

**STRUCTURAL INVESTIGATIONS IN CRYSTALS BY THE METHOD OF  
NUCLEAR MAGNETIC RESONANCE**

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1. INTRODUCTION

THE phenomenon of nuclear magnetic resonance (NMR), discovered in 1946 by Bloch<sup>33</sup> and Purcell,<sup>109</sup> belongs to a new domain of physics—radiospectroscopy. At the present time NMR has become an effective method for the study of the internal structure and the properties of matter and also of various physico-chemical processes in all states of aggregation (by 1960 the total number of publications has exceeded two thousand). In particular, extensive material has been accumulated on the investigation of nuclear resonance spectra in solids. The present review is an attempt to collect and systematize the quite numerous applications of the NMR method of obtaining information on the structure of the crystalline lattice. As is well known, structural investigations by means of NMR are a valuable supplement to the method of x-ray analysis in making more precise determinations of the position of the light nuclei† (for example, H<sup>1</sup> and F<sup>19</sup>; it should be noted that these nuclei give rise to the

most intense nuclear resonance signals). We shall not specifically discuss the application of the NMR method to the study of molecular dynamics in crystals, but shall touch on the problem of the effect of molecular motion only insofar as this is necessary for a correct understanding of structural information obtained from nuclear resonance spectra. Nor do the aims of the present review include a discussion of problems associated with relaxation phenomena and with quadrupole effects in solids. In order to facilitate the use of this review by persons without special preparation in the field of radiospectroscopy, we shall give below a resumé of the basic facts related to NMR.

If a nucleus has a nonzero spin  $I$  then its magnetic moment  $\mu$  also differs from zero. The nuclear angular momentum can have  $2I+1$  different orientations with respect to an externally applied constant magnetic field  $H_0$  (space quantization). The additional energy of the magnetic dipole is in this case equal to

$$E = -\frac{h}{2\pi} m\gamma H_0 = -\mu \frac{m}{I} H_0, \quad (1)$$

where  $m$  is the magnetic quantum number which can take on the values  $I, I-1, \dots, -I$ , and  $\gamma = \mu/(h/2\pi)I$  is the nuclear gyromagnetic ratio. Transitions between the energy levels (1) take place in accordance with the

\*Deceased.

†The coordinates of light nuclei can also be determined by means of neutron diffraction. However, this method so far is accessible only to a few laboratories.

selection rules  $\Delta m = \pm 1$ . Since the levels are equally spaced there arises the single frequency

$$\nu_0 = \frac{\gamma}{2\pi} H_0. \quad (2)$$

Often in place of the gyromagnetic ratio we use for the description of nuclear magnetism the dimensionless gyromagnetic factor  $g$ , which is equal to  $\gamma 2Mc/e$ ; here  $M$  is the proton mass,  $c$  is the velocity of light, and  $e$  is the proton charge.

Expression (2) is the basic relation in the theory of NMR. It should be noted that the same result is obtained on the basis of purely classical concepts of the motion of a magnetic dipole tracing out a cone about the direction of  $H_0$  (Larmor precession). In the commonly used magnetic fields (of the order of several thousand gauss) the Larmor precession frequencies (2) for the majority of nuclei fall in the range 1–60 Mc. In order to observe resonance absorption of energy at frequencies close to  $\nu_0$ , an alternating magnetic field of the appropriate frequency is applied to the sample containing the nuclei under investigation and situated in the field  $H_0$ . Transitions between levels are induced only by the component of the alternating field which is perpendicular to  $H_0$ .

Since the resonance frequency depends on  $H_0$  passage through the resonance region can be accomplished both by the variation of the operating frequency  $\nu$  of the apparatus, and also by a variation of the magnetic field. In the latter case  $\nu$  is fixed and the resonance frequency  $\nu_0$  varies in accordance with (2). In this case it turns out to be convenient to plot the spectrum not in terms of frequencies, but in terms of the magnetic field.

From expression (2) it can be seen that NMR can be utilized for the determination of nuclear gyromagnetic ratios, or if  $\gamma$  is already known, then it can be used for the measurement of magnetic fields (in the latter case the problem reduces to the determination of the frequency  $\nu_0$ ). Moreover, at present nuclear resonance spectra are utilized for the solution of various problems of molecular physics and physical chemistry. These applications are based on the utilization of various characteristics of the NMR lines (width, fine structure etc.), and of these we shall in future be interested only in the line shape of the NMR signal from samples in the solid phase.

Interaction between nuclear magnetic dipoles occurs in matter: each nucleus produces in the space surrounding it a certain local magnetic field which acts on neighboring nuclei.\* These local fields are the main cause of broadening of NMR lines in solids (the absorption of energy takes place in a certain

\*It is assumed that the material does not contain any paramagnetic particles. In this case we have to take into account only the magnetic interactions between the nuclei, since closed electron shells give rise only to rapidly varying (fluctuating) magnetic fields which practically do not affect the precession of nuclear moments.

frequency range, the center of which coincides with  $\nu_0$ ).

If the crystal lattice contains relatively isolated groups each with a small number of nuclear magnetic dipoles strongly interacting with one another (the so-called two-, three- and four-spin systems), the NMR spectrum becomes a multiplet spectrum. The theory of such spectra is by now well developed, and as a result of this experimental observation of such spectra enables us to obtain valuable structural information with respect to the crystal lattice. In the more general case (in the absence of isolated groups of nuclei) the theoretical calculation of the line shape turns out to be impossible, and the structural investigations are based on the measurement of certain of its integral characteristics, the so-called moments. These questions are investigated in detail below.

In the presence of thermal vibrations of appreciable amplitude or of other forms of molecular motion, the character of the local field changes. Depending on the degree of mobility of the particles the average value of the local field determining the width of the NMR lines is decreased to some extent. In order to obtain information on the structure of samples in which intensive molecular motion takes place, we have to study the NMR spectrum at low temperatures (at which the crystalline lattice is sufficiently rigid and the mobility is restricted to small thermal vibrations).

## 2. THEORY OF LINE WIDTH AND LINE SHAPE OF NUCLEAR MAGNETIC RESONANCE LINES IN CRYSTALS

a) Two-spin systems. As we have already pointed out, the dipole-dipole interaction is the principal factor that determines the shape of NMR lines in crystals. The simplest case from the point of view of theoretical discussion is the interaction between two nuclei. At the same time this case is of considerable practical interest since often a crystal lattice actually contains comparatively isolated pairs of magnetic nuclei (for example, the protons of water molecules in crystalline hydrates).

As an example we shall consider a molecule containing two atoms the nuclei of which are characterized by spin  $\frac{1}{2}$ .\* The two nuclei A and B in such a molecule are situated at a distance  $r_{AB}$  from one another (Fig. 1), and under the influence of the field  $H_0$  their spins will precess about the appropriate direction with frequencies  $\nu_{0A}$  and  $\nu_{0B}$ . The nucleus B gives rise at the point A to a local field  $H_{loc}$  (usually of the order of magnitude of a few gauss) and is itself acted upon by the local field due to the nucleus A. These fields are produced by precessing magnetic moments and, therefore, consist of two com-

\*By this assumption we exclude from consideration nuclei possessing quadrupole moments (for which  $I \geq 1$ ), and we therefore need not take into account the effect of electric fields.

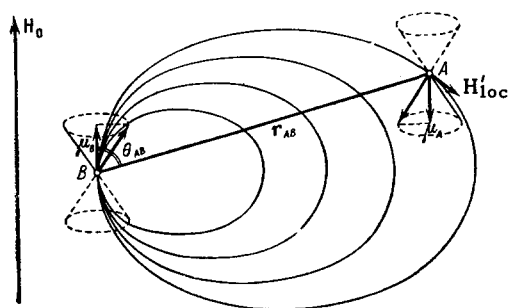


FIG. 1. Magnetic dipole-dipole interaction between two nuclei.

ponents: a constant component  $H'_{loc}$  and a variable component  $H''_{loc}$ . These components affect a nucleus differently, and we shall therefore discuss them separately.

The z-component of the magnetic moment of nucleus B gives rise at the site of the nucleus A to a constant local field  $H'_{loc}$ . The magnitude of the component of  $H'_{loc}$  parallel to the external field  $H_0$  (i.e., to the Oz axis)\* is a function of the distance between the atoms  $r_{AB}$  and of the angle  $\theta_{AB}$  between the line joining the nuclei and the direction of the external field  $H_0$  (cf. Fig. 1):

$$(H'_{loc})_z = \pm \frac{\mu_B}{r_{AB}^3} (3 \cos^2 \theta_{AB} - 1); \quad (3)$$

the "+" or "-" signs are determined by which one of the two quantum states  $m = \pm 1/2$  (which one of the two precession cones) is occupied by the nucleus B. Thus, the total constant magnetic field at the point A will be equal to

$$H = H_0 \pm \frac{\mu_B}{r_{AB}^3} (3 \cos^2 \theta_{AB} - 1). \quad (4)$$

The rotating component of the precessing magnetic moment of nucleus B gives rise at the point A to a variable local field  $H''_{loc}$ , which varies at a frequency  $\nu_{0B}$ . If  $\nu_{0A} \neq \nu_{0B}$  (in other words, if A and B are nonidentical nuclei), then the variable local field does not affect the precession. We fix the value of the external magnetic field  $H_0$  and vary the frequency of the apparatus that records the NMR. By multiplying the right hand and the left hand sides of (4) by  $\gamma_A/2\pi$ , we obtain the resonance values of the frequency for the nucleus A:

$$\nu_{res}^{(1,2)} = \nu_0 \pm \frac{\gamma_A}{2\pi} \frac{\mu_B}{r_{AB}^3} (3 \cos^2 \theta_{AB} - 1), \quad (5)$$

where  $\nu_0 = \gamma_A H_0/2\pi$ . As can be seen from (5) the spectrum consists of a doublet, the distance between the components of which depends on the positions of nuclei A and B. If resonance is observed using a macro-

\*The value of the local field usually does not exceed 10–20 gauss, i.e., as a rule  $H_0 \gg H'_{loc}$ . Under these conditions the perpendicular component of  $H'_{loc}$  produces only a small change in the orientation of the vector representing the total field, without affecting its length and without giving rise to experimentally observable effects.

scopic sample (for details see below) the intensities of the components of the doublet are equal. Indeed, nuclei B belonging to different molecules are distributed among their two quantum states corresponding to the ratio of the Boltzmann factors  $\exp(+\mu_B H_0/kT)/\exp(-\mu_B H_0/kT)$ , which is very nearly equal to unity ( $\mu_B H_0/kT$  is usually  $\gg 10^{-5}$ ). Thus, the spectrum is symmetric with respect to the frequency  $\nu_0$ ; such symmetry is in general characteristic of the shape of NMR lines due to dipole-dipole interactions of nuclei in crystals.

However, if we fix the frequency of the instrument  $\nu_0$  and vary the magnetic field within appropriate limits, then the resonance values will be given by

$$H_{res}^{(1,2)} = H_0 \mp \frac{\mu_B}{r_{AB}^3} (3 \cos^2 \theta_{AB} - 1), \quad (6)$$

where  $H_0 = 2\pi\nu_0/\gamma_A$ . Expression (6) differs from (4) only by the order of the signs of the second term. This fact is explained in the following manner: if the local field is added to the external field ["+" sign in formula (4)], then in order to obtain a resonance signal at the original frequency  $\nu_0$  the field  $H_0$  must be reduced by the same amount ["-" sign in formula (6)], and vice versa. However, since the spectrum is symmetric, we shall henceforth make no distinction in the order of signs in similar cases.

If  $\nu_{0A} = \nu_{0B}$  (in the case of identical nuclei), then, generally speaking, components of a high frequency field appear at points A and B and can induce quantum transitions similar to those induced by an external radiofrequency field. In such a case a quantum is transferred from one nucleus to the other, i.e., a simultaneous transition takes place for two nuclei (in the spin- $1/2$  case under discussion this is possible only if nuclei A and B belong to different precession cones). Such an interaction affects the value of doublet splitting, but a quantitative evaluation of this splitting is impossible within the framework of classical mechanics.\*

Pake<sup>98</sup> has carried out a quantum-mechanical calculation for the interaction of a pair of protons in water of crystallization. In the first approximation we can treat the crystal as a number of independent nuclear pairs; under these conditions the Hamiltonian operator has the following form:

$$\hat{\mathcal{H}} = -2\mu H_0 (\hat{I}_{Az} + \hat{I}_{Bz}) + 4\mu^2 r_{AB}^{-3} [\hat{I}_A \hat{I}_B - 3(\hat{I}_A \hat{i}_{AB})(\hat{I}_B \hat{i}_{AB})], \quad (7)$$

where  $\hat{i}_{AB}$  is a unit vector directed from one nucleus to the other,  $r_{AB}$  is the distance between the nuclei,  $\hat{I}_A$ ,  $\hat{I}_B$  are the nuclear spin operators. In the spin- $1/2$  case under discussion the system of two nuclei has

\*In setting up a rigorous quantitative theory the nuclei A and B are regarded as a single quantum-mechanical system whose energy levels are to be calculated. In such a case the concepts of precession cones for individual nuclei and of transitions between them are not utilized, since they do not have a rigorous physical meaning for a coupled system.

three energy levels corresponding to the possible orientations of the total spin  $I_{\Sigma}$ , which is equal to unity.\* In the absence of interaction these levels are equidistant and the transitions between them give rise to a single spectral line ( $\nu_0 = \gamma H_0 / 2\pi$ ). However, if we take into account the second term of the operator (7), then the levels are shifted, and the spectral line is split into two components. In the first approximation of perturbation theory, calculation yields the following formula for the resonance values of the field:

$$H_{\text{res}}^{(1,2)} = H_0 \pm \frac{3}{2} \frac{\mu}{r_{AB}^3} (3 \cos^2 \theta_{AB} - 1). \quad (8)$$

Compared to the case of nonidentical nuclei [formula (6)] the quantum mechanical calculation for a pair of identical nuclei gives for the magnitude of the splitting an additional factor  $3/2$ .

A given pair of protons and all the analogous (from the point of view of the direction of the line joining the nuclei) pairs in the crystal give rise to two resonance lines each of which is shifted from the center of the doublet by the amount  $3\mu r_{AB}^{-3} (3 \cos^2 \theta_{AB} - 1)/2$ . If we take into account local fields produced by the other protons, then we find that the components of the doublet are broadened (we shall discuss later in greater detail the interaction of a large number of nuclei). By taking a sample in the form of a single crystal, an elementary cell of which contains one type of proton pairs (all the  $r_{AB}$  are parallel to each other), and by investigating the dependence of the doublet splitting [cf. formulas (6) and (8)] on the orientation of the axes of the single crystal with respect to the external magnetic field, we can find the distance between the protons and the orientation in space of the line joining them. A similar investigation is possible, although it becomes more difficult, in the case of several different orientations of the vectors  $r_{AB}$ ; as the number of different directions of  $r_{AB}$  is increased a superposition of a number of doublets corresponding to different orientations occurs, and this leads to an unresolved spectrum.

If the sample containing the dipole pairs is polycrystalline, then its spectrum will be a sum of spectra for all possible orientations of  $r_{AB}$  [cf. (8)] distributed isotropically in space. We are interested in the envelope of the spectrum displayed, for example, on a magnetic field scale. In other words, we have to calculate the distribution function for the components of the doublet for all possible orientations of  $r_{AB}$ . We first consider one of the lines of the doublet corresponding to the "+" sign associated with the second term in formula (8). This line will fall in the interval between  $H_{\text{res}}$  and  $H_{\text{res}} + dH_{\text{res}}$  for all the dipole pairs whose orientation is characterized by the angle  $\theta_{AB}$  in the interval  $\theta_{AB}$  to  $\theta_{AB} + d\theta_{AB}$ . As a result

\*The fourth level, for which  $I_{\Sigma} = 0$ , plays no role, since a very strict selection rule  $\Delta I_{\Sigma} = 0$  holds (singlet-triplet transitions are forbidden).

of the aforementioned isotropic distribution of the orientations of the vectors  $r_{AB}$ , the number of orientations contained in the interval  $d\theta_{AB}$  and determining the intensity of the spectrum in the given interval is proportional to the element of area of the unit sphere

$$dS = 2\pi \sin \theta_{AB} \cdot d\theta_{AB}. \quad (9)$$

The relation between  $d\theta_{AB}$  and  $dH_{\text{res}}$  can be obtained by differentiating formula (8) with respect to  $\theta_{AB}$ :

$$dH_{\text{res}} = -9 \frac{\mu}{r_{AB}^3} \cos \theta_{AB} \sin \theta_{AB} d\theta_{AB}. \quad (10)$$

From (9) and (10) it follows that

$$|dS| = \frac{2\pi}{9 \frac{\mu}{r_{AB}^3} \cos \theta_{AB}} dH_{\text{res}}. \quad (11)$$

On expressing  $\cos \theta_{AB}$  in (8) in terms of  $H_{\text{res}}$  we finally obtain

$$|dS| = \frac{2\sqrt{3}\pi r_{AB}^3}{9\mu} \frac{1}{\sqrt{1 + \frac{2}{3} \frac{r_{AB}^3}{\mu} (H_{\text{res}} - H_0)}} dH_{\text{res}}, \quad (12)$$

where  $(H_{\text{res}} - H_0)$  varies within the following limits:

$$\frac{3\mu}{r_{AB}^3} > (H_{\text{res}} - H_0) > -\frac{3}{2} \frac{\mu}{r_{AB}^3}. \quad (13)$$

In accordance with the above discussion the coefficient of  $dH_{\text{res}}$  is proportional to the intensity of the signal in a given narrow spectral interval, i.e., it is a function of the line shape for a polycrystalline sample (on a magnetic-field scale).

