Remote nuclear quadrupole resonance in solids

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A theory is developed for remote nuclear quadrupole resonance (NQR) in solid dielectrics with transient remote excitation of crystals for various materials and various conditions of observation. Experimental studies are made to assess the possibilities of using remote NQR and NQR introscopy. Data are presented and recommendations based on theoretical and experimental investigations are formulated for the development of devices for various purposes.

1. INTRODUCTION

The successful remote detection of nuclear quadrupole resonance (NQR) signals from solids makes the method of remote NQR a promising one for applications in medicine (the detection of kidney stones), in agriculture (monitoring the distribution of fertilizer in the fields), the monitoring of technological processes in manufacturing, the search for and detection of hidden caches of explosives (mines) in the ground, in walls, and in baggage, the detection and identification of narcotics, the search for useful minerals, and so forth.

The conditions of observation of remote NQR with the use of transient methods of observation are quite different from NQR within the pickup coil. However, the absence of a theory of remote NQR and the lack of experimental studies of the optimization of remote detection of NQR have made it impossible to achieve progress in the development of the appropriate apparatus for many different practical applications.

Remote NQR is similar to the methods of NMR introscopy, which combine various means of spatial localization and mapping of NMR signals from inhomogeneous objects. In recent years NMR introscopy has been used successfully in physiological chemistry and in clinical practice, where the most important properties are its innocuous and unintrusive nature, and the sensitivity of the NMR signal to the state of the living tissue.

Unlike NMR, remote NQR does not require that a uniform static magnetic field be created in the object under study. On the other hand, because of the low intensity of the NQR signals and the necessity of working with solid materials, it is scarcely realistic to hope to obtain NQR images, and today we can only speak of obtaining NQR signals from relatively large regions of the sample, situated outside the pickup of the NQR spectrometer.

The literature contains discussions of the possibility of using nuclear quadrupole resonance for the analysis of materials that are located at short distances from the apparatus. What these authors have in mind is the case where the material is separated from the apparatus by nonmetallic opaque material: mines, explosives and narcotics in baggage, technological monitoring of the production of solid objects, the search for useful minerals, etc. Nuclear quadrupole resonance is able to distinguish nonequivalent sites of the nuclei; it gives a narrow spectral line, and it provides an unambiguous identification of the chemical compound.

To solve the problem of remote NQR it is necessary to develop the scientifically based, reliable, and unambiguous methods of remote determination of the main parameters of NQR of a solid for a wide range of conditions of observation.

The method of remote NQR implies that the signal is received from a sample that is located at a distance from the receiving apparatus of the spectrometer. This requires development of the theory of remote excitation of NQR by the transmitting system of the spectrometer and reception of the signal by the receiving antenna in the near zone.

One of the most severe drawbacks of NQR^{1-6,49} for remote investigations of matter is the low sensitivity, particularly at low frequencies, so that frequently the problem is to find the signal from samples that are placed within the coil of the spectrometer.

To implement remote NQR it is necessary to increase greatly the sensitivity of the spectrometer, which can be done by:

--reducing the noise level and interference pickup, etc, by the use of time gates and selective receiving coils;

---optimizing the signal accumulation time by the use of pulse sequences and automation of the measurements;

-the use of the techniques of Fourier spectroscopy, computer analysis of the experimental data, and correlation spectroscopy.

To study the possibility of remote NQR for obtaining NQR images it is essential to analyze theoretically and experimentally the various methods of introscopy by nuclear magnetic resonance where there is no strong polarizing magnetic field and the pure nuclear quadrupole resonance is observed.

The information content of remote nuclear quadrupole resonance can be enhanced by the use of two-dimensional, two-frequency NQR spectroscopy, which makes it possible to detect forbidden transitions, identify the nonequivalent sites of the nuclei in the crystal, and study dynamic processes in solids. The methods of cross-relaxation spectroscopy can be used to increase the sensitivity in the detection of lowfrequency NQR spectra.

2. OPTIMAL CONDITIONS FOR THE DETECTION OF REMOTE NOR

The excitation of the precession of ¹⁴N nuclei in nuclear quadrupole resonance when the sample is outside the oscillator circuit (remote nuclear quadrupole resonance)⁷⁻⁹ has its own peculiarities. Since the dimensions of the sample l are less than λ , where λ is the absorption wavelength, the radiation resistance R_{rad} of the sample is small, and therefore it is difficult to detect the reradiation outside the near zone. However, in the near zone the intensity of the radiation from the sample falls off as $1/r^3$ (Ref. 10), where r is the distance between the sample and the receiving antenna. On the other hand, the transmitting antenna (which excites the sample), can contain ferrite rods, which reduces its effective length to 1 m for an absorption wavelength of 60 m. Therefore the excitation antenna can operate in the intermediate zone (where the excitation field falls off as $1/r^2$), if the following condition is imposed on the boundaries of the sample:

$$\gamma B_1 t_{\rm w} = \pi/2, \tag{2.1}$$

where γ is the gyromagnetic ratio of the nitrogen nuclei, B_1 is the amplitude of the rf field in the pulse, and t_w is the pulse length. For a pulse power of 5 kW condition (2.1) can be satisfied at a distance of several meters from the excitation antenna.

An attempt to observe NQR of ¹⁴N in nitro groups in octogen and hexogen by the direct method of pulsed NQR, which is appropriate for remote detection, was unsuccessful. Therefore explosives planted in the ground, in walls, etc., can be observed by NQR for octogen, hexogen, and PETN only for cyclic nitrogen. Of course, the NQR spectra of the nitro groups would sharply increase the number of explosives that could be detected by this method. The NQR spectra (including from an enclosed space, like in boxes, letters, suitcases) makes possible a unique identification of the explosives and their mixtures.

The method of double NQR with only unilateral access to the sample (which is in the ground or a wall) is still difficult to implement, and therefore the NQR spectrum of trotyl and of NO_2 groups of hexogen and octogen are of importance in monitoring at airports, while the NQR spectra of cyclical nitrogen in hexogen and octogen makes it possible to detect explosives in a unilateral situation, i.e., with the use of surface rf coils.

Let us consider how a NQR signal is formed from a sample like the explosive material of a mine. In this case we consider a sample in the shape of a disk of height h and radius R, close in shape to an antitank mine. The rf pulse at the resonant frequency induces in the sample a nuclear magnetization M given by the expression

$$M = M_0 e^{-t/T_2} \cos \omega_0 t.$$
 (2.2)

The magnetic field created by the sample will be equivalent to the field that is created by the current of the circuit and a conducting ribbon of width h. The current will be equal to

$$I = M_0 h e^{-t/T_2} \cos \omega_0 t. \tag{2.3}$$

The magnetic induction created by the current I along the z axis, according to the Biot-Savart law, will be

$$B_{z} = \frac{20\pi IR}{(R^{2} + z^{2})^{3/2}} = \frac{20\pi M_{0}e^{-t/T_{2}}R^{2}h}{(R^{2} + z^{2})^{3/2}}.$$
 (2.4)

Since the volume of the sample is $V_s = \pi R^2 h$, then

$$B_{z} = \frac{20M_{0}e^{-t/T_{2}}V_{s}}{(R^{2} + z^{2})^{3/2}}.$$
 (2.5)

Let us now determine how the distance z at which the sample can be detected depends on the sample volume. We assume that the detection of the NQR, that is, the observation, occurs under the condition $B \ge B_{cr}$. We are concerned with the case $B_z = B_{z,cr}$. In this case, using expression (2.5) we obtain the following dependence on z:

$$z = \left[\left(\frac{20M_0 e^{-t/T_2} V_{\rm s}}{B_{\rm z,cr}} \right)^{2/3} \frac{V_{\rm s}}{\pi h} \right]^{1/2}.$$
 (2.6)

If the radius of the sample is small in comparison with the distance z from which the NQR signal is received, then this expression can be written in a simpler way

$$z \approx \left(\frac{20M_0 e^{-t/T_2} V_s}{B_{z,cr}}\right)^{1/3},$$
 (2.7)

where the quantity

$$k = \frac{20M_0e^{-t/t}}{B_{z,cr}}$$

is constant for a particular sample, and therefore

 T_2

$$z \approx k V_{\rm s}^{1/3}.\tag{2.8}$$

Thus the distance at which the sample can be detected does not increase linearly with the sample volume.

The sample that we used was $(CH_2)_6N_4$, in which the ¹⁴N NQR signal is observed at 3306 kHz at room temperature.

The receiving antenna contained four 400 NM ferrite rods with a diameter d=8 mm, a length 138 mm, with coils with inductances $L_1 = L_2 = L_3 = L_4$, containing 20 turns and connected in parallel. The rods with the coils were placed inside a Duralumin shield provided with slits as shown in Fig. 1. The detection of the NOR signal from ¹⁴N was verified by virtue of its disappearance when a weak magnetic field was applied. We used a disk-shaped $(CH_2)_6N_4$ sample with a weight of 50 g. The re-radiation from the sample was detected at a distance up to 17 cm from the sample without the use of signal averaging. With the use of signal averaging (with a signal-to-noise ratio $\approx n^{1/2}$, where n is the number of samples) this distance can be increased by a factor of two to three. The transmitting antenna was a spiral coil with a diameter of 200 mm made of foil-shaped fiberglass laminate. In view of the fact that

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FIG. 1. Receiving antenna.

the excitation antenna can excite large volumes (1×1) $\times 0.35$ m), the observed effect can be used for checking baggage for explosives and narcotics (hexogen, octogen, tetryl, hexotol, PVV-4, semtex, heroin, cocaine) becase this method is not bothered by the presence of metals and has a high selectivity with respect to the NQR frequency. This device is intended for checking letters, parcels, briefcases, suitcases, and for detection of bombs based on hexogen in the baggage, in the ground, and in walls. A block diagram of this apparatus is shown in Fig. 2. For explosives and narcotics there is a characteristic NQR frequency that permits identification with a probability of correct detection of 0.97. The presence of moisture, foodstuffs, common chemicals, leather, wood, plastics, etc. does not interfere with the operation of the apparatus. The minimum mass of hexogen (NQR frequency 5192 kHz) and octogen (NQR frequency 5300 kHz) is 10 g for an observation time no more than 10 s in a range of working temperatures from -30 to +40 °C, with the apparatus weighing 70 kG. The device can be used in airports and at customs stations for the monitoring of baggage.

Several methods can be used for the NQR detection of explosives and narcotics: remote NQR, the cross-relaxation method, and double NQR.¹¹⁻¹⁴ The method remote NQR described in Ref. 14, is a promising one for the

Baggage Transmitter Synthesizer Pulse Series Generator Receiver Memory Reference Voltage

FIG. 2. Block diagram of apparatus for monitoring baggage.

detection of hexotol (80% trinitrotoluene + 20% hexogen) in antitank mines without a casing and in baggage, through the detection of the ¹⁴N NQR signal at the frequency 5192 kHz.¹⁵ The separate detection at the ferrite antennas with the rf pulses passing through the baggage is possible up to 35 cm. Measurements are also possible for octogen and tetryl. The NQR characteristics of TNT are such that it is not really well suited for remote NQR, but its signal can be easily detected in double NQR and QR-NQR.¹⁶ Of course, these methods are sensitive to the presence of metals.

Usually we use as the master oscillator for remote NQR a frequency synthesizer with a stability of 10^{-8} , a remote head attached to a 3 m cable and containing the final stage of high-power transmitters (1 kW) and the receiver preamplifier. The diameter of the spiral surface coil, etched in laminated Bakelite insulation, is 25 cm and the diameter of the metal cylindrical shield is 40 cm. The shield is closed from below by a Teflon cap, and the distance between the coil and the Earth is 2 cm. The mines are searched for by moving the head over the surface of the Earth. The data in a series of pulses with detuning are accumulated in a digital memory. The entire apparatus including the power supply weighs 50 kg.

The method of cross-relaxation with the use of a U-shaped magnet extends the capability of the NQR detector. For the analysis of NOR by the method of crossrelaxation of ¹⁴N and ¹H we developed a computer program for the "Kompan" personal computer. In this development we proposed to do an averaging over the angles θ and φ in a powder. We usually used 12 960 averages. Tables I-IV show the NQR frequencies v_+ and v_- of ¹⁴N for four explosives. The transitions at the frequency v_{\perp} between the lower and middle levels) are almost independent of the static magnetic field B_0 , whereas the transition at the frequency v_+ (between the lower and upper levels) increases sharply with B_0 . The frequency $v_0 = v_+ - v_-$ also depends on B_0 , therefore the detection of antitank mines by this method with a U-shaped magnet is best done using the v_{\perp} lines. It is possible to use this method to make a universal NQR detector of antitank mines using the spectra of the nitro groups. For small asymmetry parameters η the frequency v_{-} decreases with increasing B_{0} .

