 = \frac{eQq_0}{2J(2J - 1)}\left(3m_z - \frac{3}{2}\right), \quad b = -\frac{3}{2}kM\left\langle\frac{A}{\omega^2}\right\rangle_{av},$$

$$c = -\frac{\hbar^2}{8k}M\langle A\rangle_{av}.$$

These equations are the basic ones for the analysis of the temperature dependence of the NQR frequency. The same equations can also explain its dependence on the pressure. The quantity a is directly proportional to q_0 — the static value of the principal value of the electric field gradient tensor. The quantity b can not be interpreted in such a simple manner in the case of molecular or Debye lattice oscillations, since A_i does not have a simple description in the general case. However, for certain types of oscillations (motion of the q axis around a perpendicular axis) A_i^{-1} is the moment of inertia about the axis of oscillations. It should be emphasized that a, b, and c are also functions of the volume. Therefore, observation of the variation of ν with temperature also requires the knowledge of the variation of the frequency with volume. Let us consider, for example, a perfect ion lattice. Let us assume that all the interatomic distances vary as $V^{1/3}$, where V is the crystal volume. In this case q_0 will be proportional to V, while the asymmetry parameter remains unaltered. On the other hand, q_0 does not depend on the volume in a molecular crystal. However, it is known that the value of the quadrupole coupling in a molecular lattice is 10% smaller than in a free molecule. Compression of a molecular crystal increases the hybridization of intermolecular bonds by means of bonding of neighboring molecules, which is the reason for the decrease in q_0 as the volume is decreased. Of course, most solids exhibit a behavior intermediate between these limiting cases.

In the case of two rotational oscillations about mutually perpendicular axes the temperature coefficient is given by the following expression

$$\frac{1}{\nu_0}\left(\frac{d\nu}{dT}\right) = \frac{3k}{8\pi^2}\left[\frac{e^{\frac{h\nu_a}{kT}}}{I_x\nu_a^2} + \frac{e^{\frac{h\nu_b}{kT}}}{I_y\nu_b^2}\right], \qquad (44)$$

where ν_a and ν_b are the frequencies of the rotational oscillations, I_x and I_y are the moments of inertia with respect to axes perpendicular to the direction of the quadrupole coupling. This equation shows that the magnitude of the temperature coefficient decreases as the frequency of rotational oscillations increases. This fact was utilized in reference 99 for estimating the magnitude of the frequencies of rotational oscillations in chlorates

of univalent and bivalent metals.

The dependence of the NQR frequency on the temperature was studied in a number of papers.[46,63,64,66,72,84,99,126,162,171] Suggestions were made that this dependence could be utilized for the measurement of low temperatures with a high degree of accuracy, since the measurement of temperature reduces to the measurement of the NQR frequency. At the present time such a thermometer has been constructed.[22] The properties of the thermometer are based on the temperature dependence of the NQR frequency of Cl^{35} in polycrystalline $KClO_3$. The thermometer enables us to measure temperatures in the range from 10° K to 300° K. The accuracy of temperature measurement is ±0.002° at 273° K and ±0.004° at 77° K. Chemically pure potassium chlorate was used as the sample, and this permitted very narrow absorption lines to be observed. The thermometer was calibrated in terms of primary temperature standards. This nuclear quadrupole thermometer possesses the following properties:

1) high sensitivity in determining the absolute values of the temperature;

2) simplicity and accuracy of adjustment;

3) absence of temperature hysteresis;

4) possibility of measuring temperatures over a wide range.

Such instruments can, undoubtedly, be widely used in practice.

In reference 66 an investigation is made of the temperature dependence of the quadrupole coupling of chlorine in solid derivatives of benzene. In the case of 1,2-dichlorobenzene discontinuities due to phase transitions were observed in the curves of the temperature dependence of the NQR frequency. In references 21 and 126, a study was made of the dependence of the quadrupole resonance frequency on the pressure. The pressure was varied from 1 to 104 atmospheres. A change of frequency with increasing pressure was established.