As far as the second line of the doublet is concerned, it is always symmetrical to the first line with respect to the point  $H_0$ . As a result of this the averaged distributions also have the same symmetry. The corresponding curves for both lines are shown in Fig. 2a. The resultant curve is also shown there.

In a real crystal the NMR line is broadened additionally as a result of the interaction of nuclear pairs among themselves, but often its "double hump" character is retained (Fig. 2). A measurement of the magnitude of the doublet splitting [which is equal, as can be seen from (8), to  $3\mu r_{AB}^{-3}$ ] again enables us, although with a somewhat lower degree of accuracy, to determine the internuclear distance.

Thus, the quantum mechanical treatment<sup>98</sup> of the case of nuclei distributed in a crystal in pairs enables us to obtain some information on the structure of the crystal lattice by analyzing the shape of the NMR line. The use of the NMR method for the determination of structural parameters of crystals containing pairs of neighboring nuclei will be given in Sec. 4.

b) Three- and four-spin systems. Relatively isolated groups consisting of three magnetic nuclei occur in certain solid organic compounds (methyl groups  $\text{CH}_3$ ) and in hydrates of salts (oxonium ions  $\text{H}_3\text{O}^+$ ). Andrew and Bersohn<sup>16</sup> have given a theoretical discussion of the NMR spectrum of three identical spin- $1/2$  nuclei

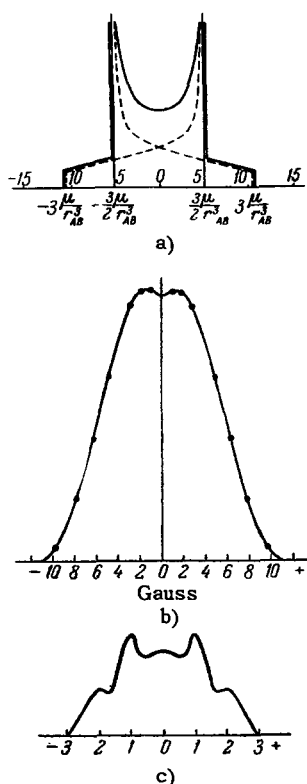


FIG. 2. a) Theoretical line shape for NMR signals in a powdered sample containing two-spin systems; the interaction between pairs of nuclei is not taken into account. b) and c) Experimentally obtained spectra for nitroguanadine<sup>113</sup> and  $\text{CCl}_3\text{COOH}$ <sup>147</sup> respectively. The first example illustrates the effect of an appreciable, and the second example of a weak, interaction between pairs of nuclei.

situated at the vertices of an arbitrary triangle. In the case of a single crystal containing identical and identically oriented triangles of nuclei, the spectrum consists of a central component and of three pairs of lines symmetrically situated with respect to the center. The distance between these lines and their relative intensities are functions of the angle coordinates specifying the orientation of the triangle with respect to the field  $H_0$ . The resonance values of the field in this case are given by the formulas

$$H_{\text{res}}^{(1)} = H_0, \quad H_{\text{res}}^{(2,3)} = H_0 \pm \frac{y}{\mu},$$

$$H_{\text{res}}^{(4,5)} = H_0 \pm \frac{3x+y}{2\mu}, \quad H_{\text{res}}^{(6,7)} = H_0 \pm \frac{3x-y}{2\mu}, \quad (14)$$

where in the case of an equilateral triangle of side  $R$  we have

$$x = \frac{3}{2} \mu^2 R^{-3} \left( \frac{1}{2} - \frac{3}{2} \cos^2 \psi \right),$$

$$y = \frac{3}{2} \mu^2 R^{-3} \left( \frac{27}{4} \sin^4 \psi - 3 \sin^2 \psi + 1 \right)^{1/2} \quad (15)$$

( $\psi$  is the angle between the external magnetic field and the normal to the plane of the triangle). From the above it can be seen that in a single crystal containing the configuration of three nuclei under discussion the line shape depends on the orientation of the crystal axis with respect to the external magnetic field.

For a polycrystalline sample, as usual, the spectrum will be obtained by summing the spectra from isotropically oriented groups. The theoretical NMR curve can be obtained by a method analogous to the one discussed by us in the case of a powder containing two-spin systems. As a result of the interaction between the different groups of nuclei, the theoretical curve for an isolated triangle is smoothed out and broadened, so that ordinarily a "three hump" curve is obtained. An experimental investigation of the shape of the NMR line of a three-spin system sometimes enables us (as will be shown in Sec. 4) to determine the position of the nuclei in the group.

A linear configuration of three spin- $\frac{1}{2}$  nuclei in the case when the magnetic moments of two nuclei are equal to one another but are different from the third one gives rise to a multiplet spectrum,<sup>141</sup> a quantitative investigation of which enables us to reach conclusions with respect to the relative position of the nuclei along the line (cf. Sec. 4).

The shape of the lines for a group of four identical nuclei ( $I = \frac{1}{2}$ ) was investigated in<sup>26,27,135,136</sup> (tetrahedron) and in<sup>70,71</sup> (parallelogram). Bersohn and Gutowsky<sup>26,27</sup> have considered the spectrum of a tetrahedral four-spin system in two cases: a) the magnetic field is directed along a two-fold or three-fold axis of symmetry, and b) the direction of the magnetic field coincides with one of the edges of the tetrahedron. In these special cases, depending on the orientation of the single crystal, the spectrum can have from seven to twenty components, which are broadened under the influence of the nuclear spins of other groups and are smeared out into one common curve that exhibits almost no multiplet structure.

The rapid increase in the complexity of the spectrum in going over from two-spin systems to three- and four-spin systems shows the futility of attempting to develop a similar theory for a still larger number of nuclei in a group (and a fortiori when no isolated groups of strongly interacting nuclei are present). In such a case a computation of the line shape would in the best case be very time-consuming; moreover, even if this could be carried out successfully, it would not be possible, because of the lack of resolution of individual components, to carry out a comparison with experiment which would be to any extent complete. In the general case by foregoing a detailed calculation of the shape of the NMR line in crystal samples we can characterize this shape by certain of its integral characteristics (cf. below).

c) Integral characteristics of the spectrum (moments). Van Vleck's theory. The concept of the moments of an NMR spectrum was introduced by Van Vleck<sup>138</sup> who developed a rigorous theory of the dipole-dipole interactions of nuclei which relates certain characteristics of the NMR lines to the structure of a solid.

The Hamiltonian operator for a system consisting of  $N$  interacting nuclear spins can be divided into two parts:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{V}, \tag{16}$$

where

$$\hat{\mathcal{H}}_0 = \gamma \hbar H_0 \sum_j \hat{I}_{zj}$$

and

$$\hat{V} = \sum_{k>j} \gamma^2 \hbar^2 r_{jk}^{-3} \{ (\hat{I}_j \hat{I}_k) - 3 (\hat{I}_j \hat{i}_{jk}) (\hat{I}_k \hat{i}_{jk}) \},$$

and where  $r_{jk}$  is the vector joining nuclei  $j$  and  $k$ ,  $\hat{i}_{jk} = r_{jk}/r_{jk}$  is the unit vector in the same direction, and  $\hat{I}_j, \hat{I}_k$  are the nuclear spin operators. The summation is extended over all  $N$  particles. The term  $\hat{\mathcal{H}}_0$  in formula (16) describes the energy acquired by the nuclear magnetic moments in an external field. It is much larger in magnitude than the term  $\hat{V}$  which corresponds to the energy of the dipole-dipole interaction (in accordance with the evaluation carried out previously, the local fields are of the order of magnitude of several gauss, while  $H_0$  in usual experiments on NMR in crystals attains values of  $5 \times 10^3$  gauss and greater).

The problem remains complex and even practically insoluble, if we set ourselves as our aim the calculation of the shape of the absorption line. Van Vleck<sup>138</sup> succeeded in showing that it is possible to calculate the quantities  $\bar{\nu}^2, \overline{\Delta\nu^2}, \overline{\Delta\nu^4}$ , etc. averaged over the line shape (for an explanation of this notation cf. below). If  $\nu_0$  is the resonance frequency corresponding to the center of the line ( $\nu_0 = \gamma H_0/2\pi$ ), while  $g(\nu)$  is a form factor (a function describing the shape of the absorption line), then the  $n$ -th moment is given in the frequency scale by

$$(\overline{\Delta\nu})^n = \overline{(\nu - \nu_0)^n} = \frac{\int_0^\infty g(\nu) (\nu - \nu_0)^n d\nu}{\int_0^\infty g(\nu) d\nu}. \tag{17}$$

Of particularly great importance is the second moment

$$\overline{\Delta\nu^2} = \frac{\int_0^\infty g(\nu) (\nu - \nu_0)^2 d\nu}{\int_0^\infty g(\nu) d\nu}, \tag{18}$$

which is also often expressed in terms of magnetic fields:\*

$$\overline{\Delta H^2} = \frac{\int_0^\infty g(H) (H - H_0)^2 dH}{\int_0^\infty g(H) dH}. \tag{19}$$

In experiments one frequently measures instead of  $g$  the derivative of this quantity with respect to  $\nu$  or  $H$ , and in this connection it is convenient to introduce the corresponding changes in the definition of the sec-

\*Often  $g(\nu)$  and  $g(H)$  are used to denote form factors normalized in such a manner that the integrals in the denominators of (18) and (19) are equal to unity. We retain the form given in the text above, as it corresponds better to the evaluation of the second moment from experimental data.

ond moment. Integrating by parts we can easily obtain (cf., for example, reference 105)

$$\overline{\Delta\nu^2} = \frac{1}{3} \frac{\int_0^\infty g'(\nu) (\nu - \nu_0)^3 d\nu}{\int_0^\infty g'(\nu) (\nu - \nu_0) d\nu} \tag{20}$$

and a completely similar expression for  $\overline{\Delta H^2}$ .

We now undertake a theoretical determination of the second moment (following Van Vleck). The following relation obviously holds

$$\overline{\Delta\nu^2} = \overline{(\nu - \nu_0)^2} = \bar{\nu}^2 + \nu_0^2 - 2\bar{\nu}\nu_0, \tag{21}$$

which shows that it is necessary to know  $\bar{\nu}^2$  and  $\bar{\nu}$  in order to determine  $\overline{\Delta\nu^2}$ . The inclusion of the dipole-dipole interaction energy in the Hamiltonian for this problem makes the usual selection rule  $\Delta m = \pm 1$  somewhat nonrigorous: transitions  $\Delta m = 0, \pm 2, \pm 3$ , appear and also, with a still lower intensity,  $\Delta m = \pm 4$  etc. This means that absorption is possible at frequencies which are integral multiples of the Larmor frequency  $\nu_0$ . However, experimentally only the single most intense line corresponding to the transition  $\Delta m = \pm 1$  is observed. We shall henceforth interpret averaging in the evaluation of the integral characteristics (17)–(21) as being carried out only within the limits of the line shape of this principal line.

Van Vleck has shown generally that if the external field is large in comparison with the local fields (i.e.,  $|\nu - \nu_0| \ll \nu_0$ ), the shape of the line corresponding to  $\Delta m = \pm 1$  is to a good approximation symmetric with respect to the Larmor precession frequency of the isolated nucleus  $\nu_0$ ; from this we obtain  $\bar{\nu} = \nu_0$ , as a result of which formula (21) can be written in the following form:

$$\overline{\Delta\nu^2} = \bar{\nu}^2 - \nu_0^2. \tag{22}$$

We also note that in virtue of the symmetry of the NMR line only its even moments differ from zero.

Thus, it is necessary to evaluate theoretically the second moment of the principal ( $\Delta m = \pm 1$ ) line, which consists as a result of the dipole-dipole interaction of a very large number of components  $\nu_{nn'}$  which are neither calculated nor observed individually (the subscripts  $n$  and  $n'$  run through all the quantum states of the coupled system of nuclear spins). Since the intensity of an individual component is proportional to the square of the matrix element  $|(\hat{I}_x)_{nn'}|^2$  this quantity can be taken as the weighting factor in carrying out the average; in this case the mean square of the frequency is given by the relation

$$\bar{\nu}^2 = \frac{\sum_{nn'} \{ \nu_{nn'}^2 |(\hat{I}_x)_{nn'}|^2 \}}{\sum_{nn'} |(\hat{I}_x)_{nn'}|^2}. \tag{23}$$

In Van Vleck's theory the quantity  $\bar{\nu}^2$  is calculated only for one line ( $\Delta m = \pm 1$ ) by using the so called "truncated" Hamiltonian operator in which the terms

corresponding to the transitions  $\Delta m = 0, \pm 2, \pm 3, \dots$  are omitted (if the complete Hamiltonian is used, then the satellite lines are also included). By utilizing the method of diagonal sums Van Vleck obtained from (23) an expression for the second moment  $\overline{\Delta\nu^2}$ . It should be noted that the value of the second moment in terms of the magnetic fields is also very useful. The relation between these two expressions is given by the formula

$$\overline{\Delta H^2} = \left(\frac{2\pi}{\gamma}\right)^2 \overline{\Delta\nu^2}. \quad (24)$$

For a single crystal containing magnetic nuclei of several different types (numbered in the following by the index  $F$ ) the mean square deviation expressed in terms of the magnetic fields is given by\*

$$\overline{\Delta H^2} = \frac{1}{N} \sum_i \left\{ \frac{3}{4} I(I+1) g^2 \mu_0^2 \sum_{k(\neq i)} (3 \cos^2 \theta_{ik} - 1)^2 r_{ik}^{-6} + \sum_F \frac{1}{3} I_F(I_F+1) g_F^2 \mu_0^2 \sum_{l_F} (3 \cos^2 \theta_{il_F} - 1)^2 r_{il_F}^{-6} \right\}. \quad (25)$$

We first consider the expression in the curly brackets, evaluated for the  $i$ -th resonating nucleus. The index  $k$  labels the resonating nuclei characterized by spin  $I$  and gyromagnetic ratio  $g$ ; the index  $l_F$  labels nuclei of type  $F$  with the corresponding characteristics  $I_F$  and  $g_F$ . Moreover, the following notation has been adopted:  $\mathbf{r}_{ik}(\mathbf{r}_{il_F})$  is a vector from the  $i$ -th nucleus to the nucleus characterized by the index  $k(l_F)$ ,  $\theta_{ik}(\theta_{il_F})$  is the angle between  $\mathbf{r}_{ik}(\mathbf{r}_{il_F})$  and the direction of the external magnetic field;  $\mu_0$  is the nuclear magneton. Summation over  $k$  and  $l_F$  extends over the whole crystal; as a result of the presence of the factor  $r_{ik}^{-6}$  (or  $r_{il_F}^{-6}$ ) this sum converges rapidly (an important role is played only by a small part of the crystal near the nucleus  $i$ —usually within a sphere of radius of approximately 10 Å).

The summation over  $i$  can be extended to all the resonating nuclei in the sample, and in this case  $N$  denotes their total number. But since the expression  $\frac{1}{N} \sum_i$  represents averaging, it is sufficient to carry out this summation over an elementary cell.

If the sample is polycrystalline, then the orientations of  $\mathbf{r}_{ik}$ ,  $\mathbf{r}_{il_F}$  are distributed isotropically in space. In such a case the factors  $(3 \cos^2 \theta_{ik} - 1)^2$  and  $(3 \cos^2 \theta_{il_F} - 1)^2$  must be averaged over a sphere.

\*Formula (25) also holds for nuclei with  $I \geq 1$ , i.e., possessing a quadrupole moment. However, it should be taken into account that expression (25) is valid in the absence of a quadrupole interaction between nuclei whose NMR is being observed. The second term in (25) remains valid in any arbitrary case. In practice calculations using formula (25) are carried out most frequently for nuclei of spin  $\frac{1}{2}$ .

The form in which (25) is written above differs somewhat from that generally used in the literature. It appears to us to be more convenient both for understanding and for practical calculations of the value of the second moment in specific crystals.

As a result of this averaging the value of the second moment for a powdered sample with several different types of magnetic nuclei assumes the form

$$\overline{\Delta H^2} = \frac{1}{N} \sum_i \left\{ \frac{3}{5} I(I+1) g^2 \mu_0^2 \sum_{k(\neq i)} r_{ik}^{-6} + \sum_F \frac{4}{15} I_F(I_F+1) g_F^2 \mu_0^2 \sum_{l_F} r_{il_F}^{-6} \right\}, \quad (26)$$

where all the notation has been already explained previously.

