

## STRUCTURE OF CHEMICAL COMPOUNDS, SPECTROSCOPY

# On the Second Moment of the Multiquantum NMR Spectrum of a Solid

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**Abstract**—New experimental data on the time dependence of an increase in the number of correlated spins under the conditions of the observation of the multiquantum NMR spectrum of a solid are processed on the basis of a microscopic theory for describing the growth of the second moment of multiquantum NMR developed by us earlier. As follows from the theory, the growth is an exponential function of time for crystals with quite diverse structures. The results are discussed on the basis of semiphenomenological models.

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Theoretical studies of an increase in the number of correlatively moving particles during the time evolution of a many-particle dynamic system were initiated at “Brussels school” (I. Prigogine) [1]. Thanks to the appearance of experimental multiquantum nuclear magnetic resonance (NMR) spectroscopy methods, we can now study the development of multispin correlations in time (e.g., see [2–10]). So far, multiquantum spectroscopy methods have been a useful tool for studying clusters and local structures, when the interpretation of multiquantum spectra is comparatively simple. The main computational algorithms have also been developed for small systems, and control of multiquantum coherences has been studied for using them in quantum calculations [11, 12].

While theoretical data on small systems can be obtained in numerical calculations, for large systems (experimental data on up to 5000 correlated spins were published [9]), which are (as distinct from small model systems) of fundamental interest for statistical physics and quantum calculations, quite different theoretical approaches are necessary. In addition, the absence of a correct theory for interpreting experimental results hinders the application of these methods to studies of ordinary solids.

The diversity of multiquantum spectroscopy methods [2–9] reduces to the irradiation of a spin system by a sequence of radiofrequency pulses that transform its spin-spin Hamiltonian into a nonsecular operator (with respect to equilibrium magnetization). Under its action, initial magnetization is transferred into various fairly complex time correlation functions of the product of various numbers  $K$  of spin operators (multispin correlations). In other words, the equilibrium density matrix  $\rho_{eq}$  transforms in a strong magnetic field into a nonequi-

librium density matrix, which can conveniently be represented as the sum of  $\rho_n$  off-diagonal elements with a certain difference of  $n$  magnetic quantum numbers called multiquantum coherences ( $n$  is the coherence order),

$$\rho(t) = \exp\{iHt\}\rho_{eq}\exp\{-iHt\} = \sum_n \rho_n(t),$$
$$\rho_n(t) = \sum_{K=n}^{K=N} \sum_p g_{Knp}(t)|Knp\rangle,$$

where  $|Knp\rangle$  is the basis operator in which  $K$  one-spin operators form the product that couples Zeeman states that differ by  $n$  units. The index  $p$  numbers different basis states with equal  $K$  and  $n$  values, and  $N$  is the total number of spins in the system. The resulting coherences are labeled by the phase shift  $\varphi$  proportional to time. The phase shift that appears is proportional to  $n\varphi$ , where  $n$  is an integer. It follows that, depending on  $n$ ,  $K$ -spin correlations are also distinguished by the number of quanta ( $n \leq K$ ) [2–4]. Next, a new sequence of pulses is applied to the system to change the sign of the nonsecular Hamiltonian mentioned above. This causes “time reversal” [2, 13, 14]; as a consequence, the system develops “backward.” The observation of the time dependence of evolution and phase  $\varphi$  allows a one- or two-dimensional Fourier spectrum to be constructed.

In usual multiquantum experiments,  $K$ -spin correlations are labeled by the phase shift about the  $Z$  axis, that is, are classified according to the number of quanta in the basis in which  $Z$  components of spin operators are diagonal ( $Z$  basis in what follows). It was, however, shown in [8] that they could also be labeled by the phase shift that appears in rotations about other axes,

for instance, the  $X$  axis. Such experiments provide additional information already in the case of a nonsecular effective Hamiltonian. Importantly, measurements of coherences in a basis different from the usual  $Z$  basis allows spin dynamics to be studied under the action of a Hamiltonian that does not change  $z$  projections. This method was used in [10, 15] to observe multispin dynamics in the  $X$  basis during free precession decay in NMR of a solid caused by the secular part of dipole-dipole interactions. In all bases, qualitatively the same picture of the development of multispin correlations in time was observed.