In some compounds[70] a temperature coefficient of opposite sign was found, i.e., the NQR frequency increased with increasing temperature. Bayer's theory, which did not take into account volume effects, is incapable of explaining a positive temperature coefficient. It is true that sometimes a positive temperature coefficient is due to the presence of side valences. In this case one can invent an explanation which does not contradict Bayer's theory. But in the majority of cases the phenomenon is nevertheless due to clearly pronounced volume effects which cancel the Bayer term in the temperature dependence.

5. ZEEMAN EFFECT IN QUADRUPOLE RESONANCE

The Zeeman effect in NQR arises when a small magnetic field is applied to the sample, which leads to a splitting smaller than the distance between the pure quadrupole energy levels.

If this splitting exceeds the pure quadrupole splitting, then one observes NMR split by quadrupole interactions. Investigations of NQR in single crystals when a weak magnetic field is simultaneously applied are of considerable interest for structural chemistry, since they can lead to far-reaching conclusions with respect to crystal structure.

Investigations of the Zeeman effect of NQR were carried out in a large number of papers.[23,24,53,65,67,125,133,137,154,155,156,157,163-165]

In the simplest case the theory of this phenomenon may be developed without any difficulty. For an isolated quadrupole nucleus we write

$$W_Q = -\frac{\mu H_0 m}{J} + \frac{eQq_{zz}[3m^2 - J(J+1)]}{4J(2J-1)}, \qquad (45)$$

where μ is the nuclear magnetic moment, H_0 is the value of the external magnetic field, m is the magnetic quantum number, J is the nuclear spin, and eQq_{zz} is the magnitude of the quadrupole coupling in frequency units.

This formula remains valid if the magnetic field is directed along the axis of symmetry of the electric field gradient, while the rf field of amplitude $2H_{10}$ is perpendicular to H_0. Figure 8 shows quadrupole energy levels split by magnetic interaction. When the magnetic field is applied, a constant increment $-(\mu H_0/J)m$ appears. In the case $m = \pm\frac{1}{2}$ it will be equal to $\mp\mu H_0/2J$, while in the case $m = \pm\frac{3}{2}$ it will be equal to $\mp 3\mu H_0/2J$ etc., and this results in a linear increase of the increment with increasing magnetic field.
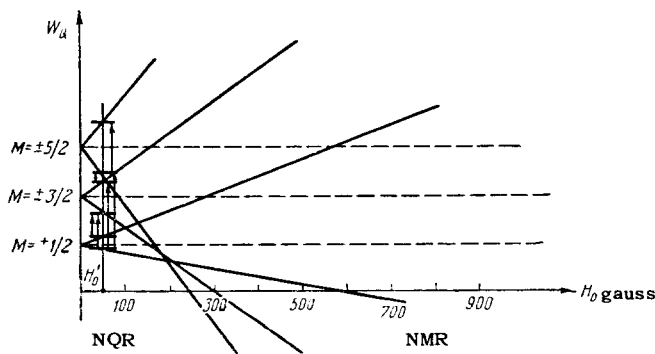

FIG. 8. Quadrupole energy levels in the presence of a magnetic field.

For the observation of Zeeman splitting in NQR

small fields of the order of 100 gauss are utilized which remove the two-fold degeneracy of the quadrupole energy levels and lead to the appearance of components in the spectrum symmetric with respect to the zero field level. In references 134, 169, and 170 the problem of the transition of NQR into NMR is investigated. In Fig. 8 it is seen that in the region of large magnetic fields we have NMR split by quadrupole interactions, while as the magnetic field is decreased a transition takes place into the region of pure quadrupole spectra.

A more complicated case, when the asymmetry parameter differs from zero, is considered in references 24 and 67. The calculation was carried out by perturbation theory, and the theory of Zeeman splitting of pure quadrupole levels was developed for half integral spin in the form which may be applied for any electric field gradient.