In a polycrystalline sample, in the case when all the resonating nuclei are structurally equivalent (transformed into each other by symmetry elements of the crystal), the expression in the curly brackets does not depend on  $i$  and, consequently, there is no need at all to take an average (with respect to  $i$ ). However, if the polycrystalline sample contains several different types of structurally nonequivalent nuclei then it is necessary to average with respect to  $i$  using appropriate weighting factors.

Formulas (25) and (26) for the values of the second moment for a single crystal and for a powder enable us to use the NMR method for the determination of certain structural parameters of a crystal lattice. As a result of quantitative investigations of the shape of the absorption line in a single crystal the following characteristics can be obtained:

- the value of the second moment  $\overline{\Delta H^2}$  for different orientations of the crystal in an external magnetic field;
- the dependence of the shape of the absorption line on the orientation (fine structure of the NMR line).

As a rule, an investigation of the line shape for a polycrystalline sample gives only the average value of  $\overline{\Delta H^2}$  (sometimes one can also observe fine structure of the type described above<sup>98</sup>).

Reference 91 reports a theoretical investigation of the maximum number of crystal lattice parameters that can be determined by studying the anisotropy of  $\overline{\Delta H^2}$  for different orientations of a single crystal.\* The value of the second moment is given as a function of the angles  $\theta$  and  $\varphi$  which define the position of  $\mathbf{H}_0$  with respect to an arbitrarily chosen coordinate system rigidly attached to the crystal under investigation. The expression obtained consists of products of 22 lattice sums (which depend on the nuclear coordinates) and different combinations of  $\cos \theta$ ,  $\cos \varphi$ ,  $\sin \theta$ ,  $\sin \varphi$  and of various powers (up to the fourth) of these quantities. The authors have shown that only 15 lattice sums are independent, while the remaining seven are linear combinations of the first 15. Thus, in principle, these 15 sums can be determined from the experimental data, and this enables us to determine 15 structural parameters appearing in these sums. However, the question arises as to which orientations

\*Reference<sup>91</sup> gives directly the calculation for only one type of magnetic nuclei in the sample; however, its results admit generalization also to the case of several types of nuclei.

of the single crystal will enable us to obtain 15 independent equations in the course of measurement of  $\Delta H^2 = \overline{\Delta H^2}(\theta, \varphi)$ . As was shown in reference 91, it is necessary to observe the anisotropy of the second moment utilizing four different axes of rotation, chosen, for example, in the following manner:  $\varphi = 0, \pi/4, \pi/2$ ;  $\theta = \pi/2$  (of course, in doing so it is possible to carry out more than 15 measurements and to eliminate partially errors from the determination of the second moments by reducing the results obtained by the method of least squares). If there are no structural data at all with reference to the single crystal, then it is possible to determine the coordinates of three nuclei in an elementary cell.\* If the dimension and the orientation of an elementary cell are known, then a complete structural determination is possible if the elementary cell contains six nuclei, etc.

d) Effect of small thermal vibrations on the observed value of the second moment. In the discussion of the shape of an NMR line and in the derivation of the formulas for the second moment in Van Vleck's theory the crystal lattice was assumed to be sufficiently rigid that it was possible to neglect the effect of thermal vibrations. However, in many cases thermal vibrations produce an appreciable effect on the shape of an NMR line. Moreover, in some crystals molecular rotation and self-diffusion occur.

The evaluation of the magnitude of the local fields and of their effect on the width of NMR lines which we have carried out earlier is not valid in the case of molecular motion (particularly if it is not confined to small vibrations). In the presence of thermal motion the local fields will vary randomly both with respect to their magnitude and direction, with the rate of variation often being quite appreciable. The presence of intense thermal motion leads to a narrowing of the NMR line both due to the reduction of the effective (average) value of the local field  $H_{10C}$ , and also as a result of the hindering of the exchange of nuclear spins, caused by  $H_{10C}''$ .

The foundations for a quantitative account of the variations in the second moment of a rigid lattice,† due to small thermal vibrations, were laid in the papers by Andrew,<sup>14</sup> Deeley and Richards,<sup>41</sup> and Gutowsky, Pake, and Bersohn.<sup>60</sup> Andrew has shown that in the presence of torsional oscillations of angular amplitude  $\alpha$  about an axis that makes an angle  $\gamma$  with the field  $H_0$  the intramolecular contribution to the second moment is diminished<sup>14</sup> by the factor  $\rho = 1 - \frac{3}{2}\alpha^2 \sin^2 \gamma$ . Deeley and Richards<sup>41</sup> introduced

\*A determination of the dimensions of the elementary cell, of its shape, and of its position with respect to the original coordinate axes requires nine parameters. One of the nuclei can, without loss of generality, be regarded as situated at the origin of an elementary cell, while for each subsequent nucleus it is necessary to determine three additional structural parameters.

†We have in mind the experimentally observed second moment of an NMR line (cf. footnote\*, p. 956).

a correction to the theoretical value of the second moment in a crystal of  $N_2H_6F_2$  (hydrazine fluoride) which takes into account the effect of vibrations of the atoms in the  $N_2H_6^{++}$  ion. The introduction of this correction reduces to the replacement of  $\sum_{ik} r_{ik}^{-6}$  in (26) by  $\sum_{ik} \overline{(r_{ik}^{-3})^2} \approx \sum_{ik} r_{ik}^{-6} (1 + 6\Delta r_{ik}^2/r_{ik}^2)$ , where the bar denotes averaging over thermal vibrations of amplitude  $\Delta r_{ik}$  (this latter quantity is evaluated approximately, for example, from the vibrational frequencies).

The two types of thermal vibrations mentioned earlier were taken into account simultaneously, and the corresponding correction to the interatomic distances obtained in NMR experiments was carried out in the paper of Ibers and Stevenson,<sup>68</sup> but these authors restricted themselves to the special case of samples in which the intramolecular contribution to the second moment was predominant, since, in their opinion, an analogous correction to the intermolecular contribution is, at best, difficult. The numerical calculations of these authors for  $NH_4Cl$ , for which the intraionic contribution to  $\Delta H^2$  is particularly large, showed that the correction due to the torsional oscillations is five times larger than the effect of the valence and deformation types of oscillations. On the other hand, in the case of  $N_2H_6F_2$  Ibers and Stevenson<sup>68</sup> obtained an almost exact mutual cancellation of corrections due to the intraionic oscillations and the torsional oscillations of the ion, and this led to an appreciable change in the results of the work of Deeley and Richards<sup>41</sup> quoted above.

e) Changes in the nuclear magnetic resonance spectrum occurring in the case of intense molecular motion. The foundations for the quantitative evaluation of the variation of the line shape for two- and three-spin systems in the presence of rotational mobility were given in references 16 and 58. Gutowsky and Pake<sup>58</sup> have carried out a theoretical calculation of the dependence of the variation of the second moment on the nature of molecular motion. The general principle effective in these cases can be briefly formulated in the following manner: the factor  $(3 \cos^2 \theta - 1) r^{-3}$  occurring in the expression for the splitting of the multiplet spectrum and for the second moment must be averaged over the molecular motion. In the case when  $\Delta H^2$  is being evaluated, the averaged expression obtained must be squared.

From the theory of Bloembergen, Purcell, and Pound<sup>35</sup> it follows that rotation or random reorientation have an effect on the NMR spectrum only when their frequencies become comparable with the line width  $\Delta\nu$ . In practice the reorientation frequencies that turn out to be effective are of the order of  $10^4 - 10^5$  cps and higher. Gutowsky and Pake have carried out calculations for an isolated system of two identical spin- $1/2$  nuclei undergoing reorientation either freely or in a potential field of symmetry  $C_n$  ( $n \geq 3$ ) about an axis perpendicular to the internuclear vector. The



reorientation frequency was assumed to be high compared to the magnitude of doublet splitting  $\nu_{\text{res}}^{(1)} - \nu_{\text{res}}^{(2)}$  [cf. formula (5)] in the rigid lattice. The doublet character of the line is preserved, and

$$H_{\text{res}}^{(1,2)} = H_0 \pm \frac{3}{4} \frac{\mu}{r_{AB}^3} (3 \cos^2 \theta'_{AB} - 1), \quad (27)$$

where  $\theta'_{AB}$  is the angle between  $H_0$  and the reorientation axis. Thus, the splitting of the spectrum depends on the direction of the axis of rotation for the pair, and not of the internuclear vector; the maximum value of the splitting is reduced by a factor two compared to a rigid system. For a polycrystalline sample the NMR line also retains its doublet character, while the splitting is halved.

The line structure for an isolated system of three nuclei in the presence of rotation has been investigated by Andrew and Bersohn.<sup>16</sup> Just as in the case of the rigid triangular system mentioned previously, we expect a spectrum consisting of a central line and of three pairs of symmetrically situated satellite lines. In the most frequently occurring case, when the reorientation axis is normal to the plane of the triangle, only one central line and one pair of satellites remain with the intensity ratio 1:2:1.

In the general case (in the absence of small isolated groups of nuclei) the line shape cannot be predicted theoretically, and the second moment of the absorption line is compared with experimental data. In the presence of rotation it is easy to calculate only the intramolecular contribution to the second moment  $(\Delta H^2)_1$ . If the rotation axis makes an angle  $\theta'$  with the direction of the field  $H_0$ , then the following formula holds

$$\begin{aligned} (\overline{\Delta H^2})_1 &= \frac{1}{4} (3 \cos^2 \theta' - 1)^2 \\ &\times \left[ \frac{1}{N} \sum_i \left\{ \frac{3}{4} I(I+1) g^2 \mu_0^2 \sum_{k(\neq i)} (3 \cos^2 \gamma_{ik} - 1) r_{ik}^{-6} \right. \right. \\ &\left. \left. + \sum_F \frac{1}{3} I_F(I_F+1) g_F^2 \mu_0^2 \sum_{l_F} (3 \cos^2 \gamma_{il_F} - 1)^2 r_{il_F}^{-6} \right\} \right], \quad (28) \end{aligned}$$

where  $\gamma_{ik, il_F}$  is the angle between the reorientation axis and the vector  $r_{ik, il_F}$ ; the remaining notation is analogous to that utilized in (25). Expression (28) gives directly the contribution to the second moment due to a single rotating group of atoms. It is also applicable to the evaluation of the intramolecular contribution to  $\Delta H^2$  in a single crystal in which all the rotational axes are parallel to one another. However, if the different molecules rotate about axes with different orientations, then it is necessary to carry out an additional averaging over all the angles  $\theta'$ .

In a polycrystalline sample the factor  $(3 \cos^2 \theta' - 1)^2/4$  becomes equal to  $1/5$  as a result of averaging over the sphere. In the special case, when all the  $\gamma_{ik}$  and  $\gamma_{il_F}$  in formula (28) are equal to  $90^\circ$  (i.e., when the rotation axes are perpendicular to the internuclear vectors), the intramolecular contribution to the second moment

for a powder is smaller by a factor four compared to  $(\Delta H^2)_1$  for a rigid lattice. We note, that an analysis of the reduction in the intramolecular contribution due to reorientations about more than a single axis was given by Powles and Gutowsky.<sup>106</sup>

The variation of the intermolecular contribution to the second moment in the case where the molecules rotate about one or about all three axes has been estimated by Andrew and Eades.<sup>18</sup> The corresponding calculations turn out to be quite awkward, since in averaging the factor  $(3 \cos^2 \theta - 1) r^{-3}$  one must take into account the variation not only of  $\theta$ , but also of  $r$ . The rotational motion by itself never reduces the intermolecular contribution to zero; if one observes in a solid an NMR line of very small width characteristic of liquids, this denotes the presence not only of rotational but also of translational motion of the molecules (self-diffusion).

The results quoted above with respect to the effect of molecular motion on the second moment require one essential qualification. As Anderson has shown (cf. reference 100, p. 45) the terms in the Hamiltonian expressing nuclear motion have no effect at all on the total second moment. However, the requirement that the second moment should remain constant as the temperature varies does not mean that the shape of the spectrum remains the same. Pake<sup>100</sup> has shown that in the presence of molecular motion the fourth moment increases, and this implies a narrowing of the central portion of the spectrum and an increase in the intensity of its outer edges. Andrew<sup>22</sup> has investigated the change in the shape of the spectrum in the presence of rotation or of random reorientation in the crystal. Intensive molecular motion gives rise (in addition to the main components considered above) to weak satellites which usually are not observed experimentally. Thus, for example, in the case of the spectrum due to a pair of nuclei the axis of rotation of which is perpendicular to the line joining them, in addition to the frequencies given by expression (5) one also obtains the frequencies  $\pm n\nu_r$ , where  $n$  is an integer, and  $\nu_r$  is the rotational frequency of the pair.

In the case of random reorientation the spectrum consists of a narrowed central part and of side bands extending on both sides from the central absorption line up to frequencies  $\nu_0 \pm 1/2\pi\tau$  (where  $\tau$  is the correlation time for the random motion).

Quite analogous side bands must occur also in other cases (in the absence of pairwise grouping of nuclei). Since they are usually too weak to be observed experimentally, one should use in comparisons with experiment the formula not for the total second moment (which, as we have already noted, coincides with the moment of the rigid lattice), but for  $\Delta H^2$  with the contribution of the side bands subtracted. Formula (28) of Gutowsky and Pake, discussed by us earlier, gives precisely this quantity.

f) Double resonance in crystals. In experiments on double resonance in solids the sample is simultaneously subjected to the action of two radiofrequency fields. Usually in this case the crystal contains two types of magnetic nuclei (A and B) with resonance frequencies  $\nu_0^{(A)} = \gamma_A H_0 / 2\pi$  and  $\nu_0^{(B)} = \gamma_B H_0 / 2\pi$ . The NMR of nuclei A is observed with simultaneous application of a strong alternating field\* of frequency  $\nu_1$  close to  $\nu_0^{(B)}$  or equal to it. The shape of the NMR line of nuclei A and its second moment are studied at different amplitudes of the strong field mentioned above and at different amounts of detuning  $\nu_1 - \nu_0^{(B)}$ . A theoretical discussion of the characteristics of the NMR line under such experimental conditions has been given in references 32 and 137. The application of a strong radiofrequency field induces corresponding transitions of nuclei B. This is accompanied by an averaging of the local field at the sites of nuclei A (the local field varies with the frequency  $\gamma_B H_2 / 2\pi$ , where  $H_2$  is the amplitude of the alternating field).

Bloch<sup>32</sup> has shown that the second moment of nuclei A does not depend on the power applied to nuclei B, and on the amount of detuning of the oscillator  $\nu_1 - \nu_0^{(B)}$ . However, this is accompanied by a change in the shape of the spectrum: the shape of the NMR line of nuclei A consists of a central narrowed component (observed experimentally) and of weak side bands (usually unobservable) arising as a result of an interaction of frequency  $\nu_1$ . Thus, the overall picture is very close to the case of the appearance of intense molecular motion discussed in reference 22.

Reference 119 contains results of an experimental verification of Bloch's calculations. The resonance of  $\text{Na}^{23}$  nuclei was observed in powdered NaF (the second moment is in this case due to the interaction both of  $\text{Na}^{23}-\text{Na}^{23}$ , and also predominantly of  $\text{Na}^{23}-\text{F}^{19}$ ). A radiofrequency field corresponding to the  $\text{F}^{19}$  resonance was applied simultaneously. As the power of this field was increased, the contribution to the second moment due to the effect of the fluorine nuclei diminished (Fig. 3). Because of certain instrumental reasons the authors did not succeed in achieving a complete averaging out of the local fields of the  $\text{F}^{19}$  nuclei, which would have enabled them to determine the magnitude of the second moment due to the  $\text{Na}^{23}-\text{Na}^{23}$  interaction. Thus, the method of double resonance in crystals in principle gives a possibility of measuring separately the contributions to the second moment due to different types of interacting nuclei.† Such a possi-

\*Usually in NMR experiments in the solid phase the amplitude of the radiofrequency field has a magnitude of a few hundredths of a gauss. The strong alternating field mentioned above has in many double resonance experiments in crystals an amplitude as high as 10 gauss.

†As has been pointed out above, the method of two radiofrequency fields is used most widely in the case when nuclei of several different types are present in the sample. The interesting experiments on double resonance of nuclei of a single type should be mentioned,<sup>74</sup> and in particular those in a two-proton system (single crystal of  $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ ); during the observation of one

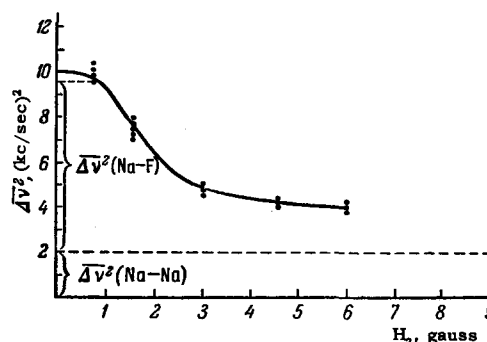


FIG. 3. Dependence of the second moment of the NMR signal of  $\text{Na}^{23}$  in powdered NaF on the amplitude of the alternating field acting on the fluorine nuclei at their resonance frequency.<sup>119</sup>  $\overline{\Delta\nu^2}(\text{Na-Na})$  and  $\overline{\Delta\nu^2}(\text{Na-F})$  are the theoretical values of the contributions to the second moment due to the effects of the Na and F nuclei respectively.

bility is unquestionably of interest for structural analysis.

