Investigation of a disordered spin system of the ^{8}Li–^{6}Li nuclei in LiF crystals by the method of β-NMR spectroscopy

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A systematic account is given of the results of experimental investigations of the transfer of the polarization of the β-active ^{8}Li nuclei to a spatially disordered spin system of the ^{6}Li nuclei in LiF crystals, carried out by the β-NMR method. The investigated effects were initiated by a single initially polarized β-active ^{8}Li nucleus formed in a nuclear reaction. An analysis of the β-ray anisotropy yielded the autocorrelation function $P_{00}(t)$ of the problem of a random walk in the disordered system when $P_{00}(t) > 0.1P_{00}(0)$. A study was made of the influence of the resonance process at the double Larmor frequency and of thermal translation of the ^{8}Li and ^{6}Li spins. The results were found to be in good agreement with the theory.

1. INTRODUCTION

A random walk in a disordered system (RWDS) is one of the topical subjects in modern physics. The interest in this topic is due to the elegance of the problem and also due to extensive applications in the physics of condensed media, optics, and spectroscopy. The system of equations [Eq. (3) below] describing the process of delocalization of the polarization (spin excitation) in a spatially disordered system of spins of the ^{8}Li and ^{6}Li nuclei discussed above is among the simplest and yet most fundamental in the RWDS theory.

From the theoretical point of view the RWDS problem requires determination of the solution of the equations just mentioned, averaged over the random spatial distribution of the donors between which an excitation can migrate. This task is very closely connected to the general problems of nonequilibrium statistical mechanics and quantum field theory,[1,2] but it is distinguished by its formal simplicity and relative ease of experimental tests.

A general theoretical solution of the RWDS problem for time intervals of moderate length can be obtained using the concentration expansion.[3] However, the problem of asymptotic approximation for long times has not yet been solved. It has been solved only using several one-dimensional models[4] and a multidimensional model of isotropic random jumps,[5,6] which have no satisfactory experimental analogs. The main experimental difficulty in the study of the long-term asymptotic behavior of an RWDS is the exponential fall of the rate of acquisition of the necessary statistics on increase in time when very small quantities have to be measured.

It is interesting to note that the problem of the long-term asymptotes of the correlation functions in the case of a random walk accompanied by polarization transfer on a regular lattice presents no difficulty from the theoretical point of view and has been basically solved at the beginning of this century, but has not yet been investigated experimentally. On the other hand, the theoretically unsolved RWDS problem has been investigated actively experimentally on the basis of the depolarization of β-active impurity nuclei (β nuclei)[7] and the delocalization of excitons,[8–11] and by measurements of the conductivity of doped semiconductors.[12] We shall consider only those systems in which the excitation transfer is initiated by the dipole–dipole interaction. The statistical data acquired in Refs. 7–9 have made it possible to study the kinetics of delocalization of the initial excitation $P_{00}(t)$ in the range of $P_{00}(t)$ of approximately one order of magnitude, which is insufficient for the attainment of the diffusion regime expected after a long time.[13] The greatest progress has been made in the experiments reported in Refs. 10 and 11 carried out using time-dependent selective laser spectroscopy, in which $P_{00}(t)$ was studied up to 0.03 and 10^{-3}, respectively. Experiments of the four-wave mixing type,[14] in which it is possible to determine directly the Fourier transform of the propagator $P(\mathbf{k}, t)$, are also very promising for RWDS studies.

The present paper gives a systematic account of the results of preliminary experimental investigations[15–17] of the transfer of the polarization from the β nuclei of ^{8}Li to a spatially disordered spin system of the ^{6}Li nuclei in LiF crystals, carried out by the β-NMR method (i.e., using magnetic resonance and relaxation of polarized β-active nuclei), which made it possible to determine directly the dependence of the polarization $\langle p_0(t)\rangle$ of an ensemble of the β nuclei on time and other parameters. An attractive feature of the β-NMR method is the identity of $\langle p_0(t)\rangle$ with the autocorrelation function $P_{00}(t) = P_{yy}(t)$ of the RWDS problem. The results obtained can be regarded as an experimental confirmation of the concentration expansion method[3] and of the semiphenomenological theory.[13] Some of the theoretical topics underlying the present investigation were discussed in Ref. 18.

The ^{8}Li–^{7}Li system differs greatly from its exciton analogs because: 1) the rate ν_{ij} of the transfer of the polarization between two spins is governed solely by the dipole–dipole interaction and can be calculated quite reliably; 2) the dependence of ν_{ij} on external magnetic fields makes it possible to control the rate of the process; 3) ν_{ij} is strongly anisotropic; 4) there is an asymmetry in respect of the transfer of the polarization from ^{8}Li to ^{6}Li and back again, as a result of which $P_{00}(t\to\infty)$ is three times larger than in the case of the transfer between identical donors; 5) the excitation is introduced into the system in an extremely localized form: initial-

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ly one β nucleus is polarized; 6) the investigated process is independent of temperature in a wide range of the latter; 7) the kinetics of the spin system can be controlled quite readily by employing strong rf fields. The extreme importance of the first of these properties should be stressed, because the reliability of the microscopic estimates of v_{ij} for the exciton transfer is considerably less; moreover, the second property is also very important because it makes it possible to carry out a more comprehensive comparison of the theory with experiment. These factors are the reasons for the investigation of the RWDS problem using the selected system of nuclei.

2. APPARATUS AND MEASUREMENT METHODS

The β-NMR spectroscopy method was developed soon after the discovery of parity nonconservation in weak interactions.[19-21] It utilizes the fact that β particles are emitted anisotropically by polarized nuclei and such emission obeys the law $W(\theta) \propto 1 + \alpha P_{00} \cos\theta$, where $W(\theta)$ is the probability of emission of β particles at an angle θ to the polarization of the β nuclei and α is a nuclear constant. Therefore, if polarized β nuclei are created in a given material and a study is made of the dependence of the angular distribution of the β particles emitted by these nuclei as a function of time, of external static and rf magnetic fields, and of temperature and pressure, it is possible to follow the evolution of the polarization of the β nuclei and thus investigate a number of processes due to the hyperfine and dipole–dipole interactions.[22] The investigated spatially disordered system of nuclei consists of the polarized β nuclei ^{8}Li formed by the capture of polarized thermal neutrons by ^{7}Li nuclei, and an isotopic impurity in the form of stable ^{6}Li nuclei, which are present in an LiF crystal. The g factors of the ^{8}Li and ^{6}Li nuclei are very similar (the difference between them is $<0.6\%$), so that in a wide range of external magnetic fields the main depolarizing process in the system of spins of the ^{8}Li–^{6}Li nuclei is cross relaxation by the flip-flop processes. This was first discovered by Bulgakov *et al.*[22] and then later by others.[23] Cross relaxation results in the transfer of the polarization from the ^{8}Li β nuclei to the nearest ^{6}Li nuclei (in LiF matrix) and its subsequent transfer back to ^{8}Li as well as to other ^{6}Li nuclei.

Figures 1 and 2 show schematically the β-NMR spectrometer. A polarized neutron beam was created by a reflection from a magnetized cobalt mirror. The flux density of these polarized thermal neutrons was 4×10^6 neutrons$\cdot$cm$^{-2}\cdot$s^{-1}. A system of guiding magnetic fields and a nonadiabatic spin flipper in the form of a thin foil[24,25] was used to reverse the direction of polarization of the neutron beam (and, therefore, the polarization of the β nuclei) relative to the external magnetic field. A mechanical chopper provided pulsed irradiation of a sample with polarized neutrons. Electrons emitted as a result of β decay were detected independently by two scintillation counters located on both sides of a sample inside the gap of an electromagnet.

The angular symmetry of β radiation was calculated using

$$\varepsilon = \frac{N(0^\circ) - N(180^\circ)}{N(0^\circ) + N(180^\circ)}, \tag{1}$$

where $N(0^\circ)$ and $N(180^\circ)$ are the numbers of the β-decay electrons recorded by a β-particle counter for two orientations of the vector representing the neutron polarization (and the polarization of the β nuclei) relative to an external static field $\mathscr{H}_0$. The asymmetry was found to be proportional to the polarization $P_{00}(t)$ of the ensemble of β nuclei averaged over the duration τ_{irr} of irradiation of a sample with neutrons and over a time $\Delta t = t_{n+1} - t_n$ the subsequent count of β particles in the n-th channel of a time analyzer:[22]

$$\varepsilon\left(t_n + \frac{\Delta t}{2}\right) = \frac{\varepsilon_0 \int\limits_{-\tau_{irr}}^{0} d\tau \int\limits_{t_n}^{t_{n+1}} dt \exp(-\lambda_0(t-\tau)) P_{00}(t-\tau)}{\int\limits_{-\tau_{irr}}^{0} d\tau \int\limits_{t_n}^{t_{n+1}} dt \exp(-\lambda_0(t-\tau))}. \tag{2}$$

Here, λ_0 is the probability of β decay and ε_0 is the extreme (i.e., in the absence of depolarization) value of the asymmetry. Time-differential measurements were carried out for $\Delta t \ll \lambda_0^{-1}$ and $\tau_{\text{irr}} \gtrsim \lambda_0^{-1}$. The dependences on external magnetic fields and on the temperature of a sample were investigated in the integral regime in which the decay electrons were counted in one time-observation channel τ_{obs}. This yielded the asymmetry $\tilde{\varepsilon} = \varepsilon(t_0 + \Delta t/2)$ with $t_0 = 0$, $\Delta t = \tau_{\text{obs}} \gg \lambda_0^{-1}$. We found that for $\lambda_0 \tau_{\text{irr}} \gg 1$ and $\lambda_0 \tau_{\text{obs}} \gg 1$ the asymmetry was $\tilde{\varepsilon} = -\varepsilon_0 \lambda_0^2 \partial P_{00}(\lambda)/\partial\lambda\,|_{\lambda=\lambda_0}$, where

$$P_{00}(\lambda) = \int\limits_0^\infty dt \exp(-\lambda t) P_{00}(t).$$

We investigated LiF single crystals of $60\times40\times2$ mm dimensions bounded by the crystallographic planes (100) (110), and (111), which were parallel to the large surface of a sample and which in turn was perpendicular to the direction of static magnetic field. The concentration of the ^{6}Li

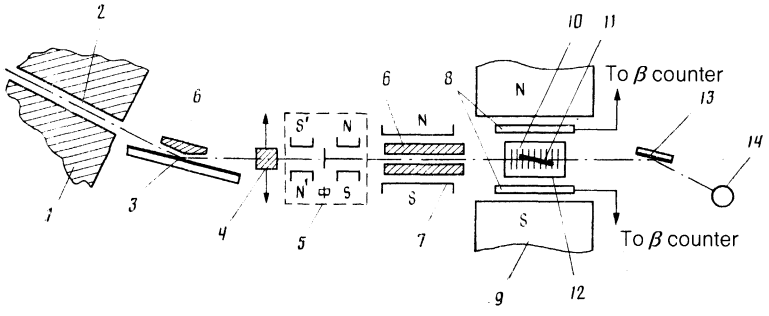

FIG. 1. Schematic diagram of the β-NMR spectrometer: 1) reactor shield; 2) collimator; 3) cobalt mirror polarizer; 4) beam chopper; 5) spin flipper (NS and $N'S'$ are magnets and F is a current-carrying foil); 6) collimator; 7) guiding field magnet; 8) β counters; 9) NMR magnet; 10) rf coil; 11) investigated sample; 12) cryostat or thermostat; 13) cobalt mirror analyzer; 14) neutron counter.