A study of the splitting of NQR lines in a magnetic field enables us to determine the asymmetry parameter for the case of spin $\frac{3}{2}$, which is of great practical significance considering that this asymmetry parameter cannot be determined by other methods. In this case the splitting turns out to depend on the orientation of the magnetic field relative to the principal axis of the electric field gradient of the crystal. Naturally, such a method requires the use of single-crystal samples: in polycrystalline samples we would observe only a broadening of the NQR lines, since in that case the small crystals are oriented completely at random.

An analysis of NQR lines split by magnetic interaction in single crystals for a given direction of the magnetic field enables us to determine the orientation of the principal axes of the electric field gradient in the neighborhood of the resonating nuclei, and this in turn enables us to obtain necessary information about crystal structure.

The theoretical investigation of these problems entailed considerable computational difficulties. In the case of small deviations from cylindrical symmetry, as we have already noted earlier, perturbation theory was used. When the asymmetry parameter vanishes, zero splitting is observed when the magnetic field is directed at an angle of 90° with respect to the axis of symmetry of the electric field gradient. However, if the asymmetry parameter differs from zero, then the magnitude of the angle between the magnetic field and the principal axis of the electric field gradient of the crystal depends on the azimuthal angle. The biggest value of the angle corresponding to zero splitting is observed when the magnetic field is situated in the $xz(\theta_x)$ plane, and the smallest

value when it is situated in the $yz(\theta_y)$ plane. Therefore, the technique of observing the dependence of the splitting of NQR lines on the angles enables us to determine the direction of the principal axes of the electric field gradient, and also of the crystallographic axes. A similar method enables us to find the greatest and the smallest angle corresponding to zero splitting (θ_y and θ_x), and this enables us to evaluate the asymmetry parameter for the case of spin $\frac{3}{2}$ in accordance with the following formula

$$\eta = \frac{3(\sin^2 \theta_x - \sin^2 \theta_y)}{\sin^2 \theta_x + \sin^2 \theta_y}. \qquad (46)$$

Sometimes it is possible to determine the asymmetry parameter also by the method of NMR split by the quadrupole interaction. Thus, Itoh et al.[115] observed the NMR of Na^{23} in a single crystal of $Na_2S_2O_3 \cdot 5H_2O$. From the magnitude of the splitting, and from the dependence of the angular position of the crystal with respect to the external magnetic field, the asymmetry parameter was determined, and in this case turned out to be equal to 0.334.

However, such investigations can be carried out only when the quadrupole coupling is very small, since for large values of the quadrupole coupling very large values of the magnetic fields would be required.

The method of pure quadrupole resonance enables one to localize the position of protons in crystals, although quadrupole resonance due to protons is naturally impossible. When protons are present in a sample an additional doublet splitting of each quadrupole resonance line occurs when a small magnetic field is applied to the sample. In reference 133 a shift of all the Zeeman components of the quadrupole spectrum was observed which was linear with respect to the increasing magnetic field in the range from 21 to 160 gauss, while the doublet splitting due to the interaction with the protons remained constant.

The splitting was observed at all angular positions of the crystal, with the exception of 90°, because the proton produces, at the point where the quadrupolar nucleus is located, a local magnetic field given by

$$H_{loc} = \frac{\mu}{r^3}(3\cos^2 \theta - 1), \qquad (47)$$

which vanishes for definite values of θ. Consequently, in this case the local field due to the protons is the cause of the internal Zeeman effect. The observation of this phenomenon enabled Livingston and Zeldes[133] to localize the position of the protons in iodic acid HIO_3. The results of the structural analysis of a single crystal of HIO_3

by the method of NMR were compared with data obtained by x-ray diffraction and neutron diffraction. The I-H distance was found to be 2.33 ± 0.02 A, and the position of the IO_3 group was also determined. At the present time observation of the Zeeman splitting of NQR lines is widely used in investigations of crystal structure.