### 3. EXPERIMENTAL METHODS

a) Radiofrequency spectrograph for quantitative study of nuclear magnetic resonance in solids. A quantitative experimental investigation of the shapes of NMR lines in crystals is made difficult by their considerable width, and often by their very low intensity. The observation of NMR signals visually on an oscilloscope screen (as is often done in investigations of liquids) is not always applicable in the case of crystalline samples and, in any case, does not guarantee a sufficiently high degree of reproducibility of the line shape. In this connection it is necessary to use a phase-sensitive detector with a narrow band amplifier to increase the signal-to-noise ratio. A radio-frequency spectrograph which enables one to determine second moments of NMR lines must satisfy the following particularly important requirements:

1) High sensitivity of the electronic circuitry, for only in the case of good signal-to-noise ratio is it possible to evaluate  $\overline{\Delta H_{\text{exp}}^2}$  with negligible statistical error.

2) Reproducibility of the shape of the NMR lines in the same sample on repeated measurements; determined, in particular, by the amplitude stability of the sensitivity.

3) High degree of stability of the magnetic field during the time of measurement,\* for to determine  $\overline{\Delta H^2}$  it is necessary to calibrate the NMR spectrum

of the components of the doublet a strong alternating field was applied simultaneously at the frequency of the second component. The theory of this problem is discussed in reference 34. The observed component is split into two lines, the distance between which agrees with the theoretically calculated value only qualitatively.

\*The presence in the phase detector of long time-constants (10–50 sec) increases the time of recording the NMR line to 30 or more minutes, and this, naturally, makes the requirements on the degree of stability of the magnetic field more stringent.

in units of the frequency scale or of the magnetic-field scale [cf. formula (20)].

At present the literature contains descriptions of radio frequency spectrographs suitable for the study of broad and weak NMR lines.<sup>11,12,42,80</sup> The principles of construction of such spectrographs and their block diagrams are generally the same; the differences concern the quality of construction of individual electronic units and of different auxiliary items (for example, the device used to measure the amplitude of the alternating field of the oscillator). Because of this we shall restrict ourselves to a brief description of the spectrograph used by us and we shall note some of its characteristic features.<sup>4</sup>

The block diagram of the spectrograph is given in Fig. 4. The magnetic field is obtained by means of an electromagnet with a pole tip diameter of 200 mm and an air gap of 40 mm. The oscillator (autodyne), in whose tank circuit the investigated substance is placed,

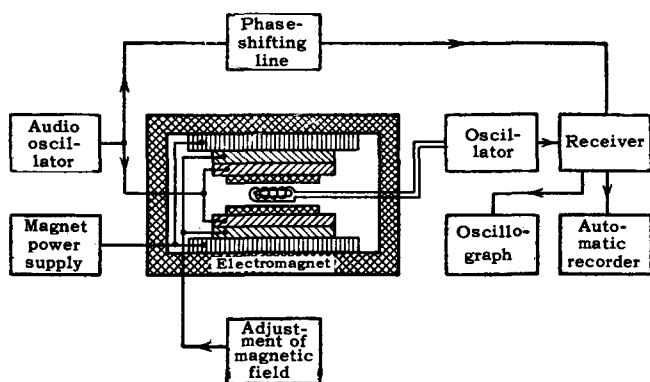


FIG. 4. Block diagram of rf spectrograph.

is a separate two-tube unit comprising the oscillator and the dividing stages. The receiver circuit has both an amplitude and a frequency channel.\* The frequency channel consists of a superheterodyne receiver with a frequency detector and its operating frequencies are in the neighborhood of 12, 14, and 16 Mc (which correspond to harmonics of the quartz crystal that stabilizes the heterodyne). The amplitude channel has the same operating frequencies, but is a receiver with direct amplification. In the investigation of liquids the signal from the low frequency amplifier is fed to an oscillo-graph (cf. Fig. 4). In this case the modulating signal (19.5 cps) which is applied to special windings on the magnet (Fig. 5) from a ZG-10 audio oscillator is at the same time used as the oscilloscope sweep.

As already mentioned, a phase-sensitive detector with a slow continuous sweep over the spectrum is used in the study of crystals to improve the signal-to-noise ratio. In this case the signal from the low frequency amplifier is fed into a narrow band amplifier

\*The amplitude channel records the variation in the amplitude of the oscillations of the oscillator at the instant of resonance, and gives the absorption component; the frequency channel responds to the deviation of the oscillator frequency and gives the dispersion component.

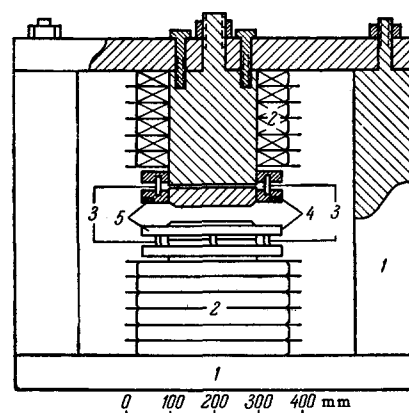


FIG. 5. Electromagnet of the rf spectrograph. 1 — yoke; 2 — field coils; 3 — adjusting volts; 4 — modulation coils; 5 — coils for small adjustments of the field.

and a phase-sensitive detector. The modulation amplitude must be several times smaller than the line width in the sample under investigation. Under these conditions the NMR signal is a sinusoidal curve whose amplitude is proportional to the slope of the line contour at the given point (at the same time a voltage of the same frequency  $\nu_{mod}$  is applied as a reference voltage to the phase-sensitive detector). Schuster's circuit,<sup>120</sup> in which the detected signal is applied to the grid of a pentode whose plate load is a double triode, is used quite frequently. The two halves of this double triode are in turn blocked and opened by the reference voltage. The output of the phase-sensitive detector (in Schuster's circuit—between the plates of the two halves of the double triode) is a voltage proportional to the cosine of the phase shift between the detected and the reference signals. In this case the useful signal which coincides in frequency with  $\nu_{mod}$  gives the dc component of the voltage, while the spectral components of the noise with  $\nu \neq \nu_{mod}$  give the ac components. The dc component is separated by an integrating circuit. The first derivative of the NMR line obtained by this method of observation is recorded on an automatic recorder (in our case EPP-09).

The continuous sweep over the crystal spectrum is accomplished either by a slow variation of the magnetic field within suitable limits, or by a variation of the oscillator frequency. The variation of the magnetic field is accomplished by means of a special device using the charge of a large capacitor (on the order of 1200  $\mu f$ ). The voltage from the capacitor is applied to a tube amplifier of sufficient power whose load consists of coils producing small shifts of the field of the electromagnet (cf. Fig. 5). Variation of the oscillator frequency for sweeping over the spectrum is utilized only in the case of the amplitude channel,\* and is achieved with the aid of a telechron

\*The detector used in the frequency channel is of high sensitivity in a fairly narrow frequency interval (of the order of 10 kc), while the width of the NMR spectrum in the solid phase frequently attains values of 100 kc and greater.

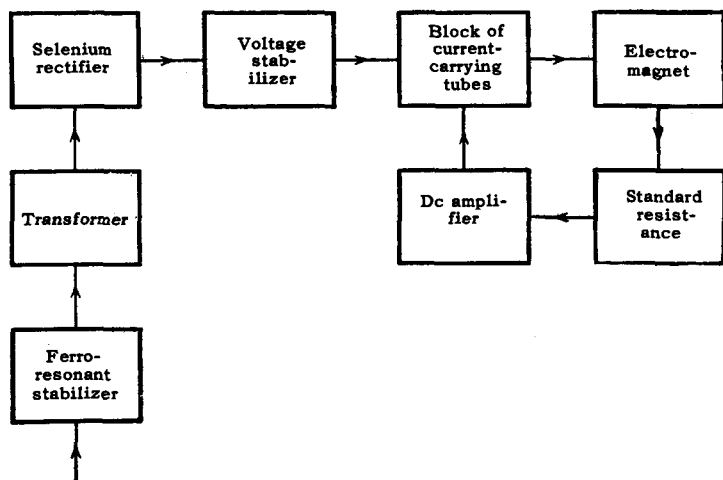


FIG. 6. Block diagram of the electronic stabilizer for the electromagnet power supply.

motor which slowly varies the capacitance in the oscillator circuit.

The magnet power supply utilizes a special high-power electronic stabilizer; the block diagram of the stabilizing system is shown in Fig. 6. The power supply for the receiver utilizes an electronic stabilizer with ripple not more than  $10^{-3}$  v, while the oscillator is powered by batteries.

b) Measurement of second moments. Instrumental corrections. For the evaluation of the second moment of an NMR line we must know:

1) the values of the function  $g(H)$  that describes the line shape (or the values of its derivative  $g' = dg/dH$ ), over the whole region in which this function differs from zero;

2) the corresponding values of  $H$  (or of  $H - H_0$ , where  $H_0$  is the resonance value of the field).\*

Thus, in recording on the chart of the automatic recorder the first derivative of the NMR line it is necessary to have a scale expressed in terms of magnetic fields, which enables us to evaluate the deviations  $H - H_0$  for any value of  $H$  within the limits of the NMR line.†

In sweeping over the spectrum by varying the field it is necessary to calibrate the connection between the current  $i$  in the auxiliary coils (5 in Fig. 5) and the variation of  $H_0$ . We have made a preliminary check of the linearity of this dependence (using the NMR signal in water). Measurements showed that within

\*In processing the experimental curve, the position of each point on the curve is measured from an experimentally determined reference point (the maximum of the absorption line, the point at which the derivative curve passes through zero, etc.). As a result of some instrumental causes this reference point may be shifted somewhat with respect to the true value of  $H_0$ . We shall return to this shift of the reference point later, in connection with the discussion of the effect of the finite rate of sweeping over the spectrum on the experimentally observed second moment.

†In interpreting NMR spectra the expression for  $\overline{\Delta H^2}$  in terms of magnetic fields is used more frequently; if the NMR spectrum is calibrated in frequency units, then the transition to magnetic fields is accomplished by means of relation (2).

the required limits ( $\pm 25$  gauss) the deviations from linearity do not exceed 2%, and no hysteresis is noticeable. The method of calibration based on the measurement of the intermediate frequency (in the frequency channel) turned out to be the most convenient one.

As we have mentioned earlier, this channel usually operates in a comparatively narrow range of intermediate frequencies (5–15 kc); however, the NMR signal can be picked out from the noise background over a considerably wider interval (up to 60 kc). The intermediate frequency was measured by means of Lissajous figures on the oscillograph screen; the calibration of the ZG-11 audio oscillator was first checked by means of the PS-10 000 scaling circuit; the accuracy of the measurement of the low frequency amounted to approximately 0.5%. The calibration process reduced to the following operations:

a) for  $i = 0$  an intermediate frequency  $f = f_0$  was established, which corresponded to the middle of the allowable frequency interval. At this stage the signal was at the center of the oscillograph screen;

b) the current  $i = i_1$  was switched on, and gave rise to a considerable increase in the magnetic field (about 6 gauss);

c) the frequency of the autodyne oscillator was varied in such a way that the signal was brought back to the center of the screen, and the new value of the intermediate frequency  $f = f_1$  was measured;

d) the shift in the field was calculated by means of the formula  $\Delta H = 2\pi(f_1 - f_0)/\gamma$ , which follows directly from (2);

e) the same operation was repeated with the current flowing in the opposite direction,  $i = -i_1$ .

Sweeping over the spectrum by varying the oscillator frequency, as we have already mentioned, is utilized only in the amplitude channel of the spectrograph. To vary the frequency, a Telechron motor with a reduction gear (2 rev/min) varied the capacitance of a cylindrical capacitor made from a micrometer screw. This additional capacitor (of the order of  $5 \mu\mu\text{f}$ ) is

connected in parallel to the variable capacitor of the oscillator circuit. In contrast to the preceding case, the calibration has to be carried out each time during the investigation of the line shape, since the result depends in an essential way on the parameters of the radio frequency coil utilized in the given experiment. Usually the oscillator frequency is measured by a heterodyne wavemeter five or six times in the course of passing through the line; the corresponding "markers" on the recorder chart calibrate the spectrum in the frequency scale.

The second moment evaluated from the experimental data exceeds somewhat the true value of  $\overline{\Delta H^2}$  due to the broadening caused by the finite modulation amplitude. A formula taking this effect into account has been derived by Andrew:<sup>15</sup> the true second moment is smaller than the experimental one by the amount  $H_m^2/4$ , where  $H_m$  is the modulation amplitude in gauss.\* The calibration of the time base required for introducing the correction can be carried out, for example, by utilizing the multiplet NMR signal of  $F^{19}$  in liquid perfluorobutyric acid ( $CF_3-CF_2-CF_2-COOH$ ) for which the value of the principal doublet splitting is well known<sup>8</sup> ( $4.47 \times 10^{-5} H_0$ ). Usually the correction due to the finite value of the modulation amplitude does not exceed 10% of the experimental value of the second moment.

The finite rate of sweep over the spectrum of the crystal utilized in connection with the phase-sensitive detector introduces distortions of the shape of the NMR line which depend on the time constant of the phase detector  $\tau_0$ . The method for introducing the appropriate correction has been developed by V. V. Moskalev and by one of the authors of the present article<sup>5</sup> (cf. also reference 13). If the signal corresponding to the derivative  $g'(H) = g'(vt)$  is applied to the input of the phase detector,<sup>†</sup> then the signal at the output is expressed by means of Duhamel's formula:<sup>10</sup>

$$B(t) = \frac{1}{\tau_0} \int_0^t g'(\tau) e^{-\frac{t-\tau}{\tau_0}} d\tau. \quad (29)$$

We note that the signal  $B(t)$  (the distorted first derivative curve) is retarded with respect to  $g'(t)$ . In particular, the experimentally observed center of the curve [the point corresponding to  $B(t) = 0$ ] is displaced with respect to the true center. In connection with the indefiniteness arising from this we write the expression for the second moment calculated from the

\*The more complete formula<sup>12</sup> includes another term which depends on the modulation frequency, but under the usual experimental conditions this term is negligibly small. Reference 62 also contains corrections to the fourth moment.

<sup>†</sup>For calculations it is convenient to set  $H = vt$ , where  $v$  is the rate of sweeping the spectrum. The time is measured from a certain instant prior to the passage through the line (i.e., when we still have  $g'(t) = 0$ ). Correspondingly,  $H$  is measured with respect to the value of the field at that instant of time.

experimental curve  $B(t)$  with respect to an arbitrary center  $t_0 + \Delta t$ :

$$\overline{\Delta H_{\text{exp}}^2} = \frac{1}{3} v^2 \frac{\int_0^\infty [(t-t_0)-\Delta t]^3 B(t) dt}{\int_0^\infty [(t-t_0)-\Delta t] B(t) dt}, \quad (30)$$

where  $t_0$  is the instant of time at which the curve  $g'(t)$  crosses the horizontal axis. All the integrals obtained in expanding the square brackets can be so transformed that the integrand contains the function  $g'(t)$  for which

$$\int_0^\infty (t-t_0)^{2k} g'(t) dt = 0 \quad (k \text{ is an integer}). \quad (31)$$

In order to achieve this we must substitute into the above integrals  $B(t)$  from (29) and interchange the order of integration, as a result of which the integral over  $t$  can be easily evaluated by parts. As a result of this we obtain the following formula for the true value of the second moment

$$\overline{\Delta H_{\text{true}}^2} = \overline{\Delta H_{\text{exp}}^2} - 2(\tau_0 v)^2 + 2h(\tau_0 v) - h^2, \quad (32)$$

where  $h = v \Delta t$ .

Since it is convenient, in practice, to evaluate the second moment with respect to the experimentally observed center, we now assume that  $h$  is equal to the displacement of the experimental center with respect to the true one, and we evaluate the quantity  $h$  analytically. This is possible to do if the passage through the line occurs not too rapidly. In such a case by the time the curve crosses the horizontal axis, the integrating circuit "forgets" the beginning of the spectrum, and reacts only to its central part which fundamentally determines the quantity  $h$ . Therefore, it is possible to approximate the first derivative of the NMR line near the center by a segment of the straight line  $g'(t) = -a(t-t_0)$ . On substituting this expression into (29) it is not difficult to show, using the obtained expression for the output voltage, that  $h = \tau_0 v$ . Thus, for a sufficiently slow passage formula (32) is simplified, and assumes the following form:

$$\overline{\Delta H_{\text{true}}^2} = \overline{\Delta H_{\text{exp}}^2} - (\tau_0 v)^2. \quad (33)$$

Formula (33) is convenient for practical use, since it does not contain the parameter  $h$ , which is not directly observed experimentally.