The quadrupole Hamiltonian in a magnetic field B_0 has the form

$$H = \frac{eQq_{zz}}{4J(2J-1)} \left[3I_z^2 - I^2 + \frac{\eta}{2} \left(I_+^2 + I_-^2 \right) \right]$$
$$-\gamma\beta B_0 \left(I_z \cos\theta + \frac{I_+ + I_-}{2} \sin\theta \cdot \cos\varphi + \frac{I_+ - I_-}{2j} \sin\theta \cdot \sin\varphi \right), \qquad (2.9)$$

where I is the nuclear spin, η is the asymmetry parameter, θ and φ are the polar and azimuthal angles of B_0 in the

TABLE I. Octogen (T=77 K).

η	<i>eQq₂₂</i> , kHz	<i>В</i> ₀ , G	ν ₊ , kHz	ν_, kHz
0,497	5457	0	5063,0	3623
		1108,3	5144,7	3542
		2216,6	5389,6	3542
		3325,0	5471,0	3542
	1	4433,2	5634,5	3461
		5542,1	5961,0	3461
	}	6650,4	6287,8	3461
	l	7758,8	6532,8	3461
	l	8867,6	6941,0	3461
0,516	6027	0	5300,0	3737,0
	1	1224,0	5383,7	3653,9
		2448,2	5552,3	3653,9
	{	3672,2	5720,1	3653,9
Į –		4896,3	5804,2	3653,9
	1	6119,8	6140,7	3653,9
	1	7345,1	6477,2	3653,9
	1	8569,1	6813,7	3653,9
1		9793,9	7066,0	3653,9
0,42	840	0	720,0	540
1		194,0	724,4	527
ł		341,2	754,0	515
		511,8	777,2	515
		682,4	788,8	515
1	1	852,9	835,2	515
1	1	1023,7	881,6	515
		1194,3	939.6	515
	1	1365,0	974,4	515
0,48	806	0	720,0	490
	1	163,7	742,4	490
	1	327,4	765,6	490
}	}	491,0	777,2	490
1	1	654,8	812,0	479
1	1	818,4	846,8	479
		982,2	893,2	479
		1146,0	982,0	479
L		1309,8	974,4	479

TABLE II. Hexogen (T = 77 K).

η	eQq ₂₂ , kHz	B ₀ , G	ν ₊ , kHz	ν_, kHz
0,608	5674	0	5180,0	3394
		1152,3	5260,4	3394
		2304,8	5422,3	3394
	1	3457,1	5665,1	3394
		4609.6	5746,0	3394
		5761,3	6069,8	3394
		6914,9	6312,5	3394
		8067,3	6636,2	3394
		9220,2	6879,0	3394
0,638	5779	0	5256	3413
		1173,7	5336,8	3413
	-	2347,4	5498,5	3413
		3521,1	5660,2	3413
		4694,9	5741,0	3413
		5868,0	6064,5	3413
		7042,9	6307,0	3413
		8216,6	6630,5	3413
		9390,9	6873,1	3413
0,614	5887	0	5319,0	3511
	i	1195,6	5570,4	3511
	1	2391,2	5739,2	3511
		3586,9	5908,0	3511
	1	4782,6	5992,4	3511
		5977,7	6330,0	3511
		7174,5	6583,2	3511
		8370,1	6920,8	3511
		9566,4	7174,0	3511
0,42	700	0	600,0	450,0
		142,1	619,3	440,2
		284,3	629,2	430,3
		426,5	648,6	430,3
		568,7	658,2	430,3
		710,8	697,0	430,3
		853,1	735,7	430.3
		995,2	784,0	430,3
		1137,5	813,0	430,3

X, Y, Z system of the electric field gradient tensor, and I_z , I, I_+ , and I_- are the spin operators.

The solution of this Hamiltonian for powders for the transitions v_+ , v_- , and v_0 is shown in Tables I-IV. We carried out 6480 averages over the angles θ and φ , which gave an accuracy of 0.11%. A detailed description of the program and a printout of the source code are given in Ref. 17. To speed up the calculations we used Quick Basic 2.0. The physics of the processes in systems of this sort is described in Refs. 9 and 18-22).

An important achievement was the development of a spin-based locator for monitoring baggage with separate excitation and detection of signals, which increases to $100 \times 100 \times 35$ cm the dimensions of the objects that can be monitored. The NQR signals were excited with surface coils, while the detection was done on the other side of the baggage with U-shaped ferrite antennas with rf coils enclosed in a shield. We used a four-channel system, similar to that for the detection of mines as the carrier is moved at a speed of 7 km/h. In the latter case only unilateral detection could be carried out.

The sensitivity of the neutron method for the detection of explosives is 40 times lower than the NQR method. Moreover, in the neutron method the presence of leather can produce improper operation. The NQR method detects explosives and narcotics according to the frequencies, which provides a high probability of reliable detection (D = 0.97). This was verified in experiments with antitank mines, models TS-2.5, TS-6, and TM-2P, which are based on hexotol. We were able to conclude that NQR is at present the best method for detection of antitank mines that do not have a metal casing.

A specific description of the quadrupole detectors for antitank mines can be found in Refs. 13-29. These detectors were used successfully by us for the first time. According to the data of A. Garroway, negative results were obtained in the USA for antitank mines (Naval Research Laboratories, Washington DC). The details of the operation with the materials can be found in Refs 30-37. The methods of attributing the NQR lines in explosives to specific chemical arrangements in the molecule are given in Refs. 30, 33, and 37. New ways have now been found to increase the sensitivity of NQR detectors of antitank mines and methods of monitoring baggage. A large number of tests have been made with PVV-4. The reference numbers were obtained from this same type of explosive (80% hexogen and 20% naphtha products) with the use of a spiral surface coil.

TABLE III. Trotyl (T = 77 K).

η	<i>eQq₁₁</i> ,kHz	B ₀ , G	ν₊, kHz	۳_, kHz
0,1396	1107	0	869,0	792,0
		224,8	914,5	775.0
		449,7	961,0	759,5
		674,5	992,0	744,0
		899,3	1038,5	744,0
		1124,0	1100,5	728,5
		1349,1	1162,5	728,5
	{	1573,9	1240,0	728,5
		1798,9	1286,5	697,5
0,1654	1131	0	895,0	801
		229,6	960,2	784
		459,4	1024,4	784
		689,1	1040,1	768
		918,8	1072,5	752
	1	1148,4	1152,2	752
	} .	1378,3	1200,3	752
		1608,0	1280,1	752
		1837,8	1344,5	736
0,1640	1083	0	857,0	767
1	{ }	219,8	918,4	750
		439,9	948,6	735
Į		659,9	994,5	720
		879,8	1025,1	720
1	1	1099,7	1101,6	705
		1319,9	1162,8	705
		1539,8	1215,0	705
ĺ	[1759,9	1300,5	705
0,1978	1095	0	875,0	767,0
}		222,2	900,4	767,0
1	1	444,8	930,1	766,0
		667,1	975,2	734,4
i		889,6	1005,6	734,4
1	ļ	1111,9	1080,2	734,4
ļ]	1334,5	1155,7	719,1
		1556,9	1200,1	719,1
		1779,3	1275,2	719,1
0,2490	1061	0	861,0	729,0
	1	215,3	917,6	729,0
		431,0	932,4	729,0
		040,4	962,0	700,3
		801,9	1006,4	700,3
		1077,3	1065,6	700,3
		1293,0	1124,8	700,3
	1	1508,5	1184,0	700,3
0 2020	1079	1724,1	1243,0	700,3
0,2929	10/8	218.9	0,888	730,0
		218,8	930,4	730,0
	1	437,9	945,2	600.0
		030,8	9/5,0	600.0
		0/3,0	1003,2	600.0
		1212 9	1125 4	600.0
		1513,0	1200 1	600.0
		1751 9	1200,1	600.0
		1751,8	1200,1	0,990

3. METHODS OF SEPARATING SIGNAL FROM NOISE

One of the acute problems in remote NQR spectroscopy and of NQR spectroscopy of 14 N in particular is the poor signal/noise (s/n) ratio. Digital signal accumulation with the use of a multi-channel analyzer as a rule is limited by the stability of the spectrometer, particularly when the sample has long spin-relaxation times. Various methods are used to increase the s/n ratio, such as lowering the

TABLE IV. PETN (T = 110 K).

n	eQq _{zr} (kHz)	<i>B</i> ₀ (G)	v ₊ , (kHz)	v_, (kHz)
0.34	1426	0	1470.0	1170.0
		289.5	1519.1	1170.0
		579.2	1568.2	1170.0
		868.9	1617.5	1097.0
		1158.5	1666.0	1097.0
		1448.0	1764.4	1097.0
		1737.9	1837.5	1097.0
		2027.5	1960.0	1097.0
		2317.3	2058.0	1097.0
0.27	1586	0	1300.0	1080.0
		322.0	1366.4	1058.4
		644.2	1411.2	1015.2
		966.3	1456.0	1015.2
		1288.5	1523.2	1015.2
		1610.4	1612.8	993.6
		1932.9	1702.4	993. 6
		2255.0	1792.0	993.6
		2 57 7.25	1881.6	993.6

sample temperature, which increases the signal by a factor of 72 at a temperature T_n =4.2 K, cooling the preamplifier, and using digital filters. In remote NQR these methods either are in principle unsuitable, or are difficult to implement technically. One can improve the advantage per unit time, that is, increase the s/n ratio with a minimum distortion of the measured curve and without degrading the resolution of the spectrum, by using differential techniques in radiospectroscopy,³⁸ where the s/n ratio and the noise are recorded separately.

All further steps in the processing of the NQR signal are carried out on the computer.

-computation of the difference (in the differential technique) simultaneously with the detection and suppression of the low-frequency interference in the region of the signal;

—correction of the zero line;

-apodization, suppression of the higher frequencies;

-Fourier transformation

--determination of the relaxation components of the exponentially-decaying curves;

--identifying the NQR lines with the various nonequivalent sites in complex spectra, etc.^{53,54}

3.1. Fast Fourier transforms

Remote NMR inevitably entails the presence of a highly nonuniform magnetic field in the region of the sample. Unlike NMR,³⁹ remote NQR does not require a strong magnetic field, which is very difficult to "expel" outside of the gap of a U-shaped magnet, and this severely restricts the possibilities of remote NMR. On the other hand, the detection of the nuclear quadrupole resonance of light nuclei by means of a unilateral coil involves a very weak signal. To increase the signal intensity, some investigators^{14,40} used rather large-volume samples to detect the signal, but this method certainly cannot always be used to separate the signal from the noise.

We have investigated the fast-Fourier-transform tech-



FIG. 3. Splitting of the ¹⁴N NQR line in $C_6H_{12}N_4$. a) Induction after a single pulse; b) spectrum after Fourier Transformation.

nique in remote NQR as one of the steps in filtering the signal from the background noise and increasing the reliability of identification of the type of material.³²

The Fourier transform method can reduce considerably the measuring time in pulsed spectroscopy. In NQR the resonance lines lie in a very broad range from kilohertz to a hundred megahertz, and the line width reaches a hundred kilohertz. To use the Fourier transform method when the band is of the order of 100 kHz wide it is necessary to use a fast analyzer with a sampling time of the order of 1 μ s. To obtain the correct line shape it is also desirable to use quadrature detection. In the experiment we used a disk-shaped sample of (CH₂)₆N₄, whose distance from the planar pickup coils could be varied.

Figure 3 shows the NQR signal of ¹⁴N at the frequency 3305 kHz at room temperature, and its Fourier transform, where the sample was placed within an ordinary solenoidal coil. The rf pulse length was $t_w = 60 \ \mu$ s, the number of samples was N = 1024, and the spacing between the measuring pulses was $t_p = 20 \ \mu$ s. One can readily see the splitting of the signal due to the dipole magnetic field of the CH₂ group.

To "increase" the resolution we recorded the induction signal with a 2.0 ms delay after the excitation pulse. (Good results were also obtained by multiplying the signal by the



FIG. 4. Decrease in the intensity of the 14 N NQR signal in urotropine for unilateral detection as a function of the distance. a) time dependence; b) spectrum.

factor $\exp[(t/T_2) - \alpha t^2]$) before carrying out the Fourier transformation.