It should be noted that a study of the splitting of NQR lines in a magnetic field is a new method of structural analysis which can yield very valuable results in many cases and can add to the information obtained by x-ray structural analysis, by neutron studies, and by nuclear magnetic resonance. The great simplicity of the experimental apparatus and the speed of obtaining and analyzing the results make the NQR method particularly valuable, considering that in this method the accuracy of determination of the internuclear distances is no less than the accuracy attained by the other methods mentioned earlier.

6. THE USE OF QUADRUPOLE RESONANCE FOR THE INVESTIGATION OF ELECTRIC FIELD GRADIENTS IN CRYSTALS

In presenting the fundamental theoretical considerations we have already partially mentioned a number of papers in which investigations were carried out which are of interest both to chemists and to crystallographers. We shall now describe in greater detail the results of the principal experiments.

Nuclear quadrupole resonance is by its nature the only method which enables us to study the potential distribution due to the electric charges in crystalline solids, since quadrupolar nuclei serve as test charges that enable us to measure this potential.

On taking into account the fact that small structural or chemical changes in the sample lead to huge shifts of the NQR frequencies compared with NMR, the importance of this method to chemistry cannot be overestimated. This field of investigation is as yet in its initial stages of development, but the results already obtained are of great interest. The first investigations in nuclear quadrupole resonance (references 2, 3, 4, 11, 16, 19, 23, 33, 34, 48, 55, 72, 74, 76, 77, 78, 109, 128, 129, 143, 145) were directed principally towards the accurate measurement of the magnitudes of the quadrupole couplings in a number of substances. At the present time the method of NQR has yielded information with respect to a large number of nuclei: Cl^{35}, Cl^{37}, Br^{79}, Br^{81}, I^{127}, Sb^{121}, Sb^{123}, As^{75}, Cu^{63}, Cu^{65}, N^{14}, B^{10}, B^{11} etc. The most

complete data on the frequencies are given in reference 132. The table gives data on the absorption frequencies[73,138,171] in substances which have been studied in greatest detail. These substances may be conveniently used for adjustment of apparatus for the study of NQR. At the present time already several hundred compounds of chlorine, antimony, iodine, copper, bromine, and nitrogen have been investigated by the NQR method. The NQR method enables us to determine the magnitude of the quadrupole coupling eQq_{zz} which depends on the nuclear and the molecular properties of the substance under investigation. If the nucleus is acted upon by only one electron, then the latter produces at the point at which the nucleus is situated the potential

$$V = \frac{e}{r}, \qquad (48)$$

where e is the electron charge and r is the distance from the electron to the center of the nucleus. Then we have

$$\frac{\partial^2 V}{\partial z^2} = \frac{e\,(3\cos^2\theta - 1)}{r^3}. \qquad (49)$$

To calculate the electric field gradient of a molecule the above expression must be averaged over the electron orbits:

$$q_i = \frac{e \int \psi_i \left(\frac{3\cos^2\theta - 1}{r^3} \right) \psi_i^* \, d\tau}{\int \psi_i \psi_i^* \, d\tau}, \qquad (50)$$

where ψ_i are the atomic wave functions. The theoretical calculation presents considerable difficulty. It may be carried through only under a number of simplifying assumptions:

1) only electrons in the valence shells are taken into account, since the filled shells are spherically symmetric;

2) S-electrons do not affect the magnitude of q;

3) if all the three p-orbits of the atom are uniformly filled, then their total effect is equal to zero;

4) when uncompensated p-electrons are present in the valence shells, the effect of all the other electrons may be neglected.