The criterion for the slowness of passage in the sense indicated above can be given by using more accurate approximations for the center of the curve. Corresponding calculations have shown that the error made by utilizing the simple formula (33) will not exceed 0.5% if the following inequality is satisfied

$$\tau_0 v < \frac{1}{6} \Delta H, \quad (34)$$

where  $\Delta H$  is the width of the absorption line measured between its points of maximum slope. In practice it is useful to choose the experimental conditions to be such that the correction  $\tau_0 v$  should not exceed 5% of the measured value of the second moment.

#### 4. STRUCTURAL INVESTIGATIONS OF CRYSTALS CARRIED OUT BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

In the discussion of fundamental theoretical problems concerning the shape of an NMR line in crystals and its integral characteristics (moments), it was found in Sec. 2 that it is possible to determine certain structural parameters of the crystalline lattice. We recall that while, generally speaking, the NMR method can be regarded only as a supplement to x-ray analysis, it is of considerable interest for the determination of coordinates of light nuclei (particularly protons).\*

The present section will be devoted to a review of the results of experiments in which structural investigations of crystals were carried out by the NMR method. At the present time there exist more than a hundred such publications, as a result of which, naturally, only some can be discussed in detail. We shall attempt to indicate the most characteristic directions followed by such investigations. At the end of the section we give as complete a table as possible of the crystals whose structure has been studied by the NMR method. The table contains brief comments on the cited original papers. Exceptions occur in the case of crystals that are discussed in greater detail in the text of the present section; in such cases only references to the literature are given.

a) Verification of the theory and certain methodological problems. The principal results of Van Vleck's theory (formulas for the moments of the NMR lines) were subjected to detailed verification experimentally. Soon after the development of this theory (in 1948) Pake and Purcell<sup>101</sup> utilized for this purpose the NMR spectrum of  $F^{19}$  in a single crystal of  $CaF_2$ . The simple distribution of  $F^{19}$  nuclei in the cubic lattice of the fluoride is well determined by x-ray structure analysis methods and is a most favorable case of evaluation of the second moment from a known structure. The value of  $\Delta H^2$  was measured for three orientations of the single crystal with respect to  $H_0$  (the direction of  $H_0$  coincided each time with one of the axes of the crystal; cf. Table I). Good agreement with the theoretically calculated value of  $\Delta H^2$  was obtained for the first two orientations. It should be noted that this verification took place soon after the discovery of NMR during a period when the technique for its observation was not yet perfected.

In 1957 a similar verification was made utilizing the same substance.<sup>37</sup> The orientations for which the second moment was measured were the same ones as

\*The sample studied must satisfy the following fundamental requirements, which follow directly from the specific features of the NMR phenomenon and of the methods of observing it (cf. Secs. 2 and 3): a) the number of unknown parameters should not be great (particularly, if the sample is a powder and not a single crystal); b) at the temperature at which the investigation is made there should be no intense molecular motion in the sample. Generally samples of approximately  $1 \text{ cm}^3$  are used.

Table I

Axis coincident with $H_0$	$\overline{\Delta H_{\text{exp}}^2}$ *		$\overline{\Delta H_{\text{th}}^2}$
	from ref. 101	from ref. 37	
[100]	$3.68 \pm 0.20 \text{ gauss}^2$	$3.49 \pm 0.22 \text{ gauss}^2$	$3.60 \text{ gauss}^2$
[110]	$2.25 \pm 0.20 \text{ gauss}^2$	$2.21 \pm 0.07 \text{ gauss}^2$	$2.24 \text{ gauss}^2$
[111]	$1.77 \pm 0.20 \text{ gauss}^2$	$1.55 \pm 0.05 \text{ gauss}^2$	$1.53 \text{ gauss}^2$

\*We note that in references 101 and 37 no correction has been made for the time constant of the phase-sensitive detector. Unfortunately, in the text of reference 37 only the rate of variation of the magnetic field is given ( $v = 0.02 \text{ gauss/sec}$ ), but the value of the time constant of the integrating circuit is not given.

before, but they were determined with greater accuracy using the NMR signal. To accomplish this the line width (between the points of maximum slope of the first derivative) was investigated as a function of crystal orientation. It turned out that small deviations of the [111] axis from  $H_0$  gave rise to a sharp increase in the line width (the author estimates the error in the determination of the orientation as  $\pm 2^\circ$ ). The results of experimental measurements of the second moment obtained in both papers and the corresponding theoretical values are given in Table I.\*

As a verification of the formula for  $\overline{\Delta H^2}$  for the case of a polycrystalline sample we can take, for example, the measurements of reference 57. The experimental value of  $\Delta H^2$  for the NMR line of  $F^{19}$  in NaF obtained with a very high degree of accuracy ( $6.21 \pm 0.05 \text{ gauss}^2$ ) agrees well with  $\overline{\Delta H_{\text{th}}^2} = 6.16 \text{ gauss}^2$ . One could cite additional similar examples.

The method proposed by Pake<sup>98</sup> for analyzing the line shape for a two-spin system was experimentally checked by the author in the same paper. Later many investigators obtained interesting structural information on the basis of this theory (cf. below).

In the investigation of crystal structure by the NMR method it is often desirable to determine from the experimental data the intramolecular and the intermolecular contributions to the second moment separately.† Andrew and Eades<sup>17,19</sup> have proposed for this purpose the method of isotopic replacement, which is not universal, but which is convenient in the case of sufficiently simple and symmetric structures. The authors

\*As can be seen from the data of Table I, even in careful work the error in the experimental determination of the second moment can amount to several per cent. However, in favorable cases the structural parameters of the crystal can be determined with a higher relative accuracy, since  $\overline{\Delta H^2}$  is inversely proportional to the sixth power of the internuclear distances.

†The most typical case is the investigation of a crystal for which the x-ray data are either nonexistent or unreliable. In such a case the NMR method is not applicable in its usual form, since the number of unknown structural parameters is too great. At the same time, if the structure of the molecule is known in its general terms, individual intramolecular structural parameters can be determined from the corresponding contribution to  $\overline{\Delta H^2}$ .

have applied this method to crystalline benzene (a), and they have also investigated 1, 3, 5-trideuterobenzene (b). We can write

$$\begin{aligned}\overline{\Delta H_a^2} &= S_1 + S_2, \\ \overline{\Delta H_b^2} &= \sigma_1 S_1 + \sigma_2 S_2,\end{aligned}\quad (35)$$

where  $S_1$  is the intramolecular and  $S_2$  is the intermolecular contribution to the second moment in the case of  $C_6H_6$ ;  $\sigma_1$  and  $\sigma_2$  are coefficients showing the factor by which the one or the other contribution is reduced in the case of deuteration. From (35) we obtain

$$\begin{aligned}S_1 &= \frac{\sigma_2 \overline{\Delta H_a^2} - \overline{\Delta H_b^2}}{\sigma_2 - \sigma_1}, \\ S_2 &= \frac{\overline{\Delta H_b^2} - \sigma_1 \overline{\Delta H_a^2}}{\sigma_2 - \sigma_1}.\end{aligned}\quad (36)$$

The quantities  $\sigma_1$  and  $\sigma_2$  can be evaluated without information about the structure of the crystalline lattice. For this we note that a replacement of any H atom by D reduces the corresponding term in formula (26) for the second moment of proton resonance by a factor

$$\frac{\frac{3}{5} I_H (I_H + 1) g_H^2}{\frac{4}{15} I_D (I_D + 1) g_D^2} = 35.82 \quad (37)$$

Assuming that the molecule is a regular hexagon, it can be easily found that  $\sigma_1 = 0.0636$ . Such a considerable decrease in the intramolecular contribution is due to the fact that deuteration affected the principal terms in the formula for  $\Delta H^2$  which describe interactions between nearest neighbors.

In order to determine  $\sigma_2$  we note that a rotation of the molecule 1, 3, 5- $C_6H_3D_3$  by  $60^\circ$  about the  $C_3$  axis interchanges the positions of H and D but brings the molecule into a position equivalent from the point of view of packing in the crystal. Therefore, one should expect that with respect to such rotations the structure will be random. In other words, in going over from  $C_6H_6$  to 1, 3, 5- $C_6H_3D_3$  for any H nucleus not belonging to the molecule under consideration the probability of replacement by a D nucleus is equal to  $1/2$ . In such a case we have

$$\sigma_2 = 0.5 + \frac{0.5}{35.82} = 0.514.$$

The big difference between  $\sigma_2$  and  $\sigma_1$  ensures a high degree of accuracy in the determination of  $S_1$  and  $S_2$  by means of formulas (36). From the experimental values  $\overline{\Delta H_a^2} = (9.72 \pm 0.06)$  gauss<sup>2</sup> and  $\overline{\Delta H_b^2} = (3.57 \pm 0.06)$  gauss<sup>2</sup> (at  $90^\circ K$ ), and also on introducing data on the second moment of monodeuterobenzene, the authors have obtained  $S_1 = (3.10 \pm 0.13)$  gauss<sup>2</sup>. The length of the side of the hexagon formed by the H atoms of the molecule calculated from the above data is equal to  $2.495 \pm 0.018$  A.

As noted in reference 19, the method described above is applicable only in those cases when  $\sigma_2$  can be evaluated from statistical considerations (in par-

ticular, this occurs if all the protons of the undeuterated molecule are equivalent). This limitation does not occur in the case of another method in which undeuterated molecules are mixed with fully deuterated ones.

b) Nuclear magnetic resonance in crystalline hydrates. In the investigation of crystalline hydrates by the method of NMR information about the structure is obtained most frequently by the method of analyzing the shape of the line, and not from its second moment. As shown in Sec. 2 the multiplet spectra of nuclear resonance are characteristic of those crystals which contain relatively isolated groups of magnetic nuclei (two-, three- and four-spin systems). In such cases it is possible in principle to calculate the spectrum theoretically and this, after comparison with the experimental spectrum, would permit one to obtain the coordinates of the nuclei of the isolated configuration mentioned above. By the NMR method it was proved that in crystalline hydrates not only water molecules are present, but also oxonium ions  $H_3O^+$ . The latter are three-spin systems. In two substances (cf. below) the spectrum of a four-spin system formed by two closely situated water molecules was also analyzed.

The first experimental investigation of crystalline hydrates was carried out by Pake,<sup>98</sup> who investigated in detail the line shape of proton resonance in the single crystal of gypsum,  $CaSO_4 \cdot 2H_2O$ . This investigation verified the theory of the line shape for a two-spin system developed by the author, and distances were obtained between the protons in the molecules of the water of crystallization. The orientations of the lines joining the protons turned out to be in agreement with those proposed on the basis of the possible directions of the hydrogen bonds. Subsequently a large number of papers was published on the investigations of crystalline hydrates.

As a first example which enables us to illustrate the possibilities afforded by the NMR method we shall consider crystalline potassium pentaborate belonging to the orthorhombic system. A characteristic feature of this substance which makes the investigation of it difficult is the presence of hydrogen not only in the molecule of the water of crystallization, but also in other structural elements of the crystal.

In 1855 the formula  $KB_5O_8 \cdot 4H_2O$  was proposed<sup>110</sup> for potassium pentaborate (we note that it was still used in a comparatively recent paper<sup>40</sup>). However, the x-ray investigation by Zachariasen<sup>149</sup> indicated the presence in the crystal of  $B_5O_{10}$  complexes as a result of which the author proposed the structural formula  $KH_2(H_3O)_2B_5O_{10}$ . The latter contains oxonium ions.

In order to obtain more precise information on the structure of potassium pentaborate, Smith and Richards<sup>129</sup> investigated the NMR signals from protons in a polycrystalline sample at liquid air temperatures. The presence of oxonium ions was not verified (the

line shape did not correspond to that expected for three-spin system). Since the existence of the  $B_5O_{10}$  complexes noted in reference 149 was not subject to doubt, the structural formula  $K(H_4B_5O_{10}) \cdot 2H_2O$  was adopted which at the present time can be regarded as finally established (cf. below).

Silvidi and McGrath<sup>126</sup> in the course of investigating a series of crystalline hydrates<sup>92, 93, 125, 127, 128</sup> have recorded the NMR spectrum of  $H^1$  in a single crystal of potassium pentaborate at room temperature. They studied the line shapes for different crystal orientations (rotation about the minor axis directed perpendicular to the magnetic field). The spectra turned out to be multiplet spectra, but in the majority of cases the individual components were poorly resolved. For the analysis of the experimental data, a standard line shape was first obtained for a single component on the basis of the spectrum showing the greatest resolution. It turned out that the curves observed experimentally could in each case be decomposed into eight standard lines situated symmetrically with respect to the common center. Of these, two doublets showed dependence on crystal orientation characteristic of two-spin systems with  $R(H \dots H) = 1.60 \pm 0.02$  Å. Thus, the presence of two molecules of water of crystallization was confirmed; their interproton vectors turned out to lie in the *bc* plane, making an angle of  $93 \pm 4^\circ$  with each other (from the symmetry of the crystal it follows that the bisector of this angle coincides with the *c* axis).

The determination of the position of the remaining protons presents a more difficult problem. Of the four standard lines belonging to them, two lines lie at the center for all orientations and coincide with each other. This means that two hydrogen atoms in the molecule occupy isolated single positions. The two remaining lines are characteristic of a two-spin system with  $R(H \dots H)$  considerably in excess of 1.60 Å.\* By using x-ray structure data and considering the possible positions of the hydrogen bonds, the author succeeded in constructing a model of the structure shown in Fig. 7. This model appears to be sufficiently well founded, even though not all its details have been established with the same degree of certainty.†

\*Such an analysis of experimental data can, generally speaking, turn out not to be unique. However, in the present case consideration only of single atoms and of two-spin system appears to be justified, since the average distribution density of magnetic nuclei in the structure is not high, and the presence of three-spin or of even more complicated systems has been excluded by the work of reference 129.

†In following reference 126 we have not touched upon the essential fact that for the minimum elementary crystal cell we need not one, but two formula units of  $K(H_4B_5O_{10}) \cdot 2H_2O$  (i.e., not two, but four molecules of water of crystallization, etc.). However, an investigation of the crystal symmetry shows that if the interproton vectors of the  $H_2O$  molecules lie in the *bc* plane their orientations must be the same pair by pair. For the two

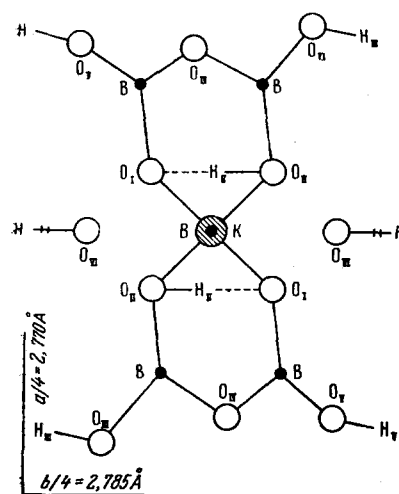


FIG. 7. Projection of the structure of potassium pentaborate on the *ab* plane according to the data of reference 126. A more detailed diagram showing the positions of the potassium, boron, and oxygen atoms in an elementary cell can be found in reference 149.

An analysis of the NMR line shape in a single crystal containing pairs of neighboring nuclei, but having a considerable number (greater than four) of different orientations of such pairs is usually made very difficult by the poorly resolved spectra. However, Lösche<sup>87</sup> succeeded in unravelling the proton resonance spectrum in Rochelle salt ( $KNaC_4H_4O_6 \cdot 4H_2O$ ), the elementary cell of which contains sixteen different orientations of molecules of water of crystallization (of these only four orientations are independent, while the others are obtained from them by applying the symmetry operations of the crystal). The NMR line shape was investigated in the case of three single crystals cut along different mutually perpendicular axes (*a*, *b*, *c*). For each differently cut crystal the shape of the NMR line was recorded by varying the orientation of the single crystal from 0 to 180° in 20° steps, i.e., a total of 30 different orientations was recorded.

In the majority of cases the line shape turned out to be unresolved; however, in individual spectra in addition to the central broad line components of a doublet were observed at the edges which permitted the determination of the orientation of one water molecule. The orientations of three additional molecules could then be immediately obtained from considerations of symmetry. Further, a calculation was made to subtract from all the experimental curves the four doublets due to the aforementioned molecules. In doing this the splitting of the doublet was evaluated in accordance with formula (8), while the shapes of the

other two-spin systems ( $H_{II}$  in Fig. 7) the model of reference 126 gives somewhat different orientations, but this difference cannot be observed in principle if the crystal is rotated only about the *a* axis. As regards the single protons, the doubling of the formula, of course, does not in any way affect their spectrum.



individual components were assumed to be the same and independent of crystal orientation.