Figure 4 shows the NQR signals from ¹⁴N for the same samples, but obtained by the surface-coil method, with the sample located at various distances l from the coil. The curve were obtained for different numbers N of data accumulation. The last signal (l=5 cm) was recorded with the least detuning, and prior the Fourier transformation it was multiplied by a factor exp (-t/32) to decrease the noise level. It can be seen that the resolving power decreases, but the application of the fast Fourier transform method makes it easy to identify the material and to increase the s/n ratio. Hence the use of the fast Fourier transform method in remote NQR with the data automatically being fed through an interface into a DVK-3 personal computer is entirely viable, even though this method with the use of preliminary data accumulation with an AI-4096 certainly increases the time spent in searching for a signal.

3.2. Correlation spectroscopy

The correlation function is widely used in physics mainly for speeding up the identification of signals masked by noise. The autocorrelation function is usually used for the analysis of the degree of correlation in random processes.

Autocorrelation can be used for the processing of data of remote NQR spectroscopy, and in Ref. 34 examples were presented that demonstrated the usefulness of this method.

The induction signal at the output of the receiving device of the NQR spectrometer after the action of the rf pulse for the case of a single resonance line can be written as

$$S(t) = S_0 \exp\left(-\frac{t^2}{2T_2^{*2}}\right) \cos \Delta \omega t, \qquad (3.1)$$

where $\Delta \omega$ is the detuning of the spectrometer away from the resonance line, which has a Gaussian shape, and T_2^* is the line width parameter.

The spectral density of the induction signal S(t) will have the form

$$S(\omega) = \sqrt{\frac{\pi}{2}} S_0 T_2^* \exp\left[-\frac{T_2^{*2}}{2} (\omega - \Delta \omega)^2\right].$$
 (3.2)

A calculation of the autocorrelation function from the signal (3.1) gives the expression

$$C_{SS}(\tau) = \int_{-\infty}^{\infty} S(t)S(t-\tau)dt$$
$$= \frac{\sqrt{\pi}}{2}S_0^2 T_2^* \exp\left(-\frac{\tau^2}{4T_2^{*2}}\right) \cos \Delta \omega \tau. \qquad (3.3)$$

The direct Fourier transform of the correlation function $C_{SS}(\tau)$ gives the spectral density of the energy

$$S^{2}(\omega) = \int_{-\infty}^{\infty} C_{SS}(\tau) e^{i\omega\tau} d\tau$$
$$= \frac{\pi}{2} T_{2}^{*2} S_{0}^{2} \exp\left[-T_{2}^{*2} (\omega - \Delta \omega)^{2}\right]. \qquad (3.4)$$

To analyze the NQR spectra of ¹⁴N we used the technique and the programs described in Ref. 41 plus additional programs for the calculation of the correlation function. Figure 5a illustrates a plot of the free-induction signal from the nitrogen nuclei in $C_6H_{12}N_4$ after the termination of the rf pulse for unilateral detection with the use of a surface coil. The measurements were carried out at room temperature and 300 points of the free-induction signal were taken with a sampling time $t_s = 10 \ \mu s$. The spectrum of this signal, obtained by the Fourier transformation of the freeinduction signal, is shown in Fig. 5b. The autocorrelation function of the free-induction signal is shown in Fig. 5c, and its Fourier transform in Fig. 5d. One can readily see the decrease in the noise level and the improvement in the resolution of the spectrum (Fig. 5d) obtained from the autocorrelation function of the free-induction signal. Because of the limited time window in which the free-



FIG. 5. Use of autocorrelation (AC) to increase signal/noise ratio in NQR of ^{14}N .

induction signal is recorded, the random noise in the freeinduction signal leads to a nonuniform noise distribution in the spectral density of the energy, with the noise amplitude falling off with increased frequency. For the case of a sinusoidal signal the increase in the amplitude s/n ratio obtained by calculation of the autocorrelation function is⁴²

$$G = \left(\frac{2BT}{2+R^{-1}}\right)^{1/2},$$
 (3.5)

where B is the band width of the signal, T is the integration time R is the power s/n ratio at the input.

In the work reported in Ref. 43, Roth used the Fourier transform of the "power free-induction signal" equal to

$$P(t) = S(t)S^{\bullet}(t), \qquad (3.6)$$

where S(t) is the complex free-induction signal. The method described in that work pertains to Fourier NMR difference spectroscopy, developed by Ernst.⁴⁴ The main achievement of this method is that the NMR spectra are independent of changes in the magnetic field and of the frequency of the spectrometer. We have used this method to find the autocorrelation function of the ¹⁴N NQR spectra in C₆H₁₂N₄. The lack of a quadrature detector allowed us to record only the real part of the complex freeinduction signal (Fig. 6a). The imaginary part of the freeinduction signal (Fig. 6b) we calculated either directly by means of the Hilbert transform (HT), which takes a great deal of computer time, or using the sine- or the cosine



FIG. 6. Calculation of the autocorrelation of a NQR spectrum.

Fourier transform (FT), as in Ref. 43. We also obtained the autocorrelation spectrum (Fig. 6f) either directly from the signals c or d, or as the Fourier transform of the previously calculated "power free-induction signal" (2.6) (Fig. 6e), which is faster.

The splitting of the NQR ¹⁴N line (Fig. 6d) gives rise to a line with a frequency Δv in the autocorrelation spectrum. The line with a frequency v_0 in the autocorrelation spectrum is due to the imperfect experimental recording of the free-induction signal, where, when the accumulation time is long, a "dip" appears in the zero line because of overloading of the receiving device after the rf pulse. This distorts the power free-induction signal (Fig. 6e) and produces the v_0 line in the autocorrelation spectrum.

The calculation of the autocorrelation function of the free-induction signal can therefore be used successfully for separating the NQR signal from the noise. A helpful technique for this purpose may also be the calculation of the autocorrelation spectrum, but NQR Fourier difference spectroscopy cannot be applied for the recording of a single line, while in the recording of multiplet NQR spectra it can complicate the problem of identification of the lines, because the symmetry properties of the autocorrelation spectrum dictate that only the shift of the frequency is determined, and not its sign.

3.3. Fourier echo spectroscopy

It is well known that the decay of the spin echo signal in NQR does not depend on the inhomogeneous broadening, but is governed only by the homogeneous broadening, so that it is possible to improve substantially the resolving power of the method in the analysis of the spin echo envelope.⁴⁵

The recording of the envelope of the spin echo signal over the spin-lattice relaxation time T_2 when it is longer than the free induction decay time T_2^* makes it faster to accumulate the NQR signal in the remote regime, and consequently facilitates the separation of the signals from the noise.

On the other hand, the analysis of "slow beats" in the spin echo envelope when the time interval between the 90° and 180° pulses is varied is frequently difficult if there are several beat frequencies.

Such problems in NQR echo arise in the study of indirect spin-spin interactions between nuclei, in the action of magnetic and electric fields on the spin echo, and in the study of the dipole-dipole interactions between close-lying nuclei. The NQR method can be made much more informative if a fast Fourier transformation is carried out on the spin echo envelope.³ Here the NQR line is effective narrowed, and one can observe the effects of high resolution in solids. However, this potential has not yet been realized.

To demonstrate the possibilities of the method of Fourier echo spectroscopy that we have worked out.^{8,46} we present a series of examples. Figure 7 shows the spin echo envelope of ¹²⁷I nuclei in crystalline I_2 at 77 K for the $\pm 1/2 \rightarrow + 3/2$ transition at the frequency 333.94 MHz. In this crystal there are indirect spin-spin interactions between the iodine atoms. It is very difficult to determine from the time-dependent picture the frequencies of the line splitting due to the spin-spin interactions. Figure 7b shows the results of a Fourier transformation of the envelope (Fig. 7a), from which we find the frequencies of the "slow beats," 9.1, 16.9, 22.1, 27.3, 36.4, and 48.1 kHz, which agree with the theoretical calculations.⁴⁷ Thus the fast Fourier transform has made it possible for the first time to see all the possible frequencies of the slow beats. In addition, the constants J and K of the indirect spin-spin interaction have been determined with greater accuracy, which is greatly affected by the dead time of the receiver.

For the ⁷⁹Br nuclei in Br_2 at 77 K, the use of the fast Fourier transform method applied to the envelope revealed four slow-beat frequencies, at 4.5, 7, 9, and 13 kHz, which



FIG. 7. a) Detection of spin echo signal from the $^{127}\mathrm{I}$ nuclei in I_2 and b) its Fourier transform.

differ from the results obtained previously from a analysis of the time picture⁴⁸ and affects the values of the constants J and K. For Br₂, J=10.4 kHz and K=1.1 kHz, while for I₂, J=28 kHz and K=1.1 kHz.

In Ref. 48, on the basis of an incomplete time plot and, accordingly, an incorrect determination of the ratio of the constants, the values J=7 kHz and K=2 kHz were found for Br₂ and J=14 kHz and K=3.5 kHz for I₂, which are quite different from the results of the present work. Four frequencies were found in Ref. 48 for the slow beats for I₂ and two for Br₂; i.e., some of the frequencies were missing.

Figure 8 shows the nuclear spin-echo envelope in $KClO_3$ at 300 K and a frequency of 28.1 MHz. The slow beats in this case result from the action of the Earth's magnetic field. The beats are seen because of the very narrow NQR lines in $KClO_3$. Figure 8b shows the results of the Fourier transformation of the echo envelope. The Earth's field splits the NQR line of ${}^{35}Cl$ in $KClO_3$ by 150



FIG. 8. a) "Slow beats" of the spin echo envelope of the 35 Cl nuclei in KClO₃ and b) the splitting of the NQR line in the Earth's magnetic field.



FIG. 9. a) Time and b) frequency dependence of the spin echo envelopes in KClO₃ in an external magnetic field of 1.4 G.

Hz, which is unobservable by the method of steady-state NQR.

The method that we developed was tested in an analysis of the NQR line shape in electric and magnetic fields. Figure 9 shows the pattern of the slow beats in KClO₃ in an external magnetic field of 1.4 G (a) and the Fourier transform (b) of this function. It can be seen that the NQR line in the magnetic field has some inflection frequencies (in this case two). According to Lucken,⁴⁹ when a magnetic field is applied the distance between the two humps in the NQR line shape of the powder for I=3/2 is equal to $2v_L\eta$, where v_L is the Larmor frequency of the ³⁵Cl nuclei in the magnetic field B_0 and η is the asymmetry parameter. Knowing the exact value of the magnetic field B_0 , one can determine the asymmetry parameter for spin 3/2, which cannot be done by any other method. An estimate gives the value $\eta=0.2$ for KClO₃.

Figure 10 shows the pattern of slow beats in a pulsed electric field of 6.3 kV/cm at the ²⁰⁹Bi nuclei in BiCl₃. The Fourier transform (b) of this function shows a complicated shape, containing three slow-beat frequencies. Three slow-beat frequencies, 4.2, 12.6, and 21 kHz, were obtained from the Fourier transform for the $7/2 \rightarrow 9/2$ transition of the Bi nuclei in BiCl₃ with E=6.3 kV/cm at 77 K, whereas in Ref. 48, on the basis of an analysis of the time dependence only one frequency was taken into account. This complicated NQR line shape for a powder in an external electric field was not taken into account by Ainbinder and Shaposhnikov;⁴⁸ rather, they assumed an idealized line shape with a single slow-beat frequency, and hence they could not explain the unequally spaced zeros of the slow beats.