If we succeed in obtaining an estimate of the magnitude of q_{zz}, then knowledge of the quadrupole coupling will enable us to calculate the quadrupole moment of the nucleus. The evaluation of q_{zz} has been carried out in certain cases in references 15, 26, 44, and 158-160. When the quadrupole moment has already been determined by another method, then knowledge of the value of the quadrupole coupling enables us to solve the inverse problem, i.e., to calculate the magnitude of the

Substance	Isotope	Temperature, °C	Resonance frequency, Mcs	Signal/noise ratio	Line width, kcs
p-C₆H₄Cl₂	Cl^{35}	27.4	34.23324 ± 0.00025	15	1.43
	Cl^{37}		26.97952 ± 0.00025	5	1.40
	Cl^{35}	16.9	34.29402 ± 0.00025	12	1.38
	Cl^{37}		27.02771 ± 0.00025	4	1.23
	Cl^{35}	0.3	34.34609 ± 0.00025	12	
	Cl^{37}		27.06887 ± 0.00025	4	
	Cl^{35}	—195	34.77540 ± 0.00025	19	
	Cl^{37}		27.40811 ± 0.00025	4	2.74
SbCl₃	Cl^{35}	25.5	19.17496 ± 0.00050	10	2.28
	Cl^{37}		15.11125 ± 0.00025	3	
	Cl^{35}	0.6	19.19916 ± 0.00050	10	2.92
	Cl^{37}		15.13058 ± 0.00025	3	
	Cl^{35}	—195	19.30468 ± 0.00050	12	3.56
	Cl^{37}		15.21522 ± 0.00025	4	
	Cl^{35}	25.5	20.40739 ± 0.00050	4	
	Cl^{37}		16.08146 ± 0.00025	1.5	
	Cl^{35}	0.6	20.47433 ± 0.00050	4	
	Cl^{37}		16.13457 ± 0.00025	1.5	
	Cl^{35}	—195	20.90767 ± 0.00050	4	
	Cl^{37}		16.47790 ± 0.00025	2	
	Sb^{121}		58.07831	5	5.18
			112.49849	3	8.07
	Sb^{123}	31.07	37.33261	5	5.32
			67.72563	3	
	Sb^{121}		58.37421	5	7.08
		0.8	112.87532	3	5.53
	Sb^{123}		37.62624	5	6.13
			67.92500	3	
NaClO₃	Cl^{35}	23.8	29.92864 ± 0.00050	9	0.57
	Cl^{37}		23.58894 ± 0.00025	3	0.52
	Cl^{35}	0.4	30.02468 ± 0.00050	15	1.35
	Cl^{37}		23.66998 ± 0.00025	4	1.13
	Cl^{35}	—195	30.63017 ± 0.00025	20	1.87
	Cl^{37}		24.14228 ± 0.00025	4	1.07
	Cl^{35}	—195	34.02341 ± 0.00025	8	5.44
CH₃Cl	Cl^{37}		26.81552 ± 0.00025	2	
C₂H₂Cl₂	Cl^{35}	—195	35.9862 ± 0.0008	8	2.6
	Cl^{37}		28.3646 ± 0.0008	2	
	Sb^{121}		48.35638	5.	9.23
			95.87212	5	14.00
	Sb^{123}	31.04	29.84304	3	11.15
			58.05708	3	
SbBr₃	Sb^{121}		48.65959	5	14.32
		0.4	96.44099	5	10.14
	Sb^{123}		30.04807	3	12.29
			58.39938	3	11.53
	Sb^{121}		44.33480	3	9.89
		30.75	88.66300	3	
	Sb^{123}		26.91568	3	
			53.81785	2	
Sb₂S₃	Sb^{121}		44.80731	5	11.16
		0.2	89.60674	3	
	Sb^{123}		27.20256	3	
			54.39268	2	

electric field gradient in the crystal. The appearance of new chemical bonds exerts a considerable influence on the magnitude of the electric field gradient of a molecule. The measurement of the magnitudes of the quadrupole couplings and of the asymmetry parameters enables us to determine the character of the chemical bond. NQR is used at present for the study of the degree of ionicity of bonds, and for the study of the type and degree of hybridization. The partially ionic nature of covalent bonds alters the charge distribution between the atoms and produces an indirect effect as a result of the change in the amount of screening of the nucleus. S-orbits are characterized by the absence of quadrupole coupling, while a p-orbit has the maximum value of quadrupole coupling. Let N_x, N_y, and N_z be the numbers of electrons in each of the three p-orbits. Then the number of uncompensated p-electrons will be given by