The curves obtained after this subtraction again showed structure which permitted further conclusions to be drawn with respect to the orientations of the H...H lines in the elementary cell. After applying this procedure twice Lösche determined the directions of all the 16 interproton vectors. The author pointed out that if the cuts from a single crystal were made in a different manner, then it would be possible to obtain at the outset a different doublet, i.e., to carry out a partial verification of the results without utilizing subtraction of lines.

In a recently published paper<sup>31</sup> the measurement of the second moments of proton resonance in crystals of Rochelle salts has been carried out for different orientations. Lösche's results have been verified in general terms (however, the more precise positions for the protons have not yet been published by the author). At the same time the structures proposed on the basis of the investigation of the polarization of infrared spectra<sup>25</sup> and on the basis of neutron diffraction<sup>122</sup> have turned out to be unreliable.

Another interesting example of the analysis of a complex NMR spectrum is afforded by the investigation<sup>63</sup> of a single crystal of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ . The authors have studied in detail the anisotropy of the multiplet spectrum and have determined the orientations of eight interproton vectors which differ in direction and which are related pair by pair by the symmetry plane of the crystal.

A study of the shape of the NMR line in crystalline hydrates of certain acids (proton resonance) showed that in these compounds the presence either of water molecules or of oxonium ions is possible.\* The difference in the line shape for a two-spin system from the case of a system of three nuclei enables us to make a choice between the two configurations referred to above.†

In the course of an investigation of the NMR spectrum of  $\text{H}^1$  in single crystals of  $\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$  (I) and  $\text{K}_2\text{SnCl}_4 \cdot \text{H}_2\text{O}$  (II)<sup>69,70,71</sup> a line shape was discovered which did not correspond to a two-spin system. In this connection the authors undertook to calculate the spectrum of a four-spin system formed by two water molecules with parallel directions of H...H (the parallelism follows from the lattice symmetry). The line shapes obtained as a result of the calculation for the different orientations of the single crystal agreed well

\*Oxonium ions have been found in  $\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ ,<sup>129</sup>  $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ ,<sup>129</sup>  $\text{HClO}_4 \cdot \text{H}_2\text{O}$ ,<sup>76,77,78,112</sup>  $\text{HNO}_3 \cdot \text{H}_2\text{O}$ ,<sup>112</sup>  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .<sup>112</sup> On the other hand in  $\text{K}(\text{H}_4\text{B}_5\text{O}_{10}) \cdot 2\text{H}_2\text{O}$ ,<sup>126,129</sup>  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ,<sup>112,72</sup>  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,<sup>98</sup>  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ <sup>75</sup> the crystal structure contains molecules of water of crystallization.

† The possibility of the formation of oxonium ions in solid hydrates of strong acids has been noted by many authors (cf., for example, references 140, 54, and 66), however, the NMR method gives the most reliable information about these ions.

with the experimental curves. The intramolecular distances H...H turned out to be equal to 1.607 Å in (I) and 1.620 Å in (II). The distances between the H...H lines of neighboring water molecules amount respectively to 3.60 and 3.90 Å. The interpretation of the NMR spectra made it possible to include both crystals in the same space group ( $V_h^9$ ), while the earlier x-ray structure investigations ascribed (II) to the group  $V_h^{16}$ .

c) Investigation of hydrogen bonds in crystals. In the study of the nature and the properties of the hydrogen bond it is of considerable interest to determine the positions of hydrogen between the atoms acted upon by the bond. With this aim in view NMR spectra of crystals are often used together with the method of neutron diffraction.

Unfortunately, the application of the NMR method to the most widely occurring and most important case of the O—H...O bonds encounters certain difficulties. Since the principal oxygen isotope  $\text{O}^{16}$  does not have a nuclear magnetic moment, the distance  $R(\text{O—H})$  cannot be determined directly. Usually some interproton distances are measured as a result of which  $R(\text{O—H})$  is calculated by using the available data on the crystal structure; however, such calculations often do not yield unique results, and this makes it necessary to introduce additional assumptions. For example, in crystalline hydrates one can directly determine the length and the direction of the vector  $\mathbf{R}(\text{H...H})$  for the  $\text{H}_2\text{O}$  molecule. In order to evaluate from these data  $\mathbf{R}(\text{O—H})$  it is necessary to know the angle HOH. Its value is either assumed (by taking standard values  $105\text{--}108^\circ$ ), or an attempt is made to determine it by means of the not always justified assumption that the protons are localized on the O...O lines.

An interesting example of the determination of the positions of the protons in the hydrogen bonds O—H...O is the investigation of the NMR signal of  $\text{H}^1$  in a single crystal of the dihydrate of oxalic acid.<sup>72</sup> The fine structure of the NMR spectrum was observed characteristic of a three-spin system with the following interproton distances:  $R(\text{H}_1... \text{H}_2) = 1.65 \text{ \AA}$ ,  $R(\text{H}_1... \text{H}_3) = 1.92 \text{ \AA}$ ,  $R(\text{H}_2... \text{H}_3) = 2.30 \text{ \AA}$ ; also the orientation of the triangle with respect to the crystallographic axes was determined. Comparison with x ray structure data enables us to conclude that  $\text{H}_1$  and  $\text{H}_2$  are protons of a molecule of water of crystallization, while  $\text{H}_3$  is the acid proton. A certain indeterminacy in the positions of the hydrogen atoms remains which is related to the fact that small displacements of the  $\text{H}_1\text{H}_2\text{H}_3$  triangles (without changing their orientation) practically do not affect the spectrum. If, however, one assumes the usual configuration for the  $\text{H}_2\text{O}$  molecule, then one obtains the structure shown in Fig. 8.

An interesting result of this work is the fact that two of the three hydrogen bonds are characterized by O—H...O angles considerably different from  $180^\circ$ . We note that a bent hydrogen bond is also found<sup>85</sup> in

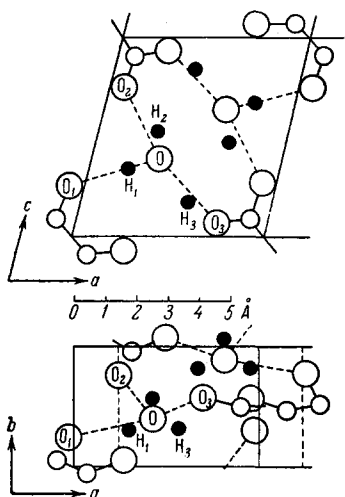


FIG. 8. One half of an elementary cell of the dihydrate of oxalic acid (the second half of the cell is completed in the direction of the  $a$  axis). The position of the protons is indicated according to the data of reference 72.

$H_3BO_3$ . In this case the angle  $BOH$  was determined from the second moment in a powder sample and turned out to be equal to  $96 \pm 2^\circ$ . The angle  $O-H \dots O$  is not given, but a measurement made on the drawing given in that article yields a value of approximately  $150^\circ$ .

In the same paper<sup>85</sup> an investigation is reported of the NMR spectrum of protons in  $KHCO_3$ . The  $HCO_3^-$  ions in this substance form dimers as a result of strong hydrogen bonds with  $R(O-H \dots O) = 2.61$  A. The measurement of the second moment in the powder enabled the authors to determine  $R(H \dots H)$  for the dimer ( $2.27 \pm 0.03$  A). A fairly rough determination of the orientation of the interproton vector from the spectrum of a single crystal led to the value  $R(O-H) \approx 1.2$  A, although even the value 1.3 A corresponding to a symmetric bond was not completely excluded.

In reference 2 we have made an attempt to determine the position of hydrogen in the  $O-H \dots O$  bond in diasporite ( $HAIO_2$ ).<sup>\*</sup> In order to do this we have calculated with the aid of formula (26) the magnitude of  $\Delta H^2$  for the  $H^1$  resonance in two cases: a) hydrogen situated exactly midway between the aforementioned oxygen atoms, and b) the  $O-H$  distance is equal to 1.00 A. We obtained 7.35 and 9.85 gauss<sup>2</sup> respectively. The theoretical values quoted above and also the experimental value  $\Delta H^2 = 9.11 \pm 0.7$  gauss<sup>2</sup> lying between them enable us to evaluate the distance  $R(O-H)$  from the NMR data. From considerations of symmetry it

\*In the x-ray structural investigation<sup>47</sup> the space group for the crystal was determined ( $V_h^{16}$ ) and also the coordinates of the  $Al^{27}$  and  $O^{16}$  atoms. On the basis of these data in reference 142, a structural model is proposed including the position of the hydrogen bonds. The distance between the corresponding oxygen atoms according to reference 142 is equal to 2.71 A, however, a calculation utilizing the atomic coordinates given in reference 47 yielded  $R(O-H \dots O) = 2.68$  A.

can be easily seen that case a) corresponds to an extremum (minimum) of the function  $\Delta H^2 = f[R(O-H)]$ . Therefore, in carrying out the interpolation we have approximated this function by the parabola  $\Delta H^2 = A[1.34 - R(O-H)]^2 + B$  with appropriate values of the constants  $A$  and  $B$ . We obtained  $R(O-H) = 1.05 \pm 0.05$  A. The comparatively large error is associated with the uniform distribution of magnetic nuclei in the crystal lattice which leads to a reduction in the dependence of  $\Delta H^2$  on  $R(O-H)$  as a result of the cancellation of the variations in the individual terms of the second moment. We note that the empirical relation between  $R(O-H)$  and  $R(O-H \dots O)$ <sup>24,97</sup> yields  $R(O-H) = 1.00 - 1.05$  A for  $R(O-H \dots O) = 2.68$  A.

In reference 141 an investigation was made of the compounds  $KHF_2$ ,  $NaHF_2$  containing a three-spin system ( $HF_2^-$  ion) which are of interest because the hydrogen bond  $F-H \dots F$  has the "anomalous" length of 2.26 A. With respect to the position of hydrogen in the  $HF_2^-$  ion various opinions had been expressed earlier; some authors<sup>53,79</sup> assumed by analogy with other substances a non-symmetric structure in which the proton was situated closer to one of the  $F^{19}$  nuclei than to the other one. However, this model leads to very large theoretical values for the second moment ( $\geq 200$  gauss<sup>2</sup>), while the experimentally obtained value of  $\Delta H^2 = 93 \pm 4$  gauss<sup>2</sup> gives convincing evidence in favor of the symmetric situation (the displacements of the H atom from the center do not exceed 0.06 A). In reference 123 the authors carried out similar measurements of the second moments in  $NH_4HF_2$ ; in this compound the  $F-H \dots F$  bond is somewhat longer (2.36 A), however, the NMR data also in this case give support to a symmetric configuration.

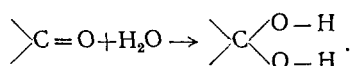
Deeley and Richards<sup>41</sup> have made a measurement of  $\Delta H^2$  for the NMR lines of  $H^1$  and  $F^{19}$  in crystalline hydrazine fluoride ( $N_2H_5F_2$ ) at temperatures of 20 and 90°K (the coordinates of the nitrogen and fluorine atoms were determined earlier in reference 82; the structure contains hydrogen bonds  $N-H \dots F$  of length  $2.62 \pm 0.02$  A). The authors calculated the second moment of the  $H^1$  resonance as a function of the position of hydrogen. In making this calculation the hydrogen bonds were assumed to be rectilinear; the intermolecular contribution to  $\Delta H^2$  was calculated on the basis of the data of reference 82. Similar calculations were made for  $\Delta H^2$  corresponding to  $F^{19}$  for different  $H \dots F$ -distances. The experimental results agree best of all with an  $N-H$ -distance of  $1.07_5 \pm 0.02$  A and an  $H \dots F$ -distance of  $1.54_2 \pm 0.01$  A. The sum of these values  $2.61_7 \pm 0.03$  A agrees well with the  $N \dots F$  distance obtained in reference 82.\*

\*It should be noted that after a refinement of the corrections for thermal vibrations was carried out in reference 68, the value obtained for  $R(N-H)$  was  $1.050 \pm 0.028$  A. Since the improved value of  $R(H \dots F)$  is not given in reference 68, it is impossible to check the agreement between the new values and the x-ray structural data.

In references 81 and 96 a measurement was made of the line width and of the second moment of the  $H^1$  resonance in a number of crystals containing  $NH_2$  groups. The principal aim of these investigations was to establish the correlation between the N—H- and N...O-distances for the hydrogen bond N—H...O. The variations in this distance are comparable to the errors of measurement by the NMR method, but, nevertheless, it is possible to deduce a semi-empirical dependence of the N—H-distance on the length of the N—H...O bond.<sup>96</sup>

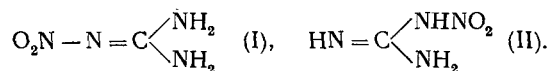
d) Choice between different models. In a number of cases the NMR method was utilized not for the determination of some structural parameter, but for making a choice between different models of a structure which qualitatively differ from one another (strictly speaking, the determination of the presence of  $H_2O$  molecules or of  $H_3O^+$  ions in the crystalline hydrate lattice discussed earlier belongs to this type of investigation).

A measurement of the second moment of the NMR line due to protons often enables one to answer the question whether a given substance is a crystalline hydrate or not; in many cases it is not even necessary to have any information on the crystal structure. The minimum second moment for a water molecule (for an H...H distance of the order of 1.65 Å) exceeds 15 gauss<sup>2</sup>. Naturally, the  $\Delta H^2$  for proton resonance in a substance which contains hydrogen only in molecules of  $H_2O$  must be somewhat larger than the value given above. As we have mentioned already, in measuring the second moment in diasporite we obtained 9.11 gauss<sup>2</sup>. This last fact enables us once again to support the point of view expressed in reference 36 in accordance with which diasporite is not a crystalline hydrate. NMR in  $Na_2CO(COO)_2 \cdot H_2O$  and in chloral hydrate<sup>29</sup> has also been utilized to obtain more precise data on the structural formulas. In both cases it was shown that the water of crystallization is absent as a result of a transition to a structure containing hydroxyls:



Further examples of the presence or absence of water molecules are contained in Table III (cf. below).

The investigation of  $\Delta H^2$  and of the fine structure of the NMR line due to  $H^1$  in powdered nitroguanidine<sup>113</sup> has enabled us to make the choice between two possible structural formulas for the molecule:



Verification was obtained for the symmetric structure (I). R (H...H) in the  $NH_2$  group is equal to  $1.77_1 + 0.01_1$  Å.

Andrew and Hyndman<sup>20,21</sup> have investigated the anisotropy of the second moment of the  $H^1$  resonance in a single crystal of urea,  $OC(NH_2)_2$ . From x-ray structural data it was known that the four atoms

(O, C, N) of the molecule lie in one plane.<sup>143,139</sup> The position of the protons remained undetermined, while the crystal symmetry permitted two possible configurations (the H...H lines of the  $NH_2$  groups lie in the same plane or perpendicular to it). The authors carried out a theoretical calculation of the magnitude of the second moment as a function of the orientation of the single crystal for the two configurations mentioned above. Figure 9 shows the experimental results and their comparison with theory; the NMR data enable us to assert definitely that the urea molecule is plane (including the hydrogen atoms).

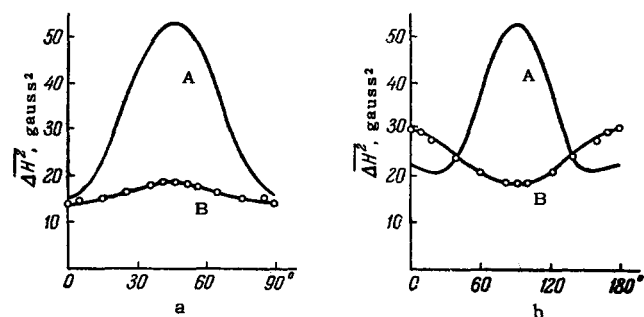


FIG. 9. Dependence on orientation<sup>21</sup> of the second moment of the NMR signal of protons in a single crystal of urea. a) Rotation of the crystal about [001]; b) rotation about [110]. Circles — experimental points, curves A for the nonplanar model, curves B — for the plane model.

Takeda and Gutowsky<sup>134</sup> have shown that the NMR method in favorable cases enables us to investigate the phenomenon of rotational isomerism in the solid phase. A measurement was carried out of the second moments of the proton resonance in  $CHCl_2CHCl_2$  and  $CHBr_2CHBr_2$  at liquid nitrogen temperature (polycrystalline samples). The theoretical calculation was carried out for the *trans*- and *gauche*-forms. The intermolecular contribution to  $\Delta H^2$  in these structures is large (30–60%), while the crystal structure is unknown. In this connection the authors estimated the intermolecular contribution to  $\Delta H^2$  approximately, on the basis of the possible packing of the molecules in the crystalline lattice. Although the error introduced by such an estimate is considerable, it is still smaller by a factor of severalfold than the expected difference of the second moments for the two isomers. As a result of a comparison of the theoretical and the experimental values of  $\Delta H^2$  it turned out that the molecules of 1,1,2,2-tetrachloroethane in the solid state are in the *gauche*-form. Attempts to prepare *trans*- $(CHCl_2)_2$  remained unsuccessful. The width of the NMR signal in this compound does not vary from  $-190^\circ C$  up to the melting point.

