Indirect methods for studying nuclear quadrupole interactions in solids

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<u>Abstract.</u> Possibilities of indirect detecting of NQR (nuclear quadrupole resonance) signals in solids are considered. Various modifications of the double NQR method are described. Capabilities of various experimental techniques are compared, and characteristic features of NQR on light integer-spin nuclei are considered. A method for taking account of the frequency shifts due to the static magnetic field is described.

1. Introduction

Nuclear quadrupole resonance (NQR) provides one of the sensitive methods for studying the intermolecular structure as well as the physical and chemical properties of a substance [1]. NQR is widely used when investigating the nature of chemical bonds, intermolecular compounds, internal motions, phase transitions, defects in crystals, etc. [2, 3]. This spectroscopic technique, first presented by Dehmelt and Krüger more than 40 years ago in Ref. [4], has gained a leading position with the expansion of the class of compounds being investigated [5, 6]. Enhancements in the element base of radio electronics and application of computers to experiments have made it possible to expand the range of applicability of above method to a variety of new scientific and applied problems solved within other branches of science. These problems include search and identification of narcotic drugs and explosives with the aid of local NQR [7, 8], remote luggage control [9, 10], etc. The development of different indirect methods for studying nuclear quadrupole interaction has opened a new perspective in applying NQR [11]. It has became possible to record resonance signals from light nuclei ²H, ⁷Li, ¹⁰B, ¹¹B, ¹⁷O, ²³Na, ²⁵Mg, etc., in a substance with the natural content of isotopes [12] and this is what accurate chemical analysis requires.

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Received 22 December 1994, revised 11 March 1996 Uspekhi Fizicheskikh Nauk **166** (7) 763–776 (1996) Translated by D Kh Gan'zha, edited by A Radzig The importance of studies in this field is verified by the fact that twelve specialists in radiospectroscopy, whose works are related to this division of physics, have been awarded the Nobel Prize. (The recent prize was adjudged to R Ernst in 1992.)

Although there are numerous reviews on NQR in the Russian literature (for example, see Refs [13 - 15]), to our opinion these problems, especially, the indirect quadrupole resonance methods are discussed insufficiently. To this connection we made an attempt to summarize the results pertaining to main indirect techniques of NQR (double NQR-NQR and double NMR-NQR) and also certain modern conceptions of their development. Undoubtedly, we does not aspire to give an exhaustive consideration of the issue because the overall bulk of information on NQR researches is really overwhelming. However, we hope that the present paper will be helpful to specialists in radiospectroscopy and students of physical departments, which are interested in nuclear quadrupole resonance.

2. Method of nuclear quadrupole resonance

Nuclear quadrupole resonance is exhibited by nuclei with spin quantum numbers $I \ge 1$ when in addition to a magnetic dipole moment they offer an electric quadrupole moment representing the degree of deviation of the shape of a nucleus from a sphere. There are two specific types of nonspherical shapes of nuclei (Fig. 1):

a) the cigar-shaped nucleus is extended along the Z' axis of the coordinate system relevant to the nuclear spin moment; in this case the magnitude of the quadrupole moment is positive;

b) the nucleus is flattened out along the Z' axis and now the quadrupole moment is negative.

There exist 2I + 1 different quadrupole moments Q since the spin projection or magnetic quantum number m can take 2I + 1 values. The quadrupole moment is the largest when m = 1. An atomic nucleus is located in the inhomogeneous electrostatic field induced by the electron shell and, hence, the energy of interaction between the nuclear quadrupole moment and gradient of the electrostatic field depends on the (nonspherical) shape of the nucleus. Reduced to the principal axes the moment is uniquely defined by two independent components q_{zz} and $\eta = (q_{xx} - q_{yy})/q_{zz}$ [2].



Figure 1. The typical deviation of the shape of an atomic nucleus from a sphere.

Here the coordinate axes are designated in such a way that the inequality $|q_{xx}| < |q_{yy}| < |q_{zz}|$ holds for the tensor components. The quantity q_{zz} is commonly referred to as the electric field gradient (EFG); η is the asymmetry parameter of the EFG tensor.

The eigenvalues of the Hamiltonian of the quadrupole interaction $\hat{\mathcal{H}}_Q$ can be found by diagonalization of the associated matrix for the *I* spin of a particular nucleus. For example, at I = 1 there appear three quadrupole energy levels:

$$E_{\pm} = \frac{1}{4} e Q q_{zz} (1 \pm \eta), \qquad E_0 = -\frac{1}{2} e Q q_{zz}.$$
(1)

Transitions between these energy levels occur under the action of a variable magnetic field onto the nuclear system and they are exhibited by selective absorption of radio-frequency radiation. Excitation of quadrupole transitions in the external radio-frequency field got the name of nuclear quadrupole resonance. The value of the EFG asymmetry parameter is limited by the inequality $0 \le \eta < 1$. The case of $\eta = 0$ corresponds to degeneration of levels $E_{\pm}(1)$. Therefore, the transition v_0 between these levels is called 'forbidden' in NQR.

The prime experimental goal of NQR is to find the parameters of quadrupole interaction eQq_{zz} and η . Intensities of resonance absorption lines are proportional to difference between the number of quanta which have been absorbed in transition from a lower level m to an upper level n and the number of quanta which have been emitted in the opposite transition. The rate of energy absorption in an isolated spin system is not zero only when the populations N_m and N_n are different and, hence, the continuous irradiation, gradually saturating the system, will inevitably stop further absorption. In this connection the specimen is usually supposed to be provided with another system for exchanging energy with the nuclei under investigation by means of some interactions. In the NQR nomenclature this system is spoken of as the 'lattice'. It includes all but spin degrees of freedom of nuclear paramagnet (vibrational, rotational, etc.). The process of energy transfer from spins to lattice is said be spin-lattice relaxation. The rate of relaxation is the second main factor (the amplitude of the irradiating field can be regarded as the first one), whereon the intensity of NQR absorption depends.

In the vicinity of a nucleus the EFG tensor is uniquely described by the quadrupole bond constant (QBC) eQq_{zz} and by parameter η calculated from the values of resonance frequencies.

Presently, most NQR researches are performed by pulse (unsteady) techniques. In the latter variable magnetic field of resonance frequency acts on the specimen by short-time intense pulses and then transient processes in the spin system are studied. Experiments with pulse excitation provide the base for direct NQR methods.

3. Features of indirect NQR detection

The deviation of the shape of an atomic nucleus from a sphere is usually small and the quadrupole moments are of the order of 10^{-23} cm². In addition, the magnitude of the quadrupole moment depends on the nuclear size and, as a result, the quantity eO is much less for light nuclei than for heavy ones and their quadrupole transitions are located within a lower frequency range. This consideration is essential because in many cases the sensitivity of the direct NQR methods decreases with frequency and it becomes very difficult to observe absorption lines even for $v \approx 1$ MHz. This is the reason why study of certain isotopes of light nuclei goes beyond the scope of the direct NQR. Low density of quadrupole nuclei in the compound under consideration presents the second natural limitation. In either case sensitivity of direct methods is insufficient and because of this indirect techniques of NQR detection should be in use.

First Herzog and Hahn enhanced the sensitivity of the method along this way to detect transitions ²³Na in the NaClO₃ single crystal [11]. They failed to detect directly weak signals of NQR from nuclei of interest and subjected the adjacent nuclei of ³⁵Cl to 180°-pulse excitation using strong spin echo from them as a reference signal. In the given sample there exist two ³⁵Cl and ²³Na spin systems (let they be designated by A and B) with dipole-dipole interactions between them, and, hence, resonance energy absorption in one of them has an immediate impact on the other. The efficiency of the system contact depends on the gyromagnetic ratio and relative distances r_{AA} and r_{AB} between nuclei AA and AB, respectively. In the single crystal involved $r_{AA} > r_{AB}$ and the attenuation of echo signal from ³⁵Cl depends primarily on the interaction between systems A and B: continuous resonance irradiation v_B at the frequency of ²³Na NQR causes the interaction Hamiltonian \mathcal{H}_{AB} to average and the spin echo from A nuclei to attenuate to a lesser extent. Here the energy absorption by system B is signalled by the difference in amplitudes of A echoes with and without the irradiation of v_B .

Thus, the example considered presents clearly the necessary conditions for experiment on double quadrupole resonance to be performed. Namely, the specimen should have two kinds of nuclei: A (with strong signal of nuclear resonance) and B (of interest); these two spin systems should be bound by dipole-dipole interactions. Methods of double NQR differ primarily in the choice of a specific spin system for providing reference signal and in the way of the energy exchange between spins A and B. In all their diversity the modern double techniques can be explicable on the basis of a single thermodynamic analogy. Two spin subsystems A and B in a specimen may be considered as two thermal reservoirs with a heat-conductive rod between them. One reservoir has a high heat capacity, it is an analog of A spins; another reservoir possesses a low heat capacity, it is an analog of B spins. If reservoir B is heated by a resonance radio-frequency field, it is hardly possible to measure the new, changed temperature of the reservoir because the heat capacity of the spin system is low. However, if system B is heated for a long time and the rod shows a high heat conductivity, the temperature of reservoir A with high heat capacity will vary significantly. This variation can be measured and the rise in A-system temperature will provide an indirect evidence of resonance energy absorption by system B. The lower is the initial temperature of reservoir A and the higher is the heat conductivity of the rod, the stronger is the effect. Thus, three main stages of experiment on double nuclear quadrupole resonance may be distinguished:

1) spin system A is first cooled down;

2) *B*-spins are heated (by radio-frequency irradiation or in other way) and they are brought in contact with *A*-spins;

3) changes in A system are measured.