The most important characteristics of multiquantum spectroscopy necessary for applied (e.g., structural) studies and the understanding of the physics of irreversible processes are the time dependences of multiquantum coherences, which, in turn, determine the distribution of the intensities of coherences of various orders in the multiquantum spectrum. The overwhelming majority of authors use the simplest statistical model suggested in [2, 3] and the ensuing Gauss form of the distribution of coherences of various orders,

$$g_n(\tau) \sim Sp\{\rho_n(\tau)\rho_{-n}(\tau)\} \sim \exp(-n^2/N(\tau)). \quad (1)$$

The  $N(\tau)/2$  variance in this model is determined by the number of spins  $N(\tau)$  between which dynamic correlation is established during preparation time  $\tau$  because of dipole-dipole interaction. This number called the number of correlated spins or effective cluster size increases with preparation time  $\tau$ . Note that the experimental dependences often cannot be described by dependence (1) (e.g., see [6]). Therefore, it is at the least necessary to use a value similar in meaning to  $N(\tau)$  but based on first principles and independent of the model.

Such a value can be the second moment  $\langle n^2(\tau) \rangle$  of the distribution of various order coherence intensities in multiquantum spectroscopy [16]. For a Gauss distribution, this moment coincides with the variance  $N(\tau)/2$  in (1). For a distribution of another form, it also characterizes the number of correlated spins (effective cluster size). The equation that relates this moment to the correlation function of the product of four spin operators taken at various time moments was obtained by Khitrin as early as 1997 [16]. The first attempt at calculating this correlation function was made by us quite recently [17] because of the extreme complexity of calculations.

Calculations of four-spin time correlation functions substantially more complex compared with two-spin functions that appear in usual NMR observations were performed in [17] with improving the methods and approaches that we developed and successfully used to calculate two-spin time correlation functions.

In this work, the time dependence of the four-spin time correlation function for  $\langle n^2(\tau) \rangle$  was described using time-dependent spin projection operators, for which expansions into the complete system of orthonormalized operators were constructed. Calculations were performed for three model examples corre-

sponding to different spin systems of solids. It was shown that, in usual solids, an increase in coherences depended on time exponentially. This is in agreement with the experimental data [9, 15] on both spin systems described by the Hamiltonian of the secular dipole-dipole interaction part and systems described by a nonsecular effective Hamiltonian typical of multispin NMR spectroscopy.

In nonmetallic diamagnetic solids, the mean reason for broadening of the NMR absorption spectrum is the secular part of internuclear dipole-dipole interaction [18], which fully determines the dynamics of the nuclear spin system,

$$\begin{aligned} H_d &= \sum_{i \neq j} b_{ij} S_{zi} S_{zj} + \sum_{i \neq j} a_{ij} S_{+i} S_{-j} = H_{zz} + H_{ff} \\ &= \sum_{i \neq j} b_{ij} S_{zi} S_{zj} + \sum_{i \neq j} a_{ij} (S_{xi} S_{xj} + S_{yi} S_{yj}) \\ &= \sum_{i \neq j} \{ H_{dij}^{zz} + H_{dij}^{xx} + H_{dij}^{yy} \}, \end{aligned} \quad (2)$$

where  $b_{ij} = \gamma^2 \hbar (1 - 3 \cos^2 \theta_{ij}) / 2 r_{ij}^3$ ,  $a_{ij} = -b_{ij}/2$ ,  $\hat{r}_{ij}$  is the vector between spins  $i$  and  $j$ ,  $\theta_{ij}$  is the angle between the  $\hat{r}_{ij}$  vector and a constant external magnetic field, and  $S_{\alpha i}$  is the  $\alpha$  component ( $\alpha = x, y, z$ ) of the vector spin operator at node  $i$ . Here and throughout, energy is expressed in frequency units.

Hamiltonian (2) is basic for "spin alchemy." It transforms under the action of radiofrequency pulses into other Hamiltonians of interest to researchers [19]. For instance, in traditional multiquantum NMR spectroscopy [2–4], the effective Hamiltonian

$$H_{eff} = \sum_{i \neq j} c_{ij} (S_{zi} S_{zj} - S_{yi} S_{yj}) = \sum_{i \neq j} \{ H_{dij}^{zz}/2 + H_{dij}^{yy} \} \quad (3)$$

is prepared.