$$U_p = \frac{N_x + N_y}{2} - N_z. \tag{51}$$

From this we obtain

$$q_{zz} = U_p q_0, \tag{52}$$

where q_0 is the contribution made by one uncompensated p-electron. The number of uncompensated p-electrons may be calculated on the basis of a number of simplifying assumptions. Consider a halogen atom which forms a single bond which increases the number of its electrons to a complete shell of eight. If the bond is formed only by means of p-orbits, and does not have an ionic character, then $N_x = N_y = 2$, $N_z = 1$ and $U_p = 1$. In a chlorine molecule $U_p = 0.99$ which indicates the p-character of the bond practically without any trace of ionic properties. The magnitude of the quadrupole coupling per uncompensated p-electron was measured by Jaccarino and King:[139]

$$eQq_0 = -109.74 \text{ Mcs.}$$

Let us assume that α is the percentage content of S-coupling, while β is the relative weight of the bond of ionic type. Then we have

$$U_p = (1 - \beta)(1 - \alpha). \tag{53}$$

Thus, an increase in the degree of ionicity and of the S-nature of the bond leads to a decrease in the quadrupole resonance frequency, and therefore measurement of quadrupole couplings in molecular crystals enables us to draw conclusions with respect to the degree of participation of individual structures.

A large number of papers (references 51, 61, 94, 95, 100, 117, 130, 119, 129, 137, 144, 151, and 168) is devoted to the investigation of bond char-

acter. In reference 137 a study was made of the type of bond hybridization of chlorine in a number of compounds. The asymmetry parameter and the absorption frequency were measured. The observed quadrupole frequencies were extrapolated to zero temperature in order to reduce the influence of lattice vibrations. On taking into account the following expressions

$$\left. \begin{array}{l} eQq_{zz} = -\left(\frac{\alpha}{2} - \beta\right) eQq_0, \\[2mm] eQq_{yy} = -\left(\frac{\alpha}{2} + \frac{\beta}{2}\right) eQq_0, \\[2mm] eQq_{zz} = \left(\alpha - \frac{\beta}{2}\right) eQq_0, \\[2mm] \eta = \frac{\beta}{2\alpha - \beta}, \end{array} \right\} \tag{54}$$

it was possible to elucidate the character of participation of the individual simplest structures in bond formation. In reference 102 a study was made of NQR in five chlorates. As has already been noted, a rigorous interpretation of the observed NQR frequencies is difficult, since the evaluation of the electric field gradient is associated with calculations involving many-electron systems involving unknown bond type and degree of hybridization. On taking into account the fact that the magnitude of the quadrupole coupling in chlorates is considerably smaller than 109.74 Mcs it was possible to draw conclusions with respect to the partial ionicity and S-hybridization of chlorine bonds; d-hybridization, as a rule, plays no essential role. The effect of the shape of the ClO_3^- pyramid on the NQR frequency in chlorates was taken into account. Indeed, chlorine forms three bonds with oxygen atoms. Let us calculate the electric field gradient corresponding to one bond. For the sake of simplicity we consider that the asymmetry parameter is equal to zero, i.e., we choose the coupling tensor in the form

$$q_{z'z'} \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{55}$$

On taking into account the variation of the tensor when the z' axis is rotated, we obtain the average field gradient due to the three bonds along the axis of symmetry of the ClO_3^- pyramid:

$$q_{zz} = \frac{3}{2}(3\cos^2\theta - 1) q_{z'z'}, \tag{56}$$

where θ is the angle between the Cl—O direction and the axis of symmetry of the pyramid, and $q_{z'z'}$ is the electric field gradient corresponding to one bond. Formula (56) made it possible to calculate,