Before we proceed to particular techniques, there is a need to introduce the basic theoretical concepts used to describe the physical processes gone in double resonance, namely, the rotating coordinate system and the spin temperature.

The equation of motion of the nuclear magnetic moment in a constant magnetic field \mathbf{B}_0 has the form

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \gamma \left[\boldsymbol{\mu} \times \mathbf{B}_0 \right]. \tag{2}$$

According to this equation the magnetic moment $\boldsymbol{\mu}$ precesses around the field vector \mathbf{B}_0 with the angular velocity $\gamma B_0 = \omega_0$ (Larmor frequency). In a coordinate system X', Y', Z' rotating around the laboratory system X, Y, Z with a certain angular velocity, Eqn (2) becomes $d\boldsymbol{\mu}/dt = \gamma[\boldsymbol{\mu} \times \mathbf{B}_0] + [\boldsymbol{\omega} \times \boldsymbol{\mu}]$. Let $\omega/\gamma = B'$ and $B_0 - B' = B_{\text{eff}}$ (B_{eff} is the effective field). Then Eqn (2) in the rotating coordinate system (RCS) takes the form $d\boldsymbol{\mu}/dt = \gamma[\boldsymbol{\mu} \times \mathbf{B}_{\text{eff}}]$. Thus, the magnetic moment in RCS remains unchanged in magnitude and direction.

Let a radio-frequency magnetic field $\mathbf{B}_1 \cos \omega t$ be applied perpendicularly to the vector \mathbf{B}_0 . It may be presented as a superposition of two equal fields rotating with equal angular velocities in opposite directions. The resonance is affected only by the field rotating in the same direction in which the Larmor precession proceeds. In RCS the field \mathbf{B}_1 is constant and the effective field is, consequently, equal to $\mathbf{B}'_{\text{eff}} = (\mathbf{B}_0 - \boldsymbol{\omega}/\gamma) + \mathbf{B}_1$; thus, $d\boldsymbol{\mu}/dt = \gamma[\boldsymbol{\mu} \times \mathbf{B}'_{\text{eff}}]$. It follows from the last equation that, for example, the nuclear magnetic moment $\boldsymbol{\mu}$ precesses in RCS around the vector \mathbf{B}'_{eff} with the angular velocity $\boldsymbol{\omega}' = \gamma \mathbf{B}'_{\text{eff}}$. Let θ be the angle between the vectors \mathbf{B}'_{eff} and \mathbf{B}_0 . The value of the angle is determined from the equation $\tan \theta = |\mathbf{B}_1|/|\mathbf{B}_0 - \boldsymbol{\omega}/\gamma|$. Clearly, $\theta = \pi/2$ for $\boldsymbol{\omega} = \boldsymbol{\omega}_0$ and Eqn (2) can be rewritten in the form

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \gamma \left[\boldsymbol{\mu} \times \mathbf{B}_1 \right]. \tag{3}$$

This means that the magnetic moment μ precesses around the vector \mathbf{B}_1 . Thus, in the classical formulation the implication of RCS is that the influence of the magnetic field \mathbf{B}_0 on the magnetic moment of a nucleus can be made arbitrary small when $\boldsymbol{\omega} \rightarrow \boldsymbol{\omega}_0 = \gamma \mathbf{B}_0$.

Passing to the quantum-mechanical representation in NQR, the quadrupole interaction Hamiltonian of a spin system can be written for $\mathbf{B}_0 = 0$ as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{Q} + \hat{\mathcal{H}}_{pr} + \hat{\mathcal{H}}_{DD} \,. \tag{4}$$

Here $\hat{\mathcal{H}}_Q$ is the Hamiltonian of quadrupole interactions, $\hat{\mathcal{H}}_{pr}$ is the Hamiltonian of interaction with the oscillating field $\mathbf{B}_1 \cos \omega t$, $\hat{\mathcal{H}}_{DD}$ is the Hamiltonian of dipole-dipole interactions. Passing on to RCS is accomplished by means of the unitary operator

$$\hat{U} = \exp(i\hat{A}t), \quad \hat{A} = \frac{1}{2}\omega\hbar\sum_{i}\left[\left(\hat{I}_{z}^{i}\right)^{2} - \frac{1}{3}\hat{I}(\hat{I}+1)\right].$$

The transformed Hamiltonian takes the form

$$\hat{\mathcal{H}}' = \hat{U}\hat{\mathcal{H}}\hat{U}^* = \frac{1}{2}\hbar(\omega_{\rm Q} - \omega)\sum_{i} \left[\left(\hat{I}_z^i\right)^2 - \frac{1}{3}\hat{I}(\hat{I} + 1) \right] \\ + \hbar\omega_1\hat{I}_x + \mathcal{H}_{\rm DD}', \qquad (5)$$

where the secular part of the Hamiltonian of dipole-dipole interactions \mathcal{H}'_{DD} commutes with the Hamiltonian $\hat{\mathcal{H}}_Q$. This transformation does effectively weaken the quadrupole interaction of nuclei and enhance the influence of terms $\omega_1 \hat{I}_x$ and $\hat{\mathcal{H}}_{DD}$ in NQR and may be referred to as transition to rotating coordinate system or representation of interactions. It should be noted that, unlike NMR, this procedure does not match a real mechanical rotation.

The concept of spin temperature was framed in NMR in application to the two-level spin system with dipole-dipole interactions. If this system is placed in a constant magnetic field $B_0 \gg B_{\text{loc}}$, where B_{loc} are the local magnetic fields created by adjacent nuclei, the gaps between energy levels can approximately be taken the same for all nuclei in the system. If the energy equilibrium is violated in some way, the spin system would return to the equilibrium state in a characteristic time $T_2 \sim (\gamma B_{\rm loc})^{-1}$. On this basis a special quantity $\theta_{\rm S}$ is introduced for the spin system and it represents the probability through the Boltzmann's distribution function $\exp[E_i/(k\theta_S)]$ that the system is in the state with an energy E_i . By analogy with thermodynamics the quantity $\theta_{\rm S}$ was called spin temperature. In real crystalline bodies each nuclear system possesses its own spin temperature differing from the lattice spin temperature and tends to the latter with the time constant T_1 . Since spin-spin interactions are usually much stronger than spin-lattice interactions and, hence, $T_1 \gg T_2$, then the spin system can be regarded as temporarily isolated from the lattice (either of them can be in the equilibrium state with its own heat capacity and temperature).

Thus, let us consider an equilibrium two-level spin system in a magnetic field \mathbf{B}_0 . If the value of B_0 decreases to B'_0 in a time less than T_1 , the entropy of the spin system would not change. In this case the spin temperature lowers because the entropy is a function of the ratio B_0/θ_S . The spin temperature takes a new value $\theta_S = (B'_0/B_0) \theta_S$. If the induction of the field $B'_0 \approx 10^{-3}$ T is of the same order as those of internal magnetic fields, the spin temperature θ'_S could be lower for a while than the lattice temperature θ_L . In zero external field the spin system comes to equilibrium with the lattice in a time T_{1D} and the latter is always smaller than the time T_1 in strong magnetic fields (subscript D means that the magnetic field is of the same level as internal fields that dipole moments of spins produce). The process of decreasing the spin temperature of a system is termed adiabatic demagnetization. This process is fully reversible: the system can be returned to the initial state by rapidly turning on the magnetic field B_0 . As we shall see later, adiabatic demagnetization plays an important part in experiments on double resonance.

4. Methods of double nuclear quadrupole resonance

It should be stressed that the double NQR techniques appeared not as replacements to direct methods but rather as their additions in situations when the latter failed to give adequate results. Historically, double resonance techniques developed simultaneously with direct pulse NQR methods, moreover, investigations were frequently made in parallel: one specimen was studied by direct method and by DNQR to cross-check the results.