When an electric field is applied the NQR line shape is determined by the convolution of the line-shape function in zero field, $g(\omega)$, with the function $\eta_E(\omega)$, which describes the shape of the single-crystal line in an electric field E (Ref. 50):



FIG. 10. a) Beats in the spin echo envelope of 209 Bi nuclei in BiCl₃ in a pulsed electric field of 6.3 kV/cm and b) spectrum of the beats.

$$I_E(\omega') = \int_{\omega' - \Delta \omega_E}^{\omega' + \Delta \omega_E} \eta_E(\omega) g(\omega', \omega) d\omega.$$
(3.7)

According to Plancherel's theorem, the Fourier transform of expression (3.7), i.e., of the convolution, is equal to the product of the Fourier transforms of the cofactors of the convolution. The function $F[\eta_E(\omega)]$ in the case of a pulsed electric field modulates the spin echo envelope after twopulse excitation. For the case of a powder and with $E\perp B_1$ this envelope varies according to⁵¹

$$F[\eta_E(\omega)] \sim \frac{2}{\tau} \left\{ [1 - (\Delta \omega_E \tau)^{-2}] \sin(\Delta \omega_E \tau) + \frac{\cos(\Delta \omega_E \tau)}{\Delta \omega_E \tau} \right\}.$$
(3.8)

From the experimental data one usually determines the NQR line shape factor in a field "B" and the frequency shift by the formula for the zeros of the echo beats

$$\frac{\Delta\omega_E\tau}{1-B(\Delta\omega_E\tau)^2} = \tan(\Delta\omega_E\tau). \tag{3.9}$$

The accuracy in the determination of the frequency shift can be significantly increased by using the Fourier transform of the spin echo envelope. For example, if the beats of the spin echo envelope in the compound GeI₄ for the ¹²⁷I nuclei ($1/2 \neq 3/2$, $v_Q = 225.088$ MHz, E = 15 kV/cm),⁵² as shown in Fig. 11a are recorded by a synchronous detector, then they will have the shape shown in Fig. 11b. For comparison, Fig. 11c shows the theoretical curve (2) with $\Delta v_E = 15$ kHz. Figures 11d, and 11e show the Fourier transforms of the curves b and c, respectively, taken at 4096 points ($\Delta \tau = 0.5 \ \mu s$).

The NQR line shape for an asymmetry parameter $\eta \neq 0$ in a magnetic field is similar to that in an electric field, a fact that must be taken into account in developing a theory of slow beats in powder samples.



FIG. 11. Fourier NQR echo spectrum of ¹²⁷I in GeI₄ in an electric field.

The Fourier transform (b) of the spin echo envelope of the 75 As nuclei in AsBr₃ is shown in Fig. 12. The figure shows the splitting of the arsenic lines due to the direct dipole-dipole interactions with the bromine nuclei.

These investigations show that working in the time domain with the slow beats in the NQR spin echo envelope reveals many features of the phenomenon that have led to an incorrect analysis of the results.⁴⁸ In particular, the theoretical calculations of the spin echo envelope in a pulsed electric field with a single slow-beat frequency⁴⁸ are not supported by experiment, which indicates the incorrect averaging in the powder sample, as well as the not completely correct calculational method of Das and Saha, which is appropriate only for zero detuning. The spin-echo envelope recorded by varying the time interval between the 90° and



FIG. 12. a) Decay of the spin echo amplitude and b) NQR line splitting of 75 As in AsBr₃ due to the heteronuclear dipole-dipole interaction.

the 180° pulses is similar to the decay in the magnetization recorded in the multi-pulse experiment of Carr and Purcell.

The method of Fourier echo spectroscopy developed for NQR makes it possible to obtain experimental results more reliable than those obtained by an analysis of the curves in the time domain. Moreover, the use of the Fourier echo spectroscopy permits optimization of the data accumulation time for improvement of the s/n ratio.

3.4. The maximum entropy method in NQR

The maximum entropy method and its different variants is used in the spectral analysis, for the detection of a signal with given parameters above the noise background. In recent years these methods have begun to be used to reduce the noise level and increase the resolution in the analysis of NMR spectra,⁵⁵ in electron spin resonance,⁵⁶ and in nuclear quadrupole resonance.⁵⁷ Compared to ordinary NQR with discrete Fourier transforms, the maximum entropy method also makes it possible to increase the sensitivity in recording two-dimensional NQR spectra.⁵⁸ For the simultaneous improvement in the resolution and the suppression of the noise in nuclear magnetic resonance, this method is used in combination with the deconvolution (inverse convolution) with, for example, a Lorentzian line shape.^{59,60}

Nuclear quadrupole spectroscopy has its own peculiarities, associated not only with differences in instrumentation, but also with the range of frequencies, the widths of the spectral lines, and the intensities of the signals. Following Laue *et al.*,⁶¹ we look for the spectrum⁵⁷ using the "Cambridge" algorithm, which has been described in detail in Ref. 62. This maximum entropy algorithm consists of sifting among the possible test spectra for the highest entropy H and the smallest mean square statistical deviation χ^2 of the real data M_t from the test data \overline{M}_t that are observed for a hypothetical spectrum \overline{n}_v . The experimental data M_t represent the decay of the free-induction signal and are fed to the computer from the ¹⁴N NQR spectrometer. The normal operation of the algorithm presupposes the correct phasing of the experimental data.

The data M_t are found as the inverse Fourier transform of the test spectrum \bar{n}_v . The final result does not depend on the starting point of the iterations, i.e., on the initial test spectrum.

Since the entropy H is a nonlinear function, the program goes through an iteration process in which the test spectrum must be changed many times, $\bar{n}_v \rightarrow \bar{n}_v + \delta n_v$. The variation of the test spectrum

$$\delta n_{\nu} = u \frac{\partial \chi^2}{\partial \bar{n}_{\nu}} + v \frac{\partial H}{\partial \bar{n}_{\nu}}$$
(3.10)

proceeds in the direction of lowering χ^2 and increasing H; here u and v are coefficients and

$$\frac{\partial H}{\partial \bar{n}_{v}} \sim \operatorname{const-ln} \bar{n}_{v}.$$
 (3.11)



FIG. 13. Use of the maximum entropy method in remote detection of NQR of ^{14}N .

In the use of the inverse Fourier transform the test data \bar{n}_v are transformed from the frequency domain to the time domain

$$\bar{M}_t = \exp(-kt) \sum_{\nu=0}^{N-1} \bar{n}_{\nu} \exp(-2\pi i \nu t N^{-1}). \quad (3.12)$$

They reproduce the measurement process. The gradient $\partial \chi^2 / \partial \bar{n}_v$ is found as the Fourier transform of the quantity

$$\frac{\partial \chi^2}{\partial \bar{M}_t^*} = 2(\bar{M}_t - M_t)\sigma_t^{-2}.$$
(3.13)

Both of the Fourier transformations are carried out on a function first multiplied by exp(-kt) for stability of the numerical procedure.

The iteration process terminates when $\chi^2 \approx N$ (the number of points of the spectra) and when $\nabla \chi^2$ and ∇H are parallel. The data analysis was done with the program "MME", developed and appended to the program written for the analysis of NQR data and described in Ref. 41. Figure 13 illustrates the effectiveness of the maximum entropy method for the analysis of remote NQR signals: Curve *a* is the ¹⁴N NQR spectrum from C₆H₁₂N₄ for unilateral detection with a surface coil and curve *b* is the same spectrum after 10 MME iterations. The number of points in this example is 512.

The use of the maximum entropy method has shown that it is an effective method of mathematical data processing of NQR signals that increases the signal/noise ratio. This is important because the number of sweeps available in collecting the data is limited by the stability of the spectrometer and the experimental time. Naturally, the maximum entropy method can be used only for signals for which the s/n ratio is greater than unity.



FIG. 14. Calculated sensitivity profile of a round surface coil.

B_z/I_r (T/A) \cdot 10⁻⁶



FIG. 15. The quantity B_z/I as a function of z for single-turn coils of different radius: 1) R = 5 cm; 2) R = 10 cm; 3) R = 15 cm; 4) R = 20 cm.

3.5. Receiving and transmitting antennas

In the simplest case for the application of remote NQR, a planar round surface coil can be used that serves both as the transmitting and receiving antenna, and is placed above the region where the sample is located. Because of the nonuniformity of the rf field of this coil, it receives the NOR signal from the region of the sample bounded by the circumference of the coil to a depth into the sample from the center of the coil about equal to the coil radius. We have calculated the sensitivity profile of such a coil of radius R for a plane lying parallel to the plane of the coil at a different distance l. This profile is shown in Fig. 14. The sensitivity is indicated by the vertical coordinate. The side of the base of the cube in which this profile is plotted is equal to 2R and its center coincides with the center of the coil. The surface-coil method was used with a standard pulsed NQR spectrometer⁶³ after a simple modification of the pickup. To increase the sensitivity with increasing distance from the sample, it was found advisable to increase the diameter of the plane coil, which leads to difficulties associated with preparing and tuning of large rf coils, as well as shielding them from interference.

In the spectrometer the receiving and transmitting coils can be different. The two-coil design reduces the direct reception of the signal during the time of the rf excitation pulse, but it should be kept in mind that in some cases when the receiving and transmitting antennas are mutually perpendicular the NQR signal cannot be detected.

To study samples at a distance from the NQR sensor, coils can be used that are in the form of two solenoids with current flow in opposite directions⁶⁴ or that have ferrite cores,⁶⁵ thus increasing the amplitude of the rf field and improves the uniformity of the field at the location of the sample.

To "extend" the rf field outside of the bounds of the coil one can use opposed coils. The results obtained by Rath *et al.*⁶⁶ led to the conclusion that opposed coils pro-

vide a more uniform B_1 field and a better spatial selectivity than ordinary rf coils. Opposed coils can be used either as the excitation coil or as the receiving coil. When a single coil is used its dimensions must be chosen so that its detection properties dominate over its excitation properties.¹⁴ As the dimensions of the surface coil are increased the uniformity of the field is improved when the coil is used as the irradiation coil and the sensitivity is improved when it is used as the receiving coil, and thus the power requirements of the spectrometer and the resonant frequency of the circuit are reduced. The use of high-Q remote coils constitutes the principal obstacle to decreasing the recovery time of the system after the irradiation pulse. Unfortunately, in the NQR of low-frequency nuclei such as ¹⁴N, it is necessary to deal not only with a low signal intensity and the long times T_1 , but also the short times T_2^* .

If the z axis is taken perpendicular to the plane of the irradiation coil out from its center and B_z is the magnetic induction along the z axis, R is the radius of the irradiation coil, and I is the current in the ring, then the optimum relation between R and z is given as $R = \sqrt{2}z$. The uniformity of the magnetic field along the z axis can be increased by increasing the diameter of the irradiating coil. The dependence of the quantity B_z/I on z for a single-turn coil is shown in Fig. 15. It can be seen that for $R \sim 15$ cm the field B_z falls off by at most a factor of two with increasing z up to 16 cm. Thus the optimum distance z for the detection of NQR will be of the order of the radius of the irradiation surface coil.

Let us assume that for some reason we cannot achieve the condition of 90° pulses, Eq. (2.1), by increasing the power of the pulse transmitter (the power in a pulse cannot exceed 2–4 kW). The power requirements of the pulses can be considerably reduced by the use of the optimum detuning of the rf carrier pulses.

The maximum amplitude of the induction signal that can be fed into the coil after the operation of the rf pulse, for conditions of a uniform rf field B_1 , is given for a powder⁶⁷ by

$$\langle \bar{I}_i \rangle_{B_1} = \frac{N \hbar \omega_Q}{3kT} \frac{\sin P - P \cos P}{P^2}, \qquad (3.14)$$

where $P = 2\gamma B_1 t_w$. Then the 90° condition for the rf pulse will be

$$2\gamma B_1 t_{\rm w} \approx 0.66\pi. \tag{3.15}$$

For a planar transmitter coil and a relatively large sample, as in our case, the B_1 field is nonuniform and the concept of a 90° condition has no meaning in the usual sense. At first, as the rf pulse is lengthened, the amplitude of the induction signal increases, and then remains essentially constant during the time that the 90° condition, when it ceases to be satisfied of one element of the sample, begins to be satisfied for another element.

For the case of unilateral detection we used two planar transmitting-receiving coils. The first is a planar coil mounted in a litz-wire fashion: the inner diameter of a winding is 50 mm and the outer diameter is 100 mm. The second coil is a planar spiral coil printed on a fiberglass laminate of diameter 200 mm. It should be noted that the operating coils must be well shielded, since there is a great deal of interference in the operating range, and the larger the radius of the coil, the more difficult is it to eliminate the interference.

It is therefore clear that with a comparatively lowpower transmitting oscillator it is possible to detect NQR signals from ¹⁴N at a considerable distance from the irradiating surface coil, which is simultaneously used as the receiving coil for the receiving circuit.

The prospects for the development of remote NQR are linked with the development of a technique that will substantially increase the sensitivity of the spectrometer.