Results for solid tetrabromoethane depend on the method of crystallizing the sample: in the case of monotonic cooling down to  $-90^\circ C$  the *gauche*-form is produced from the supercooled liquid. However, if the crystallization is carried out at temperatures be-

tween  $-45^\circ$  and  $-25^\circ\text{C}$  from a liquid previously super-cooled down to  $-65^\circ\text{C}$ , then the trans-form is produced. On heating the trans-form of  $\text{CHBr}_2\text{CHBr}_2$  the NMR line does not change up to  $-20^\circ\text{C}$ ; at  $-20^\circ\text{C}$  the line width increases as a result of a partial transition of the sample into the gauche-form.

e) Investigation of incompletely ordered (statistical) structures. In studying NMR in a solid with an incompletely ordered structure it is very difficult to obtain detailed information on the positions of nuclei. However, certain averaged quantities can be determined which depend on the nature of the lack of ordering.

In references 6 and 2 (cf. also reference 3) we have published the results of investigations of five different samples of carbon monofluoride (obtained by fluoridation of graphite). This substance was first synthesized by Ruff and Bretschneider<sup>118</sup> in 1934. The process of the fluoridation of graphite proceeds differently depending on the temperature and the pressure and in the limit gives rise to the compound  $(\text{CF})_n$ . In practice samples were obtained<sup>117</sup> up to  $(\text{CF}_{0.988})_n$ . In reference 118, on the basis of not completely sufficient x-ray data, a possible structural model for carbon monofluoride was proposed, which, however, was later rejected. In 1947 a new x-ray investigation was carried out<sup>117</sup> and a model was constructed which did not contradict experimental facts. In accordance with reference 117, the fluorine is bonded to the carbon by covalent chemical bonds. The positioning of carbon atoms in layers is retained, but the bonds within a layer become single, as a result of which the angles between them approach tetrahedral angles ("corrugated" layers of C atoms). A distance of 1.4 Å has been assumed for the C-F bond, and a distance of 1.54 Å for the C-C bond. We note that in a later paper<sup>102</sup> the authors reached, generally speaking, similar conclusions with respect to the crystal structure of  $(\text{CF})_n$ .

We have calculated the second moment of the NMR line of  $\text{F}^{19}$  for the model of reference 117 on the assumption of complete fluoridation, i.e., on the basis of the chemical formula  $(\text{CF})_n$ . The calculation was carried out with a degree of accuracy of the order of 0.5%, and, therefore, the specific position of the atoms in the neighborhood of the given nucleus was taken into account within a sphere of radius 7.5 Å; outside this sphere the sum in Van Vleck's formula was replaced by an integral. We obtained  $\overline{\Delta H^2} = 9.25$  gauss<sup>2</sup>. In the case of incomplete fluoridation, i.e., in the case of the compound  $(\text{CF}_x)_n$  ( $x < 1$ ), it can be easily shown that the value of the second moment can lie between the following limits:

$$9.25x \leq \overline{\Delta H^2} \leq 9.25. \quad (38)$$

The lower limit holds in the case of a completely random distribution of the vacancies (sites unoccupied by F atoms); the upper limit occurs in the case when

relatively large (tens of Å) completely fluoridated regions alternate with unfluoridated ones (i.e., those retaining the graphite structure).

The experimental results obtained by us and their comparison with theory are shown in Table II. The second moment was calculated after taking the average of not less than three experimental curves; a correction was made for finite modulation amplitude, and the effect of the time constant of the phase-sensitive detector was taken into account.

Table II

Sample No.	Degree of fluoridation, $x$	$\overline{\Delta H^2}_{\text{exp}}$ in gauss <sup>2</sup>	$\overline{\Delta H^2}$ -theoretical limits in gauss <sup>2</sup>
1	0.966	$9.08 \pm 0.35$	8.94—9.25
2	0.874	$8.37 \pm 0.40$	8.08—9.25
3	0.779	$7.76 \pm 0.35$	7.20—9.25
4	1.0	$8.37 \pm 0.40$	9.25
5	1.0	$6.34 \pm 0.50$	9.25

As can be seen from the data for sample No. 1 the discrepancy between  $\overline{\Delta H^2}_{\text{exp}}$  and the possible theoretical values lies within experimental error. Thus, the model of reference 117 does not contradict data obtained from the NMR spectrum.\* The theoretical limits for  $\overline{\Delta H^2}$  are in this case separated by a very small interval, and it does not appear to be possible to draw any conclusions with respect to the nature of the distribution of the few vacancies.

In the case of samples No. 2 and 3 which are incompletely fluoridated the observed value of the second moment lies between the theoretical limits (somewhat closer to the lower limit). Therefore, one can conclude that the nature of the distribution of the atoms is intermediate between the two extreme cases mentioned previously. Moreover, apparently the concept of a random distribution of vacancies is closer to reality than the assumption of the presence of fluoridated and unfluoridated regions of large size.

The completely fluoridated samples No. 4 and 5 exhibit an anomaly which is particularly sharply pronounced in the latter case. Such a deviation of the experimental second moment from the theoretical limits apparently indicates a difference between the crystal structure of sample No. 5 and the model of reference 117 used by us to explain the results for the first three samples.

Another example of a crystal in which investigations of such type are possible is topaz. As is well known, atoms of fluorine and hydroxyl groups are present in the structure and replace one another isomorphically. An investigation of the NMR signals of  $\text{H}^1$  and  $\text{F}^{19}$  enables us to determine the ratio between them without destroying the crystal.<sup>3</sup> Measurement of the second moments of both resonances must in favorable

\*For comparison it can be pointed out that the model of reference 118 leads to  $\overline{\Delta H^2} \sim 2$  gauss<sup>2</sup>, which irreconcilably contradicts the experimental data given above.

cases give us information on the nature of the distribution of the F atoms and of the OH groups (random distribution or presence of regions predominantly containing occupants of one type). Since the magnetic moments of  $H^1$  and  $F^{19}$  are close to one another, the investigation must be based fundamentally on the fact that the dipole-dipole interactions for nuclei of different types are less effective than for nuclei of the same type (coefficients  $\frac{3}{5}$  and  $\frac{4}{15}$  in Van Vleck's formula).

In connection with investigations of incompletely ordered crystal structures, the work of Richards and Yorke<sup>115</sup> deserves brief mention. They have determined the ratio of the number of protons in the aromatic and the aliphatic groups for a series of samples of different types of carbons (a detailed recapitulation of this interesting paper is hardly appropriate here,

since carbons have in general no crystalline structure). In developing the methodology of such investigations, the authors measured second moments for the proton resonance in 17 individual hydrocarbons and for two mixtures of known composition. The analysis of the data obtained shows that for this class of substances the values of  $\overline{\Delta H^2}$  can be predicted with a good degree of accuracy on the basis of a simple additive scheme. The solution of the inverse problem (the determination of the distribution of protons between the different groups on the basis of a measured second moment) is not unique. However, by making use of certain additional considerations the authors succeeded in obtaining estimates for the ratio of the numbers of protons in aromatic and aliphatic groups which are in good agreement with the data of other methods.

Table III

This table lists substances for which some structural parameters have been determined by means of the method of nuclear magnetic resonance. The form in which the formulas are written and the ordering of the substances follows that adopted in Chemical Abstracts. In many cases we have also given another more customary way of writing the chemical formula. The table does not include crystals, information about which is restricted to the discovery and investigation of molecular mobility or the measurement of the magnitude of the second moment (without any further interpretation). We have utilized the following abbreviations: FS - fine structure of NMR lines, M - molecular mobility, T - text. The latter indicates that the substance in question has been discussed in some detail in the text of this review (this refers principally to § 4).

Substance	Reference	Notes
1. $Ag_2H_3IO_6$	30	Confirmation that this substance is not a crystalline hydrate.
2. $AlHO_2(\gamma)$ , $AlOOH$	63	$\overline{\Delta H^2}$ in a powdered sample. Confirmation of structure. <sup>95</sup> It was not possible to obtain more accurate proton positions.
3. $AlHO_2$ , $HAIO_2$	2	T
4. $AlH_3O_3(\alpha \text{ and } \gamma)$ , $Al(OH)_3(\alpha \text{ and } \gamma)$	63	$\overline{\Delta H^2}$ in powdered samples for two modifications: bayerite ( $\alpha$ ) and hydrargillite ( $\gamma$ ). The structure previously proposed <sup>94</sup> for ( $\gamma$ ) has been confirmed, while that proposed <sup>146</sup> for ( $\alpha$ ) has been rejected.
5. $BF_3 \cdot H_2O$	50	$\overline{\Delta H^2}$ and FS in a polycrystalline sample. In the case of slow cooling the non-ionized form $BF_3 \cdot H_2O$ is obtained with $R(H \dots H) = 1.62 \text{ \AA}$ and $R(B-F) \approx 1.39 \text{ \AA}$ . In the case of rapid freezing the $BF_3 \cdot OH^-$ and $H_3O^+$ ions apparently remain in the structure.
6. $BF_3 \cdot 2H_2O$	50	$H^2$ and FS in polycrystalline sample. In the case of slow cooling the non-ionized form $BF_3 \cdot 2H_2O$ is obtained with $R(H \dots H) = 1.54 \text{ \AA}$ (average for two apparently non-equivalent water molecules). By making use of the data on $BF_3 \cdot 2D_2O$ one obtains $R(B-F) = 1.38 \text{ \AA}$ . In the case of rapid freezing the $BF_3 \cdot OH^-$ and $H_3O^+$ ions apparently remain in the structure.
7. $BF_4^-Rb$ , $RbBF_4$	103	$\overline{\Delta H^2}$ in a powdered sample. $R(B-F)$ in the tetrahedral $BF_4^-$ ion is equal to $1.43 \pm 0.03 \text{ \AA}$ .
8. $BH_3O_3$ , $H_3BO_3$	65	T
9. $BH_4^-K$ , $KBH_4$	49	M. $\overline{\Delta H^2}$ in a powdered sample. $R(B-H)$ has been determined for the $BH_4^-$ ion ( $1.255 \pm 0.02 \text{ \AA}$ ).

Table III

Substance	Reference	Notes
10. $\text{BH}_4\text{Na}$ , $\text{NaBH}_4$	49	M. $\overline{\Delta\text{H}^2}$ in a powdered sample. $\text{R}(\text{B}-\text{H})$ has been determined for the $\text{BH}_4^-$ ion ( $1.255 \pm 0.02 \text{ \AA}$ ).
11. $\text{BH}_4\text{Rb}$ , $\text{RbBH}_4$	49	M. $\overline{\Delta\text{H}^2}$ in a powdered sample. $\text{R}(\text{B}-\text{H})$ has been determined for the $\text{BH}_4^-$ ion ( $1.255 \pm 0.02 \text{ \AA}$ ).
12. $\text{B}_3\text{H}_6\text{KO}_{10} \cdot 2\text{H}_2\text{O}$ , $\text{K}(\text{H}_4\text{B}_3\text{O}_{10}) \cdot 2\text{H}_2\text{O}$	126, 129	T
13. $\text{BaBr}_2 \cdot \text{H}_2\text{O}$	92	FS in a single crystal. The orientations of the interproton vectors have been determined (they are all identical) and also $\text{R}(\text{H} \dots \text{H}) = 1.56 \pm 0.02 \text{ \AA}$ . Hydrogen bonding occurs in this structure $\text{O}-\text{H} \dots \text{Br}$ .
14. $\text{BaBr}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$	128	FS is in single crystal. $\text{R}(\text{H} \dots \text{H})$ in water is equal to $1.61 \pm 0.01 \text{ \AA}$ . The orientation of the only interproton vector in the elementary cell has been determined.
15. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	127	FS in a single crystal (rotation about the a and c axes). $\text{R}(\text{H} \dots \text{H}) = 1.57-1.59 \text{ \AA}$ ; orientations of four interproton vectors have been determined. The probable positions of the H atoms have been indicated (hydrogen bonds $\text{O}-\text{H} \dots \text{O}$ and $\text{O}-\text{H} \dots \text{Cl}$ occur in the structure).
16. $\text{BaCl}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , $\text{Ba}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$	132, 128	FS in a single crystal. The orientations of the interproton vectors and $\text{R}(\text{H} \dots \text{H}) = 1.56 \text{ \AA}$ have been determined. The results of reference 132 have been checked in reference 128. Within experimental error agreement has been obtained.
17. $\text{BrH}_4\text{N}$ , $\text{NH}_4\text{Br}$	56, 60	$\overline{\Delta\text{H}^2}$ in a powdered sample. $\text{R}(\text{N}-\text{H})$ in the $\text{NH}_4^+$ ion is equal to $1.025 \pm 0.005 \text{ \AA}$ . In reference 60 $\overline{\Delta\text{H}^2}$ in a powdered sample. After correction for torsional oscillations has been made $\text{R}(\text{N}-\text{H}) = 1.031 \pm 0.004 \text{ \AA}$ .
18. $\text{BrH}_4\text{P}$ , $\text{PH}_4\text{Br}$	58	$\overline{\Delta\text{H}^2}$ in a powdered sample. Experimental data do not contradict the value $\text{R}(\text{P}-\text{H}) = 1.42 \text{ \AA}$ , obtained for $\text{PH}_4\text{I}$ .
19. $\text{C}_2\text{Br}_2\text{F}_4$ , $\text{CF}_2\text{BrCF}_2\text{Br}$	61	M. $\overline{\Delta\text{H}^2}$ in a polycrystalline sample. The molecules are either exclusively or predominantly in the trans-form.
20. $\text{C}_2\text{Cl}_2\text{F}_4$ , $\text{CF}_2\text{ClCF}_2\text{Cl}$	61	M. $\overline{\Delta\text{H}^2}$ in a polycrystalline sample. The molecules are either exclusively or predominantly in the trans-form.
21. $\text{C}_2\text{Cl}_4\text{F}_2$ , $\text{CFCl}_2\text{CFCl}_2$	61	M. $\overline{\Delta\text{H}^2}$ in a polycrystalline sample. The molecules are either exclusively or predominantly in the gauche-form.
22. $\text{CF}_x$ , $x \leq 1$	2, 3, 6	T
23. $\text{CHKO}_3$ , $\text{KHCO}_3$	85	T
24. $\text{CH}_3\text{NO}$ , $\text{HCONH}_2$	81, 96	$\overline{\Delta\text{H}^2}$ in a powdered sample. N-H-distance $1.036 \pm 0.025 \text{ \AA}$ (on the assumption that the angle $\text{HNN} = 120^\circ$ ). Cf. Sec. 4.
25. $\text{CH}_4\text{N}_2\text{O}$ , $\text{OC}(\text{NH}_2)_2$	20, 21, 84, 144	References 20 and 21: T. Reference 81: $\text{R}(\text{N}-\text{H}) = 1.077 \pm 0.007 \text{ \AA}$ . M. Reference 144: $\overline{\Delta\text{H}^2}$ in a single crystal. $\text{R}(\text{N}-\text{H}) = 1.02 \pm 0.01 \text{ \AA}$ on the assumption that the angle $\text{HNN} = 120^\circ$ .
26. $\text{CH}_4\text{N}_2\text{S}$ , $\text{SC}(\text{NH}_2)_2$	45, 46	M. The temperature dependence of the width of an NMR line is explained if we assume rotation of molecules of plane or almost plane configuration about the C-S bond.
27. $\text{CH}_4\text{N}_4\text{O}_2$ , $\text{CN}_2\text{O}_2(\text{NH}_2)_2$	113	T

Table III (continued)