Compared with original works, we here use the notation  $c_{ij} = b_{ij}/2$  and perform cyclic permutation of spin projections. Recently, the time dependences of various order coherence intensities in a multiquantum spectrum were measured in [10, 15] for a system with usual dipole Hamiltonian (2). It was shown that the behaviors of systems described by Hamiltonians (2) and (3) qualitatively coincided.

The experimental intensity of multiquantum coherences is determined by the time correlation function

$$\begin{aligned} &\Gamma_\varphi(t, \tau) \\ &= Sp\{U^+(\tau)U_\varphi U(t)S_x U^+(t)U_\varphi^+ U(\tau)S_x\} / Sp\{S_x^2\}. \end{aligned} \quad (4)$$

Here,  $U(t)$  is the evolution operator with the Hamiltonian of internal interaction  $H_d$  from (2) (or the Hamiltonian of this interaction transformed by radiofrequency pulses into some new nonsecular effective Hamiltonian

$H_{\text{eff}}$  (3)),  $U_\varphi = \exp(i\varphi S_x)$  is the operator of rotation through angle  $\varphi$  about the  $x$  axis, and  $S_x = \sum_i S_{xi}$  is the  $x$  component of the total spin of the nuclear system. For generality, we use the notation  $\tau$  for the evolution with time reversal. The condition  $t = \tau$  corresponding to experiments will be satisfied in the final equations.

$n$ -Order coherence intensity is obtained from (4) after the Fourier transform (integration in the  $n\varphi$  variable). It was, however, shown in [16] that this should not necessarily be done for determining the second moment of various order coherence intensity distribution in a multi-quantum spectrum. Instead, the equation

$$\begin{aligned} \langle n^2(t) \rangle &= -d^2 \Gamma_\varphi(t, t) / d\varphi^2 |_{\varphi=0} \\ &= -Sp\{[S_x, S_x(t)]^2\} / Sp\{S_x^2\}, \\ S_x(t) &= U(t)S_x U^\dagger(t) \end{aligned} \quad (5)$$

can be used.

This equation is easy to generalize to  $t \neq \tau$ ,

$$\langle \langle n^2(t, \tau) \rangle \rangle = \langle n^2(t, \tau) \rangle / 2 + \langle n^2(\tau, t) \rangle / 2; \quad (6)$$

$$\begin{aligned} \langle n^2(t, \tau) \rangle &= 2 \sum_{i,j,f,q} \{Sp\{S_{xi} S_{xf} S_{xj}(t) S_{xq}(\tau)\} / Sp\{S_x^2\} \\ &\quad - Sp\{S_{xj} S_{xi}(t) S_{xf} S_{xq}(\tau)\} / Sp\{S_x^2\}\}. \end{aligned} \quad (7)$$

At  $t = \tau$ , we obtain

$$\langle \langle n^2(t, \tau) \rangle \rangle = \langle n^2(t, t) \rangle = \langle n^2(t) \rangle. \quad (8)$$

At  $t \neq \tau$   $\langle n^2(t, \tau) \rangle$  contains an imaginary part, which disappears in (6) after symmetrization.

Direct calculations of four-spin time correlation functions in (5) or (8) is a very complex and cumbersome problem. In [17], the four-spin correlation function was expanded in powers of time with the isolation and summation of the main sequences of contributions (diagrams) in the approximation of large spatial dimensionality lattices ( $d \rightarrow \infty$ , where  $d$  is the space dimension). Below, we consider the dependence of  $\langle n^2(t) \rangle$  on the properties of the  $S_x(t)$  amplitudes of the expansion in the complete system of orthonormalized operators [20–25],

$$S_x(t) = \sum_{j=0}^{\infty} A_j(t) |j\rangle. \quad (9)$$

Similar expansions were repeatedly used in non-equilibrium statistical mechanics (e.g., see [20–25]) to describe various time correlation functions.