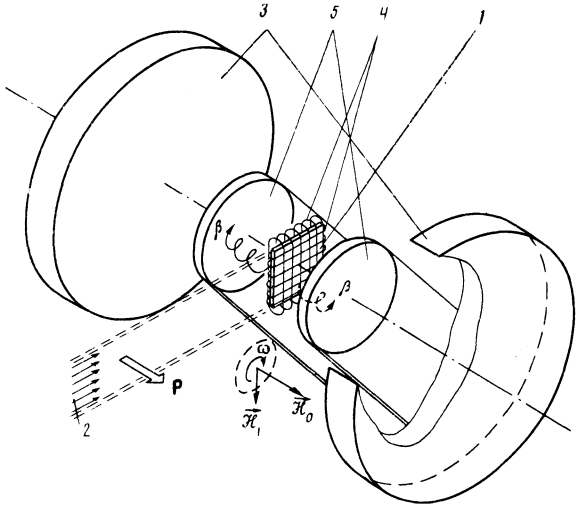

FIG. 2. Sample and magnet of the β-NMR spectrometer: 1) sample; 2) polarized neutron beam with polarization p; 3) poles of a magnet creating a field $\mathcal{H}_0$; 4) coils providing rf fields $\mathcal{H}_1$; 5) scintillation detectors for β electrons and fiber optical waveguides.

isotope was 3.21(3)%. Two coils, used to generate rf fields at the nuclei in a sample, were wound directly on the sample and the axes of these coils were mutually perpendicular. This made it possible to apply two rf fields simultaneously. A sample was heated in a special thermostat. The half-life $T_{1/2}$ of the ^{8}Li nuclei was 0.84 s ($\lambda_0 = \ln 2/T_{1/2} = 0.825\ \text{s}^{-1}$). The spins of the ^{8}Li, ^{7}Li, ^{6}Li, and ^{19}F nuclei were $I = 2$, $L = 3/2$, $S = 1$, and $F = 1/2$, respectively, and the g factors were $g_I = 0.8267$ (Ref. 26), $g_L = 2.171$, $g_S = 0.8220$, and $g_F = 5.257$.

3. THEORY

We investigated experimentally the following processes of spin dynamics of the polarized β-active ^{8}Li nuclei in LiF crystals for different types of interaction of the β nuclei with the environment and on application of different perturbations to the spin system in a crystal:

1) the depolarization in the field $\mathcal{H}_0$ because of cross relaxation in the ^{8}Li–^{6}Li system and because of the ^{6}Li–^{6}Li flip-flop processes at room temperature of the sample and in the absence of rf fields;

2) the same depolarization process, but under the conditions when strong rf fields were applied to the ^{7}Li and ^{19}F nuclei and accelerated the flip flop processes of the spins of both ^{6}Li and ^{8}Li nuclei;

3) the depolarization because of cross relaxation and application of an rf field at the frequency of the two-spin resonance $\omega_I + \omega_S$, where ω_I and ω_S are the Larmor frequencies of the ^{8}Li and ^{6}Li nuclei, respectively;

4) the depolarization because of the cross relaxation at high temperatures of a sample (in the presence of the translational diffusion of the lithium nuclei).

We shall now describe briefly each of these processes.

3.1. Depolarization because of cross relaxation in a spatially disordered system of the ^{8}Li–^{6}Li nuclei

It was shown in Refs. 22 and 23 that, in LiF crystals in fields $\mathcal{H}_0 > 100$ G, the depolarization (more accurately the delocalization of the polarization) of the ^{8}Li nuclei occurred because of cross relaxation with the ^{6}Li nuclei. The kinetics of this process was described by the following equations:[27,28,18]

$$\frac{\partial p_i}{\partial t} = -\sum_j (\nu_{ji} p_i - \nu_{ij} p_j), \qquad p_i(t=0) = \delta_{i0}, \tag{3}$$

where $p_i = \bar{I}_i^z$ is the polarization of the i th nucleus in the ^{8}Li–^{6}Li system, where $i = 0$ corresponds to ^{8}Li and $i \neq 0$ to ^{6}Li. The transition rates ν_{ij} are described by

$$\nu_{ij} = \frac{\nu_0 r_0^6}{r_{ij}^6}(1 - 3\cos^2\theta_{ij})^2, \qquad i \neq 0 \neq j, \qquad \nu_{ii} = 0, \tag{4}$$

where

$$\nu_{j0} = \frac{\nu_1 r_0^6}{r_{j0}^6}(1 - 3\cos^2\theta_{j0})^2, \qquad \nu_{0j} = \xi\nu_{j0}, \qquad \xi = \frac{I(I+1)}{S(S+1)} = 3,$$

$$\nu_0 = (\pi/6)\,(g_S^2\beta_n^2/\hbar r_0^3)^2 S(S+1) g_c(0),$$

$$\nu_1 = (\pi/6)\,(g_I g_S \beta_n^2/\hbar r_0^3)^2 S(S+1) g_c(\Delta).$$

Here, $\mathbf{r}_{ij}$ is the vector representing the distance from the spin i to the spin j; θ_{ij} is the angle between the external field $\mathcal{H}_0$ and $\mathbf{r}_{ij}$; r_0 is the distance between the nearest lithium nuclei in an LiF crystal ($r_0 = 2.85$ Å); β_n is the nuclear magneton; $g_c(\Delta)$ is the normalized profile function of the cross relaxation (PFCR); Δ is the difference between Larmor frequencies of ^{8}Li and ^{6}Li.

In the occupation number representation,[18,27] which involves introduction of a quantity $\tilde{P}_{\mathbf{xy}}(t)$ representing the polarization of a site $\mathbf{x}$ in a crystal at a moment t on condition that at $t = 0$ only the site $\mathbf{y}$ is polarized, Eq. (3) becomes

$$\frac{\partial \tilde{P}_{\mathbf{xy}}}{\partial t} = -\sum_{\mathbf{z}} (n_{\mathbf{z}}\nu_{\mathbf{zx}}\tilde{P}_{\mathbf{xy}} - n_{\mathbf{x}}\nu_{\mathbf{xz}}\tilde{P}_{\mathbf{zy}}), \qquad \tilde{P}_{\mathbf{xy}}(t=0) = \frac{n_{\mathbf{y}}}{c}\delta_{\mathbf{xy}}. \tag{5}$$

Here, $\nu_{\mathbf{xz}} = \nu_{ij}(\mathbf{r}_i = \mathbf{x}, \mathbf{r}_j = \mathbf{z})$, $n_{\mathbf{x}}$ is the occupation number of the site $\mathbf{x}$, which can be equal to 1 or 0 when the site $\mathbf{x}$ is either occupied or not by the ^{6}Li spin; an ^{8}Li nucleus is located at the site $\mathbf{y}$. The configurational average is $\langle n_{\mathbf{z}} \rangle = c$, where c is the dimensionless concentration of the ^{6}Li isotope. From the theoretical point of view this problem reduces to the calculation of the polarization $P_{00}(t)$ of the β nuclei of ^{7}Li, averaged over the random distribution of the ^{8}Li and ^{6}Li spins in a crystal. A survey of calculations of such quantities can be found in Refs. 1 and 18. The natural time scale of the problem is set by the Förster constant β_0 defined by the relationship

$$\left\langle \exp\left(-\sum_i \nu_{ij} t\right)\right\rangle = \exp(-(\beta_0 t)^{1/2}),$$

$$j \neq 0, \quad \beta_0 = \frac{512}{243}\pi^3 c^2 \nu_0, \tag{6}$$

which applies to the fcc lattice in what is known as the low-concentration limit when $c \to 0$, whereas $\beta_1 t$ is finite. If

$\beta_1 t < 1$, a satisfactory solution of the problem can be obtained using the concentration expansion[3]

$$P_{00}(t)=\exp\left\{-\left(\frac{\beta_1 t}{\xi+1}\right)^{1/2}-\alpha\beta_1 t\right\}, \quad \beta_1=\frac{\beta_0\nu_1}{\nu_0}. \tag{7}$$

The parameter α depends on $\mathscr{H}_0$ and cannot be calculated using the expressions and data given in Refs. 3 and 18. If $\mathscr{H}_0 = 0$, $\nu_1 = \nu_0$, and $\xi = 3$, we find that $\alpha = 0.013$. Equation (7) is accurate up to terms proportional to c^2 inclusive. The same expression was proposed in Ref. 29 in the lowest order of c for the simpler situation when $\xi = 1$ and the transition rates ν_{ij} are isotropic; it also follows directly from the results of Ref. 30.