4. TWO-DIMENSIONAL TWO-FREQUENCY NQR SPECTROMETER IN REMOTE OPERATION

The main problem in remote NQR is to achieve longrange detection of compounds in which all the other parameters are already known, unlike in the case of ordinary (not remote) NQR, which is used as an instrument for studying matter at the molecular level. In addition, there exist a range of problems where the parameters of the NQR must be determined using only the remote mode of operation (nondestructive monitoring of biological objects, measurements in media that are corrosive or dangerous to life, etc.). Moreover, before addressing the problem of the remote detection of explosives and narcotics, it is necessary to determine the principal, most characteristic parameters of NQR of these materials. It is therefore necessary to discuss for a time a new method, whose effectiveness is retained under the conditions of remote NQR detection.

Progress in nuclear quadrupole resonance is in many ways bound up with the development of pulsed methods. The two-frequency method is an important one of these;⁶ it *provides additional information on the nonlinear proper*ties of a spin system. In Ref. 9 we pointed out for the first time that twofrequency methods based on NQR are equivalent to a twodimensional NMR frequency experiment. Here, the offdiagonal signals of the two-dimensional spectrum, which indicate the transfer of magnetization between different states, are equivalent to the additional signals of the twodimensional quadrupole echo.

At the present time two-dimensional (2D) spectroscopy in high-resolution NMR in a strong magnetic field has been well worked out.⁶⁸ This is the two-dimensional correlation spectroscopy (COSY), where two spectra are mutually correlated on the basis of the bonding, or other cases where the exchange or cross-relaxation transitions lead to cross-peaks in the 2D NMR spectra.

The method of 2D spectroscopy has been applied successfully to NMR and NQR in zero field,^{69,70} but the technique of cycling the field and indirect detection greatly complicate the apparatus and increase the experimental time; moreover, it is possible to operate only in the low-frequency region (below 1 MHz).

We have established a connection between the time of appearance of the two-frequency signals in the program "kvadrat" and the coordinates of the cross-peaks of the 2D NQR spectrum, and have implemented experimentally two-dimensional NQR spectroscopy for the direct method of detection. Such an approach to obtaining twodimensional NQR signals has been developed for the first time. The advantage of this method is mainly the large increase in the number of compounds that can be detected—particularly in the region of high NQR frequencies.

The sensitivity of 2D experiments cannot be higher than that of 1D experiments, but frequently it is necessary to make a large number of 1D experiments in order to obtain the same information; that is, the information content of the two-dimensional experiment per unit time is much greater than even though the sensitivity is low. The two-frequency NOR methods, in particular the method of two-frequency spin echo, was developed in 1967.³ In fact, these were the first two-dimensional experiments of a pulsed type in radio-frequency spectroscopy, and were carried out prior to the NMR experiments.⁶⁸⁻⁷⁰ It is true that computer techniques were applied earlier in NQR experiments. This probably explains why the first twodimensional experiments are attributed to Jeener.⁶⁸ The two-frequency spin echo spectra³ already contain all the information that can be obtained from computerized twodimensional NQR spectra (quantum beats, the assignment of the lines).

By the use of computer techniques in the twofrequency method one can obtain a two-dimensional image of the NQR spectra.

An increase in the clock frequency to 53 MHz in modern personal computers (in the PC "Kompan" the clock rate is 12 MHz) would greatly shorten the signal accumulation time in remote NQR and in two-dimensional spectroscopy.

A typical two-dimensional experiment consists of four parts: the preparation, the evolution, the mixing, and the



FIG. 16. Two-dimensional NQR spectrum of ¹⁴N from urea.

detection.⁷¹ During the preparation part, a coherent, nonequilibrium state of the spin system is created. During the evolution, the spin system develops under the action of the effective Hamiltonian, which, as necessary, is varied by turning on and turning off resonance, homo- and heteronuclear decoupling, magic numbers of rotations, etc. During the mixing there is a transfer of the magnetization, which is also characteristic of the system under study. In the detection stage the magnetization is determined by the measurement of the signal $S(t_1, t_2)$, where t_1 is the duration of the evolution period and t_2 is the time of observation of the signal during the detection.

The function $S(t_1,t_2)$ is then subjected to a twodimensional complex Fourier transformation and is converted to a two-dimensional spectrum, which is used for the study of material systems with a complicated spectrum, in which complicated exchange processes occur.

In strong-field NMR the 2D technique, by virtue of the correlation of the various pwoder spectra, can sometimes be used to create a characteristic and interpretable model.

In principle, it is possible to apply to remote NQR all the methods that have been worked out for twodimensional high-resolution NMR,⁶⁸ and thus it is possible to study exchange or cross-correlation processes with the aid of the cross-peaks. However, this concept in NMR is of no interest with respect to solids, since NMR powder spectra in a strong field do not contain any additional information. Experimental two-dimensional NMR or NQR spectra in zero field (not remote) for deuterated systems were reported for the first time in Ref. 69, and for the case of excitation with a low-frequency pulsed field in Ref. 70. Two-dimensional NMR and NQR (I=1) spectroscopy in zero field⁶⁹ has proved to be suitable for the analysis of complex spectra. However, even though the technique with circulation of the field⁶ involves a sharp increase in the sensitivity of the NQR spectrum of ¹⁴N and ²H in the low-frequency region below 1 MHz, two-dimensional spectroscopy in zero field requires a large expenditure of time in the experiment, since for each cycle of variation of the field no more than one point of the two-dimensional function $S(t_1,t_2)$ is recorded, and even this may require signal accumulation. The main point is that this technique essentially is inapplicable to remote NQR.

While in the ordinary (direct) pulse method of detection the two-dimensional response function $S(\tau,t')$ is recorded after two rf pulses, the Fourier transform makes it possible to obtain the two-dimensional spectrum $S(\omega_1,\omega_2)$ even under remote conditions; here τ is the delay time between the pulses t' is the instantaneous time reckoned from the time the second pulse is applied.

In Fig. 16 we illustrate an experimental twodimensional ¹⁴N NQR spectrum that we took⁷² in this way at 77 K from CO(NH₂)₂ at the frequency $v_{\perp} = 2917.7$ kHz (the detuning relative to the specified frequency is laid out along the axes). The corresponding one-dimensional spectrum is shown in Fig. 17. The function $S(\tau,t')$ was recorded in the experiment over 128×128 points. On the topogram of this spectrum one can readily see the asymmetry of the two-dimensional spectral line, caused by the difference in the relaxation times T_2^* and T_2 in this compound. The experimentally recorded envelope of the induction signal at the nuclear quadrupole resonance has a non-Gaussian shape and does not have cylindrical symmetry about the origin $t_1 = t_2 = 0$. As a result, the two-dimensional pure absorption peak also does not have cylindrical symmetry and is accompanied by a "star-like effect." This effect can be eliminated in a number of cases by a Lorentz-Gaussian 2D transformation.⁶⁸

The Fourier transformation is ordinarily used in radio



FIG. 17. a) Echo signal in urea at the frequency $v_{+} \approx 2911$ kHz at 77 K, $t_{w} = 50 \mu s$, $t'_{w} = 100 \mu s$, $t_{p} = 20 \mu s$; and b) Fourier transform of the urea echo using 4096 signal points.

spectroscopy in the spectral analysis of the response of spin systems. In other areas of study, in holography, for example, a technique that has lately been used successfully for information processing is the Hartley transform,⁷³ which has a number of advantages in the analysis of large sequences of real one-dimensional and two-dimensional data. Unlike the Fourier transform, which maps a real function into the complex plane and is asymmetrical in *i*, with the Hartley transform the direct and inverse transformations are only in the real region, and it possesses the symmetry mentioned above. The handling of real data does not require operations with complex quantities, and therefore the Hartley transform algorithm uses only half the machine time used for the Fourier transform.

The discrete Hartley transform

$$H(v) = N^{-1} \sum_{\tau=0}^{N-1} f(\tau) \cos(2\pi v \tau N^{-1})$$
(4.1)

makes it possible to obtain the power spectrum without the use of the complex plane, directly from H(v) with the use of the relation

$$P(v) = (H(v))^{2} + (H(N-v))^{2}.$$
(4.2)

The analysis by the discrete Hartley transform of twodimensional digital images also has advantages over the discrete Fourier transform. Bearing this fact in mind, to obtain two-dimensional power spectra in NQR we used the two-dimensional discrete Hartley transform in addition to the discrete Fourier transform:

$$H(v_{1},v_{2}) = \frac{1}{N_{1}N_{2}} \sum_{\tau_{1}=0}^{N_{1}-1} \sum_{\tau_{2}=0}^{N_{2}-1} f(\tau_{1},\tau_{2})$$
$$\times \cos[(2\pi v_{1}\tau_{1}N_{1}^{-1}) + (2\pi v_{2}\tau_{2}N_{2}^{-1})].$$
(4.3)

Representing the two-dimensional spectra in the form of absolute values of expression (4.3), (the square root of the power spectrum), we eliminate the necessity of making a phase correction. It is true that the 2D spectrum represented as absolute values has a much poorer resolution compared to the pure absorption mode, and therefore we did not use this scheme for the spectra that have closelying peaks.

The known method of obtaining 2D NMR spectra has the following drawbacks in NQR spectroscopy.⁶⁸ When there are non-equidistant systems of energy levels, then in the case of NQR there is no known way of mixing whereby the magnetization can be transferred via the excitation of forbidden transitions in systems with spin I=1, 5/2, 7/2, and so forth. As a result, even when the working frequency of the NQR Fourier spectrometer is tuned so as to encompass the entire region where the spectral lines may possibly lie, the two-dimensional NQR spectrum will not contain cross-peaks that show how the spectral lines relate to the same nucleus. Therefore with the known way of obtaining 2D NQR spectrum one loses a significant part of the information concerning the system being studied.

Moreover, tuning the frequency of the NQR Fourier spectrometer to record the entire NQR spectrum requires each time a new measurement of $S(t_1, t_2)$ and a calculation of $S(\omega_1, \omega_2)$, which greatly increases the time required to obtain the 2D spectrum.

We have proposed a method for increasing the information content and reducing the time required to collect 2D NQR spectra by measuring and analyzing the twofrequency NQR spin-echo signals at adjacent transitions.⁷⁴

This goal is achieved in the following way. In the familiar method of recording 2D spectra, which includes measuring the transverse magnetization in the form of a two-dimensional function of the instantaneous time and the time of evolution after the stages of preparation, evolution and mixing, and subsequent two-dimensional Fourier transformation, one records the net magnetization due to the mixed transitions of one and the same nucleus after the creation of coherent nonequilibrium states and mixing with the aid of a two-frequency pulse sequence program. This method is different from others in that during the time of preparation of the spin system and during the mixing period two pulse frequencies are used at the same time, with frequencies close to those of adjacent transitions of the nuclei under study. The varying magnetization is recorded by not just a single receiving device, tuned to a single frequency, but by two, tuned to the two operating frequencies, and the detection is done by two synchronous detectors.

For a spin quantum number I=5/2 and zero asymmetry parameter of the crystal electric field gradient, $\eta=0$,





the transition $\pm 1/2 \rightarrow \pm 5/2$ has zero transition probability, and cannot be observed.³

We have excited the transitions $\pm 1/2 \rightarrow \pm 3/2$ in the ¹²⁷I nuclei (14.7 MHz) and $\pm 3/2 \rightarrow \pm 5/2$ (29.4 MHz) in CdI₂ by a pair of pulses of duration t_w and t'_w separated by a time interval τ (using the program "kvadrat").

The responses $S_1(\tau,t)$ and $S_2(\tau,t)$ of the spin systems at the frequencies ω_1 and ω_2 after the two pulses were fed into the "Kompan" personal computer, they were summed, and from this function we carried out a twodimensional complex Fourier transformation; here t is the instantaneous time counted from the start of the second pulse. The two-dimensional spectrum $S(\omega_1, \omega_2)$ was constructed and the plotted out on the printer with the program "Surfer."

In the NQR spectrum of 127 I in CdI₂ shown in Fig. 18



FIG. 19. Two-dimensional spectrum of ${}^{127}I$ in CdI₂ obtained by the standard method.



FIG. 20. Block diagram of a two-dimensional two-frequency NQR spectrometer. MO—master oscillator; FC—frequency channel; CD synchronous detector; AD—analog/digital converter.

one can see, in addition to the transitions at the frequencies ω_1 (14.7 MHz) and ω_2 (29.4 MHz), a transition at ω_3 (44.1 MHz), which is absent in the single-frequency variant. In addition, one can see cross-peaks with coordinates (14.7, 29.4) MHz and (29.4, 14.7) MHz, including the corresponding forbidden transitions: (14.7, 44.1) MHz and (29.4, 44.1) MHz (Refs. 21 and 75).