The expansion in orthogonal operators given in the beginning of this paper was in turn used in calculations of multi-quantum coherence amplitudes [2–9]. In this expansion and in (9), different basis operators are, however, used. In the first equation, the universal basis is formed by all possible products of operators of projections of various system spins. This is convenient for calculations of small clusters. As the number of one-spin

operators  $K$  increases, the number of basis operators grows exponentially. To overcome mathematical difficulties, uncontrollable approximations are usually introduced. For instance, exact dynamic equations are replaced with random walk equations in the Liouville space. At the same time, Eq. (9) uses the basis constructed for a particular Hamiltonian and the initial operator  $|0\rangle = S_x$  rather than the universal basis. Each next operator is obtained from the previous one after calculation of the commutator with the Hamiltonian according to the recurrent equation

$$\begin{aligned} |1\rangle &= i[H, |0\rangle], \quad |k+1\rangle = i[H, |k\rangle] + v_{k-1}^2 |k-1\rangle \\ &\quad (\text{for } k \geq 1), \end{aligned}$$

$$v_k^2 = Sp\{\langle k+1|k+1\rangle\} / Sp\{\langle k|k\rangle\}.$$

Note that, along with the products of spin projection operators, the  $|j\rangle$  orthogonal operators also contain the products of spin-spin coupling constants. This also substantially distinguishes the basis under consideration from the universal  $|K_{np}\rangle$  basis mentioned above.

The abandonment of basis universality allowed the authors of [20–25] to make progress in studies of the dynamics of many-particle systems, at least, for some model Hamiltonians or in calculations of time correlation functions simpler than those considered in this work.

For definiteness, let us consider a spin system with Hamiltonian (2). The  $A_j(t)$  amplitudes are then multi-spin one-quantum time correlation functions. The largest possible number of summations over lattice indices (the number of different spins) in these functions increases as  $j$  grows and equals  $j+1$ . The system of differential equations

$$\dot{A}_0(t) = v_0^2 A_1(t), \quad (10)$$

$$\dot{A}_k(t) = A_{k-1}(t) - v_k^2 A_{k+1}(t) \quad (\text{for } k \geq 1)$$

was obtained for  $A_j(t)$  [20–25]. To avoid confusion, we must mention some difference in the definition of  $A_j(t)$  amplitudes between [20] and [21–24]. The difference is the  $(i)^j$  multiplier. We selected the variant used in [21–24], when  $A_j(t)$  does not contain an imaginary part because the  $(i)^j$  multiplier is included in the definition of the  $|j\rangle$  operator. The  $\{v_k\}$  parameters whose values determine the solution to system (10) are written unambiguously in terms of the moments of the NMR absorption line [20]. In particular,

$$v_0^2 = M_2 = \frac{9}{4} \sum_j b_{ij}^2, \quad v_1^2 = (M_4 - M_2^2) / M_2, \quad (11)$$

$$v_2^2 = (M_2 M_6 - M_4^2) / (M_4 - M_2^2) M_2,$$

where  $M_2$ ,  $M_4$ , and  $M_6$  are the second, fourth, and sixth moments of the NMR absorption line.

Substituting (9) into (5) yields

$$\langle n^2(t) \rangle = \sum_{j=1}^{\infty} \sum_{j'=1}^{\infty} A_j(t) A_{j'}(t) S_p \{ \langle j' | [S_x, [S_x, |j\rangle]] \} / S_p \{ S_x^2 \}. \quad (12)$$

For crystals with a large number of the nearest neighbors  $Z$ , the main contribution containing the largest possible number of summations over various lattice indices can be written with  $j = j'$  in (12). Indeed, when we pass from the operator  $|j\rangle$  to  $|j+1\rangle$ , the largest possible number of spin operators with various spin indices constituting the orthogonal operator increases by one. Double commutation with  $S_x$  does not change the number of operators and only changes their projections. For instance,  $S_{y_i} \rightarrow S_{z_i} \rightarrow S_{y_i}$ . The  $|j\rangle$  and  $|j'\rangle$  operators should therefore contain equal numbers of spin operators for their scalar product to be nonzero. Note that, if only the  $H_{zz}$  part of Hamiltonian (2) is used, the  $j = j'$  contribution is the only nonzero contribution in (12) [26].

At the same time, for total Hamiltonian (2) at large  $|j\rangle$ , the orthogonal operator can also contain contributions with a smaller number of lattice indices, because, as recommended in [20], the  $|j\rangle$  operator is constructed by the subtraction (summation) of the  $|j'\rangle$  operators with  $j' < j$  with quite definite coefficients. These corrections are, however, on the order of  $\sim (1/Z)^p$ , where  $p > 0$ , and are small at a large number of neighbors  $Z$  [27].