Thus, the first method of double quadrupole resonance used initially as a special approach in observing the spectrum of ²³Na in the single-crystal chlorate [11] (see above), was later enhanced by Hahn and coworkers who called it spin-echo double resonance (SEDR) [16]. The strong signal with high signal-to-noise ratio usually observed from nuclei ³⁵Cl, ⁵⁵Mn, ⁷⁹Br, ⁸¹Br or ¹²⁷I was used there as a reference one [17]. The essence of the method is as follows. Three pulses are applied to a specimen with quadrupole nuclei of two kinds A and B (Fig. 2): 90° -180°-pulses with carrier of the A resonance frequency and, simultaneously with the second pulse of the first pair, another 180°-pulse but with resonance frequency carrier pertaining to B nuclei. If the second frequency coincides with ω_B for the absorption line of B-spins, the amplitude of echo signal from A nuclei is smaller than in the case of ordinary two-pulse program because the 180° B-pulse inverts the local dipole magnetic field and, thus, changes the phase of precession for A nuclei. This bears witness to resonance energy absorption by B system. In this case the gain in sensitivity in comparison to the direct observation of NQR with B nuclei is expressed by means of the formula [17]:

$$\frac{\Delta V_A}{V_B} = \frac{1}{e} \frac{\mu_A \omega_A \gamma_A^2 \langle \Delta \omega_{AB}^2 \rangle}{\mu_B \omega_B \gamma_B^2 \langle \Delta \omega_{AA}^2 \rangle} , \qquad (6)$$

where ΔV_A is the decrement of amplitude of echo signal from nuclei A, V_B is the amplitude of signal with nuclei B, μ_A and μ_B are the magnetic moments of nuclei A and B, $\langle \Delta \omega_{AB}^2 \rangle$ is the second moment of the absorption line of A nuclei resulting



Figure 2. The scheme of an experiment on spin-echo double resonance.

from their interaction with *B* nuclei; $\langle \Delta \omega_{AA}^2 \rangle$ is the second moment of nuclei *A*. It follows from formula (6) that the greater the difference between the resonance frequencies of *A* and *B* nuclei, the higher is the sensitivity. In addition, *B* nuclei should have half-integer or integer spin but for $\eta \approx 0$. Otherwise their dipole-dipole interactions with *A* spins will be weak and the second moment $\langle \Delta \omega_{AB}^2 \rangle$ in the numerator in formula (6) reduces to zero with an accuracy of the first order of the perturbation theory. This is none other as the familiar effect of 'quenching' of dipole-dipole interactions between integer and half-integer spins in solids [18]. The linkage between two nuclear systems can be enhanced for integer spins of *B* at $\eta > 0$ by application of an external constant magnetic field B_0 . However, in polycrystalline samples this leads to an undesirable broadening of resonance lines.

The resolution of double spin-echo resonance depends generally on the width of the absorption line of *B* nuclei and it is high for single crystals. The range of applicability of the method, thanks to its high sensitivity restricted only by the signal-to-noise ratio in system *A*, extends to a variety of nuclei with half-integer spins. For example, NQR was exhibited by ²³Na, ³⁹K, ⁴¹K, ¹³³Cs, ⁸⁵Rb, ⁸⁷Rb nuclei in different chlorates [16], etc. It is also possible to study integer spins, including those of deuterium for $\eta \sim 0$, i.e. in the case of degenerate energy levels. Unfortunately, the case of major practical importance, when $\eta > 0$, goes beyond the scope of SEDR unless the sample is a single crystal.

The alternative research line in double resonance is presented by the technique based on steady radio-frequency irradiation of sample. Under the name of steady doublequadrupole resonance in rotating coordinate system it was initially used to observe NQR of isotopes ³⁹K, ⁴⁰K, ⁴¹K in chlorates [19]. The major characteristic feature of this technique consists in application of two steady radio-frequency fields to the spin system in such a way that the frequency $\omega = \omega_A + \Delta \omega$ of the first field $B_{1A} \cos(\omega t)$ differs by the detuning $\Delta \omega$ from the resonance frequency of A nuclei and the frequency of the second field $B_{1B}\cos(\omega_B t)$ coincides with the resonance frequency of *B*-spins. The field B_{1A} provides for establishing the equilibrium nuclear magnetization along the effective field vector in system A. The field B_{1B} brings about heat exchange between A- and B-spins in the equilibrium system provided that

$$\alpha_A \gamma_A \mathbf{B}_{1A} = \alpha_B \gamma_B \mathbf{B}_{1B} \,, \tag{7}$$

where $\alpha = \sqrt{I(I+1)} - m(m-1)$. The duration of thermal contact is limited by the time of cross-relaxation. Therefore, the phase of the field B_{1B} is periodically changed by 180° to provide for continuous heating of A spins [20]. If the frequency ω_B coincides with one of the quadrupole transitions in *B*-nuclei, the magnetization of system A in RCS decreases. This decrease exhibited by the change in the absorption signal of NQR from A nuclei does indicate that the resonance has occurred.

The sensitivity of the double steady method versus that of the direct pulse NQR on *A*-nuclei is determined by the expression

$$\sigma = \sigma_{\text{pulse}} \, \frac{B_{1A}}{2\sqrt{B_{1A}^2 + B_{\text{loc}}^2}} \, \frac{T_{1A}}{T_{1A} + T_{AB}} \,, \tag{8}$$

where T_{AB} is the cross-relaxation time for systems A and B; B_{loc} is the total induction of local magnetic fields. The peak

value is attained for the detuning $\Delta \omega = (B_{1A}^2 + B_{loc}^2)^{1/2}$. Thus, the sensitivity of the method is sufficient to study many isotopes of uncommon quadrupole nuclei [21, 22]. The serious drawback of steady double resonance is that high stability and switching rate are difficult to realize for a powerful radiofrequency magnetic field. It should also be stressed that the major obstacle to the widespread employment of the two methods we considered is a limited number of chemical compounds, in one sample of which there is, along with Bnuclei of interest, a second quadrupole system A with strong resonance signal. Therefore, we concentrate our attention on a more widespread version of DNQR, which is the double nuclear-magnetic nuclear-quadrupole resonance. In this method a weak quadrupole signal from B-nuclei is recorded by a change in strong signal from magnetic nuclei (usually, protons).

Double NMR-NQR methods are commonly classified by conditions wherein contact between systems A and B occurs [12, 13]. On this basis the following methods are distinguished:

1) DNQR in a strong magnetic field (in the rotating coordinate system);

2) DNQR in zero magnetic field (in the laboratory coordinate system);

3) DNQR in a weak magnetic field.

Depending on particular mechanism of intersystem thermal contact, these types of double resonance can be implemented in different ways that we are now going to consider.

1. Double resonance technique in a strong magnetic field, developed by Hartmann and Hahn [23], is the oldest one pertaining to double NMR-NQR. To arrange the experimental cycle, spin systems A and B are polarized in a constant external magnetic field \mathbf{B}_0 and retained there till magnetization reaches equilibrium. Then the sample is exposed to a radio-frequency field \mathbf{B}_{1A} perpendicular to \mathbf{B}_0 , with the same frequency as the resonance NQR frequency for system A in the field \mathbf{B}_0 : $\omega_A = \gamma_A \mathbf{B}_0$. The sample is irradiated for a time within which 90°-pulse lasts ($\gamma_A B_{1A} \tau = \pi/2$). In the coordinate system rotating around the vector B_0 with the angular frequency ω_A , the magnetization vector \mathbf{M}_A for A-spins precesses about the effective field vector \mathbf{B}_{eff} . After cessation of a pulse, the phase of the radio-frequency field is changed by $\pi/2$ and \mathbf{M}_A becomes parallel to the field \mathbf{B}_{1A} preventing the decay of magnetization of A-spins with the time constant of spin-spin interaction T_{2A} . This phenomenon was called spinlocking in RCS. For times less than the spin-lattice relaxation time T_{1A} , spin temperatures θ_A of A-system in RCS and laboratory system $\theta_{\rm L}$ are related by the expression

$$\theta_A = \frac{\theta_{\rm L} B_{1A}}{B_0} \,. \tag{9}$$

Since $B_{1A} \ll B_0$, the temperature θ_A is much less than temperature θ_L (i.e. A-spins cool down as a result of spinlocking in RCS). Following this adiabatic demagnetization, the sample is exposed to the second radio-frequency field B_{1B} (Fig. 3) perpendicular to B_0 . This field provides a thermal contact between systems A and B. The radiation frequency correlates with the level splitting of the quadrupole system $\Delta E_B = \hbar \omega_B$. Using the equation for spin magnetization along the radio-frequency magnetic field

$$M_B = \frac{CB_{1B}}{\theta_B} \,, \tag{10}$$



Figure 3. The scheme of radio-frequency irradiation of the sample in the experiment on double resonance in a rotating coordinate system.

where $C = \gamma_B \hbar I (I+1) N_B / (3k)$ is the Curie constant, *I* is the spin of a *B* nucleus, N_B is the number of *B*-spins in the sample, k is the Boltzmann's constant, and considering the initial zero value of the system magnetization along the \mathbf{B}_{1B} direction, we can conclude that the spin temperature θ_B in RCS is infinitely large [12]. The \mathbf{B}_{1B} amplitude is calculated by means of formula (7) with allowance made for approximate equality between the energy level splittings for systems A and B in RCS. The last expression is called the Hartmann-Hahn condition. The phase of the field \mathbf{B}_{1B} is periodically changed by 180° to ensure an efficient energy transfer after the spin temperature equalization in both systems as a result of dipoledipole interactions. The spin temperature θ_B goes then negative and system B gets 'hotter' than system A. After completion of the radio-frequency irradiation with the pulse B_{1B} , second 90°-pulse B_{1A} is applied to record the decaying residual magnetization of the system. The drop of free induction allows information on the change in temperature of A-spins and on the onset of quadrupole nuclei resonance to be gained.