Had the spins of ^{6}Li been distributed on a regular lattice, the asymptote corresponding to large values of t would have been of the diffusion type: $P_{00}(t) \propto t^{-3/2}$. In spite of many theoretical investigations of a random walk in a disordered system, the diffusion asymptote was predicted only in the approach developed in Ref. 13 (see also Refs. 28, 1, and 18). Elsewhere it was concluded that $\ln P_{00}(t)$ has in the low-concentration limit a power-law asymptote in terms of t. A special feature of the theory of Ref. 13 is a self-consistent allowance for the fact that in the problem under discussion a site y can be regarded as reliably occupied by an ^{8}Li spin, whereas in the rest of the medium there is one impurity spin per $1/c$ lattice sites on the average, which is also true of some fine-structure analytic memory functions associated with the long-range nature of the dipole–dipole interaction. A semiphenomenological system of equations describing this process is formulated in Ref. 13. Matching of the first two terms of the asymptotes for long and moderate times yielded[13]

$$P_{00}(t)=Q_0(t)+\xi\frac{1-Q_0(t)}{(\mu\beta_0(t+\tau))^{1/2}}\left(1+\frac{\varphi}{(\mu\beta_0(t+\tau))^{1/2}}\right), \tag{8}$$

where $Q_0(t) = \exp(-(\beta_1 t)^{1/2})$, $\varphi = 2.09$, $\mu = 0.889$, and $\mu\beta_0\tau = 5.11$. An experimental method of time-dependent selective laser spectroscopy was used in Ref. 11 to show that if $\beta_1 = \beta_0$, then Eq. (8) describes the delocalization of excitons right up to $P_{00}(t) > 10^{-3}$ in the case of a somewhat different, also predicted theoretically, set of the parameters φ, μ, τ, and ξ. The difference between these parameters was due to the angular dependences of the transition rates ν_{ij} and also due to the difference between the spins of ^{8}Li and ^{6}Li.

A regular method was proposed recently[31] for calculation of the diffusion coefficient of spatially disordered systems, which was a further development of the theory of Ref. 32. Application of this method to incoherent exciton transport gave (in agreement with the experimental data of Ref. 14) a diffusion coefficient which was half that predicted by the semiphenomenological theory[13] (the diffusion coefficients predicted by the theories in Refs. 13 and 33 were identical). Assuming that such a reduction occurred also for all the components of the spin diffusion tensor of the investigated ^{8}Li–^{6}Li system in LiF and introducing a refinement which made the expression valid up to terms $\sim\beta_1 t$ when $\beta_1 t \ll 1$, we obtained once again Eq. (8) subject to the following modifications (see Ref. 18):

$$Q_0=\exp[-(\beta_1 t)^{1/2}-0{,}278\beta_1 t],$$

$$\varphi=2{,}09, \quad \mu=0{,}445, \quad \mu\beta_0\tau=5{,}11. \tag{8'}$$

The number 0.278 in Q_0 corresponds to $\mathscr{H}_0 = 153.4$ G. In the more general case the value of Q_0 should be determined using Eq. (94) and Table II from Ref. 18. Attempts to use this expression for Q_0 in Eq. (8) with the initial values of the parameters φ, μ, and τ results in a less accurate description of the experimental data.

3.2. Depolarization due to cross relaxation under conditions of rf excitation at the Larmor resonance frequencies of the host spins

As pointed out already in the preceding section, the application of a weak magnetic field ($\gtrsim 150$ G) to an LiF crystal suppressed almost completely all the ^{8}Li depolarization mechanisms with the exception of cross relaxation with the ^{6}Li nuclei. Since the half-life of ^{8}Li was limited ($T_{1/2} = 0.84$ s), the time evolution of the process of delocalization of the polarization of ^{8}Li in the ^{8}Li–^{6}Li system in LiF and, consequently, the feasibility of detection of the asymptotic (diffusion) regime depended strongly on the cross relaxation rate, which was proportional to the PFCR. This rate can be varied in the field $\mathscr{H}_0 \approx 150$ G by selecting the crystallographic orientation of a sample, altering the density of the ^{6}Li spins, or deliberately changing the width of the ^{8}Li and ^{6}Li resonance lines by the application of strong (i.e., of amplitudes exceeding the amplitudes of the local fields in a crystal) rf fields to a crystal of LiF (narrowing by the Bloch method).

The motion of spins induced by such rf fields reduced the width of the profile function of the nuclear magnetic resonance (PFNMR) $g_r(\omega)$ and of the PFCR $g_c(\omega)$, representing a convolution of the PFNMRs of ^{8}Li and ^{6}Li. The narrowing was effective (i.e., all the rates ν_{ij} increased) as long as $g_c(\Delta) \sim g_c(0)$, where Δ is the difference between the Larmor frequencies of the ^{8}Li and ^{6}Li nuclei. In the case of very narrow lines it was found that $g_c(\Delta) \ll g_c(0)$ and the spin dynamics of these nuclei was independent, because $\nu_{i0} \ll \nu_{kl}$, where $i \neq 0$ and $k \neq 0 \neq l$. In the absence of narrowing the PFNMR and PFCR were nearly Gaussian, because the phase relaxation time of the ^{8}Li and ^{6}Li nuclei was less than the flip-flop time of the nuclei in the immediate environment. When narrowing occurred in the experiments under discussion, the difference between these times increased even further, so that we assumed throughout the PFNMR and PFCR were Gaussian functions with the second moments related by $M_2^c = M_2^r(^8\text{Li}) + M_2^r(^6\text{Li}) \approx 2M_2^r(^8\text{Li})$. For simplicity, we ignored the unimportant difference between the second moments of the PFNMRs of ^{8}Li and ^{6}Li, because the difference between their g factors did not exceed 0.6%. An allowance for the static correlation of the local fields (i.e., a correlation created by the immobile spins of the host material) at the ^{8}Li and ^{6}Li nuclei had practically no effect on the PFCR (Ref. 34) and, therefore, we ignored this effect also.

The application of strong rotating rf fields with amplitudes $\mathscr{H}_{1L}$ and $\mathscr{H}_{1F}$ and with frequencies $\tilde{\omega}_L \approx \omega_L$ and $\tilde{\omega}_F \approx \omega_F$, where ω_L and ω_F are the Larmor frequencies of the ^{7}Li and ^{19}F nuclei, respectively, changed the second moment M_2^r of the PFNMR of ^{8}Li as follows:[35,36]

$$M_2^r = M_{20}^{II}\cos^2\vartheta_L + M_{20}^{IL}\cos^2\vartheta_F,$$
$$\cos\vartheta_L = \frac{\omega_L - \tilde{\omega}_L}{\omega_L^{eff}}, \quad \cos\vartheta_F = \frac{\omega_F - \tilde{\omega}_F}{\omega_F^{eff}},$$
$$\omega_L^{eff} = [\omega_{1L}^2 + (\omega_L - \tilde{\omega}_L)^2]^{1/2}, \quad \omega_F^{eff} = [\omega_{1F}^2 + (\omega_F - \tilde{\omega}_F)^2]^{1/2}, \tag{9}$$
$$\omega_{1L} = \frac{g_L\beta_n\mathcal{H}_{1L}}{\hbar}, \quad \omega_{1F} = \frac{g_F\beta_n\mathcal{H}_{1F}}{\hbar}.$$

Here, M_{20}^{1L} and M_{20}^{1F} are the contributions made to the second moment of the PFNMR β nuclei by the nuclei ^{7}Li and ^{19}F in the absence of narrowing (if $\vec{\mathcal{H}}_0 \| [111]$, then $M_{20}^{1L}/(2\pi)^2 = 1.53$ kHz^2 and $M_{20}^{1F}/(2\pi)^2 = 0.64$ kHz^2). The problem of delocalization of the polarization in the system of the ^{8}Li–^{6}Li nuclei in the presence of narrowing can be reduced to the problem considered in Sec. 3.1, but with other transition probabilities ν_{ij}, proportional to the new values of the PFCR.

We investigated narrowing of the PFNMR by subjecting a sample to a weak scanning rf field with an amplitude $\mathcal{H}_1$ and a frequency ω which was varied near the Larmor frequencies of ^{8}Li and ^{6}Li. One-spin Larmor resonances and multispin satellite resonances at frequencies $\omega = \omega_K \pm \omega_L^{\text{eff}}$, where $K = \{I, S\}$, could then occur in the system.[35,36] The influence of the latter resonances in the experiments described below was slight. The origin of these satellites of the Larmor frequencies was related to the renormalization, in strong rf fields, not only of the Zeeman interaction, but also of the secular part of the dipole–dipole interactions. In the presence of a scanning field the system of equations (3) considered in the Laplace representation

$$p_0(\lambda) = \int_0^\infty dt\, e^{-\lambda t} p_0(t)$$

was transformed to

$$\lambda p_0 = 1 - R_I p_0 - \sum_j (\nu_{j0}p_0 - \nu_{0j}p_j), \tag{10a}$$
$$\lambda p_{i\neq 0} = -R_S p_i - \nu_{0i}p_i + \nu_{i0}p_0 - \sum_{j\neq 0}(\nu_{ji}p_i - \nu_{ij}p_j), \tag{10b}$$
$$R_I = \pi\omega_{1I}^2 g_r(\omega - \omega_I) + R_{Sat}(\omega - \omega_I - \omega_L^{eff}) + R_{Sat}(\omega - \omega_I + \omega_L^{eff}), \tag{10c}$$
$$R_S = \pi\omega_{1S}^2 g_r(\omega - \omega_S) + R_{Sat}(\omega - \omega_S - \omega_L^{eff}) + R_{Sat}(\omega - \omega_S + \omega_L^{eff}). \tag{10d}$$