Next, we put

$$S_p \{ \langle j | [S_x, [S_x, |j\rangle]] \} / S_p \{ S_x^2 \} = F(j) S_p \{ \langle j | j \rangle \} / S_p \{ S_x^2 \}. \quad (13)$$

Here,  $F(j)$  is some function of  $j$ , and (13) is actually its definition. According to [20],

$$S_p \{ \langle j | j \rangle \} / S_p \{ S_x^2 \} = \prod_{k=0}^{j-1} v_k^2,$$

and we eventually obtain

$$\langle n^2(t) \rangle = \sum_{j=1}^{\infty} A_j^2(t) F(j) \prod_{k=0}^{j-1} v_k^2. \quad (14)$$

It follows from the aforesaid and (14) that calculations of the second moment of a multi-quantum spectrum are a very complex many-particle problem. It requires deep comprehension with invoking all the available, including phenomenological, results.

The dependence of  $v_k^2$  on  $k$  determines the time dependences of the  $\{A_j(t)\}$  time correlation functions (e.g., see [23, 24]). For this reason, we will consider the asymptotic (at large time  $t$  values) behavior of  $\langle n^2(t) \rangle$  from (14) for several models depending on the behavior

of the  $v_k^2$  functions. This will in turn allow us to select the model that correctly describes experimental results.

The  $F(j)$  functions of the integral argument can be approximated by the sum of a first-degree polynomial and an oscillating function,

$$F(j) = aj + c + (-1)^j (bj - c). \quad (15)$$

Equation (15) is fairly general in character, and its  $\{a, b, c\}$  coefficients can be found if the  $|j\rangle$  operators are known for the selected model.

Below, we consider three models with the dependences  $v_k^2 \sim \text{const}$ ,  $v_k^2 \sim k$ , and  $v_k^2 \sim k^2$ . The situation with  $v_k^2 \sim \text{const}$  starting with some  $k$  value will be referred to as "parameter quenching." This situation was, in particular, considered in [22, 25], where the  $\{A_j(t)\}$  amplitudes were written in the form of different Bessel functions. Since the time asymptotics of Bessel functions of one type depend on time almost identically, we can use much simpler results obtained in [22] for our purposes. In addition, the corollaries to the results obtained in [25] can be considered.

A scheme for parameter quenching suggested in [22] was based on the assumption according to which  $v_0^2 = (1/2)\mu^2$ , and  $v_j^2 = (1/4)\mu^2$  if  $j \geq 1$  ( $\mu = (2M_2)^{1/2}$ ). We then have  $A_j(t) = 2^j \mu^{-j} J_j(\mu t)$ , and  $\langle n^2(t) \rangle$  takes the form

$$\langle n^2(t) \rangle = 2 \sum_{j=1}^{\infty} J_j^2(\mu t) F(j). \quad (16)$$

After the summation of the series [28], (16) becomes

$$\langle n^2(t) \rangle = c + a(\mu t)^2 [J_0^2(\mu t) + J_1^2(\mu t)] - (a+b)\mu t J_0(\mu t) J_1(\mu t) - c J_0(2\mu t). \quad (17)$$

At  $\mu t \gg 1$ , the substitution of the asymptotic equations for the Bessel functions in (17) yields

$$\langle n^2(t) \rangle \cong c + 2a\mu t/\pi + ((a+b)/\pi) \cos(2\mu t) - c/\sqrt{\pi\mu t} \cos(2\mu t - \pi/4). \quad (18)$$

Interestingly, the linear growth of  $\langle n^2(t) \rangle$  with time (Eq. (18)) was observed experimentally [7] for fluoroapatite quasi-one-dimensional crystals.

An example of a linear dependence of  $\{v_k\}$  parameters on  $k$  is provided by the Gauss form of  $A_0(t)$  time correlation functions (and, therefore, the Gauss form of the NMR absorption spectrum),

$$A_0(t) = \exp(-M_2 t^2/2). \quad (19)$$

We then have

$$v_k^2 = (k+1)M_2. \quad (20)$$

The NMR absorption spectra with a Gauss shape appear in modeling dipole-dipole interactions by inter-

action with an infinite radius (the van der Waals model). For this model, explicit equations for the  $|j\rangle$  operators and  $A_j(t)$  functions were found in [26],

$$A_j(t) = (t^j/j!) \exp(-M_2 t^2/2). \quad (21)$$

Substituting the required  $F(j)$  values in general form (15) into (14) and performing the summation yields

$$\langle n^2(t) \rangle = c + aM_2 t^2 + (-c - M_2 t^2 b) \exp(-2M_2 t^2). \quad (22)$$