from the observed absorption frequency, the magnitude of the electric field gradient contributed by each individual bond. It should be noted that the factor $(\frac{3}{2})(3\cos^2\theta - 1)$ vanishes for $\theta = 54°44'$; for a similar reason NQR may be observed in perchlorates only at very low frequencies. In sodium chlorate the distance of the chlorine atom from the O_3 plane is equal to 0.48 A, while the average Cl—O distance is 1.48 A, from which it follows that $q_{zz} = -1.02\,q_{z'z'}$. In potassium chlorate the distance of the chlorine atom from the O_3 plane is equal to 0.50 A, and the average Cl—O distance is 1.48 A. Therefore $q_{zz} = -0.99\,q_{z'z'}$.

Thus, the electric field gradient in chlorates is a negative quantity. If the variation in $q_{z'z'}$ is not taken into account, then the value obtained for the ratio of frequencies in chlorates of sodium and potassium is close to the experimentally observed value, 1.03. A similar calculation for barium chlorate led to $q_{zz} = -1.00\,q_{z'z'}$. Taking all this into account, the conclusion can be drawn that the principal contribution to the electric field gradient in the neighborhood of chlorine nuclei in chlorates is made by their immediate surroundings.

On taking into account the fact that the electric field gradients of the pyramid and of the individual bond are very close to one another, the number of uncompensated p-electrons corresponding to each bond can be evaluated directly from the initial data. An attempt to take into account the effect of more distant atoms has led to considerable difficulties.

If NQR is studied in the same compound for different isotopes, the ratio of the quadrupole moments can be obtained with a great degree of accuracy. Thus, in reference 131 the ratio of the quadrupole moments of the iodine isotopes was measured from NQR data in SnI_4:

$$\frac{eQ(I^{129})}{eQ(I^{127})} = 0.7011213 \pm 0.00015.$$

In references 29 and 75 the ratio of the quadrupole moments of the gallium isotopes has been measured:

$$\frac{eQ(Ga^{69})}{eQ(Ga^{71})} = 1.5867 \pm 0.0004.$$

Similar measurements have been carried out for the isotopes of chlorine,[127] for the isotopes of copper,[99] for the isotopes of antimony,[171] etc.

Many investigations are devoted to the study of the influence of chemical affinity on the quadrupole resonance frequency. Livingston[130] has studied NQR in chlorine derivatives of methane. A fine structure of the NQR lines was observed due to the nonequivalent position of the nuclei in the crys-

talline lattice. In this case the quadrupole coupling (which is equal to twice the value of the frequency) was evaluated as the average of several values. When the temperature dependence was investigated in all cases an increase in frequency was observed with decreasing temperature. A gradual replacement of hydrogen atoms by chlorine in methane led to a smooth increase in the quadrupole coupling, amounting approximately to 4.5 Mcs for each additional atom of chlorine. Similarly, a complete replacement of hydrogen atoms by F in CH_3Cl, CH_2Cl_2 and $CHCl_3$ led to an increase in the coupling, amounting on the average to 2.9 Mcs. When hydrogen is replaced by a halogen the chlorine-carbon bond becomes less ionic in character, owing to the polarization by the electronegative halogen, which leads to an increase in the NQR frequency. In reference 35 the Cl^{35} resonance was investigated in five chlorobenzenes containing different numbers of chlorine atoms. It was found that the resonance frequency increases in proportion to the increasing number of chlorine nuclei in the molecule. Similar investigations were also carried out in the case of iodine in a number of iodine-substituted methanes.[109] A large number of investigators succeeded in observing the fine structure of NQR due to the nonequivalent positions of the resonating nuclei in the crystalline lattice.[3,4,17,31,34,39,62,74,84,111,130,173,174,178] In certain cases (for example, in antimony trichloride) the appearance of fine structure, apparently, cannot be explained by the nonequivalent positions of the chlorine atoms in the crystalline lattice. A number of papers[65,168] is devoted to the study of the conjugate and the double bond character of the bonds.