Here, R_I and R_S are the total rates of the resonant depolarization of the ^{8}Li and ^{6}Li nuclei by the rf fields, whereas the terms $\pi\omega_{1K}^2 g_r(\omega - \omega_K)$, where $\omega_{1K} = -g_K\beta_n\mathcal{H}_1$, allow for the influence of the Larmor resonances of these nuclei in Eqs. (10c)–(10d). The rates R_{Sat} of the satellite Larmor resonances of the ^{8}Li and ^{6}Li nuclei were ($K = \{I, S\}$)

$$R_{Sat}(\omega - \omega_K \pm \omega_L^{eff}) = \frac{5\pi}{2}\left(\frac{\omega_{1K}\omega_{1L}}{(\omega_L^{eff})^2}\right)^2\left(\frac{g_K g_L \beta_n^2}{\hbar}\right)^2 \times \sum_i \left(\frac{1 - 3\cos^2\vartheta_i}{r_i^3}\right)^2 g_S(\omega - \omega_K \pm \omega_L^{eff}), \tag{11}$$

where the summation was carried out over the lithium sublattice of an LiF crystal around a specific spin of type K; $g_s(\omega - \omega_K \pm \omega_L^{\text{eff}})$ is the profile function of a satellite resonance, representing a Gaussian with a second moment equal to the sum $M_2^L + M_2^r$ of the second moments of PFNMR and of the ^{7}Li and ^{8}Li nuclei, and in the presence of narrowing it was found that

$$M_2^L = M_{20}^{LL}\left(\frac{1 - 3\cos^2\vartheta_L}{2}\right)^2 + M_{20}^{LF}\cos^2\vartheta_L\cos^2\vartheta_F, \tag{12}$$

which for the $\vec{\mathcal{H}}_0 \| [111]$ orientation gave $M_{20}^{LL}/(2\pi)^2 = 13.2$ kHz^2 and $M_{20}^{LF}/(2\pi)^2 = 4.4$ kHz^2. As in Refs. 37, 35, and 36, we used what are called the one-spin second moments

$$M_2^L = \frac{\text{Sp}[H_{Sec}, L_i^+][L_i^-, H_{Sec}]}{\text{Sp}\, L_i^+ L_i^-}$$

(where H_{Sec} is the secular[38] part of the spin–spin interactions), which represent five-ninths of the van Vleck second moments in the case of identical spins and are equal to the latter in the case of different nuclei. Their application ensures a much better agreement with the widths of multispin resonances. The expressions for the calculation of M_2^{LL} and of other second moments were given in Ref. 36.

Naturally, the considerable difference between the values of R_I and R_S was primarily due to the difference between the frequency offsets, i.e., between the arguments of the resonance profile functions, and not to the dependences of the quantities ω_{1I} and ω_{1S} on the g factors of ^{8}Li and ^{6}Li.

We calculated $P_{00}(t) = \langle p_0(t)\rangle$ using the following quite effective method.[16] The sum in Eq. (10b) was replaced with a simpler expression $K(\lambda + R_s)p_i$, which—for a suitable selection of the function $K(\lambda)$—predicted correctly all the important properties of the term being ignored. The system of equations obtained in this way was exact in the principal order in c and could have the exact solution and it could be averaged like the system discussed in Ref. 39. The result then obtained was

$$P_{00}(\lambda) = \langle p_0(\lambda)\rangle = \frac{\xi}{\rho_I + K}\int_0^\infty \exp\left[-\frac{\rho_S\xi y}{\rho_I + K} - \left(\frac{\xi\beta_1}{\pi(\rho_I + K)}\right)^{1/2} J(y)\right] dy, \tag{13}$$

where

$$J(y) = 2y\int_0^1 \exp(-yx^2)(1 - x^2)^{1/2}\, dx,$$
$$K = K(\rho_S), \quad \rho_I = \lambda + R_I, \quad \rho_S = \lambda + R_S.$$

Comparing this expression for $R_I = R_S = 0$ with the Laplace transforms of Eqs. (7) and (8), we could determine numerically the unknown function $K(\lambda)$ and then apply Eq. (13) to interpret the integral β-NMR measurements, because in the case when $\lambda_0\tau_{\text{irr}} \to \infty$ and $\lambda_0\tau_{\text{obs}} \to \infty$ the observed asymmetry of β particles was related directly to $P_{00}(\lambda)$ by

$$\bar{\varepsilon}=-\varepsilon_0\lambda_0^2\frac{\partial}{\partial\lambda}P_{00}(\lambda)\,|_{\lambda=\lambda_0}. \qquad (14)$$

In an analysis of the experimental data we introduced corrections to this expression allowing for the finite nature of the quantities $\lambda_0\tau_{\text{irr}}$ and $\lambda_0\tau_{\text{obs}}$.

3.3. Depolarization due to cross relaxation in the presence of rf radiation of frequency $\omega_I+\omega_S$ representing a two-spin resonance of ^{8}Li and ^{6}Li

This process can be described by the following equations:[15,40]

$$\frac{\partial p_i}{\partial t}=-\sum_j(\nu_{ji}p_i-\nu_{ij}p_j)-\sum_j(\mu_{ji}p_i+\mu_{ij}p_j),\quad p_i(t=0)=\delta_{i0}, \qquad (15)$$

where the rates of the elementary resonant two-spin transitions are given by

$$\mu_{ij}=\xi_i\mu_{ij}^0\left(\frac{r_0}{r_{ij}}\right)^6(3\cos 2\vartheta_{ij})^2,\quad \xi_0=\xi=3,\quad \xi_{i\neq 0}=1,$$
$$\mu_{ij}^0=\frac{\pi}{6}\left(\frac{\mathscr{H}_1}{\mathscr{H}_0}\right)^2\left(\frac{g_ig_j\beta_n^2}{\hbar r_0^3}\right)^2S(S+1)g_r^{(2)}(\omega-\omega_i-\omega_j). \qquad (16)$$

Here, $g_r^{(2)}(\Delta)$ is the profile function of a two-spin resonance line for which we used the approximation by a Gaussian with a second moment equal to twice the second moment PFNMR of ^{8}Li or ^{6}Li; g_i and ω_i are, respectively, the g factor and the Larmor frequency of the ith spin in the ^{8}Li–^{6}Li system; $\mathscr{H}_1$ is the amplitude of the rotating rf field. An analysis of the first terms of the concentration expansion[14,15] gives

$$P_{00}(t)=\langle p_0(t)\rangle=\exp\left(-(\beta_et)^{1/2}/2-\alpha_e\beta_et\right), \qquad (17)$$

where

$$\beta_e=\beta_1(1+{}^{27}/_4\gamma^{1/2})^2,\quad \alpha_e=0{,}014(1+21{,}5\gamma^{1/2}),$$
$$\gamma=\mu_{i0}^0/\nu_0\sim(\mathscr{H}_1/\mathscr{H}_0)^2\ll 1.$$

It is recognized here that $\xi=3$ and $\beta_0\approx\beta_1$ and the value of α_e is given for $\mathscr{H}_0=153.4$ G. Our calculations were carried out in the principal order in γ. Equation (17) indicates that the relative change $\delta\beta/\beta_1=(\beta_e-\beta_1)/\beta_1=\text{const}\ \gamma^{1/2}$ in the effective rate of depolarization in a disordered system is considerably higher than the ratio of the elementary rates $\mu_{i0}^0/\nu_0\sim\gamma\ll 1$. The physical side of the enhancement of the depolarization process lies in the fact that two-spin resonance violates the law of conservation $\Sigma_ip_i=1$ typical of cross relaxation and could be used to ensure total depolarization for closely spaced pairs of ^{8}Li–^{6}Li nuclei [pairs of this kind determine the behavior of $P_{00}(t)$ in the limit $\beta_et\leqslant 1$].

This cause for the enhancement effect associated with violation of the laws of conservation is quite common in the physics of relaxation processes. Similar enhancement occurs also in all orders of the concentration expansion, in agreement with the semiphenomenological analysis[41] developed to describe the exponential stage of the kinetics of the concentration self-quenching of the luminescence.

3.4. Depolarization due to cross relaxation in the presence of translational diffusion of lithium nuclei

The influence of the spatial motion of the lithium ions on the process of delocalization of the polarization in the ^{8}Li–^{6}Li system of an LiF crystal became significant at temperatures $T>500$ K. An increase in T enhanced the effectiveness of cross relaxation so that the spatial diffusion of the lithium nuclei began to overtake the spin–spin delocalization of the polarization. The main relaxation mechanism then became the transfer of the polarization to the ^{6}Li spins that approach in ^{8}Li, and the subsequent transfer of the polarization still further because these nuclei fly apart in space.[14,42]

A quantitative description of the process was provided by generalizing the concentration expansion, developed for the case of statistical disorder, to allow for the translational and spatially uncorrelated motion of the nuclei. In the principal order in respect of the concentration of the ^{6}Li nuclei, it was found that

$$\langle p_0(t)\rangle=\exp[-M(t)],\quad M(t)=c\sum_{\mathbf{r}}[1-b_0^{(1)}(\mathbf{r},t)]. \qquad (18)$$

Here, $b_0^{(1)}(\mathbf{r},t)$ is the polarization of an ^{8}Li nucleus interacting with only one-spin ^{6}Li, which at the moment t is separated by $\mathbf{r}$ from ^{8}Li which is true also if an allowance is made for all the preceding translational motion of both spins.[1,17]

In the case of slow motion, when the frequency $\varkappa$ of the lithium ion jumps is low compared with the cross relaxation frequency ν_1, in the limit of a continuous spectrum the main correction to $\varkappa$ and to the static limit $[M(t,\varkappa=0)=(\beta_1t)^{1/2}/2]$ agrees with the semiclassical approximation for the propagator near its singularity $\cos^2\vartheta_{ij}=1/3$, where the cross relaxation probability [see Eq. (4)] vanishes.[17] Consequently, if $\xi=3$, we obtain

$$M(t)=(\beta_1t)^{1/2}/2+1{,}69c\varkappa^{1/4}\nu_1^{1/4}t. \qquad (19)$$

On the basis of its derivation, the above expression is valid as long as the second term is small compared with the first, i.e., when $\varkappa^{3/4}\nu_1^{-1/4}t^{1/2}\ll 1$. In the case when $\varkappa^{3/4}\nu_1^{-1/4}t^{1/2}\gg 1$ and $\varkappa/\nu_1\ll 1$, we can calculate $M(t)$ using a method developed in the theory of scattering of slow particles (scattering length theory).[17,43] It is then found that $M(t)$ is of the same form as in Eq. (19), but it has a somewhat larger numerical coefficient (amounting to 1.76) in the second term. In a comparison of the theory with experiment, we ignored the difference between these coefficients.