Thus, in comparison with the previous technique, the experiment of Hartmann and Hahn shows that the sample dwells all the time in a steady magnetic field B_0 , parameters of which affect the 'reference' signal of A-system. The sensitivity of the method is given by the equation [13]:

$$\sigma = \frac{\sigma_A}{e} \left[1 - \exp\left(-\frac{T_{1A}}{T_{AB}}\right) \right],\tag{11}$$

where σ_A is the signal-to-noise ratio in detection of NMR signal of system A, T_{1A} is the spin-lattice relaxation time for system A in RCS; T_{AB} is the cross-relaxation time for A and B systems; e is the charge of an electron. It follows from formula (11) that the sensitivity of DNQR in a rotating coordinate system is independent of the NQR frequency and also that it is greater by several orders in magnitude than spin-echo double resonance (in this conclusion we regard to the ratio T_{1A}/T_{AB}). The resolution is limited here by the line broadening because of interaction between systems A and B and it is equal to $\Delta\omega_B \approx (2-10) \Delta\omega_A$.

The capabilities of this method allows it to be used for high-sensitive investigations of NQR on nuclei 2 H, 7 Li, 23 Na, 43 Ca with the natural contents of isotopes [24 – 26, 13, 14].

The major drawback of this variety of DNQR is the obligatory use of single-crystal samples with large spin-lattice relaxation times since the experiment is conducted in a constant magnetic field \mathbf{B}_0 .

2. Method of double nuclear resonance in zero magnetic field (in laboratory coordinate system) developed by Redfield [27], Slusher and Hahn [28] contributed to the extension of the 'magnetic field cycling' technique of Ramsey and Pound [29] to investigations of NQR. In this case the steady magnetic field \mathbf{B}_0 is used for adiabatic demagnetization of spin system A when the field intensity is rapidly decreased to the level of the internal magnetic field B_{loc} in the specimen. The process of periodical change of the external magnetic field intensity from the steady value B_0 to B_{loc} during the experiment is referred to as cycling. Thus, the experimental cycle include the following steps (Fig. 4): the sample is held in the field B_0 till the magnetization of system A reaches equilibrium; the field B_0 is adiabatically decreased by switching it off (or by moving the sample to the region where the field is lacking) and, as a result, the spin temperature θ_A drops; the sample is irradiated by the radio-frequency field \mathbf{B}_{1B} and system A and B are brought into thermal contact; the field \mathbf{B}_0 is applied once again and the residual magnetization of A-spins is measured (usually, by the induction signal after the 90°-pulse \mathbf{B}_{1A} at the NMR frequency). Clearly, the interaction of two spin systems can take place when the Hartmann-Hahn condition is satisfied. In this case B_{loc} plays the role of B_{1A} . However, the intensity B_{1B} should be rather high (of order 10^{-2} T) and this leads to a significant NQR-line broadening. Therefore, this method is rarely used in this variant.



Figure 4. The general scheme of an experiment on double resonance in a laboratory coordinate system: τ is the duration of radio-frequency irradiation of the quadrupole system.

Systems A and B are brought into contact through

- thermal mixing in the zero external magnetic field [30];
- solid-effect mechanism (DRSE) [31];

 irradiation at frequencies of coupled multiplets (DRCM) [32].

Each of these methods has its own peculiar features. In the case of thermal mixing the radio-frequency field \mathbf{B}_{1B} is modulated in frequency:

$$\omega = \omega_B + \Delta\omega \cos(\Omega t) \tag{12}$$

or in phase (at a frequency of $\alpha_A \gamma_A B_{1A}$ (7)). Here $\Omega = (3\gamma_B^2 B_{1B} + \Delta)^{1/2}$, $\Delta \omega = (\langle \Delta \omega_{AB}^2 \rangle)^{1/2}$, Δ is the inhomogeneous NQR-line broadening, B_A is the inverse spin temperature, ω_B is the frequency of one of the NQR transitions. The action of the field leads to the establishment of a contact between systems A and B and this contact is spoken of as thermal mixing. If the frequency ω_B matches one of the NQR transitions, the spin temperature θ_A changes significantly and the decrement of the induction signal in the field **B**₀ provides an indirect information on the energy absorption by *B*-spins.

Since systems A and B are in continuous contact throughout the time when the sample is irradiated by the field B_{1B} , the method is highly sensitive. For $T_{1B} > T_{AB}$ and high spindiffusion rate the latter equals [33]:

$$\sigma = \frac{\sigma_A}{e} \left[1 - \exp\left(-\frac{T_{\rm 1D}}{T_{AB}}\right) \right]. \tag{13}$$

This makes it possible to detect low-frequency NQR transitions in nuclei such as ¹⁷O, ³⁹K, ⁹⁵Mo, ⁹⁷Mo with natural contents [34, 35]. Unfortunately, nuclei with integer spins cannot be subjected to above procedure because dipole-dipole interactions between systems *A* and *B* are suppressed in zero magnetic field. Thermal mixing has also the following limitation: the sample must be irradiated by a high-intensity field \mathbf{B}_{1B} for small γ_B and this leads to NQR-line broadening and, in some cases, to direct proton absorption in the frequency range $\omega < 0.5$ MHz.

Partly, the cited limitations can be overcome using solideffect [36]. This effect manifests itself in additional transitions at frequencies $\omega_B \pm \omega_A$, where ω_B and ω_A are the resonance frequencies of systems *A* and *B*. These simultaneous transitions in quadrupole and magnetic systems are induced by dipole-dipole interactions in the sample and they provide intensive energy exchange to the point of total demagnetization of *A*-spins. The probability of a solid-transition is equal to

$$W = \frac{\omega_{1B}^2}{\Delta\omega_A} \frac{4\Delta\omega_{AB}^2}{\omega_A^2} , \qquad (14)$$

where $\omega_{1B} = \gamma_B B_{1B}$ is proportional to B_{1B}^2 . To this connection the efficient thermal contact between systems *A* and *B* is attained by the choice of the optimal value of the irradiating field B_{1B} [37]. From the quantum-mechanical standpoint the solid-effect occurs because energy states of spins mixes as a result of dipole-dipole interactions between systems *A* and *B*. The possibility of exciting the solid-transitions depends on the ratio of relaxation times in a particular sample. Especially, the inequalities $\omega_+ T_{1D} \ge 1$ and $\omega_+ T_{1B} \leqslant 1$, where $\omega_+ = \omega_B + \omega_A$, must hold. The last inequalities can be considered as the conditions for solid-transitions to occur. Additional transitions appear in double resonance spectra as a distinctive

multiplet structure of NQR lines and they can cause significant line broadening. Generally the resolution of the method is determined by the width of the proton resonance which is close to $\Delta \omega_A \ge \Delta \omega_B$.

The major advantage of DRSE is its high sensitivity. It is by $(N_A\gamma_A)/(N_B\gamma_B)$ times more sensitive than the direct method. Moreover, both the nuclei with half-integer spins and nuclei with integer spins can be investigated [38] (for example, nitrogen ¹⁴N in polycrystalline samples [39, 40]). At the same the dependence of the method sensitivity on the suppression of dipole-dipole interactions makes it impossible to attain the estimated magnitude of the sensitivity for integer spins in zero magnetic field. Usually the sample is irradiated by the field **B**_{1B} in a weak auxiliary field $B_0 \simeq 10-50$ G and this brings about an additional NQR-line broadening. Besides, the DRSE technique is not applicable to samples with large times T_{1B} [41] and to nuclei, whose quadrupole transitions occur at frequencies lower than 200 kHz, in the region of direct proton absorption.

In double resonance with coupled multiplets [42] the sample is simultaneously irradiated at two frequencies in zero magnetic field. The detuning $\omega_{2B} - \omega_{1B}$ is of the order of $\Delta \omega_{AB}$ for protons in the nearest neighbourhood of nuclei *B* with which they form dipole multiplets. The radio-frequency field **B**₁ saturates the quadrupole system at one of the NQR frequencies while the field **B**₂ provides an intensive thermal contact between systems *A* and *B*. The action at frequencies ω_{1B} and $\omega_{2B} = \omega_{1B} + \omega_A$ brings about a decrease in the inverse temperature β_A in comparison with its initial value $\beta_{\text{loc}} = \beta_0 B_0 / \beta_{\text{loc}}$ and, thus, this phenomenon is equivalent to the solid-effect at the frequency ω_+ with continuous irradiation of quadrupole nuclei. The sensitivity of the method can be calculated from formula (13), where

$$T_{AB}^{-1} \simeq \frac{N_B}{N_A} \frac{\omega_{\rm 1D}}{\Delta \omega} \left(\frac{\Delta \omega_{\rm D}}{\Delta \omega_A} \right)^2, \tag{15}$$

here N_B , N_A are the numbers of relevant nuclei in the sample; $\Delta\omega_{\rm D}$ is the frequency difference in a dipole multiplet. Thanks to two-frequency saturation the sample can be irradiated by weaker fields than in the case of thermal mixing without any loss in overall sensitivity. This makes it possible to study polycrystalline samples with low natural content of an isotope [42], including ¹⁷O nuclei [43]. The resolution of the DRCM is specified by the quantity $\Delta\omega_{\rm D}$ and it is comparable with that of the solid-effect technique.