Figure 19 shows a two-dimensional NQR spectrum of 127 I in CdI₂ at T = 298 K, obtained by the one-frequency method.⁷⁴

This method of obtaining 2D NQR spectra can be implemented by any two-frequency NQR pulse spectrometer with Fourier transform capabilities. A block diagram of the apparatus for obtaining two-dimensional twofrequency NQR spectra by the direct method is shown in Fig. 20. The pulsed coherent NQR spectrometer has two independent channels of excitation and reception of the signals of the two-frequency echo. The operating frequency is provided by MO1 and MO2 master oscillators (using a Ch6/31 frequency synthesizer). The programmer PG generates the series of pulses and controls the operation of the entire spectrometer. The signals at the frequencies ω_1 and ω_2 of adjacent transitions are picked up by the receivers, and after detection by the synchronous detectors SD1 and SD2, they are converted to digital form by the analog-todigital converters AD1 and AD2. The signals of the twofrequency spin echo from the two transitions, which represent the time-dependent responses of the sample to the two-frequency excitation sequenced according to the "kvadrat" program, for example, are entered into the memory of a microcomputer through matching device. In a single measurement one row of the two-dimensional function $S(\tau,t)$ is recorded, corresponding to the given τ . The programmer changes the delay τ between pulses with the required step, that allows a recording of the entire matrix $S(\tau,t)$.

Let us now consider the excitation of a two-frequency spin echo of the ¹⁴N nuclei. The times that the twofrequency echo signals appear for the ¹⁴N nuclei according to the program "kvadrat"⁷⁶ are shown in Table V. The Fourier transform of the function $S(\tau,t)$, where τ is the time interval between pulses makes it possible to obtain the two-dimensional NQR spectrum. It can be seen from Table

Excitation Frequencies	Carrier Frequency	Appearance Time of Two-Frequency Echo	Coordinates in the Two-dimensional
¥_,¥_	¥+	0	ν ₊ , 0
		τ	¥_, ¥_
		21	ν ₊ , 2ν ₊
		$2\tau - \frac{\nu}{\nu_+}\tau$	ν ₊ , ν ₊ + ν ₀
		$\tau + \frac{\nu}{\nu_+}\tau$	$\nu_{+}, \nu_{+} + \nu_{-}$
	<u>۷_</u>	0	ν_, 0
		τ	ν_, ν_
ļ		21	v_, 2v_
}		$\tau + \frac{\nu_+}{\nu}\tau$	v_, v_ + v
		$\frac{\nu_+}{\nu}\tau$	ν_, ν ₊
v ₊ , v ₀	ν ₊	0	ν_, 0
		Ŧ	v ₊ , v ₊
		$2\tau - \frac{\nu}{\nu_{+}}\tau$	$\nu_{+}, \nu_{+} + \nu_{0}$
		$r + \frac{\nu_{-}}{\nu_{+}}r$	$\nu_{+}, \nu_{+} + \nu_{-}$
		2r	v ₊ , 2v ₊
	<i>v</i> 0	0	ν ₀ , 0
		τ	^v o ^{, v} o
		2r	v ₀ , 2v ₀
		$\frac{\nu_{+}}{\nu_{0}}$ r	۳ ₀ , ۳ ₊
		$\tau + \frac{\nu_+}{\nu_0}\tau$	$\nu_0, \nu_0 + \nu_+$
ν_, ν ₀	_۲	0	ν_, 0
		Ŧ	vv_
		$\frac{\nu_+}{\nu}\tau$	¥_, ¥_
		21	v_, 2v_
		$\tau + \frac{\nu_+}{\nu}\tau$	$\nu_{-}, \nu_{-} + \nu_{+}$
	ν _o	0	v ₀ , 0
		τ	۳0, ۳0
		27	v ₀ , 2v ₀
		$\frac{\nu_{+}}{\nu_{0}}\tau$	ν ₀ , ν ₊
		$r + \frac{\nu}{\nu_0}r$	$\nu_0, \nu_0 + \nu_+$

V that the cross-peaks of the two-dimensional spectrum are equivalent to the times of appearance of the signals in the two-frequency method.

If the one-dimensional NQR spectrum of ¹⁴N contains more than one or two lines we inevitably encounter the problem of correlating the multiplets and identifying the coupled transitions. This and other more detailed information on the spin system is provided by two-dimensional NQR spectroscopy.

We have established⁷⁶ a connection between the times of appearance of the two-frequency spin echo signal for the "kvadrat" program (I=1) and the coordinates of the 2D NQR spectrum. We calculate the complex intensities of the peaks of the 2D spectra, the amplitudes for the transfer of coherence, and establish a relation between the 2D NQR spectra and the various sequence programs of the twofrequency excitation. Of particular interest is the symmetry of the 2D spectra.

The reaction of the spin system after the preparation and mixing pulses according to the "kvadrat" program will be described by the density matrix

$$\rho(\tau,t) = S(\tau,t)\rho_0 S^{-1}(\tau,t), \qquad (4.4)$$

where

$$S(\tau,t) = \exp(-iH_Q t) \exp(-iH_1^{(M)} t'_w)$$
$$\times \exp(-iH_Q \tau) \exp(-iH_i^{(P)} t_w);$$

t is measured from the start of the second pulse, and the indices P and M denote the Hamiltonians of the interaction with the rf field at the preparation and mixing stages, respectively.

The net signal at the detection stage can be represented without taking into account the line width as^{68}

$$G(\tau,t) = \sum_{m,n} \exp (i\omega_m^{(d)}t) Z_{\mp \omega_m \omega_n} \exp(\mp i\omega_n^{(e)}\tau),$$
(4.5)

where $Z_{\mp \omega_m \omega_n}$ defines the intensity and the phase of the peak with the coefficients $[\omega_m^{(d)}, \mp \omega_n^{(e)}]$. The superscripts d and e denote the frequencies that are related to the periods of detection and evolution. Let us consider the case of echo and anti-echo signals in the two-dimensional spectrum (the N and P peaks.⁶⁸ It is evident that the coherences excited in the preparation stage contribute only to the anti-echo signal (the P peak).

The complex amplitude of the coherences after the preparation stage for the "kvadrat" program can be obtained in the form of the matrix elements

$$P_{\omega_n} = \frac{\hbar N}{3kT} \begin{pmatrix} i\cos\varphi \cdot \sin\alpha \cdot [\sin^2\varphi\omega_0 + \cos\alpha(\cos^2\varphi\omega_+ + \sin^2\varphi\omega_-)] \\ \sin\varphi \cdot \sin\alpha \cdot [\cos^2\varphi(1 - \cos\alpha)\omega_0 - \cos\alpha\omega] \\ i\sin\varphi \cdot \cos\varphi \cdot (1 - \cos\varphi)[\sin^2\varphi(1 - \cos\alpha)\omega_0 + \omega_- + \omega_+ \cos\alpha] \end{pmatrix} \begin{pmatrix} \omega_+ \\ \omega_- \\ \omega_0 \end{pmatrix}$$
(4.6)

where $\alpha = \gamma B_1 \sin \theta t_w$, n = +, -, 0.

The complex amplitude for the transfer of coherence from the transition with the frequency ω_n to the transition with the frequency $-\omega_m$ during the mixing process in this same program will be determined by the matrix elements $P_{-\omega_-\omega_-}$

$$= \begin{pmatrix} -\omega_{+} & -\omega_{-} & -\omega_{0} \\ \cos^{2}\varphi \cdot \sin^{2}\alpha' & i\sin\varphi \cdot \cos\varphi \cdot \sin^{2}\alpha' & -\sin\varphi \cdot \cos^{2}\varphi \cdot \sin\alpha'(1-\cos\alpha') \\ i\sin\varphi \cdot \cos\varphi \cdot \sin^{2}\alpha' & -\sin^{2}\varphi \cdot \sin^{2}\alpha' & -i\sin^{2}\varphi \cdot \cos\varphi \cdot \sin\alpha'(1-\cos\alpha') \\ \sin\varphi \cdot \cos^{2}\varphi \cdot \sin\alpha'(1-\cos\alpha') & -i\sin^{2}\varphi \cdot \cos\varphi \cdot \sin\alpha'(1-\cos\alpha') & -\sin^{2}\varphi \cdot \cos^{2}\varphi(1-\cos\alpha')^{2} \end{pmatrix} \begin{pmatrix} \omega_{+} \\ \omega_{-} \\ \omega_{0} \end{pmatrix}$$

$$(4.7)$$

where $\alpha' = \gamma B_1 \sin \theta t_w$; m, n = +, -, 0.

The matrix elements of the operator of an observed quantity can be written as

$$I_{\omega_m} = (\sin \theta \cdot \cos \varphi, \quad -i \sin \theta \cdot \sin \varphi, \quad \cos \theta). \quad (4.8)$$

Then the complex amplitudes of the two-frequency spin echo signals and the N-peaks of the 2D NQR spectrum will be equal to the product of the matrix elements

$$Z_{-\omega_m\omega_n} = I_{\omega_n} R_{-\omega_m\omega_n} P_{\omega_n}.$$
(4.9)

In the simpler cases, where the preparation and the mixing of the systems occur with a single rf pulse at the frequency ω_+ or ω_- the complex amplitudes of the coherences will be equal, respectively, to

$$P_{\omega_n} = \frac{\hbar N \omega_+}{3kT} \begin{pmatrix} -i\sin\alpha \cdot \cos\alpha \\ 0 \\ 0 \end{pmatrix} \begin{matrix} \omega_+ \\ \omega_- \\ \omega_0 \end{matrix}$$
(4.10)

where $\alpha = \gamma B_1 \sin \theta \cdot \cos \varphi t_w$, and

$$P_{\omega_n} = \frac{\hbar N \omega_-}{3kT} \begin{pmatrix} 0 \\ -\sin \alpha \cdot \cos \alpha \\ 0 \end{pmatrix}^{\omega_+}_{\omega_-}, \qquad (4.11)$$

where $\alpha = \gamma B_1 \sin \theta \cdot \sin \varphi t_w$.

The complex amplitudes for the transfer of coherences will be, respectively,

$$R_{-\omega_{m}\omega_{n}} = \begin{pmatrix} -\omega_{+} & -\omega_{-} & -\omega_{0} \\ \sin^{2} \alpha' & 0 & 0 \\ 0 & 0 & i \sin \alpha' \\ 0 & -i \sin \alpha' & 0 \end{pmatrix} \begin{pmatrix} \omega_{+} \\ \omega_{-} \\ \omega_{0} \end{pmatrix} (4.12)$$

 $R_{\omega_m \omega_n}$

here
$$\alpha' = \gamma B_1 \sin \theta \cdot \cos \omega t'_{-}$$
 and

$$R_{-\omega_{m}\omega_{n}} = \begin{pmatrix} -\omega_{+} & -\omega_{-} & -\omega_{0} \\ 0 & 0 & 0 \\ 0 & -i\sin^{2}\alpha' & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \omega_{+} \\ \omega_{-} \\ \omega_{0} \end{pmatrix}$$
(4.13)

where $\alpha' = \gamma B_1 \sin \theta \cdot \sin \varphi t'_w$.