A comparison with the exact equation obtained in [26] gives  $a = 2$ ,  $c = 1/2$ , and  $b = -1$ . It follows that, for this model,

$$\begin{aligned} \langle n^2(t) \rangle &= 1/2 + 2M_2 t^2 \\ &+ (M_2 t^2 - 1/2) \exp(-2M_2 t^2); \end{aligned} \quad (23)$$

that is, the time dependence of an increase in the second moment of a multiquantum spectrum is quadratic. Note that a linear dependence of the  $\{v_k\}$  parameters on  $k$  can be obtained for real lattices when dipole-dipole interaction (2) contains  $zz$  interaction only [30].

The quadratic dependence of the  $v_k^2$  parameters on  $k$

$$v_k^2 = (k+1)(k+2)v_0^2 \quad (24)$$

appears when the  $A_0(t)$  time correlation function is selected in the form

$$A_0(t) = 1/ch^2 t. \quad (25)$$

In (25), the time is dimensionless,  $t \rightarrow t(M_2/2)^{1/2}$ . According to [24], we then have

$$A_j(t) = (1/ch^2 t)(tch)^j/j!. \quad (26)$$

Substituting  $F(j)$  in form (15) into (14) and performing summation, we obtain

$$\begin{aligned} \langle n^2(t) \rangle \\ = e + 2ash^2 t - c(ch2t)^{-2} - 2bsh^2 t(ch2t)^{-3}. \end{aligned} \quad (27)$$

Equation (27) describes the exponential growth of the second moment of a multiquantum spectrum with time. Note that strengthening of the time dependence as space dimension increased was observed experimentally [5, 7]. A power law was suggested. We will show that the experimental results reported in recent works [9, 15] are well described by an exponential dependence. This functional dependence also follows from microscopic theory [17]. Lastly, calculations performed in [28, 30] using exact equations for eight moments of correlation function spectra lead to a quadratic dependence of  $v_k^2$  on  $k$  in three-dimensional lattices.

Time correlation functions of form (25) were used to describe the general properties of some dynamic systems [24]. As far as we know, this time correlation function was for the first time used to describe paramagnetic

spin systems by Blume and Hubbard [31]. They obtained this function by solving an approximate equation they used for an autocorrelation function of the type  $Sp\{S_{xi}S_{xi}(t)\}/Sp\{S_{xi}^2\}$  in an isotropic Heisenberg paramagnetic. For nuclear spin systems coupled by secular dipole-dipole interaction, such a function  $(1/sh^2 t)$  was suggested in [32] as a trial function for describing the  $A_0(t)$  nonoscillating component of free precession decay in NMR spectra. This free precession decay component is determined by the contribution of "far environment" spins [33].

The analysis performed above shows that a correct microscopic description primarily requires taking into account multispin processes similar to those that occur among a large number of far environment spins and form NMR spectrum wings [34–37]. According to [29], the  $v_k^2 \sim k^2$  dependence corresponds to the exponential shape of the wings found in these works.

An increase in the number of correlatively moving spins with time was studied by multiquantum NMR spectroscopy in many experimental works. The behavior of the largest number of correlated spins observed thus far, 5000, was studied for adamantane in recent works [9], where evolution with Hamiltonian (3) was observed. Lastly, the time dependence of the number of correlated spins in  $\text{CaF}_2$  crystals, the generally recognized model object for spin dynamics studies [33, 34], was studied in one of the most recent works [15]. Measurements were performed up to  $N = 96$ . The intensity distributions in the multiquantum spectra were close to normal (Eq. (1)) in both works. The second distribution moments were therefore determined by selecting the Gauss function with the same width at half-height. More exactly, the  $K = N(t) = \langle n^2(t) \rangle$  value called the number of correlated spins was found. The time dependences of this value are shown in Fig. 1 and 2 in semi-logarithmic coordinates. As follows from our experimental data processing, the results for these quite differently organized crystals are well described by the dependence