Substance	Reference	Notes
28. $\text{CH}_6\text{AlN}_3\text{S}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ $\text{C}(\text{NH}_2)_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	89, 1	Reference 89: M. FS in a single crystal for different orientations (rotation about the a and c axes). $R(\text{H} \dots \text{H}) = 1.63 \text{ \AA}$ . The orientations of the interproton vectors have been determined. A conclusion has been drawn that the $\text{Al}^{3+}$ ions, apparently, lie on the $C_3$ axes. Two possible variants of the position of the $\text{H} \dots \text{H}$ lines in the guanadinium ion are indicated. Reference 1: FS obtained by rotating the crystal about three mutually perpendicular axes. On the basis of an earlier study <sup>9</sup> which led, in principle, to the determination of the structure of the crystal a model is proposed for the positioning of the water molecules around the $\text{Al}^{3+}$ ions. A choice is made between two variants of the orientation of the $\text{H} \dots \text{H}$ lines of the guanadinium ion proposed in reference 89.
29. $\text{C}_2\text{H}_2\text{Cl}_2\text{O}_2$ , $\text{CCl}_2\text{COOH}$	55, 146, 147	In reference 55 an investigation was made of the NMR spectrum in a powder and in a single crystal. The existence of the dimer $R(\text{H} \dots \text{H}) = 2.56 \pm 0.02 \text{ \AA}$ has been proved. There exist two orientations of the interproton vectors at an angle of $31^\circ 30'$ with respect to each other. In references 146 and 147 it was found as a result of investigations using a polycrystalline sample that $R(\text{H} \dots \text{H}) = 2.48 \pm 0.04 \text{ \AA}$ .
30. $\text{C}_2\text{H}_2\text{Br}_4$ , $(\text{CHBr}_2)_2$	134	T
31. $\text{C}_2\text{H}_2\text{Cl}_4$ , $(\text{CHCl}_2)_2$	134	T
32. $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$	72, 112	T
33. $\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$ , $\text{CH}_2\text{ClCOOH}$	146	$\overline{\Delta\text{H}^2}$ in a polycrystalline sample. It did not turn out to be possible to give by the NMR method a reliable proof of the formation of a dimer.
34. $\text{C}_2\text{H}_3\text{Cl}_3\text{O}_2$ , $\text{CCl}_2\text{CH}(\text{OH})_2$	29	T
35. $\text{C}_2\text{H}_4\text{Cl}_2$ , $(\text{CH}_2\text{Cl})_2$	56	$\overline{\Delta\text{H}^2}$ in a powdered sample. $R(\text{H} \dots \text{H})$ in the $\text{CH}_2\text{Cl}$ group is equal to $1.71 \pm 0.02 \text{ \AA}$ . From this value it follows that the angle $\text{H}-\text{C}-\text{H}$ is somewhat smaller than the tetrahedral angle.
36. $\text{C}_2\text{H}_4\text{N}_2\text{O}_2$ , $\text{NH}_2 \cdot \text{COCONH}_2$	96	T. $\overline{\Delta\text{H}^2}$ in a powdered sample. $\text{N}-\text{H}$ -distance is equal to $1.039 \pm 0.013 \text{ \AA}$ (on the assumption that the angle $\text{HNH} = 120^\circ$ ).
37. $\text{C}_2\text{H}_3\text{NO}_2$ , $\text{NH}_2\text{CH}_2\text{COOH}$	81, 121	$\overline{\Delta\text{H}^2}$ in a powdered sample. It was shown that the structure is an ionic one: $\text{NH}_3^+\text{CH}_2\text{COO}^-$ . $R(\text{N}-\text{H}) = 1.074 \pm 0.014 \text{ \AA}$ . <sup>81</sup>
38. $\text{C}_2\text{H}_6\text{N}_2\text{O}_4$ , $\text{N}_2\text{H}_5\text{C}_2\text{O}_4$	107	$\overline{\Delta\text{H}^2}$ and an analysis of the line shape in a powdered sample. Apparently, the structure consists of $\text{N}_2\text{H}_5^+$ and $\text{HC}_2\text{O}_4^-$ ions.
39. $\text{C}_2\text{H}_{10}\text{N}_3\text{O}_4$ , $(\text{N}_2\text{H}_5)_2\text{C}_2\text{O}_4$	107	$\overline{\Delta\text{H}^2}$ in a powdered sample. The crystal consists of $\text{C}_2\text{O}_4^-$ and $\text{N}_2\text{H}_5^+$ ions.
40. $\text{C}_4\text{H}_2\text{FeO}_4$ , $\text{H}_2\text{Fe}(\text{CO})_4$	28	Investigation of $\overline{\Delta\text{H}^2}$ in a polycrystalline sample at $20^\circ\text{K}$ . The existence of proton pairs is assumed, even though no fine structure was observed; $R(\text{H} \dots \text{H}) = 1.88 \pm 0.05 \text{ \AA}$ . It is concluded that the protons are bonded directly to the iron atom, with $R(\text{Fe}-\text{H})$ very small (of the order of $1.1 \text{ \AA}$ ).
41. $\text{C}_4\text{H}_4\text{KNaO}_6 \cdot 4\text{H}_2\text{O}$ , $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	31, 87	T
42. $\text{C}_4\text{H}_4\text{O}_2$	48	The NMR data confirmed the structural formula $\text{CH}_2 = \underset{\text{O}-\text{C}=\text{O}}{\text{C}}-\text{CH}_2$

Table III (continued)

Substance	Reference	Notes
43. $C_4H_8Cl_4Pt_2$ , $(C_2H_4PtCl_2)_2$	111	$\overline{\Delta H^2}$ and FS in a powdered sample. Some information is obtained on the deformation of the $C_2H_4$ molecule in the crystal.
44. $C_6H_3D_3$	19	T
45. $C_6H_5D$	19	T
46. $C_6H_6$	17, 19	T
47. $C_6H_{12}N_4$ , $N_4(CH_2)_6$	7, 144	Reference 144: $\overline{\Delta H^2}$ in a powdered sample. On the assumption that $R(C-H) = 1.09-1.10$ A the angle HCH is expected to be smaller than the tetrahedral angle. Reference 7: $\overline{\Delta H^2}$ in a powdered sample. The best agreement between the experimental and the theoretical values of the second moment is obtained for $R(C-H) = 1.10-1.11$ A (the angle HCH is a tetrahedral angle).
48. $C_3Na_2O_5 \cdot H_2O$ , $Na_2CO(COO)_2 \cdot H_2O$	29	T
49. $CaF_2$	37, 101	T
50. $CaHO_4P \cdot 2H_2O$ , $CaHPO_4 \cdot 2H_2O$	75	$\overline{\Delta H^2}$ and FS in a single crystal, and with less reliable results in a powdered sample. For water of crystallization $R(H \dots H) = 1.59 \pm 0.03$ A; the orientations of the interproton vectors are determined with respect to the crystal axes. It is shown that the positions of the acid proton proposed earlier are erroneous (more probable variants are given).
51. $CaO_4S \cdot 2H_2O$ , $CaSO_4 \cdot 2H_2O$	98	T
52. $Cd_3O_{12}S_3 \cdot 8H_2O$ , $3CdSO_4 \cdot 8H_2O$	63	T
53. $ClHO_4 \cdot H_2O$ , $HClO_4 \cdot H_2O$	76, 77, 78, 112	T
54. $ClH_4N$ , $NH_4Cl$	56, 60, 27	Reference 56: $\overline{\Delta H^2}$ in a powdered sample. $R(N-H)$ in the $NH_4^+$ ion is equal to $1.025 \pm 0.005$ A. Reference 60: $\overline{\Delta H^2}$ in a powdered sample. After the correction for torsional oscillations has been made $R(N-H) = 1.038 \pm 0.004$ A. Reference 27: $\overline{\Delta H^2}$ in a single crystal. $R(N-H) = 1.032 \pm 0.005$ A.
55. $Cl_2Cu \cdot 2H_2O$ , $CuCl_2 \cdot 2H_2O$	73	FS in a single crystal (rotation about the b axis) at room temperature. The interproton vectors of the $H_2O$ molecules lie in the ac plane and make angles of $\pm (37.5 \pm 1.5^\circ)$ with the a axis. $R(H \dots H) = 1.60$ A. It is noted that these results disagree with the results of reference 104 carried out by a somewhat different method at low temperatures.
56. $Cl_4CuH_8N_2 \cdot 2H_2O$ , $(NH_4)_2CuCl_4 \cdot 2H_2O$	73	FS in a single crystal for a rotation about the c axis. The interproton vectors of the water molecules are parallel to the diagonals of the base of the tetragonal cell. $R(H \dots H) = 1.59$ A.
57. $Cl_4CuK_2 \cdot 2H_2O$ , $K_2CuCl_4 \cdot 2H_2O$	73	FS in a single crystal for a rotation about the c axis. The interproton vector of the water molecules are parallel to the diagonals of the base of the tetragonal cell. $R(H \dots H) = 1.62$ A.
58. $Cl_4HgK_2 \cdot H_2O$ , $K_2HgCl_4 \cdot H_2O$	69, 70, 71, 125	T
59. $Cl_4K_2Sn \cdot H_2O$ , $K_2SnCl_4 \cdot H_2O$	69, 70, 71, 125	T
60. $Cl_4H_2Pt \cdot 2H_2O$ , $H_2PtCl_6 \cdot 2H_2O$	129	T
61. $Cu_4O_{16}Si_8 \cdot (H_2O)_8$ , $(CuSiO_3 \cdot H_2O)_8$	133	FS in a single crystal. The orientations of the molecules of water of crystallization and the interproton distance (1.59 A) have been determined.



Table III (continued)

Substance	Reference	Notes
62. $\text{FH}_4\text{N}$ , $\text{NH}_4\text{F}$	43, 56	$\overline{\Delta\text{H}^2}$ in a powdered sample. $\text{R}(\text{N}-\text{H})$ in the $\text{NH}_4^+$ ion is equal to $1.025 \pm 0.005 \text{ \AA}$ . Reference 43: $\text{R}(\text{N}-\text{H}) = 1.04 \pm 0.01 \text{ \AA}$ . Reference 56: $\text{R}(\text{H}-\text{F}) = 1.64 \pm 0.02 \text{ \AA}$ .
63. $\text{F}_2\text{HK}$ , $\text{KHF}_2$	141	T
64. $\text{F}_2\text{HNa}$ , $\text{NaHF}_2$	141	T
65. $\text{F}_2\text{H}_2\text{N}$ , $\text{NH}_4\text{HF}_2$	123	T
66. $\text{F}_2\text{H}_6\text{N}_2$ , $\text{N}_2\text{H}_6\text{F}_2$	41	T
67. $\text{F}_6\text{GeNa}_2$ , $\text{Na}_2\text{GeF}_6$	3, 7	M. $\overline{\Delta\text{H}^2}$ in a powdered sample at room temperature and at $160^\circ\text{K}$ . The NMR data for $\text{F}^{19}$ do not correspond to the structure proposed in papers on x-ray structure. <sup>38, 39</sup>
68. $\text{F}_6\text{K}_2\text{Ti}$ , $\text{K}_2\text{TiF}_6$	67	$\overline{\Delta\text{H}^2}$ in a powdered sample. $\text{R}(\text{Ti}-\text{F})$ in the $\text{TiF}_6^{2-}$ ion is equal to $(1.916 \pm 0.02) \text{ \AA}$ . The NMR data give no basis for assuming that the ion possesses any asymmetry which was assumed in the x-ray structural paper. <sup>124</sup>
69. $\text{F}_6\text{Na}_2\text{Si}$ , $\text{Na}_2\text{SiF}_6$	3, 7	M. $\overline{\Delta\text{H}^2}$ in a powdered sample at room temperature and at $160^\circ\text{K}$ . The NMR data for $\text{F}^{19}$ do not correspond to the structure proposal in the x-ray structural references 38, 39.
70. $\text{F}_6\text{Na}_2\text{Ti}$ , $\text{Na}_2\text{TiF}_6$	3, 7	M. $\overline{\Delta\text{H}^2}$ in a powdered sample at room temperature and at $160^\circ\text{K}$ . The NMR data for $\text{F}^{19}$ do not correspond to the structure proposed in the x-ray structural references 38, 39.
71. $\text{HNO}_3 \cdot \text{H}_2\text{O}$	112	T
72. $\text{H}_2\text{KN}$ , $\text{KNH}_2$	51	$\overline{\Delta\text{H}^2}$ and FS in a powdered sample. $\text{R}(\text{H} \dots \text{H})$ in the $\text{NH}_2^-$ ion is equal to $1.63 \pm 0.03 \text{ \AA}$ from which it follows that the $\text{HNH}$ angle, apparently, lies in the range $103-109^\circ$ .
73. $\text{H}_2\text{MgO}_2$ , $\text{Mg}(\text{OH})_2$	44	$\overline{\Delta\text{H}^2}$ in a single crystal. The absorption line shape for different orientations exhibits a $60^\circ$ periodicity which confirms the expected hexagonal positioning of the protons. A determination is made of the parameter $\rho = 0.69 \pm 0.02 \text{ \AA}$ which characterizes the distance between the planes containing the hydrogen atoms.
74. $\text{H}_2\text{MoO}_4$ , $\text{MoO}_3 \cdot \text{H}_2\text{O}$	88	$\overline{\Delta\text{H}^2}$ and FS in a powdered sample. It is shown that the substance is a crystalline hydrate.
75. $\text{H}_2\text{O}$	84	$\overline{\Delta\text{H}^2}$ in a polycrystalline sample at $90^\circ\text{K}$ . Comparison with neutron diffraction data leads to the values of $\text{R}(\text{O}-\text{H}) = 1.01 \text{ \AA}$ and angle $\text{HOH} = 104.5^\circ$ .
76. $\text{H}_2\text{O}_4\text{S} \cdot \text{H}_2\text{O}$ , $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$		T
77. $\text{H}_2\text{O}_4\text{S} \cdot 2\text{H}_2\text{O}$ , $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	129	Analysis of the line shape in a powdered sample. The following structures are possible: $(\text{H}_3\text{O})_2\text{SO}_4$ or $(\text{H}_3\text{O})\text{HSO}_4 \cdot \text{H}_2\text{O}$ . The former is the more probable one.
78. $\text{H}_2\text{O}_4\text{Se} \cdot \text{H}_2\text{O}$ , $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$	129	T
79. $\text{H}_3\text{NO}_3\text{S}$	52	The NMR method is used to establish the structure of $\text{NH}_3^+\text{SO}_3^-$ .
80. $\text{H}_3\text{NO}_4\text{S}$ , $\text{NH}_3\text{OSO}_3$	114	M. $\overline{\Delta\text{H}^2}$ and FS in a polycrystalline sample at 20, 90 and $293^\circ\text{K}$ . The structure of $\text{H}_3\text{NO} \cdot \text{SO}_3$ is confirmed; $\text{R}(\text{H} \dots \text{H}) = 1.72 \pm 0.03 \text{ \AA}$ .
81. $\text{H}_4\text{IP}$ , $\text{PH}_4\text{I}$	108	$\overline{\Delta\text{H}^2}$ in a powdered sample. $\text{R}(\text{P}-\text{H})$ in the $\text{PH}_4^+$ ion is equal to $1.42 \pm 0.02 \text{ \AA}$ .

Table III (continued)

Substance	Reference	Notes
82. $H_4MoO_3, MoO_3 \cdot 2H_2O$	<sup>88</sup>	$\overline{\Delta H^2}$ and FS in a powdered sample. It is established that this substance is a crystalline hydrate. After corrections for zero-point vibrations have been introduced $R(H \dots H)$ has turned out to be equal to $1.56 \pm 0.03 \text{ \AA}$ .
83. $H_6N_4O_6, N_2H_6(NO_3)_2$	<sup>107</sup>	$\overline{\Delta H^2}$ , and also an analysis of the line shape in a polycrystalline sample. The structure contains $N_2H_6^{++}$ ions with $R(H \dots H) = 1.71 \pm 0.015 \text{ \AA}$ .
84. $H_6N_2O_4S, N_2H_6SO_4$	<sup>107</sup>	$\overline{\Delta H^2}$ , and also an analysis of the line shape in a polycrystalline sample. The structure contains $N_2H_6^{++}$ ions with $R(H \dots H) = 1.71 \pm 0.015 \text{ \AA}$ .
85. $H_{10}N_4O_4S, (N_2H_5)_2SO_4$	<sup>107</sup>	$\overline{\Delta H^2}$ in a powdered sample. The crystal consists of $SO_4^{--}$ and $N_2H_5^+$ ions; for the latter a possible structure is given.
86. $H_{11}IN_2O_6, (NH_4)_2H_3IO_6$	<sup>30</sup>	Confirmation that this substance is not a crystalline hydrate.
87. $Li_2O_4S \cdot 2H_2O, Li_2SO_4 \cdot 2H_2O$	<sup>99, 130, 131, 64, 93</sup>	Reference 99: FS in a single crystal. A determination is made of two orientations of the interproton vectors which lie approximately in the [100] plane and which make angles of approximately $\pm 45^\circ$ with the c axis. This indicated an inaccuracy in the earlier x-ray structure determination, <sup>130</sup> and this was later confirmed by a repetition of the x-ray investigation. <sup>86</sup> References 130 and 131: $\overline{\Delta H^2}$ in a single crystal and in a powdered sample, FS in a single crystal (rotation about the b axis), $R(H \dots H) = 1.57 \text{ \AA}$ ; the interproton vectors make an angle of $46 \pm 2^\circ$ with the b axis. Reference 64: The same. $R(H-H) = 1.59 \text{ \AA}$ . One interproton vector makes angles $\alpha_0 = 92.5^\circ$ , $\beta_0 = 51^\circ$ , $\gamma_0 = 52^\circ$ with the positive directions of the a, b, c axes; the second can be obtained from the first one by a rotation of $180^\circ$ about the b axis. Reference 93: FS in a single crystal (rotation about the a, b, c axes and also about the direction of one of the interproton vectors). Anomalies which are difficult to explain are noted in the values of the doublet splitting (deviations from Pake's theory <sup>98</sup> ). The data given in the article on the orientation of the interproton vectors do not quite agree with the symmetry $C_2^2$ determined by x-ray methods. <sup>86</sup>

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