If the motion is fast ($\varkappa\gg\nu_1$), we can expand $M(t)$ as a continued fraction in $\nu_1/\varkappa$. Then, to within terms $(\nu_1/\varkappa)^2$ inclusive, we obtain

$$M(t)=Zc\nu_1t, \qquad (20)$$

where

$$Z(\vec{\mathscr{H}}_0\|[100])=8{,}6\frac{1-5{,}1\nu_1}{\varkappa+6{,}4\nu_1},$$
$$Z(\vec{\mathscr{H}}_0\|[110])=12{,}3\frac{1-11{,}4\nu_1}{\varkappa+14{,}3\nu_1},$$
$$Z(\vec{\mathscr{H}}_0\|[111])=13{,}5\frac{1-8{,}4\nu_1}{\varkappa+10{,}5\nu_1}.$$

An allowance for the quadrupole interaction of the ^{8}Li nuclei with the diffusing lithium vacancies was made by us using perturbation theory. The relationship between the effective frequency $\varkappa$ or with the jumps of the lithium ions and the characteristics of vacancies in a lithium fluoride crystal was described by the expressions

$$\varkappa = c_v \tau_v^{-1}, \quad c_v = \exp(S_f/k - h_f/kT),$$

$$\tau_v^{-1} = \nu_D \exp(S_m/k - h_m/kT), \qquad (21)$$

or c_v is the concentration of the lithium vacancies; τ_v^{-1} is the frequency of their jumps; ν_D is the Debye frequency of LiF; S_f and S_m are the entropies, whereas h_f and h_m are the enthalpies of the formation and migration of a lithium vacancy, respectively; k is the Boltzmann constant; T is the absolute temperature.

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1. Depolarization of the ^{8}Li nuclei in an LiF crystal due to cross relaxation in a disordered system of ^{8}Li–^{6}Li nuclei, and its acceleration by an rf field

The depolarization of ^{8}Li was measured in the case of natural (unaccelerated) cross relaxation for two orientations of LiF crystals: with the [100] and [111] axes oriented parallel to the magnetic field $\vec{\mathscr{H}}_0$ (Figs. 3a and 3b). The cross relaxation parameters and the results of an analysis of the experimental data are presented in Tables I and II.

The depolarization in the case of accelerated cross relaxation processes was determined for a sample of LiF with the $\vec{\mathscr{H}}_0 \| [111]$ orientation, where $\mathscr{H}_0 = 153.4$ G. A crystal was exposed to two strong rf fields, one of amplitude $\mathscr{H}_{1L} = 3.1(3)$ G and of frequency $\tilde{\omega}_L/(2\pi) = 256$ kHz and the other of amplitude $\mathscr{H}_{1F} = 8(1)$ G and of frequency $\tilde{\omega}_F/(2\pi) = 620$ kHz. The frequencies of these fields were close to the Larmor frequencies of the stable nuclei ^{7}Li and ^{19}F, which under the experimental conditions were 253.8 and 614.7 kHz, respectively. The theoretical cross relaxation rates were then calculated from the expressions in Eq. (4) on the assumption that the PFCR was a Gaussian with the second moment $M_2^c = 2M_2^r$, where M_2^r were calculated from Eq. (9) using the rf field parameters (Table I). Since the exposure to these rf fields induced multispin processes, resulting in additional depolarization of the β nuclei,[37] the rf field parameters were selected so as to minimize the influence of these processes in the investigated crystal.[36] Calculations indicated that the rate of depolarization due to these multispin processes did not exceed $10^{-3}\beta_0$. The experimental data on the PFNMR of the ^{8}Li nuclei and on the kinetics of the depolarization of these nuclei in LiF crystals in the case of natural and accelerated cross relaxation processes were given in Figs. 3 and 4. Fitting of the theoretical curves based on Eqs. (7) and (8) to the experimental data was carried out allowing for the relationship between β_1 and β_0: $\beta_1 = \beta_0 \exp(-\Delta^2/2M_2^c)$, where Δ is the difference between the Larmor frequencies of ^{8}Li and ^{6}Li (in a field of 153.4 G this difference was $\Delta/2\pi = 0.55$ kHz). The fitting was in fact carried out using one parameter, which was β_0. The $\varepsilon(t)$ and $\tilde{\varepsilon}(\nu)$ dependences were analyzed simultaneously.

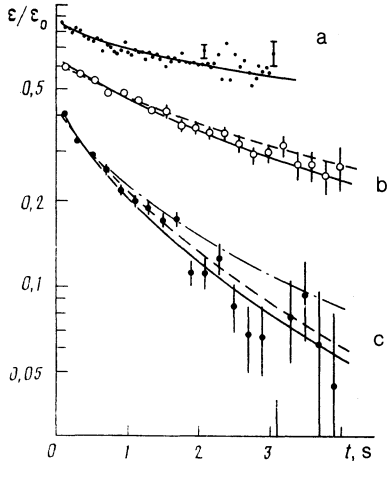

FIG. 3. Time dependences of the asymmetry of β radiation emitted by the ^{8}Li nuclei in LiF: a) natural cross relaxation for $\vec{\mathscr{H}}_0 \| [100]$, where $\mathscr{H}_0 = 218$ G, $\tau_{irr} = 0.42$ s, $\varepsilon_0 = 6.73(5)\%$; b) natural cross relaxation when $\vec{\mathscr{H}}_0 \| [111]$, where $\mathscr{H}_0 = 153.4$ G, $\tau_{irr} = 2.37$ s, $\varepsilon_0 = 5.93(4)\%$; c) accelerated cross relaxation process when $\vec{\mathscr{H}}_0 \| [111]$, where $\mathscr{H}_0 = 153.4$ G, $\tau_{irr} = 2.4$ s, and $\varepsilon_0 = 6.19(4)\%$. The continuous curves are calculated using Eq. (8), the dashed curves are calculated using Eq. (7), and the chain curves are calculated using Eq. (8′); in case b the chain curve lies between the dashed and continuous curves.

The fact that the experimental values of β_0 and β_1 obtained in the $\vec{\mathscr{H}}_0 \| [111]$ orientation in the absence of acceleration were somewhat higher than the theoretical values was explained by a slight quasi-Lorentzian narrowing of the PFCR, which was due to dynamic correlations of local fields at the nuclei participating in the cross relaxation process[17,44] (PFCR was practically Gaussian only when the flip-flop processes of the host spins were ignored). This effect is discussed in greater detail in Sec. 4.3. The discrepancy between the experimental and theoretical values of β provided a measure of the error resulting from the use of Eqs. (7), (8), and (8′) when $\beta_0 t \lesssim 5$. The difference between the experimental and theoretical parameters under acceleration conditions was possibly related to the fact that, firstly, the PFCR was influenced by the flip-flop processes of the spins surrounding the β nucleus and, secondly, because the real rate W_{MS} of multispin processes could exceed the theoretical estimate by a factor of $10^{-3}\beta_0$. For example, matching of the calculated and experimental values of β could be achieved simply by assuming that $W_{MS} \approx 0.05\beta_0$. Using our data, we concluded that Eqs. (7), (8), and (8′) were not in conflict with the experimental data in the case when $\beta_0 t < 15$.

4.2. Depolarization of the ^{8}Li nuclei in an LiF crystal due to cross relaxation in an ^{8}Li–^{6}Li system in the presence of an rf field of frequency $\omega_I + \omega_S$ of the two-spin resonance of these nuclei

Our experiments were carried out on an LiF single crystal with the $[111] \| \vec{\mathscr{H}}_0$ orientation using a field $\mathscr{H}_0 = 153.4$ G. Since the crystal was annealed during the preparatory stages, we expected it to be free of internal stresses. This was in agreement with an investigation[45] of the influence of defects on the Larmor resonance of ^{8}Li at various temperatures when the characteristic temperature of the annealing of radiation defects (lithium vacancies) was found to be 60–70 K and right up to 300 K there was no influence of defects on the Larmor resonance.

The experimentally determined line profile of the two-spin resonance $\omega_I + \omega_S$ and the dependence of the asymme-

TABLE I. Theoretical parameters of the ^{8}Li–^{6}Li cross relaxation in LiF.

Orientation of sample in field $\mathscr{H}_0$	$\mathscr{H}_0$, G	ν_0, s^{-1}	ν_1, s^{-1}	β_0, s^{-1}	β_1, s^{-1}	$M_2^c/(2\pi)^2$, kHz^2
$\mathscr{H}_0 \parallel [100]$	218	6,43	6,34	0,43	0,424	27,7
$\mathscr{H}_0 \parallel [111]$	153,4	16,3	15,8	1,09	1,06	4,3
$\mathscr{H}_0 \parallel [111]$ *	153,4	49(3) **	36(3) **	3,3(2) ***	2,4(2) ***	0,47(8) **

*In the presence of acceleration.
**The errors in the theoretical values in the presence of acceleration are due to the experimental errors in $\mathscr{H}_{1L}$ and $\mathscr{H}_{1F}$.
***For these values of β_0 and β_1 the coefficent α in Eq. (7) is 0.028 (Ref. 3).

try of the β radiation on time and on the amplitude of $\mathscr{H}_1$ (when $\omega = \omega_I + \omega_S$) are plotted in Figs. 5–7. The continuous curves in these figures [calculated using Eq. (17)] were obtained for the value $\beta_1 = 1.32(2)\ s^{-1}$. The theoretical value was $\beta_1 = 1.06\ s^{-1}$. The discrepancy between these values could be due to the reasons discussed in Sec. 4.1. The dependences $\varepsilon(t)$ were described satisfactorily by Eq. (17) right up to $\beta_1 t \approx 5$.