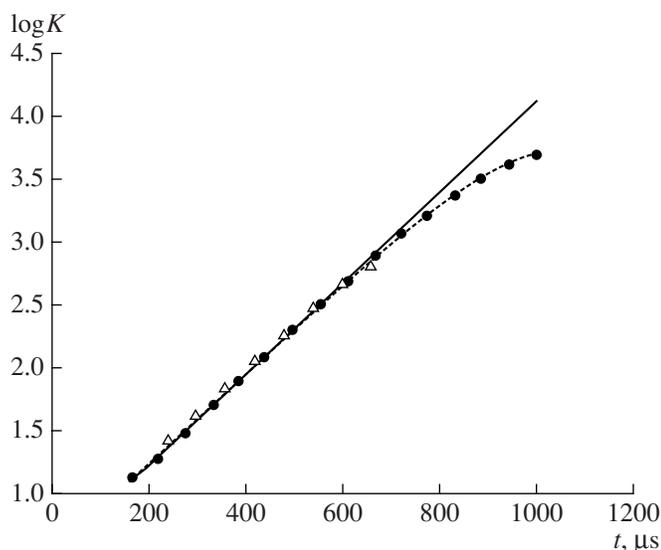
$$N(t) = A_e \exp\{a_e t\}. \quad (28)$$

For adamantane, the parameters in (28) (see Fig. 1) found by the method of least squares were

$$A_e^{(A)} = 3.24, \quad a_e = 0.0083 \text{ (1/}\mu\text{s)} = 0.3(M_2)^{1/2}. \quad (29)$$

To obtain the dimensionless value in (29), we used the theoretical second moment of the NMR absorption spectrum of adamantane calculated in [5],  $(M_2)^{1/2} = 4.19 \text{ kHz}$ . In [9], no experimental  $M_2$  value was given, but, as follows from the free precession decay data, it was close to theoretical.

The  $N(t)$  time dependence described by (28) is shown in Fig. 1, where decimal rather than Napierian



**Fig. 1.** Increase in the number of correlated spins with time in adamantane; triangles are the experimental data from [9, 2004], and solid circles, the experimental data from [9, 2006]. The solid line corresponds to calculations by (28), and the dashed line, to the approximation (32) taking into account relaxation.

logarithms are plotted along the vertical axis. That is, Eq. (28) is transformed as

$$\log N(t) = 0.0036t + 0.51.$$

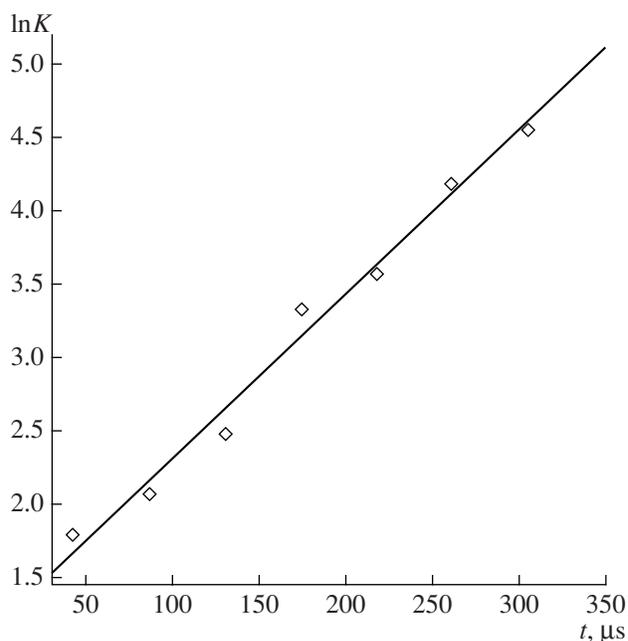
Triangles in Fig. 1 correspond to the experimental results obtained by Suter in 2004 [9], and solid circles, to his results of 2006 [9]. The figure shows that the results of 2004 (triangles) begin to deviate from the exponential function earlier than solid circles (data of 2006). It can therefore be expected that deviations from the exponential dependence of the rate of growth of the number of correlated spins are of instrumental origin. For instance, the cycle time of the apparatus used in 2006 was 55  $\mu\text{s}$  against 60  $\mu\text{s}$  in 2004 [9].