The complex amplitudes of the P peaks of the 2D NQR spectrum are also determined by the product (4.9), but the values of the transfer of the coherences will here be different. For example, for the two-frequency mixing (ω_+ and ω_-) according to the "kvadrat" program, we have

$$= \begin{pmatrix} \omega_{+} & \omega_{-} & \omega_{0} \\ \cos \alpha' \cdot (\sin^{2} \varphi + \cos^{2} \varphi \cdot \cos \alpha') & i \sin \varphi \cdot \cos \varphi \cdot \cos \alpha' (1 - \cos \alpha') & -\sin \varphi \cdot \sin \alpha' (\sin^{2} \varphi + \cos^{2} \varphi \cdot \cos \alpha') \\ -i \sin \varphi \cdot \cos \varphi \cdot \cos \alpha' (1 - \cos \alpha') & \cos \alpha' \cdot (\cos^{2} \varphi + \sin^{2} \varphi \cdot \cos \alpha') & i \sin^{2} \varphi \cdot \cos \varphi \cdot \sin \alpha' (1 - \cos \alpha') \\ \sin \varphi \cdot \sin \alpha' (\sin^{2} \varphi + \cos^{2} \varphi \cdot \cos \alpha) & i \sin^{2} \varphi \cdot \cos \varphi \cdot \sin \alpha' (1 - \cos \alpha') & (\cos^{2} \varphi + \sin^{2} \varphi \cdot \cos \alpha') (\sin^{2} \varphi + \cos^{2} \varphi \cdot \cos \alpha') \\ \end{pmatrix} \omega_{+}$$

w

and for a single mixing pulse at the frequency ω_+ and $\omega_$ we have, respectively,

$$R_{\omega_{m}\omega_{n}}^{(+)} = \begin{pmatrix} \omega_{+} & \omega_{-} & \omega_{0} \\ \cos^{2} \alpha' & 0 & 0 \\ 0 & \cos \alpha' & 0 \\ 0 & 0 & \cos \alpha' \end{pmatrix} \omega_{+} \qquad (4.15)$$
$$R_{\omega_{m}\omega_{n}}^{(-)} = \begin{pmatrix} \omega_{+} & \omega_{-} & \omega_{0} \\ \cos \alpha' & 0 & -\sin \alpha' \\ 0 & \cos^{2} \alpha' & 0 \\ \sin \alpha' & 0 & \cos \alpha' \end{pmatrix} \omega_{+} \qquad (4.16)$$

The two-frequency spin-echo signals and the N and P peaks of the 2D NQR spectrum of ¹⁴N for various programmed sequences are illustrated in Fig. 21. The diagonal and cross peaks in this figure are shown for simplicity as absolute values, although in reality in the transfer of coherence they have different phases depending on the lengths of both the preparation and the mixing pulses. The same can be said of the amplitudes of the peaks of the 2D spectra, which for simplicity are shown equal. Moreover, the nonuniformity of the internal electric fields at the resonant nuclei causes the signals to be elongated to an extent determined by the width factor $1/T_2^*$ along the "comb" in the 2D spectrum, passing through the origin of the coordinate system, a feature that also is not shown in Fig. 21. The relaxation mechanisms of the spin system will determine the shape of the lines in the 2D NQR spectrum, as will the law of the decay of the echo, including the solid echo, with allowance for the dipole-dipole interaction of two kinds of spins.

(4.14)

Thus we have obtained the amplitudes and phases of the lines of the 2D NQR spectra recorded with various two-frequency excitation programs. This capability makes it possible to optimize the experimental arrangement with the use of two-frequency 2D NQR spectroscopy of ¹⁴N to determine the correlation of the transitions of coupled spin systems by the transfer of coherence from one transition to another in the mixing process.

Figure 22 shows a two-dimensional NQR spectrum of ¹⁴N in $C_3H_6N_6O_6$. The diagonal cross section of the spectrum corresponds to a one-dimensional spectrum (the v_+ and v_- lines). Because of the coarse scale, the close-lying triplet lines due to the three nonequivalent nitrogen sites are not resolved in the main peaks or in the cross peaks. The intensities of the cross peaks depend on the durations of the excitation pulse lengths. The two-dimensional NQR spectra of ¹⁴N in the high-frequency region were obtained in this investigation for the first time with the use of the special program for the "Kompan" computer.

The two-dimensional spectrum similarly obtained from the response of the NQR system to two-frequency excitation according to the "kvadrat" program⁶ is wholly equivalent to the spectrum with cross peaks discussed above. Conversely, knowing the positions and intensities of the cross peaks in the two-dimensional spectrum, one can determine the times of appearance and the intensities of the two-frequency signals in the "kvadrat" program.

In this way, the use of the two-frequency method in two-dimensional NQR spectroscopy opens up new possi-



FIG. 21. Two-frequency programs and 2D NQR spectrum (I=1).

bilities for enhancing the information content, while the use of the two-dimensional spectra has allowed us to propose a new means of attributing the NQR lines to specific nonequivalent sites of the nitrogen nucleus in the crystal.

The appearance of forbidden transitions in the twodimensional spectrum is due to mixing of the quantum states during the two-frequency excitation. Both the main signals and the cross peaks of the two-dimensional spectrum have intensities and phases that are determined by the duration and initial phases of the excitation pulses. The excitation of forbidden transitions and the presence of cross peaks in the case of several nonequivalent sites of the nuclei in the sample permit a unique identification of the NQR lines. Thus we have shown for the first time that forbidden transitions can be observed in the twodimensional NQR spectra.

The proposed method of obtaining two-dimensional NQR spectra has the following advantages over existing methods:

1. A greatly enhanced information content of the twodimensional NQR spectra due to the appearance of cross peaks, which belong to one nucleus and forbidden transitions.

2. Faster acquisition of the 2D spectrum because of the simultaneous recording of the two-frequency signals from adjacent transitions.

3. A much larger number of compounds that can be studied, particularly in the high-frequency region.

The principal difficulties associated with remote 2D spectroscopy are related to the low signal levels of remote NQR and the poor resolution of the lines. At the same time the 2D regime can be used successfully for identifying the NQR lines in the study of explosives.

5. NUCLEAR QUADRUPOLE RESONANCE IN EXPLOSIVES

A number of papers^{14,39,77} have been devoted to the detection of NQR of ¹⁴N in nitro compounds. These papers have focused mainly on the measurement of the parameters of the NQR spectra for cyclic nitrogen, and only in a small



FIG. 22. Two-dimensional NQR spectrum of C₁H₆N₆O₆.

number of compounds—the NQR spectrum of the nitro groups that have low-intensity lines in the frequency range 0.5-1 MHz.

In this investigation we have used the method of double NQR (Refs. 5 and 6) and also the direct-pulse method with signal averaging.⁹ The experimental results are shown in Table VI, where on the basis of the measured frequencies v_{+} and v_{-} we calculated the quadrupole interaction constants eQq_{zz} and the asymmetry parameters η . The data for the temperature dependence of the NQR frequency of some explosive materials can be found in Ref. 12.

TABLE VI.

Material	ν₊, kHz	י _{-י} kHz	cQq _{zz} , kHz	η	Temperature, Method
Trotyl	869	792	1107	0,1396	77 K
	895	801	1131	0,1654	Direct Method
	857	767	1083	0,1640	and
j –	875	767	1095	0,1978	DNQR
	861	729	1061	0,2490	
	888	730	1078	0,2929	
Hexogen	5118	3394	5674	0,608	77 K
	5256	3413	5779	0,638	Direct Method
	5319	3511	5887	0,614	
}	600	450	700	0,420	110 KDNQR
Octogen	5063	3623	5457	0,497	300 K
	5300	3737	6027	0,516	Direct Method
	720	540	840	0,42	ł
	720	490	806	0,48	110 K DNOR
TEN	1470	1170	1426	0,34	110 K
	1300	1080	1586	0,27	DNQR

The experiment showed that the detection of the NQR signal at the frequencies 5192 kHz in $N_3(CH_2)_3 \cdot (NO_2)_3$ and 5300 kHz in $N_4(CH_2)_4(NO_2)_4$ in the remote NQR regime⁹ is possible at room temperature even at distances of 20 to 25 cm from a sample having a weight more than 10 g. The other lines are too weak for remote detection.

However, the NQR lines of 14 N for the cyclic nitrogen when cooled to 298 K have been detected at the frequencies 5300, 5063, 3737, and 3623 kHz, and in hexogen (the strongest lines) at 5192 and 3410 kHz. These lines can readily be detected in mixtures of these explosives with trotyl, and with a surface coil they can be used to detect antitank mines based on hexotol under the ground (to 10 cm).

The time required to detect mines with a detection probability D=0.97 and a probability of a false indication F=0.03 in an area of 1 m² is 10 s, and with multichannel devices a prototype device is possible that for n=4 can travel on an armored vehicle with a speed of 7.6 km/h and detect 100% of the antitank mines in its path.

On the other hand, for the frequencies of cyclic nitrogen in octogen and hexogen, although they are suitable of detecting antitank mines, the enemy can artificially suppress the NQR signals from the mine by the use of pulsed rf interference.

In this case one can have recourse to the NQR spectrum of ¹⁴N of the nitro groups, which we have obtained for the first time by the method of ¹H–¹⁴N double nuclear quadrupole resonance with a selective magnetic field. We have calculated the NQR spectral parameters, i.e., the

TABLE VII.

K _{A-B}	h
$K_{C-C} = 1$ $K_{C-N} = 0.41$ $K_{N-N} = 0.82$	$h_{\rm c} = 0$ $h_{\rm N} = 2 - 2.4$ $h_{\rm N} = 1.3 - 1.5$
$K_{\text{C-CH}_3} = 1$	$h_{\rm CH_3} = -0.5$

quadrupole interaction constant eQq_{zz} and the asymmetry parameter η , using the formula of Ref. 9:

$$eQq_{zz} = \frac{2}{3}(v_{+} + v_{-}),$$

$$\eta = 3(v_{+} - v_{-})(v_{+} + v_{-})^{-1}.$$
(5.1)

The NQR method allows us to measure in chemical compounds the quadrupole interaction constant eQq_{zz} and the asymmetry parameter η of the electric field gradient tensor of the crystal.³ The asymmetry parameter η , unlike eQq_{zz} , depends strongly on ρ , the degree of double bonding of the chemical bond, since

$$\eta = \frac{3(N_x - N_y)}{2N_z - N_x - N_y},$$
(5.2)

where N_x , N_y , and N_z are the populations of the P_x , P_y , and P_z orbitals. For a spin quantum number I = 1 (¹⁴N) we have

$$\rho = \frac{2}{3} \left| \frac{eQq_{zz}}{eQq_0} \right| \eta, \tag{5.3}$$

where $eQq_0 = 8400$ kHz is the quadrupole interaction constant for the nitrogen atom per one unbalanced P electron. Here

$$\rho = 2 \sum_{i} c_i^2, \tag{5.4}$$

where c_i are the orthonormalized coefficients in the expansion of the wave functions of the *i*th atom and the summation is taken over the unfilled orbitals.

The calculations of ρ for three nitro compounds were carried out by Hofman's method of MO LCAO on the Kompan computer with the parameters of the heteroatoms as given in Table VII.

Table VIII lists the experimental and theoretical values of ρ of the three nitro compounds. By means of a regres-

TABLE VIII.

Compound	eQq _{22'} kHz	η	ρ Exp.	$\boldsymbol{\rho}_{\mathrm{Theor.}}$
1. $N_4(CH_2)_4(NO_2)_4$ Cyclic Nitrogen	5742	0,5065	0,2308	0,2316
NO,	823	0,450	0,0294	0,0293
2. C ₆ H ₃ (NO ₂) ₃ CH ₃	1107	0,1563	0,0137	0,0137
	1078	0,2465	0,0210	0,0223
3. $N_3(CH_2)_3(NO_2)_3$	5780	0,620	0,2844	0,2865
Cyclic Nitrogen				
NO ₂	700	0,420	0,0233	0,0267

sion analysis program we studied the connection between ρ_{theor} and η for different kinds of regression. We obtained the following results:

Linear regression:

$$\eta = 1.09316\rho + 0.2887419, \tag{5.5}$$

correlation coefficient R = 0.789882; geometric regression:

$$\eta = 0.9301297 \rho^{0.3143765},\tag{5.6}$$

exponential regression:

R = 0.7918453;

$$\eta = 0.2701423 \cdot 18.26075^{\rho},$$
 (5.7)
 $R = 0.695412.$

Thus formula (5.5) can be used for theoretical predictions of the asymmetry parameter η in nitro compounds from calculations of the degree of double-bonding ρ of the nitrogen chemical bonds.

6. CONCLUSIONS

The practical results obtained show that with nuclear quadrupole resonance methods it is possible to detect in a few seconds the spectra of samples that are situated at not too large distances from the measuring coil. This permits the NOR method to be used to address a number of problems that cannot be solved by other means. We have designed and constructed a device⁷⁸ for remote NQR and have shown that the maximum signal for the corresponding distances can be achieved by optimizing the mean power $\langle B_1 \rangle$ of the rf pulse acting with a detuning $\Delta \omega$. To determine the depth and position of the detected object a means has been developed based on finding the detuning in a strong, nonresonance multipulse sequence. Theoretical expressions have been derived for the intensities of the ¹⁴N NOR signals for single crystals and powder, and for the variation of the signal intensity of NQR of ¹⁴N in urotropine and hexogen as a function of the distance between the sample and the surface coil. The use of Fourier transforms in remote NQR of ¹⁴N significantly reduces the time to record the spectra by pulsed spectrometry.

A method has been proposed for increasing the sensitivity of remote NQR of 14 N by two-frequency excitation of the spin system and application of a weak magnetic field to the sample.