Of considerable interest also is the study of the effect of impurities on the electric field gradient in crystals. In references 68 and 179 a study was made of solid solutions of paradichlorobenzene in a number of isomorphic compounds. It was found that the intensity of the NQR line decreases with increasing impurity as

$$A = A_0 \exp(-NC), \tag{57}$$

where C is the molar concentration of the impurity, N is a characteristic number which represents the number of resonating nuclei interacting with one molecule of the impurity. An evaluation of these characteristic numbers for different compounds enabled conclusions to be drawn with respect to the volume occupied by a molecule of the impurity in the crystal. In reference 179 a study was made of the solid solution of paradichlorobenzene in paradibromobenzene. For the observation of the NQR phenomenon, a nonstationary technique[29,30,43,56,57,107,110]

was used in which the rf field was applied to the sample in the form of pulses, and the spin echo phenomenon was observed. It was found that the spin-lattice relaxation time does not depend on the composition of the sample. However, T_2^* falls off very rapidly from 3.1×10^{-4} sec in pure para-dichlorobenzene down to 0.15×10^{-4} sec in a sample with 20 percent (molar) of paradibromobenzene. Thus, the principal effect is the broadening of the absorption line due to the appearance of distortions in the electric field gradient in the neighborhood of the chlorine nuclei.

We have also studied solid solutions of antimony in benzene and in potassium chloride. Samples of $SbCl_3$ were sealed in vacuo into test tubes with side arms containing definite quantities of the impurity which were later introduced into the sample. Mixtures of antimony trichloride with KCl or C_6H_6 were melted, and solid solutions with up to 22% KCl and up to 8% C_6H_6 were investigated. It was found that a larger characteristic number corresponds to benzene.

The above brief examination of the principal applications of quadrupole resonance shows that this method is of considerable interest to the chemist studying problems of the formation of chemical bonds. On taking into account the insignificant material expenditures required for setting up the apparatus, one can say that the NQR method can be practically utilized in every laboratory. The wide range of problems which may be solved with the aid of nuclear quadrupole resonance makes this method very promising. Therefore, further development of investigations in this direction undoubtedly will lead to the solution of a number of problems associated with the theory of solids.

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Translated by G. Volkoff

Translator's Comments — This 28-page review paper must have been written just prior to the publication of the much more extensive 223 page excellent monograph by Das and Hahn[1] on the same subject, as it contains no reference to the latter, nor to the 118 page review paper by Cohen and Reif[2] on the topic of NQR effects in NMR studies of solids which is very briefly discussed in section 5 of the present paper.

The author states that one of his aims is to give a survey of Soviet work in NQR. In his bibliography he refers to two papers by Semin and Fedin (90, 91 on his list), who have worked with Wang's regenerative circuit (171), to seven papers (96-102) by himself, and to one paper by Skripov (161) who apparently has contributed, along with Kushida, Benedek and Bloembergen (126) and Wang (171), to generalizing Bayer's (20) theory of the temperature dependence of NQR. Grechishkin's own papers (96-102) deal with determination of T_1 and with width of NQR lines in several chlorates, and with evaluation of various instrumental factors. Figures 2-7 describe the author's equipment and illustrate his results. Figure 4 is a modification of Hopkins' circuit (113), and Fig. 6 is Schuster's circuit (149). The remaining two Russian references (124, 180) deal with determinations of vibrational frequencies by other methods. Thus, Soviet work in NQR seems as yet not to be very extensive.

The rest of the paper is devoted to work done outside the U.S.S.R. which, with the exception of one or two recent papers (e.g. 126), is covered more fully in the reviews by Das and Hahn[1] and by Cohen and Reif.[2] However, the Soviet work is not included in these two reviews, so that the present paper is useful in bringing it to our attention.

[1] T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Supplement 1, Solid State Physics, Academic Press, 1958.

[2] M. H. Cohen and F. Reif, Quadrupole Effects in Nuclear Magnetic Resonance Studies of Solids, Solid State Physics **5**, 321 (1957), Academic Press.