In addition to previous cases, in zero external magnetic field over the frequency range $\omega_{1B} \leq 200$ kHz the interaction between systems *A* and *B* can proceed subject to continuous thermal contact [44]. The nature of this phenomenon is very simple: direct dipole-dipole interactions lead to energy absorption by system *A* in a wide frequency range and any pair of quadrupole levels with an appropriate gap between them can continuously exchange energy with protons in the course of irradiation. The intensity of continuous thermal contact depends on degree of overlapping the absorption spectra of nuclei *A* and *B* in zero magnetic field [45]. The method that relies on this effect can be used for detecting the low-frequency transitions of light nuclei (see the next section).

3. Double resonance in a weak magnetic field possesses the most universal method among DNQR since it is efficient for studying half-integer as well as integer spins. In contrast to the above techniques the sensitivity of which is weaker for nuclei with integer spins in zero external fields, this method exploits the stronger interaction between systems A and B in a certain intermediate field $B'_0 \gg B_{loc}$, while quadrupole systems are exposed to radio-frequency irradiation in the absence of B'_0 in order to prevent the line broadening of ω_B and resolution decrease [13]. In the process of adiabatic demagnetization accomplished by cycling the magnetic field B_0 , a moment comes at its certain value when the Zeeman splitting of the proton system becomes equal to one of the quadrupole frequencies ω'_B : $B'_0 = \omega'_B / \gamma_A$. The energy level equalization in two systems brings about heat exchange between them as a result of spin-flip transitions induced by dipole-dipole interactions. Similar contact is reproduced upon switching on the field \mathbf{B}_0 . The method that relies on this process of interaction of quadrupole and magnetic systems of the sample is referred to as double resonance with level crossing (DRLC) [46]. The cross-relaxation proceeds for a time $\tau_{\rm cr}$ when the interaction condition $\omega_A \simeq \omega'_B$ is satisfied. Since the adiabatic switching rate for the magnetic field B_0 must comply with the expression $dB_0/dt \ll \gamma_A B_{loc}$, then the limiting value τ_{cr} is restricted to the ratio $\Delta \omega_A / \omega_{A0}$, where $\omega_{A0} = \gamma_A B_0$. Multiple cross-relaxation is also possible when $n\omega'_B \simeq m\omega'_A$, where *n*, *m* are the integers, but the probability of such process is much lesser. For n = m = 1 we have $\tau_{\rm cr} \simeq \Delta t (\Delta \omega_A / \omega_{A0})$, where Δt is the time for which ω_{A0} decreases to $\omega_{\rm D} = \gamma_A B_{\rm loc}$. Level crossing leads to equalization of spin temperatures in systems A and B. In this case magnetization of A-spins is partly transferred to 'hotter' Bspins and, as a result, quadrupole system usually cools down. The sample is subsequently exposed to radio-frequency radiation \mathbf{B}_{1B} in the zero external magnetic field and if frequency coincides with the resonance frequency ω_B of a certain transition in the *B*-system then the level populations of the latter equalize and B-spins heat up. On return of the sample to the field \mathbf{B}_0 , level crossing occurs in the opposite order. The heated B-system gives a part of its energy to Aspins, thus decreasing their polarization and causing additional heating. If the radiation frequency does not match the resonance ω_B , the state of the *B*-system as well as the inverse spin temperature β_A would not change. The resultant temperature β_A is determined in the field \mathbf{B}_0 by the induction signal amplitude after the 90°-pulse application at a frequency of ω_{A0} .

For long relaxation times T_{1A} and T_{1B} the level-crossingprocess can be repeated multiply for one cycle of retuning the frequency ω_B [13]. To this end an intermediate magnetic field B'_0 is superimposed as a meander with a frequency of about 10 Hz in such a way that the condition $\omega_0 \simeq \gamma_A (B_0^{\prime 2} + B_{loc}^2)^{1/2}$ is satisfied; and the irradiation by the field B_{1B} is performed in fields B_{loc} (Fig. 5). The sensitivity of the method is given by the expression $\sigma_B = \sigma_A (\Delta M/M_0)$ (ΔM is the change of the residual proton magnetization due to saturation of the quadrupole transition at the end of the experimental cycle) and it is usually by two or three orders in magnitude greater than the sensitivity of direct NQR. Particularly, the advantage of DRLC is that its sensitivity remains practically the same as the detected frequency decreases down to very low values. This makes it possible to apply this method to studying light nuclei with small quadrupole moments. In fact the quantity σ_B depends on the values of T_{1B} , T_{1D} , N_B/N_A [13, 26] and in this particular case it is a maximum for $T_{1B} \gg \tau_{\rm irr}$, $T_{1D} \ll \tau_{\rm irr}$ and it is a minimum for $T_{1B} \ll \tau_{irr}$, where τ_{irr} is the time for which quadrupole system is exposed to radio-frequency radiation in local fields. In consideration of DRLC we



Figure 5. The scheme of experimental cycle with multiple level crossing.

presumed that the cross-relaxation occurs only when B_0 changes; however, it is possible for integer spins (for example, when I = 1) with a small asymmetry parameter that $\omega_0 \leq \gamma_A B_{\text{loc}}$ throughout the time τ_{irr} . In this case the method is naturally goes into the double resonance method with continuous thermal contact [45].

Intensities of detected spectral lines depend heavily on population ratios for levels in *B* systems. On application of a magnetic field to the sample, however, quadrupole frequencies change and, for specific values of B'_{0i} , levels of NQR intersect. Mixing of NQR levels brings about a disorder in their crossings with the magnetic levels of system *A* and, subsequently, to redistribution of spectral line intensities. The last effect is especially strong in multilevel systems and this is one of the drawbacks of the method. The second drawback offers a low sensitivity for nuclei with integer spins, not having direct bonds with protons.

However, advantages of the method is more important than its drawbacks. DRLC is used to study half-integer and integer spins in polycrystalline samples with nuclei of ²H, ⁷Li, ¹⁰B, ¹⁴N, ¹⁷O, ²³Na [47–50], etc., as a universal high-sensitive method with high resolution (the last parameter depends on the linewidth $\Delta \omega_B$ for small radio-frequency radiation levels in zero external magnetic field).

We considered the main types of double NMR-NQR. Sometimes several other methods are used for indirect detection of nuclear quadrupole resonance. Among them are double resonance with selective pulses (DRSP) [51] used to record low-frequency spectra of NQR [52 – 54]; method of cross-relaxation spectroscopy [55] ensuring high sensitivity for a characteristic time $T_{1A} \ge T_{1B}$ and used to detect NQR signals from nuclei ¹³⁷Ba [56], ³⁵Cl [57], ¹⁴N [58], etc. It should be stressed that the spin-echo double resonance possesses the highest sensitivity while DRLC and DRSP have the greatest resolution (comparable with that of direct NQR methods).

The choice of the experimental double-resonance technique is based on information about parameters of nuclei to be studied and about the properties of a particular sample. Optimal conditions for experiment are determined with regard to the spin-lattice relaxation times T_{1B} , T_{1A} and T_1 of quadrupole and proton systems, respectively. The time T_{1A} depends on temperature in very complex fashion, therefore, preliminary study is usually performed to minimize this time in order to reduce the cycle duration t_c . The time is considered to be optimal when $t_c \gtrsim T_{1A}$. At the same time the spin-lattice relaxation time in zero external magnetic field T_{1D} for an operational temperature chosen should not be very small. If it is less than the switching time for the magnetic field B_0 in the course of adiabatic demagnetization, i.e. $T_{1D} \lesssim \Delta t$, then DNQR is impossible. The ratio of times T_{1B} and T_{1D} defines the mechanism of interaction between systems A and B. Frequently, several effects superimpose. The following typical cases can be distinguished:

(1) $T_{1B} \ll T_1$ and either solid-effect or thermal mixing dominates;

(2) $T_{1B} \gg T_1$ and proton system is polarized as a result of level crossing (DRLC dominates, resolution in a spectrum is at maximum);

(3) $T_{1B} \sim T_1$ and the system contact occurs through superposition of DRSE and DRLC effects.