The numerical coefficient in front of $\gamma^{1/2}$ in the expression for β_e, obtained by the fitting method, was 6.0(3), whereas its theoretical value was 6.75. Clearly, the excess of the theoretical value above the experimental result was due to neglect of the fact that a certain volume ($\sim r_0^3$) was forbidden for ^{6}Li around the β nucleus of ^{8}Li. The dashed curve in Fig. 6 represents the results of fitting, carried out on the assumption that the enhancement of the effect (Sec. 3.3) did not occur, i.e., that the resonant depolarization was a monoexponential process. However, this hypothesis was in poor agreement with available data [$\chi^2/n = 81/19$, against the value 24/19 obtained using Eq. (17)]. An experimental determination of the second moment of the $\omega_I + \omega_S$ resonance (Fig. 6) gave $M_2/(2\pi)^2 = 5.5 \pm 1.5\ kHz^{-1}$, which was not in conflict with the theoretical value 4.2 kHz. If the depolarization process had been due to the quadrupole interactions of ^{8}Li with crystal defects (the resonance would then have occurred at frequencies $2\omega_I$, practically equal to $\omega_I + \omega_s$), the theoretical value of the second moment would have been 8.6 kHz^2.

4.3. Depolarization of the ^{8}Li nuclei in LiF crystals at high temperatures

Figures 8–10 give the experimental and calculated data on the influence of the temperature of LiF crystals on the depolarization of β-active ^{8}Li impurity nuclei. This influence became significant at temperatures $T > 500$ K. This was due to translation between vacancies of the lithium nuclei, which accelerated greatly the cross relaxation process. The dependences $\varepsilon(t)$ plotted in Fig. 10 confirmed the predicted change in the kinetics of the depolarization of ^{8}Li from that described by the expression $\ln P_{00} \propto -(\beta_1 t)^{1/2}$, valid in the absence of motion at room temperature, to $\ln P_{00} \propto -\beta_1 t/c$, valid in the case of quite rapid motion of the lithium nuclei at temperatures $T > 600$ K. An analysis of all the data was made using the Arrhenius approximation for the frequency of the translation jumps of lithium $\varkappa = \varkappa_0 \exp(-h/kT)$. We also allowed for the quadrupole interaction of ^{8}Li with the diffusing lithium vacancies and postulated that the constant of the interaction with the latter at the minimum approach distance was $\beta_Q = 3\omega_Q = 2\pi \cdot 11.7(4)$ kHz (Ref. 45). In fields < 150 G we allowed for the depolarization associated with the cross relaxation of ^{8}Li with ^{7}Li and ^{19}F.

In an analysis of $\tilde{\varepsilon}(\mathscr{H}_0)$ one should bear in mind that $[\beta_1 t/(\xi+1)]^{1/2}$ in Eq. (17) was calculated in the approximation of a continuous medium using

$$M^{(1)}(t) = \frac{c}{\xi+1} \sum_r [1 - \exp(-(\xi+1)\nu_{r0} t)]$$

representing the first term of the expansion of $M(t)$ in powers of the concentration.[3] The continuous medium approximation is valid when $c \to 0$ and $\beta_1 t$ is finite or, which is equivalent, when $c \ll 1$ and $\exp(-(\xi+1)\nu_1 t) \ll 1$. In high fields the last inequality is no longer obeyed and calculations carried out using the exact expression for $M^{(1)}(t)$ predict a stronger dependence of the polarization on $\mathscr{H}_0$ than does Eq. (7).

The results of an analysis of $\tilde{\varepsilon}(\mathscr{H}_0)$ at room temperature allowing for this refinement and also assuming a Gaussian PFCR with a variable second moment M_2^c are repre-

TABLE II. Results of analysis of experimental data.

Orientation of sample in field $\mathscr{H}_0$	Using Eq. (7)		Using Eq. (8)		Using Eq. (8′)	
	β_0, s^{-1}	β_1, s^{-1}	β_0, s^{-1}	β_1, s^{-1}	β_0, s^{-1}	β_1, s^{-1}
$\mathscr{H}_0 \parallel [100]$	0,46(2)	0,45(2)	0,48(2)	0,47(2)	0,44(2)	0,43(2)
$\mathscr{H}_0 \parallel [111]$	1,37(2)	1,32(2)	1,22(2)	1,18(2)	1,24(2)	1,20(2)
$\mathscr{H}_0 \parallel [111]$ *	5,6(2)	4,4(2)	4,4(2)	3,2(2)	4,4(2)	3,4(2)

*In the presence of acceleration

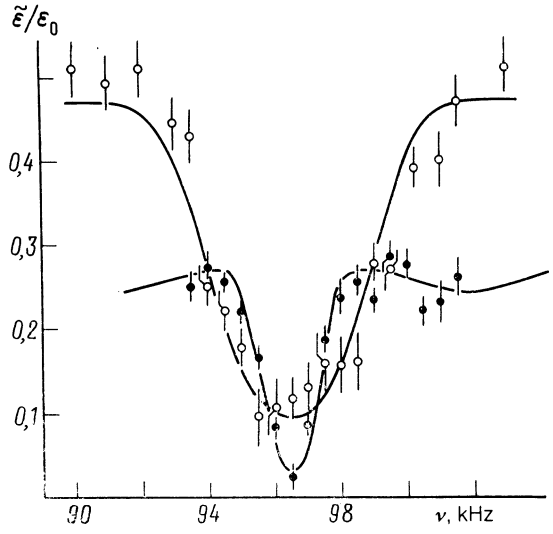

FIG. 4. Curves representing the β-NMR spectrum of the ^{8}Li nuclei in LiF crystal with the [111] axis parallel to the field $\vec{\mathscr{H}}_0$ on application of a small-amplitude scanning field $\mathscr{H}_1$ of frequency ν, $\mathscr{H}_0 = 153.4$ G: ○) in the absence of strong rf fields in a sample, $\mathscr{H}_1 = 0.025(1)$ G, $\tau_{irr} = \tau_{obs} = 4.1$ s, $\varepsilon_0 = 6.19(4)\%$; ●) in the presence of strong rf fields (with parameters given in Sec. 4.1), $\mathscr{H}_1 = 0.022(2)$ G, $\tau_{irr} = 2.4$ s, $\tau_{obs} = 3$ s, $\varepsilon_0 = 6.19(4)\%$. The results of the calculations based on Eqs. (7), (8), and (8′) are indistinguishable in this figure.

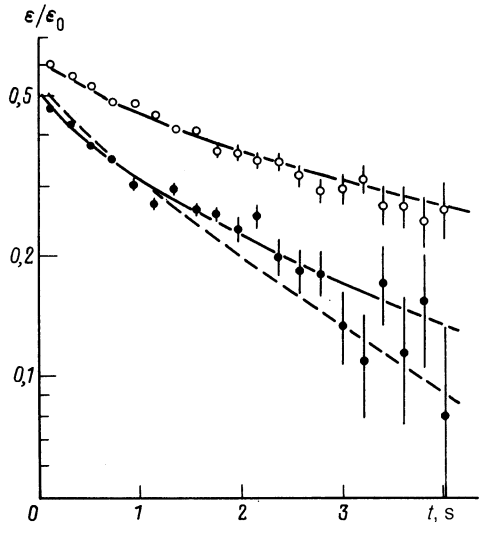

FIG. 6. Time dependences of the asymmetry of the β radiation emitted by the ^{8}Li nuclei in LiF; $\vec{\mathscr{H}}_0 \| [111]$, $\mathscr{H}_0 = 153.4$ G, $\tau_{irr} = 2.4$ s, $\varepsilon_0 = 5.93(4)\%$: ○) natural cross relaxation in the ^{8}Li–^{6}Li system (in the absence of the rf field); ●) in the presence of an rf field of frequency $(\omega_I + \omega_S)/2\pi = 192.8$ kHz and of amplitude $\mathscr{H}_1 = 10.4$ G. The continuous curves are calculated on the basis of Eq. (17) and the dashed curves represent a check of the hypothesis of an exponential resonant depolarization (see Sec. 4.2).

sented by the continuous curves in Fig. 8 and give a somewhat higher value of $M_2^c = 6.4(4)$ kHz^2 than fitting using the continuous medium approximation [5.9(4) kHz^2]. The theoretical value of M_2^c for a rigid lattice obtained ignoring correlations between local fields was 10.2 kHz^2. Fitting of the data using the parameters β_0 and M_2^c [when the relationship $\beta_1 = \beta_0 \exp(-\Delta^2/2M_2^c)$ was obeyed; Δ is the difference between the Larmor frequencies of ^{8}Li and ^{6}Li] clearly ensure a better agreement with the experiments [dashed curve in Fig. 8, $M_2^c = 5.9(4)$ kHz^2, $\beta_0 = 0.68(2)$ s^{-1}, for $\beta_0^{theor} = 0.71$ s^{-1}], but the discrepancy in the values of M_2^c remained considerable. This discrepancy was still there when an allowance was made in Eq. (18) both for three-particle clusters [i.e., when $M(t)$ included the next, proportional to c^2, term in the concentration series] and of the static correlation of the local fields.[34] The correlation appeared in its pure form when the spins of the host matrix (^{7}Li and ^{19}F) were immobile relative to spin pairs (^{8}Li–^{6}Li or ^{6}Li–^{6}Li) participating in the cross relaxation process and it resulted in a slight narrowing of the PFCR. This difference between the second components probably implied the existence of a dynamic correlation between the local fields.[44] The first reports of such effects were given in Ref. 7 (see also Ref. 28).