The possibilities of searching for explosives in hidden locations by means of nuclear quadrupole resonance of nitrogen nuclei have also been examined in Refs. 24, 27, and 79–81.

Numerical methods applied by us in NQR spectroscopy have been described in Refs. 57 and 34. Our proposed method of two-frequency, two-dimensional nuclear quadrupole resonance spectroscopy make it possible to observe forbidden transitions and attribute the lines to a single nonequivalent site in complex spectra with the assistance of the cross peaks.⁸²

Further developments in remote nuclear quadrupole resonance will lead to the development of practical monitoring instruments.

- ¹T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, Solid State Physics, Supplement 1, Academic Press, New York (1958).
- ²G. K. Semin, T. A. Babushkina, and G. G. Yakobson, *Applications of* NQR in Chemistry [in Russian], Leningrad (1972).
- ³V. S. Grechishkin, Nuclear Quadrupole Interactions in Solids [in Russian], Nauka, Moscow (1973).
- ⁴I. A. Safin and D. Ya. Osokin, Nuclear Quadrupole Resonance in Nitrogen Compounds [in Russian], Nauka, Moscow (1977).
- ⁵V. S. Grechishkin and V. P. Anferov, Adv. Nuclear Quadrupole Resonance, Vol. 4, 71 (1980).
- ⁶V. S. Grechishkin, V. P. Anferov, and N. Ya. Sinyavsky, Adv. Nuclear Quadrupole Resonance, 5, 1 (1983).
- ⁷V. S. Grechishkin, Z. Naturforsch. A 45, 559 (1990).
- ⁸V. S. Grechishkin, Tajan, P. R. China, (1990), p. 15.
- ⁹V. P. Anferov, V. S. Grechishkin, and N. Ya. Sinyavskii, *Nuclear Spin Resonance. New Methods* [in Russian], Leningrad State University (1990).
- ¹⁰ R. W. P. King, H. R. Mimno, and A. H. Wing, *Transmission Lines, Antennas, and Waveguides*, Mcgraw-Hill, New York (1945).
- ¹¹R. A. Marino, J. Mol. Struct. 111, 323 (1983).
- ¹²R. J. Karpowicz and T. B. Brill, J. Phys. Chem. 87, 2100 (1983).
- ¹³S. V. Anferova, V. S. Grechishkin, and V. P. Anferov, Teor. Exp. Khim. No. 2, 237 (1985).
- ¹⁴T. Hirschfeld and S. M. Klainer, J. Mol. State 58, 63 (1980).
- ¹⁵ V. S. Grechishkin and G. V. Mozzhukhin, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 2, 118 (1991).
- ¹⁶ V. S. Grechishkin and A. V. Bodnya, Inventor's certificate [Russian], No. 314658 (1990).
- ¹⁷ V. S. Grechishkin and T. N. Rudakov, Deposited in VINITI, No. 3480-V90.
- ¹⁸V. S. Grechishkin, Zh. Strukt. Khim. No. 4, 171 (1991).
- ¹⁹V. S. Grechishkin and I. R. Kutaeva, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 8, 121 (1991).
- ²⁰V. S. Grechishkin, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 8, 119 (1991).
- ²¹ V. S. Grechishkin and N. Ya. Sinyavskii, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 8, 73 (1991).
- ²²V. S. Grechishkin, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 9, 126 (1991).
- ²³ V. S. Grechishkin, T. N. Rudakov, V. P. Anferov, A. I. Kalyutik, and G. N. Chursin, Inventor's certificate [Russian], No. 265282 (1987).
- ²⁴ V. S. Grechishkin, V. P. Anferov, A. I. Kalyutik, G. M. Chursin, and N. M. Sitnikov, Oboronnaya Tekhnika No. 7, 16 (1986).
- ²⁵ V. S. Grechishkin, V. P. Anferov, and A. V. Belyakov, Inventor's certificate [Russian], No. 227392 (1985).
- ²⁶ V. S. Grechishkin, T. N. Rudakov, and V. B. Ganopol'skii, Inventor's certificate [Russian], No. 274627 (1988).
- ²⁷ V. P. Anferov, V. S. Grechishkin, G. V. Mozzhukhin, and N. Ya. Sinyavskii, Inventor's certificate [Russian], No. 278728 (1988).
- ²⁸ V. S. Grechishkin, G. V. Mozzhukhin, and A. V. Bodnya, deposited in VINITI, No. 4791-V88.
- ²⁹ V. S. Grechishkin, A. A. Shpilevoi, and N. Ya. Sinyavskii, deposited in VINITI, No. 433-B89.
- ³⁰ V. S. Grechishkin, R. V. Grechishkina, and O. V. Starovoitova, Zh. Fiz. Khim. 58, 770 (1989).
- ³¹ V. S. Grechishkin, A. A. Shpilevoi, and G. V. Mozzhukhin, deposited in VINITI, No. 4194-V89.
- ³² V. S. Grechishkin, N. Ya. Sinyavskii, and G. P. Alekseenko, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 1, 117 (1990).
- ³³ V. S. Grechishkin, and M. L. Zlatogorskii, Zh. Strukt. Khim. No. 6, 135 (1990).
- ³⁴ N. Ya. Sinyavskii and V. S. Grechishkin, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 1, 123 (1991).
- ³⁵T. N. Rudakov, V. S. Grechishkin, and A. V. Belyakov, Inventor's certificate [Russian], No. 303327 (1990).
- ³⁶ V. S. Grechishkin and O. V. Starovoitov, Fiz. Tverd. Tela (Leningrad) 32, 1601 (1990) [Sov. Phys. Solid State 32, 936 (1990)].
- ³⁷ V. S. Grechishkin, A. A. Shpilevoi, and T. N. Rudakov, deposited in VINITI, No. 5226-V90.
- ³⁸T. Dohler and H. Dohler, Arbeitstagung "Moderne Methoden und Ergebnisse der Fertkorper-NMR-Spektroskopie. 29, Nov.-3 Dez. Eisenach-Wartburg (1982), p. 18.
- ³⁹ A. De Los Santos. W. L. Rollwitz, and J. D. King, Bull. Am. Phys. Soc. No. 29, 72 (1984).
- ⁴⁰ A. V. Bodnja, V. S. Grechishkin, G. V. Moshukhin and T. N. Rudakov,

IXth AMPERE Summer School, Sept 20-26, Novosibirsk (1987), p. 312.

- ⁴¹ N. Ya. Sinyavskii and V. S. Grechishkin, deposited in VINITI, 12 July 1988, No. 5578-V88.
- ⁴² J. Max, Methodes et Techniques de Traitement du Signal et Applications aux Mesures Physiques, Masson, Paris (1985).
- ⁴³K. Roth, J. Chem. Soc. Faraday Trans. 2. 83, 1427 (1987).
- ⁴⁴R. R. Ernst, J. Magn. Reson. 4, 280 (1971).
- ⁴⁵ V. S. Grechishkin, S. I. Gushchin, and V. A. Shishkin, JETP Lett. 7, 44 (1968).
- ⁴⁶ V. S. Grechishkin, and N. Ya. Sinyavskii, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 11, 122 (1989).
- ⁴⁷V. S. Grechishkin, N. E. Ainbinder, S. I. Gushchkin, and V. A. Shishkin, Zh. Eksp. Teor. Fiz. 55, 787 (1968), [Sov. Phys. JETP 28, 407 (1968)].
- ⁴⁸N. E. Ainbinder and J. G. Shaposhnikov, Adv. in NQR. 3, 67 (1978).
- ⁴⁹E. A. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, New York (1969).
- ⁵⁰R. W. Dixon and N. Bloembergen, J. Chem. Phys. 41, 1739 (1964).
- ⁵¹G. K. Semin, S. A. Petukhov, V. M. Burbello, V. A. Egorov, and A. A. Boguslavskii, Izv. Akad. Nauk SSSR Ser. Fiz. **45**, 528 (1981) [Bull. Acad. Sci. USSR Phys. Ser. **45**(3), 64 (1981)].
- ⁵²S. A. Petukhov, Candidate's dissertation in the Physical and Mathematical Sciences, Perm (1985).
- ⁵³V. P. Anferov, G. S. Beloglazov, and V. N. Surkov, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 0, 26 (1985); deposited in VINITI July 15, 1987, No. 6229.
- ⁵⁴ V. P. Anferov, L. S. Kivaeva, and V. N. Surkov, deposited in VINITI, No. 5068-V38 (1989).
- ⁵⁵S. Sibisi, J. Skilling, G. Brereton, E. D. Laue, and J. Staunton, Nature, 311, 446 (1984).
- ⁵⁶R. A. Jackson, J. Magn. Reson. 75, 174 (1987).
- ⁵⁷ N. Ya. Sinyavskii, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 12, 91 (1990).
- ⁵⁸E. D. Laue, M. R. Mayger, J. Skilling, and J. Staunton, J. Magn. Reson. **68**, 14 (1986).
- ⁵⁹F. Ni. G. C. Levy, and H. A. Scherata, J. Magn. Reson. **66**, 385 (1986).
- ⁶⁰M. A. Delsuc and G. C. Levy, J. Magn. Reson. 76, 306 (1988).
- ⁶¹ E. D. Laue, J. Skilling, J. Staunton, S. Sibisi, and R. G. Brereton, J. Magn. Reson. **62**, 437 (1985).
- ⁶² J. Skilling and R. K. Bryan, Mon. Not. R. Astron. Soc. 211, 111 (1984).
- ⁶³ N. Ya. Sinyavskii, Nuclear Quadrupole Resonance, Interuniversity collection, Kaliningrad, State University, Kaliningrad, No. 1, 13 (1976).
- ⁶⁴J. L. Engle, J. Magn. Reson. 37, 547 (1980).
- ⁶⁵ R. A. Assink, E. Fukushima, A. A. V. Gibson, A. R. Rath, and S. B. W. Roeder, J. Magn. Reson. 66, 176 (1986).
- ⁶⁶ A. R. Rath, S. B. W. Roeder, and E. Fukushima, Rev. Sci. Instrum. 56, 402 (1985).
- ⁶⁷S. Vega, J. Chem. Phys. **61**, 1093 (1974).
- ⁶⁸ R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Oxford University Press, Oxford (1990).
- ⁶⁹A. M. Thayer, J. M. Millar, and A. Pines, Chem. Phys. Lett. **129**, 55 (1986).
- ⁷⁰R. Kreis, Dissertation, Zurich Technischen Hochchule (1989).
- ⁷¹A. Bax, Two-Dimensional Nuclear Magnetic Resonance in Liquids, Delft University Press, Dordrecht, Holland (1982) [Nauka, Novosibirsk (1989)].
- ⁷² N. Ya. Sinyavskii, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 5, 113 (1991).
- ⁷³ R. N. Bracewell, *The Hartley Transforms*, Oxford University Press, New York (1986) [Mir. Moscow (1990)].
- ⁷⁴N. Ya. Sinyavskii and V. S. Grechishkin, Announcement of inventor's certificate [Russian], of January 21, 1991, MKI 01 24/00 (affirmative decision November 25, 1991).
- ⁷⁵V. S. Grechishkin and N. Ya. Sinyavskii, Fiz. Tverd. Tela (Leningrad) 33, 1875 (1991) [Sov. Phys. Solid State 33, 1053 (1991)].
- ⁷⁶N. Ya. Sinyavskii and V. S. Grechishkin, deposited in VINITI December 13, 1990, No. 6221-V90.
- ⁷⁷S. M. Klainer, T. V. Hirschfeld, and R. A. Marino, Fourier Transform Nuclear Quadrupole Resonance Spectroscopy. Fourier, Hadamad, and Hilbert Transforms, Plenum Press, New York (1982).

- ⁷⁸ A. V. Bodnya, V. S. Grechishkin, and G. V. Mozzhukhin, deposited in VINITI, NO. 4791-V33.
- ⁷⁹V. P. Anferov, V. G. Kuznetsov, and N. Ya. Sinyavskii, Inventor's certificate [Russian], No. 305856, December 1, 1989.
- ⁸⁰ V. S. Grechishkin, N. Ya. Sinyavskii, and G. V. Mozzhukhin, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 7, 61 (1992).
- ⁸¹V. S. Grechishkin, Appl. Phys. A 55, 505 (1992).
- ⁸²V. S. Grechishkin and N. Ya. Sinjavsky, Z. Naturforsch. A 47, 430 (1992).
- ⁸³ V. S. Grechishkin and R. V. Grechishkina, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 10, 125 (1992).

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