Measurements of T_{1A} are usually conducted using a saturation technique. To this end the time interval τ between 90°-pulses in the NMR radiation sequence is determined, for which the magnetization of the sample is $\mathbf{M} = 0.63 \,\mathbf{M}_0$, where \mathbf{M}_0 is the steady-state magnetization. The time T_{1A} is found from the relation [13]:

$$\mathbf{M} = \mathbf{M}_0 \left[1 - \exp\left(-\frac{\tau}{T_{1A}}\right) \right].$$
(16)

The value of T_{1D} can be calculated from the dependence of the M amplitude on the time τ' for which the sample holds in zero field without irradiation:

$$T_{\rm 1D} = \frac{\tau_2' - \tau_1'}{\ln(M_1/M_2)} \,. \tag{17}$$

The accuracy of the last measurement is rather low (about 20%) due to the influence of level crossing on the magnetization. Therefore, this estimate can be used only for evaluation purposes.

The quadrupole system relaxation is generally described by several times T_{1B} [2]. There are 2*I* and I - 1/2 relaxation times for integer and half-integer spins, respectively. It is usually impossible to measure T_{1B} for most light nuclei with the aid of direct NQR because of small signal-to-noise ratio. To this connection the experimental conditions for DNQR are chosen using the measurement technique based on adiabatic demagnetization [59]. It was initially used to determine relaxation times with nuclei of nitrogen ¹⁴N [60]. The sample is adiabatically demagnetized and it is then retained in zero external field for a time τ_i and irradiated by the reading 90°-pulse at the resonance frequency of the quadrupole system. The spin-lattice relaxation time is found from the relation

$$I = I_0 \exp\left(-\frac{\tau}{T_{1B}}\right) + I_\infty , \qquad (18)$$

where I, I_0 , I_∞ are the induction signal amplitudes for $\tau = \tau_i$, $\tau = 0$ and τ_∞ , respectively. This method was used by the authors, for example, to determine T_{1B} for ²H nuclei in polycrystalline samples. The measurement error was about 10%. We failed to detect signals from ⁶Li nuclei because of the small signal-to-noise ratio.

One of perspective lines in expanding the possibilities of DNQR is to combine it with a two-frequency technique [15]. In Ref. [61] the authors showed for nuclei of nitrogen ¹⁴N that the intensity of a detected line v_{-} can be increased by

simultaneous saturation at the frequency v_0 . And vice versa, the intensity of the line v_0 increases when the transition v_- is simultaneously saturated. In this way the sensitivity of DNQR can be increased four times. At the same time an additional irradiation of the sample at the v_+ frequency pertaining to one of the nonequivalent positions of a nucleus in the crystal leads to the situation in which all other spectral lines of NQR are detected on a weaker level. The signal intensities of other nonequivalent positions are unchanged in this case. The last property does not affect the sensitivity of the method but it can be used for qualifying resonance lines in complex spectra of NQR as emitted by a nucleus in the nonequivalent position [62].

5. Investigation of light quadrupole nuclei with integer spins by DNQR

Among eighty eight quadrupole nuclei there are only seven with integer spins. ¹⁴N and ¹⁰B nuclei are most extensively studied by DNQR methods [14, 63, 15] since they are widely used in industrial chemical compounds. Nuclei ²H and ⁶Li presents the major complexity for the method owing to smallness of their EFG tensors and because of low natural abundances (0.015% and 7.2%, respectively). NQR signals from these nuclei are very weak and, as a result, absorption lines cannot be detected directly even for a large number of stored signals. The location of spectral lines of deuterium and lithium in the direct proton absorption area (≤ 200 kHz), apart from the effect of suppression of dipole-dipole interactions, also contributes to the complexity of study. At the same time these experiments provide a unique opportunity for studying electronic structure of molecules. In particular, EFG of deuterium with a shell consisting of a single 1selectron and exhibiting high-energy excited states depends essentially on changes in electron densities of neighbouring atoms in the molecule. This makes it possible to use the EFG as a sensitive indicator of the change in electron density of molecules, presence of hydrogen bond, etc.

There are several ways to enhance the sensitivities of the main DNQR techniques in detecting weak signals for integer spins [15, 44, 50, 61]. In particular, double resonance with level crossing can be made more efficient in studying nuclei with integer spins and without direct proton bonds by using an auxiliary 'selective' field [64]. In this case the sample is held throughout establishing/removing the field B_0 for a time $\Delta t \simeq (3-5) T_{AB}$ in constant magnetic field $B'_0 = \omega_B / \gamma_A$, the intensity of which matches the energy exchange condition for systems A and B and retunes with a change in the frequency of irradiation of quadrupole nuclei. In this context the term 'selective' refers to preferential action of the field B_0 onto the spin system. The prolongation of contact between systems A and B when ω_B and the frequency of one of the quadrupole transitions coincide makes it possible to get a stronger signal of NQR. This technique can be realized with the use of an additional solenoid through which the sample will go when it is mechanically moved out of the field \mathbf{B}_0 into zero field [64]. The only difficulty is that the field \mathbf{B}_0' must be retuned in synchronism with the high-frequency field in each experimental cycle.

However, the use of a selective field does not eliminate the drawbacks of the method when studying superlight nuclei with low natural content. The sensitivity of DRLC is limited by the ratio of resonant spins in systems *A* and *B*. The number of 'spin-flip' transitions in the course of irradiation of

quadrupole nuclei cannot exceed the total number of *B*-spins and is limited by the degree of *B*-system polarization in the process of proton magnetization. Until energy level equalization, *B* nuclei can make only a fixed number of 'spin-flip' transitions. Therefore, detection of NQR spectra by the level-crossing method becomes already inefficient when the content of quadrupole nuclei is less than 10% of the total number of protons in the sample. In most cases, it is also impossible to get use of advantages of double resonance solid-effect in studying ²H and ⁶Li because of large spinlattice relaxation times in the system of *B*-spins.

The best technique in this case is shown by the double resonance with a continuous thermal contact [45, 65]. It prolongs the energy exchange between spin systems A and B to the extreme point of polarization decaying. The intensity of absorption of radio-frequency field energy by a system of dipoles with magnetic dipole-dipole interactions between them is equal in zero external field to

$$I = hv \,\frac{hv}{k\theta_{\rm S}} f(v) \,B_1^2\,,\tag{19}$$

where v is the radiation frequency; B_1 is the amplitude of the irradiating magnetic field; hv is the energy delivered to the system; $hv/(k\theta_S)$ is the relative probability of absorption; f(v) is the matrix element of the distribution function. If a weak magnetic field \mathbf{B}'_0 is applied to the sample, the function f(v) peaks at the following frequencies: 0; $(\gamma_A/(2\pi))B'_0$; $2(\gamma_A/(2\pi))B'_0$; $3(\gamma_A/(2\pi))B'_0$, etc. Usually separate peaks of f(v) do not resolve for small $B'_0 < B_{\text{loc}}$ and there appears only a single line broadened into high-frequency range. As an example Fig. 6 shows spectra of proton absorption for dipole



Figure 6. A portion of the proton absorption spectrum for a common hexagonal ice (a) and for a crystal hydrate $MgCl_2 \cdot 10D_2O \cdot 2C_6H_{12}N_4$ (b) at 120 K.

reservoir placed in distilled water (a) and crystal hydrate $MgCl_2 \cdot 10D_2O \cdot 2C_6H_{12}N_4$ (b) at 120 K. The shape of absorption lines is approximated by the function $v^2 \exp(-v^2/(2\Delta^2))$, where $\Delta = 45 \text{ kHz}(a)$ and $\Delta = 40 \text{ kHz}(b)$.

Continuous thermal contact between systems A and B is made when the high-frequency portion of the function f(v) in the region of quadrupole transitions is high enough to establish a link between A and B system and at the same time it is small enough for the direct proton absorption to dominate. One way to provide these conditions is to irradiate the sample in advance by an auxiliary magnetic field \mathbf{B}_{1A} with a frequency of 50 Hz in zero static field $(B_0 = 0)$ and to saturate then one of the quadrupole transitions by the field \mathbf{B}_{1B} (Fig. 7a) [13]. In spite of the gain in sensitivity (by a factor of 1.5–3.5) with the preliminary heating of A-spins, the method discussed does not possess the required characteristics for studying ²H and ⁶Li nuclei when their concentrations are small.



Figure 7. Schemes of experiments for improving thermal contact between systems *A* and *B* with double resonance in a laboratory coordinate system in the cases of low-frequency irradiating (a) and constant magnetic (b) fields.