The dynamic correlation was related to the influence of motion (flip-flop processes) of spins in the host matrix on the PFCR. The presence of the correlation effects in the PFCR became dependent on the vector $\mathbf{r}_{ij}$ joining the cross-relaxing spins located at the sites i and j. When the motion of the host matrix spins was approximated by a normal random process, it was found that the PFCR $g_{ij}(\omega)$ could be represented in the form[18,44]

$$g_{ij}(\omega) = \int_{-\infty}^{+\infty} \frac{dt}{2\pi} \exp(i\omega t) \left\langle \exp\left(i \int_0^t d\tau (\hat{\omega}_{loc}^i(\tau) - \hat{\omega}_{loc}^j(\tau)) \right) \right\rangle$$
$$= \int_{-\infty}^{+\infty} \frac{dt}{2\pi} \exp(i\omega t) \exp\left[-2 \int_0^t d\tau (t-\tau) (\Lambda_{ii}(\tau) - \Lambda_{ij}(\tau)) \right]. \quad (22)$$

Here,

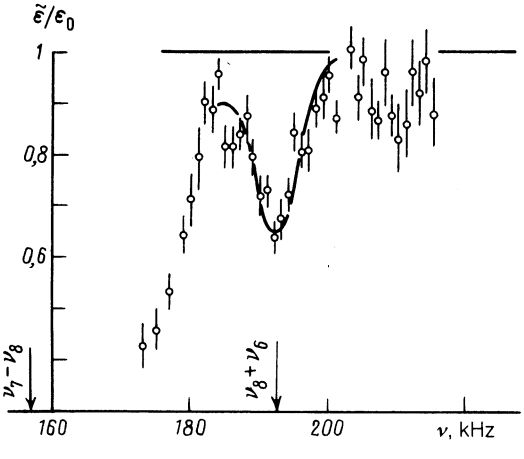

FIG. 5. Curve representing the β-NMR spectrum of the ^{8}Li nuclei in LiF in the region of a two-spin resonance at $\omega_I + \omega_S$; $\vec{\mathscr{H}}_0 \| [111]$, $\mathscr{H}_0 = 153.4$ G, ν is the frequency of a scanning rf field of amplitude $\mathscr{H}_1 = 10.4$ G, $\tau_{irr} = 2.4$ s, $\tau_{obs} = 4.1$ s, $\varepsilon_0 = 6.19(4)\%$.

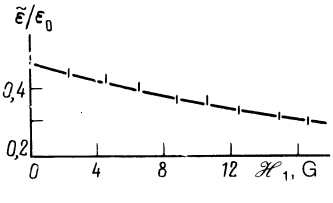

FIG. 7. Dependence of the asymmetry of the β radiation emitted by the ^{8}Li nuclei in an LiF crystal on the amplitude $\mathscr{H}_1$ of an rf field of frequency 204 kHz corresponding to a two-spin resonance $\omega_I + \omega_S$ in a field $\mathscr{H}_0 = 162.7$ G, $\vec{\mathscr{H}}_0 \| [111]$, $\tau_{irr} = 2.45$ s, $\tau_{obs} = 3$, $\varepsilon_0 = 5.69(4)\%$. An analysis of the data is made on the basis of Eq. (17).

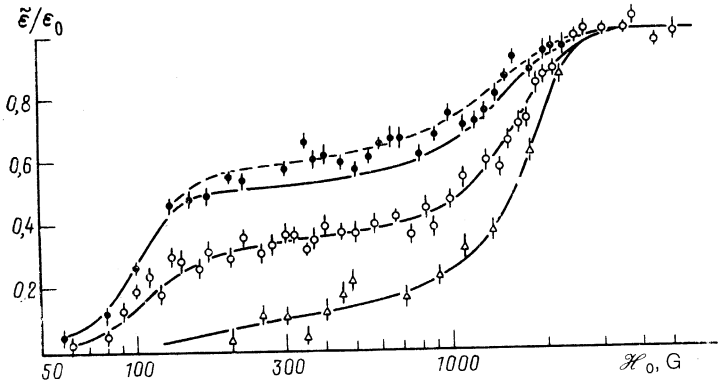

FIG. 8. Dependence of the asymmetry of the β radiation emitted by the ^{8}Li nuclei in LiF on the magnetic field $\vec{\mathscr{H}}_0 \| [110]$ at different temperatures of a sample, $\tau_{irr} = \tau_{obs} = 4.1$ s, $\varepsilon_0 = 7.36(12)\%$: ●) 296 K, $M_2^c = 6.4(4)$ kHz^2; ○) 540 K, $M_2^c = 7.5(4)$ kHz^2; △) 577 K, $M_2^c = 7.1(4)$ kHz^2. The theoretical value of M_2^c for the [110] orientation was 10.1 kHz^2.

$$\Lambda_{ij}(\tau) = \langle \hat{\omega}^i_{loc}(\tau)\, \hat{\omega}^j_{loc} \rangle$$

is the correlation function of the local fields created by the z components of the spins of the matrix at a given pair of nuclei; $\Lambda_{ii}(\tau)$ is a smoothly falling function of τ, whereas $\Lambda_{ij}(\tau)$ (here and later it is assumed that $i \neq j$) passes through a maximum and falls to zero in the limit $\tau \to \infty$.

If we adopt a realistic approximation developed in Refs. 44 and 18, the quantities Λ_{ii} and Λ_{ij} are positive for any value of τ [see Eq. (12) in Ref. 18]:

$$\Lambda_{ii}(0) - \Lambda_{ij}(0) = M_2^c,$$

where M_2^c is the second moment of the PFCR found allowing for the correlation between the local fields. The case when Λ_{ii} and Λ_{ij} are independent of τ corresponds to a purely static correlation, whereas for $\Lambda_{ij}(0) = 0$ and the functions Λ_{ii} and Λ_{ij} dependent on τ there may be a purely dynamic correlation, whereas for $\Lambda_{ij}(0) \neq 0$ the static and dynamic correlations appear simultaneously. It is clear from Eq. (22) that the dynamic correlation may not alter M_2^c, but it does result in quasi-Lorentzian narrowing of the PFCR and this effect is stronger than the analogous narrowing of the PFNMR, in qualitative agreement with the experimentally observed narrowing of both profile functions.

An analysis of the results does not allow us to determine independently $\varkappa_0$ and h, but it can be used to find the ratio $h/\ln \varkappa_0 = 0.104(1)$, where h is in electron volts and $\varkappa_0$ is in reciprocal seconds. It follows from the physical meaning that at $T_0 = h/(k \ln \varkappa_0) \approx 540$ K the time $(\varkappa c^{2/3})^{-1}$ taken by lithium to travel a distance equal to their average distance ($\sim r_0 c^{1/3}$) between the ^{6}Li nuclei in LiF becomes comparable with the reciprocal of the rate $(\nu_1 c^2)^{-1}$ of cross relaxation of the two spins ^{8}Li and ^{6}Li located at the average distance. This gives $\varkappa c^{2/3} \propto \nu_0 c^2$ (or in the case under discussion, $\varkappa \sim 1\ \text{s}^{-1}$), which defines the region of the greatest sensitivity of the β-NMR method to the translational motion of the nuclei. Using $\nu_D = 1.5 \times 10^{18}\ \text{s}^{-1}$ (Ref. 46) and the sum $S_j + S_m = 2.3$k (Ref. 47), we found that $\varkappa_0 = 1.8 \cdot 10^{15}\ \text{s}^{-1}$ and $h = 1.58$ eV. Determination of the thermal mobility of the lithium ions in LiF, carried out by other methods at higher temperatures $T > 800$ K (Ref. 48) and at $T > 920$ K (Ref. 49), gave values $\varkappa_0 = 1.7 \cdot 10^{16}\ \text{s}^{-1}$, $h = 1.81$ eV and $\varkappa_0 = 1.3 \cdot 10^{17}\ \text{s}^{-1}$, $h = 1.90$ eV, respectively. Our data used together with the values of $\varkappa_0$ from Ref. 48 or Ref. 49 would have given $h = 1.69$ and 1.85 eV, respectively. Therefore, on conversion to the enthalpy of activation, our results differed from those, for example, reported in Ref. 48 by 0.1 eV, i.e., by 6%. This scatter was typical of determination of the enthalpy of activation by different methods. It should also be mentioned that an analysis of the data of Ref. 48 deduced from measurements of the rate $1/T_1$ of the ^{19}F nuclei, unaffected by the quadrupole interaction (because the spin of ^{19}F was 1/2), gave values of $\varkappa_0$ and h practically identical with those obtained by us.

The acceleration of the ^{8}Li–^{6}Li cross relaxation observed at high temperatures was due to the motion of thermal-equilibrium lithium vacancies characterized by $h = h_f + h_m$. Had the vacancies been of radiation origin, we would have had $h \approx h_m$. The value $h_m = 0.65$–0.75 eV was reported in Refs. 47 and 48. The conclusion of observation of thermal-equilibrium vacancies was in agreement with the results of Ref. 45 reported earlier, where the radiation vacancies created as a result of formation of β nuclei ^{8}Li in LiF because of the (n, γ) reaction caused by thermal neutrons, were observed only at $T < 80$ K. When the temperature of the crystal was increased, these vacancies were annealed and at 300 K they were absent from spheres of $\approx 4r_0$ radii surrounding the ^{8}Li nuclei.[15,40]

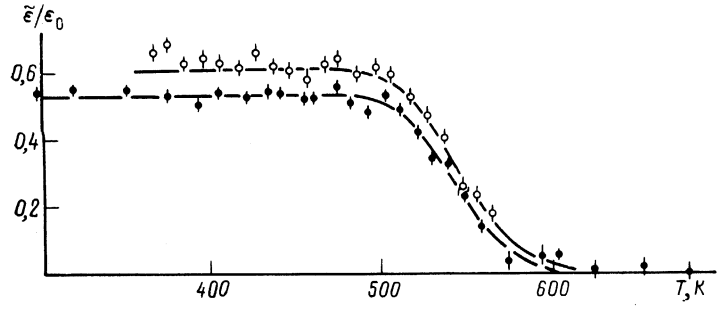

FIG. 9. Dependences of the asymmetry of the β radiation emitted by the ^{8}Li nuclei on the temperature of an LiF crystal, $\mathscr{H}_0 = 200$ G, $\tau_{irr} = \tau_{obs} = 4.1$ s, $\varepsilon = 7.36(12)\%$: ○) $\vec{\mathscr{H}}_0 \| [100]$; ●) $\vec{\mathscr{H}}_0 \| [110]$.