To describe dependence “curving” in Fig. 1, it is reasonable to assume that, by virtue of some circumstances of instrumental origin (nonuniformity of external fields, inaccuracy of phase measurements, and relaxation because of correction terms to the effective Hamiltonian, which is the stronger the longer the cycle time), each multiquantum spectrum component with number  $M$  decreases according to the Gauss multiplier  $\sim \exp(-fM^2)$ . The condition for the spectrum width at half-height then takes the form

$$\exp(-M^2/N(t) - fM^2) = 1/2. \quad (30)$$

It follows that deviations from the ideal dependence can be described by the equation

$$N_{1/2}(t) = N(t)/(1 + fN(t)), \quad (31)$$



**Fig. 2.** Increase in the number of correlated spins with time in fluorite; squares are the experimental data from [15], and the solid line corresponds to calculations by (28).

or

$$\log N_{1/2}(t) = \log N(t) - \log(1 + fN(t)). \quad (32)$$

The corresponding curve at  $f = 1.2 \times 10^{-4}$  is shown in Fig. 1 (dashed line).

For  $\text{CaF}_2$ , data processing with the use of the method of least squares yields

$$A_e = 3.32, \quad a_e = 0.0112 \text{ (1/}\mu\text{s)} \quad (33)$$

in Eq. (28).

The authors of [16] did not specify crystal orientation with respect to the external magnetic field. We cannot therefore compare the exponent in (33) with the second moment value for fluorite.

The time dependence of the number of correlated spins given by (28) likely means that each new spin of the correlated cluster becomes a warranted and independent producer of correlations. As a result, there is some physical analogy with chain reactions (branching processes). An explosive increase in the number of correlations, which can be expected for such a time dependence, is likely suppressed by various relaxation processes (including those mentioned above), which will possibly be discussed elsewhere. At the same time, almost all authors (see above) model the growth of the number of correlations by random walk in the Liouville space to describe the time dependence of  $N$ . This results in power  $N(t)$  dependences. As a rule, such modeling is motivated by purely qualitative considerations presented most clearly by Fel'dman at the All-Moscow

Seminar on Magnetic Resonance in 2006. Let us analyze them.<sup>1</sup>

Let us consider a sphere filled by spins. We can estimate the time when the spin in the center of the sphere begins to feel a spin on its surface. This time qualitatively corresponds to the time of cluster formation of all spins inside the sphere. If spins are coupled by dipole-dipole interaction, it is reasonable to assume that this time equals time  $t$  determined by the condition

$$\omega_d t \approx 1,$$

where  $\omega_d$  is the characteristic “dipole frequency,”  $\omega_d \sim 1/R^3$ . The number of spins  $N$  inside the sphere can be estimated as

$$N \sim R^d,$$

where  $d$  is the space dimension. Therefore, clearly,

$$N \sim t^{d/3}.$$

In particular, at  $d = 3$ , we find that the number of correlated spins increases linearly with time. The diffusion model proper of excitation transfer from the center of the sphere to the surface then gives

$$N \sim t^{d/(3/2)},$$

which qualitatively coincides with the preceding result.

However, any diffusion-character description gives the rate of the growth of the number of correlations determined by a diffusion jump and weakly depending on correlations already formed. For this reason, processes of the growth of the number of correlations are linear (additive) in diffusion models, whereas, in reality, they are nonlinear (multiplicative) as follows from our analysis.

Note that the experimental substantiation of the independence of the dynamics of separate correlated cluster spins is contained in [9, 16], where it is shown that the decoherence (correlation weakening) rate depends on the number of spins in the cluster  $K$  as  $K^{1/2}$ . Indeed, the observed dependence of the rate of coherence loss was explained in [38], where it was assumed that each spin in the cluster relaxes independently of the other spins, and the relaxation function of each spin in the cluster is Gaussian. The function of relaxation of the cluster of  $K$  spins should then also be Gaussian, and its exponent should be proportional to  $Kt^2$ . A decrease by  $e$  times is determined by the condition  $Kt^2 \sim 1$ , or  $t \sim 1/K^{1/2}$ .

For large  $K$  values, the particular form of the relaxation dependence is unimportant. Only the parity of the corresponding time function is of importance. Everything else is “taken care of” by the central limiting theorem.

<sup>1</sup>E.B. Fel'dman. Private communication. Institute of Radio Engineering and Electronics, Russian Academy of Sciences, 2006.

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