Better sensitivity is achieved when a weak constant magnetic field \mathbf{B}'_0 is applied to the sample in intervals between irradiations of the quadrupole system with the field \mathbf{B}_{1B} [65]. The former is modulated by sinusoidal sound-frequency half-waves (~ 20 Hz). The radio-frequency field B_{1B} acts in antiphase in the absence of \mathbf{B}_0 . Thus, *B*-spins are alternately heated up and brought in contact with protons (Fig. 7b). The value of \mathbf{B}'_0 is varied through the range $(0-20) \times 10^{-4}$ T to ensure intensive energy exchange. This technique is applicable to a variety of compounds with ²H in natural concentrations [65]. The major drawback of this method is the limitation on the intensity of radio-

frequency irradiation of quadrupole nuclei. In most cases the required level of the field is unattainable since the direct proton absorption becomes essential even for $B_{1B} \gtrsim 3 \times 10^{-6}$ T. Figure 8a shows the spectrum of ²H we obtained by this technique in water frozen down to 120 K with the 0.5% content of D₂O. The line patterns are distorted as a result of direct proton absorption. The transition at a frequency of v_0 was not detected.



Figure 8. NQR spectra of deuterium in a sample of hexagonal ice with the 0.5% content of ²H, detected with the use of the conventional double resonance technique with a continuous thermal contact (a) and with our method (b) at T = 120 K.

To eliminate the last drawback we propose another approach. With it the advantages of continuous linkage mechanism can be realized more fully. To this end the static field B_0 is modulated by rectangular sound-frequency pulses and alternated with pulses of static magnetic field B' perpendicular to \mathbf{B}_0 (i.e. in parallel to the axis of the radiofrequency coil \mathbf{B}_{1B}) (Fig. 9). The field \mathbf{B}' imposed in the course of irradiation of quadrupole nuclei eliminates (through the action on the proton system) the direct proton absorption in the case of strong \mathbf{B}_{1B} . Clearly, \mathbf{B}' must have the optimal value for each transition: if it is exceeded, the sensitivity of the method does not increase because of the spectral line broadening; if the value is not reached, the direct proton absorption prevents signal detection. The optimal value of B' can be determined by locating the extremum of the functional dependence of the type

$$F(B') = \frac{(W_B + W'_B) W_B^{-1}}{(W_A + W'_A) W_A^{-1}},$$
(20)



Figure 9. The scheme of experiment for detecting DNQR of integer spins in the low-frequency range.

where W_B and W'_B are the probabilities of transitions in a quadrupole system, W_A and W'_A are the probabilities of direct proton absorption in zero magnetic field and in the field B, respectively [66]. The maximal value of F(B') corresponds to the optimal value of B'. The function F(B') approaches unity as B' decreases to zero.

Formula (20) is applicable to different quadrupole nuclei irrespective of their spin *I*. The denominator of the right-hand side is generally given by the expression: $1 + \cos(\arctan B'/B_{loc})$. The numerator can be calculated with the perturbation theory to sufficient accuracy since the magnetic part of the Hamiltonian is small in this case $(\gamma_B B' \ll eQq_{zz})$.

In particular, if I = 1 and the asymmetry parameter is small ($\eta < 0.1$), the transition frequencies are [67]:

$$v_{1,2} \simeq 3K + (\eta^2 K^2 + D^2 \cos^2 \theta)^{1/2},$$

$$v_{1,3} \simeq 3K - (\eta^2 K^2 + D^2 \cos^2 \theta)^{1/2},$$
 (21)

where $K = eQq_{zz}$, $D = \gamma_B B'$ is the factor presenting the severity of exposure to the constant magnetic field; θ is the polar angle of the spherical coordinate system. The relevant probabilities of transitions in collinear fields $(\mathbf{B}_{1B}||\mathbf{B}')$ take the form

$$W'_{B1,2} \simeq W_{B1,3} \simeq D_1^2 \frac{(\eta^2 K^2 + D^2 \cos^2 \theta)^{1/2}}{D^2 \cos \theta},$$
 (22)

where $D_1 = \gamma_B B_{1B}$.

We obtained (22) by averaging over all possible directions of the vector \mathbf{B}' in the coordinate system pertaining to the principal axes of the EFG tensor. This result is valid for polycrystalline samples. If $\eta > 0.1$, the probabilities of transitions are as follows

$$W'_{B1,2} \simeq \frac{1}{2} D_1^2 \frac{\eta K(9 - \eta^2)}{9D^2(1 - \eta)\cos\theta},$$

$$W_{B1,3} \simeq \frac{1}{2} D_1^2 \frac{\eta K(9 - \eta^2)}{9D^2(1 + \eta)\cos\theta}.$$
(23)

It can be easily shown that the resonance transition in the spin system not perturbed by the field *B* is characterized in powder by the probabilities $W_{B1,2} \sim W_{B1,3} \sim D_1^2/3$. Thus, all terms in formula (20) are known.

The sensitivity of detection of nuclei with integer spins in a low-frequency range (≤ 200 kHz) can be increased through application of the last technique 100-fold in comparison with the DRLC. In addition, 'forbidden' v_0 transitions in the vicinity of the maximal proton absorption are also become accessible to observation. For comparison, Fig. 8b shows the spectrum of ²H for hexagonal ice enriched with deuterium $(0.5\% D_2O)$. This spectrum was taken using the last technique. The duration of the experimental cycle was 180 s, the time for which the sample was placed into auxiliary fields was 6 s, the field amplitude was equal to $B_{1B} = 5 \times 10^{-6}$ T. The spectrum of the complex $MgCl_2 \cdot 10D_2O \cdot 2C_6H_{12}N_4$ with hydrogen bond was taken similarly (Fig. 10). The detection of v_0 transitions makes it possible to uniquely classify lines as those of four nonequivalent positions of deuterium in the molecule.



Figure 10. The NQR spectrum of ²H in the complex MgCl₂ · 10D₂O · 2C₆H₁₂N₁₄ made by the scheme in Fig. 9 at T = 120 K. The duration of the cycle is 130 s; the time for which the sample is placed into zero field is 8 s; the field amplitude is $B_{1B} = 10^{-5}$ T.

As a compound with natural content of ⁶Li we used a sample of lithium phosphate LiH₂PO₄ \cdot H₂O. Figure 11b shows absorption lines after ten data storages. Figure 11a shows the same spectral range but the spectrum was taken using the conventional DRLC technique, all other factors being the same. The comparison testifies that the method is capable to increase the efficiency of DNQR signal detection for nuclei with integer spins in the low-frequency range.

Frequency shifts resulting from the action of static magnetic fields can be taken into account using formulae of the perturbation theory or numerical methods. In the latter case the solution to a secular equation is found for the specific nuclear spin. Since the consideration of the Zeeman effect in polycrystals requires averaging over angles θ and φ of the



Figure 11. DNQR spectra of ⁶Li in the sample LiH₂PO₄ · H₂O detected by the DRLC (a) and by our technique (b). The cycle duration is 90 s; the time for which the sample is retained in the zero field is 4 s; the field amplitude is $B_{1B} = 5 \times 10^{-6}$ T.

spherical coordinate system, we diagonalized matrices of spin Hamiltonian for I = 2;3 to simplify the problem. The coefficients of the resultant polynomials of fifth and seventh powers are cumbersome to be presented here; they may be found in [66]. These equations can then be solved easily using a standard program.

One of the most important tasks (for application purposes) is to improve methods of NQR detection with nuclei of nitrogen ¹⁴N. Successful works of Russian scientists [15, 7] have lead to significant advances in this field. In particular, methods of detection and remote monitoring of the presence of explosives [9, 10] were developed in the course of complex studies on local NQR [7] and on direct pulse method with a large coil. For the first time NQR was studied in the Tetryl and PETN explosives. Optimal frequencies for remote experiments were selected (for example, $\omega = 5192$ kHz in hexogen). As a result antitank mines and plastic explosives can now be detected remotely by the NQR method.

At present techniques for detection of narcotic drags by NQR are under development. American scientists have achieved a significant progress in this field. For example, 'Quantum Magnetics' (USA) manufactured appliances with irradiating coil of 170 litres in volume for monitoring frozen fish products. In Russia these studies are hindered now by the lack of funds.

The weak signal level of ¹⁴N in most explosives and narcotic drugs makes it necessary to use indirect methods of quadrupole resonance to find absorption lines and to establish spectral parameters. In this situation satisfactory results can be achieved by the use of various DNQR techniques and of cross-relaxation spectroscopy. In particular we detected spectra of ¹⁴N in cocaine (at room temperature) and in codeine phosphate by the DNQR method with auxiliary magnetic fields: $C_{17}H_{21}NO_4 - eQq_{zz} = 5081$ kHz, $\eta = 0.04$; $C_{18}H_{21}NO_3 \cdot H_3PO_4 - eQq_{zz} = 1207$ kHz, $\eta = 0.35$. In this way complex mixtures like 'hashish' and 'opium' were also studied. This made it possible to propose a number of recommendations on remote detection of narcotic drugs.

Clearly, further development of indirect techniques based on nuclear resonance would expand the range of applicability of NQR in topical applied problems.

6. Conclusions

In this article we considered the principal modifications of the indirect method for studying nuclear quadrupole interactions in solids. The emphasis was placed on comparison of features relevant to these techniques and on possibilities of their improving. As numerous investigations show, double NQR methods remain one of the perspective lines of studies in spite of a wide adoption of the high-resolution NQR technique. In many cases these methods are the only ones with which a perfect chemical analysis of complex industrial mixtures can be conducted, narcotic drugs and explosives can be found and identified, intermolecular structure of synthesized pharmacological preparations can be studied, etc.