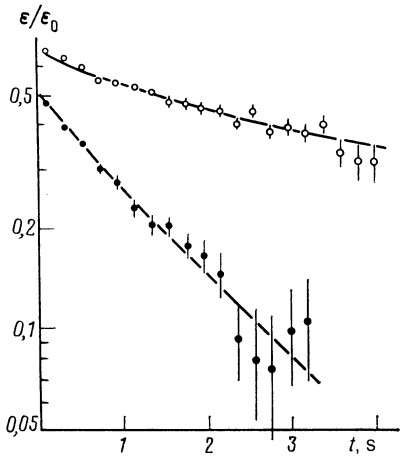

FIG. 10. Time dependence of the asymmetry of the β radiation emitted by the ^{8}Li nuclei in an LiF crystal, $\mathscr{H}_0 = 200$ G, $\mathscr{H}_0 \| [110]$, $\tau_{irr} = 2.4$ s, $\varepsilon_0 = 7.36(12)\%$, recorded at two different temperatures: ○) 296 K; ●) 540 K.

5. CONCLUSIONS

An investigation of the cross relaxation process in the spatially disordered system of the ^{8}Li–^{6}Li nuclei in an LiF crystal demonstrated that Eq. (8), based on a semiphenomenological theory[13,18] of a random walk and a microscopic refinement of Eq. (8′) (based on Refs. 31 and 18), describes satisfactorily the experimental data right up to $\beta_0 t < 15$, i.e., for $P_{00}(t) > 0.1P_{00}(0)$. This conclusion was in agreement with the results of Ref. 11, where similar expressions were used to describe delocalization of excitons right up to $\beta_0 t < 100$. However, apart from a difference in respect of the method, the system investigated by us differed from that considered in Ref. 11 by a different angular dependence of the probability of the transfer of the polarization (i.e., a different cross relaxation rate) and a difference between the spins of ^{8}Li and ^{6}Li. The cumulant form of Eq. (7) in the concentration expansion provided a reliable basis for obtaining the values of the microscopic parameters from the experimental data in the range $\beta_0 t \leqslant 5$. A comparison of the experimental interaction constants with the theory provided information on the real profile function of the cross relaxation process and on the dynamic correlation of the local magnetic fields.

The experimental data on the depolarization of the ^{8}Li nuclei accompanied by simultaneous processes of cross relaxation and two-spin resonance [in the range of the values $P_{00}(t) > 0.1P_{00}(0)$] in the disordered ^{8}Li–^{6}Li spin system were in satisfactory agreement with the theoretical expressions obtained on the basis of the concentration expansion and indicating enhancement of the resonant depolarization in the disordered system. The observed effect was useful in practical spectroscopy when estimating the influence of weak relaxation processes.

The concentration expansion[3] provided a quantitative description of a random walk in the disordered ^{8}Li–^{6}Li system in the presence of spatial motion of the lithium nuclei [when $P_{00}(t) > 0.1P_{00}(0)$]. The values of the parameters describing the motion of thermal-equilibrium vacancies agreed with those obtained by other methods. However, the sensitivity of β-NMR spectroscopy to slow motion of lithium nuclei (with the jump frequency $\sim 1\ s^{-1}$) was superior to the sensitivity of other nuclear spectroscopic methods.

[1] F. S. Dzheparov, S. V. Stepanov, and V. E. Shestopal, Preprint No. 133 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1987).
[2] F. S. Dzheparov and V. E. Shestopal, Izv. Vyssh. Uchebn. Zaved. Fiz. No. 6, 77 (1987).
[3] F. S. Dzheparov, V. S. Smelov, and V. E. Shestopal, Pis'ma Zh. Eksp. Teor. Fiz. **32**, 51 (1980) [JETP Lett. **32**, 47 (1980)].
[4] S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, Rev. Mod. Phys. **53**, 175 (1981).
[5] P. J. H. Denteneer and M. H. Ernst, Phys. Rev. B **29**, 1755 (1984).
[6] F. S. Dzheparov and V. E. Shestopal, Preprint No. 141 [in Russian], Institute of Theoretical and Experimenal Physics, Moscow (1989).
[7] M. I. Bulgakov, A. D. Gul'ko, F. S. Dzheparov, and S. S. Trostin, *Problems in Magnetic Resonance* [in Russian], Slavyanogorsk (1981), p. 54.
[8] C. R. Gochanour and M. D. Fayer, J. Phys. Chem. **85**, 1989 (1981).
[9] D. E. Hart, P. A. Anfinrud, and W. S. Struve, J. Chem. Phys. **86**, 2689 (1987).
[10] O. K. Alimov, M. Kh. Ashurov, T. T. Basiev *et al.*, Preprint No. 160 [in Russian], Lebedev Physics Institute (1983); M. Kh. Ashurov, T. T. Basiev, A. I. Burshteĭn *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 98 (1984) [JETP Lett. **40**, 841 (1984)].
[11] V. P. Gapontsev, F. S. Dzheparov, N. S. Platonov, and V. E. Shestopal, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 460 (1985) [JETP Lett. **41**, 561 (1985)].
[12] A. R. Long, Philos. Mag. B **59**, 377 (1989); A. R. Long, J. McMillan, N. Balkan, and S. Summerfield, Philos. Mag. B **58**, 153 (1988).
[13] F. S. Dzheparov, Radiospektroskopiya No. 13, 135 (1980).
[14] L. Gomez-Jahn, J. Kasinski, and R. J. D. Miller, J. Phys. (Paris) **46**, Colloq. 7, C7-85 (1985).
[15] Yu. G. Abov, M. I. Bulgakov, S. P. Borovlev *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. **50**, 2354 (1986).
[16] Yu. G. Abov, M. I. Bulgakov, S. P. Borovlev *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. **52**, 460 (1988).
[17] Yu. G. Abov, M. I. Bulgakov, S. P. Borovlev *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. **52**, 1699 (1988).
[18] F. S. Dzheparov, Zh. Eksp. Teor. Fiz. **99**, 982 (1991) [Sov. Phys. JETP **72**, this issue (1991)].
[19] F. L. Shapiro, Usp. Fiz. Nauk **65**, 133 (1958).
[20] D. Connor, Phys. Rev. Lett. **3**, 429 (1959).
[21] Yu. G. Abov, O. N. Yermakov, A. D. Gulko *et al.*, Nucl. Phys. **34**, 505 (1962).
[22] M. I. Bulgakov, S. P. Borovlev, A. D. Gul'ko *et al.*, Preprint No. 150 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1976).
[23] F. Fujara, H. J. Stöckmann, H. Ackermann *et al.*, Z. Phys. B **37**, 151 (1980).
[24] A. D. Gul'ko, S. S. Trostin, and A. Hudoklin, Nucl. Instrum. Methods **34**, 88 (1965).
[25] M. I. Bulgakov, A. D. Gul'ko, and S. S. Trostin, Preprint No. 100 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1981).
[26] A. Winnacker, D. Dubbers, F. Fujara *et al.*, Phys. Lett. A **67**, 423 (1978).
[27] F. S. Dzheparov and A. A. Lundin, Zh. Eksp. Teor. Fiz. **75**, 1017 (1978) [Sov. Phys. JETP **48**, 514 (1978)].
[28] F. S. Dzheparov, Radiospektroskopiya No. 15, 20 (1983).
[29] D. L. Huber, D. S. Hamilton, and B. Barnett, Phys. Rev. B **16**, 4642 (1977).
[30] V. P. Sakun, Fiz. Tverd. Tela (Leningrad) **14**, 2199 (1972) [Sov. Phys. Solid State **14**, 1906 (1973)].
[31] F. S. Dzheparov, Pis'ma Zh. Eksp. Teor. Fiz. **52**, 894 (1990) [JETP Lett. **52**, 269 (1990)].
[32] C. R. Gochanour, H. C. Andersen, and M. D. Fayer, J. Chem. Phys. **70**, 4254 (1979).
[33] H. Scher and M. Lax, Phys. Rev. B **7**, 4491, 4502 (1973).
[34] F. S. Dzheparov and S. V. Stepanov, *Modern NMR and ESR Methods in Solid-State Chemistry* [in Russian], Chernogolovka (1990), p. 74.
[35] F. S. Dzheparov and S. V. Stepanov, Preprint No. 139 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1982).
[36] Yu. G. Abov, M. I. Bulgakov, S. P. Borovlev *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. **47**, 2299 (1983); Preprint No. 66 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1984).
[37] Yu. G. Abov, M. I. Bulgakov, A. D. Gul'ko *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **35**, 344 (1982) [JETP Lett. **35**, 424 (1982)].
[38] A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder*, Clarendon Press, Oxford (1982).
[39] E. N. Bodunov, Izv. Akad. Nauk SSSR Ser. Fiz. **42**, 303 (1978).

[40] Yu. G. Abov, M. I. Bulgakov, S. P. Borovlev *et al.*, Preprint No. 111 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1985).
[41] A. I. Burshtein and V. P. Sakun, Chem. Phys. Lett. **103**, 205 (1983).
[42] Yu. G. Abov, M. I. Bulgakov, S. P. Borovlev *et al.*, Preprint No. 134 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1987); Preprint No. 26, Institute of Theoretical and Experimental Physics, Moscow (1989); Hyperfine Interactions **61**, 1319 (1990).
[43] I. V. Aleksandrov, *Theory of Magnetic Relaxation* [in Russian], Nauka, Moscow (1975).
[44] F. S. Dzheparov, Izv. Akad. Nauk SSSR Ser. Fiz. **54**, 1694 (1990).
[45] M. I. Bulgakov, S. P. Borovlev, A. D. Gul'ko *et al.*, Preprint No. 138 [in Russian], Institute of Theoretical and Experimental Physics, Moscow (1978); Pis'ma Zh. Eksp. Teor. Fiz. **27**, 481 (1978) [JETP Lett. **27**, 453 (1978)].
[46] V. A. Kuchin and V. L. Ul'yanov, *Elastic and Anelastic Properties of Crystals* [in Russian], Énergoatomizdat, Moscow (1986).
[47] M. Lazaridou, C. Varotsos, K. Alexopoulos, and P. Varotos, J. Phys. C **18**, 3891 (1985).
[48] M. Eisenstadt, Phys. Rev. **132**, 630 (1963).
[49] A. I. Naumov and V. B. Ptashnik, Fiz. Tverd. Tela (Leningrad) **10**, 3710 (1968) [Sov. Phys. Solid State **10**, 2950 (1969)].

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