The possibilities of DNQR have not been exhausted yet. Introduction of the latest radio-electronic developments into experiment, construction of new installations and modernization of old ones will undoubtedly expand the range of applicability of the method.

One of the perspective lines of inquiries is to conduct experiments combining magnetic field cycling and twofrequency excitation of spin systems. The use of crossrelaxation spectroscopy makes it possible to fill up the data obtained earlier in NQR studies.

It is extremely important to generalize and systematize incessantly experimental results through formation of mobile data-bases [68, 69] in which the main operational information about experiments have to be stored. The wide capabilities of methods of double nuclear quadrupole resonance will eventually justify the expenditure and hardship of organizing the experiments of this kind.

References

- Grechishkin V S Usp. Fiz. Nauk 69 189 (1959) [Sov. Phys. Usp. 2 699 (1959)]
- Grechishkin V S Yadernye Kvadrupol'nye Vzaimodeistviya v Tverdykh Telakh (Nuclear Quadrupole Interactions in Solids) (Moscow: Nauka, 1973)
- Semin G K, Babushkina T A, Yakobson G G Primenenie YaKR v Khimii (Application of Nuclear Quadrupole Resonance to Chemistry) (Moscow: Khimiya, 1972)
- 4. Dehmelt H-G, Krüger H Naturwiss. 37 111 (1950)
- Grechishkin V S, Ainbinder N E Usp. Fiz. Nauk 80 597 (1963) [Sov. Phys. Usp. 6 566 (1964)]
- Grechishkin V S, Ainbinder N E Usp. Fiz. Nauk 91 (4) 645 (1967) [Sov. Phys. Usp. 10 237 (1967)]
- Grechishkin V S, Sinyavskii N Ya Usp. Fiz. Nauk 163 95 (1993) [Phys. Usp. 36 980 (1993)]
- 8. Hirschfeld T, Klainer S M J. Mol. Struct. 58 63 (1980)
- 9. Grechishkin V S Appl. Phys. A 55 505 (1992)
- 10. Grechishkin V S Appl. Phys. A 58 63 (1994)
- 11. Herzog B, Hahn E L Phys. Rev. 103 148 (1956)
- Anferov V P, Grechishkin V S, Grechishkina S V Izv. Akad. Nauk SSSR Ser. Fiz. 42 (10) 2164 (1978)
- 13. Edmonds D T Phys. Reports 29 (4) 233 (1977)
- 14. Porte A L Ann. Rep. Prog. Chem. 80 149 (1983)

- Anferov V P, Grechishkin V S, Sinyavskii N Ya Yadernyi Spinovyi Rezonans: Novye Metody (Nuclear Spin Resonance. New Methods) (Leningrad: Leningrad State University, 1990)
- 16. Emshwiller M, Hahn E L, Kaplan D Physics 39 (3) 218 (1990)
- Kirchanov V S, Dresvyankin B V, Grechishkin V S *Izv. Akad. Nauk* SSSR Ser. Fiz. 42 (10) 2173 (1978)
- 18. Leppelmeier G W, Hahn E L Phys. Rev. 141 724 (1966)
- 19. Jones E P, Hartmann S R Phys. Rev. Lett. 22 867 (1969)
- 20. Jones E P, Hartmann S R Phys. Rev. B 6 757 (1972)
- 21. Ramachanran R, Narasimhan P T J. Mol. Struct. 111 53 (1983)
- 22. Goldburg W, Lee M Phys. Rev. Lett. 7 321 (1963)
- 23. Hartmann S R, Hahn E L Phys. Rev. 128 2042 (1962)
- 24. Walstedt R E, McArthur D A, Hahn E L Phys. Lett. 15 7 (1965)
- 25. Ragle J L, Sherk K L J. Chem. Phys. 50 3553 (1969)
- 26. Blinc R, in *Advances in Nuclear Quadrupole Resonance* (2) (London: Heyden, 1975) p. 71
- 27. Redfield A G Phys. Rev. 130 589 (1963)
- 28. Slusher R E, Hahn E L Phys. Rev. Lett. 12 246 (1964)
- 29. Ramsey N F, Pound R V Phys. Rev. 81 278 (1951)
- 30. Goldman M, Landesman A Phys. Rev. 132 610 (1963)
- 31. Seliger J et al. *Phys. Status Solidi* **25** 422 (1974)
- 32. Brosnan S G P, Edmonds D T J. Magn. Resonance 45 440 (1981)
- 33. Bleich H E, Redfield A G J. Chem. Phys. 55 5405 (4) (1971)
- 34. Poplett I J F, Smith J A S J. Chem. Soc. Faraday Trans. II (GB)77 761 (1981)
- Poplett I J F, Smith J A S J. Chem. Soc. Faraday Trans. II (GB) 77 1155 (1981)
- Anferova S V, Grechishkin V S, Sinyavskiĭ N Ya Izv. Vyssh. Uchebn. Zaved. Ser. Fiz. 28 (1) 110 (1985)
- Goldman M Spin Temperature and Nuclear Magnetic Resonance in Solids (Oxford: Clarendon Press, 1970) [Translated into Russian (Moscow: Mir, 1972)]
- 38. Anferova S V, Grechishkin V S Zh. Fiz. Khim. **5**7 2544 (1983)
- 39. Anferova SV, Grechishkin VS, Mozzhukhin GV Zh. Strukt. Khim.
- 27 (1) 55 (1986)
 40. Edmonds D T, Hunt M J, Mackay A L J. Magn. Resonance (USA) 9 66 (1973)
- 41. Beletski A et al. Pribory Dlya Nauchnykh Issledovanii 57 (3) 80 (1986) [Rev. Sci. Instrum. 57 (3) 393 (1986)]
- 42. Smith J A S J. Mol. Struct. 58 1 (1980)
- 43. Maragalit J, Shporer M J Magn. Res. 43 340 (1981)
- Grechishkin V S, Anferov V P, Sinyavskii N Ya, in Advances in Nuclear Quadrupole Resonance (5) (London: Heyden, 1983) p.1
- 45. Edmonds D T, Mailer J P G J. Magn. Resonance (USA) 26 93 (1977)
- 46. Koo Y C, Hahn E L Bull. Amer. Phys. Soc. 13 32 (1968)
- Day R O, Hadipour N L, Ragle J L J. Magn. Resonance (USA) 67 466 (1986)
- 48. Yukio H, Keiter E A, Broun T J. Magn. Resonance (USA) 67 202 (1986)
- Kunwar A L, Gutowsky H S, Oldfield E J. Magn. Resonance (USA) 58 359 (1984)
- Seliger J, Zagar V, Blinc R J. Magn. Resonance A (USA) 106 214 (1994)
- 51. Millar J M et al. J. Chem. Phys. 83 (3) 934 (1985)
- 52. Kreis R, Suter D, Ernst R R Phys. Lett. 118 160 (1985)
- 53. Zax D B et al. J. Chem. Phys. 83 (10) 4877 (1985)
- 54. Zax D B et al. Nature (London) 312 (5992) 351 (1984)
- 55. Goldman M C Seanc. Acad. Sci. Paris (246) 1058 (1958)
- 56. Mc Grath J W, Silvidi A A J. Chem. Phys. **36** 1496 (1962)
- 57. Nakamura S, Enokiya H J. Phys. Soc. Jpn. 18 183 (1963)
- Bavin P M G, Stephenson D, Smith J A S Z. Naturforsch. Teil A (Germ) 41a 195 (1986)
- 59. Anferov V P et al. J. Mol. Struct. 83 89 (1982)
- Anferov V P et al. Izv. Vyssh. Uchebn. Zaved. Ser. Fiz. 30 (7) 88 (1987)
- 61. Grechishkin V S, Anferov V P, in *Advances in Nuclear Quadrupole Resonance* (4) (London: Heyden, 1980) p. 71
- 62. Grechishkin V S, Mikhal'kov V M Zh. Fiz. Khim. 59 24 (1985)
- Safin I A, Osokin D Ya Yadernyi Kvadrupol'nyi Rezonans v Soedineniyakh Azota (Nuclear Quadrupole Resonance in Nitrogen Compounds) (Moscow: Nauka, 1977)
- 64. Anferov V P, Starovoitova O V Zh. Fiz. Khim. 63 (1) 225 (1989)

- 65. Edmonds D T, Mailer J P G J. Magn. Resonance (USA) **29** 213 (1978)
- 66. Anferov V P, Shpilevoi A A Dep. in VINITI No 824-B93 (1993)
- 67. Negita H J. Chem. Phys. 44 1734 (1966)
- 68. Chihara H The NQR-News Letter (2) 1 (1993)
- Grechishkin V S Izv. Vyssh. Uchebn. Zaved. Ser. Fiz. 36 (5) 121 (1993)