Spin-fluctuation spectrum, phase relaxation, and NMR of β-active ^{8}Li nuclei in LiF crystals: from the method of memory functions to cumulant expansions

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The magnetic-resonance shape function $g(\omega)$ of impurity β-active ^{8}Li nuclei has been measured in LiF by β-NMR spectroscopy. The external magnetic field was oriented along the [001], [011], and [111] axes of the single crystals in different measurements. The function $g(\omega)$ varies over nearly five orders of magnitude. The hypothesis of normal fluctuations of the local magnetic field at impurity nuclei, combined with the general principles of the theory of irreversible processes, leads to a quite general and elementary description of the phase relaxation of these nuclei. This description is convenient for interpreting experiments.

1. Phase relaxation is a fundamaental elementary part of all processes in physical kinetics. The simplest manifestations of this relaxation are seen in the theory of radiation in vacuum and in the kinetics of low-density gases, in which collective processes are usually unimportant, at least in 3D systems.[1-3] Nuclear spin systems in paramagnetic phases constitute another limiting case, in which the phase relaxation is governed nearly completely by collective effects. However, the relaxation has received essentially no study from this point of view. We believe it is for this reason that there is still no satisfactory description of the phase relaxation of impurity nuclei.

Current research on phase relaxation in multispin problems is developing in several directions. The first is a simple, pragmatic description of this effect in terms of memory functions and the first few moments of a resonance line, i.e., the first time derivatives of the correlation function $g(t)=\langle I_+(t)I_-\rangle_0/\langle I_+I_-\rangle_0$ $[\langle ...\rangle_0 = \mathrm{Tr}(..\,.)/\mathrm{Tr}1]$ at $t=0$ (see Ref. 4 and the literature cited there). Here the Heisenberg evolution of the spin operator I_+ is determined, as usual, by the secular part of the dipole–dipole interaction. A second research direction focuses on oscillations of this correlation function in homonuclear systems.[4,5] A third direction consists of attempts to explain[6,7] the exponential behavior of the spectral density of spin fluctuations, i.e., the NMR lineshape function

$$g(\omega)=\int_{-\infty}^{\infty} g(t)\cos(\omega t)\frac{dt}{2\pi}, \tag{1}$$

at large values of ω which have been observed experimentally in Ref. 8 and, in a narrower variation range of $g(\omega\ )$, in the studies cited in Sec. I, Part 3, of the monograph by Abragam and Goldman.[4] A fourth and important research direction was opened up in Refs. 9–11, where the model of a normal random process was

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introduced in phase relaxation theory to describe fluctuations in local fields. The greatest success of this theory so far has been in explaining the contraction of the motion.[12] This contraction was later described, no less successfully, by the method of memory functions along the first of these research directions. The idea of Anderson, Weiss, and Kubo was developed significantly in some studies summarized in Ref. 13. Unfortunately, that approach (except for the numerical simulation) was not pursued to the point of a satisfactory quantitative description of experimental data.

We believe that the possibilities of the Anderson-Weiss-Kubo theory are far from exhausted, for the following reasons. 1) We do not as yet have a satisfactory solution of the problem of the motion of a spin in a 3D fluctuating field. 2) In the analysis of spin correlation functions of impurity nuclei in the case of a 1D local field, the ideas of the general theory of irreversible processes have not been utilized thoroughly. The first of these deficiencies was corrected in part by Zobov,[7] who also showed that in the limit of a large number of neighbors (more precisely, in the limit of an infinite dimensionality) the fluctuations of the local fields constitute a normal random process.

Correcting the second deficiency is the purpose of the present study. We have measured the NMR line of impurity nuclei over a broad range $g(\omega) \geqslant 10^{-5} g(\omega=0)$ for various orientations of the magnetic field. We have observed that when the motion of the local fields at the impurity nuclei is modeled by a relativistic normal random process,[14,15] it is possible to obtain a good description of the experimental data if, in the evaluation of the correlation function of these fields, $K(t) = \langle \hat{\omega}_{loc}(t) \hat{\omega}_{loc} \rangle$, we correctly take account of the circumstance that this function is determined by the evolution of the z components of the spins of the host (or matrix) nuclei of the crystal: At small values of t, this correlation function is an analytic function of t^2. As t increases, the collective nature of the spin evolution of the host nuclei is manifested. We first have $\ln K(t) \propto -t$, while the long-term asymptotic behavior of $K(t)$ is of a diffusion nature: $K(t \to \infty) \propto t^{-3/2}$. The reason is that the resultant z component of each species of host spins is an additive integral of motion.

2. The NMR lineshape function $g(\omega)$ of β-active impurity nuclei ("β-nuclei"), namely, ^{8}Li ($T_{1/2}=0.84$ s, $I=2$), was measured in LiF single crystals in a magnetic field $H_0=2984.9(3)$G at room temperature. The accuracy of the fields was limited by variations of the field in the sample ($=10^{-5}$). The concentration of paramagnetic centers did not exceed 10^{-5}. Estimates show that the effect of paramagnetic impurities on the results is negligible. The possibility of carrying out precise measurements of this sort had been demonstrated previously.[8] The experimental apparatus and measurement procedure are described in detail in Refs. 16 and 17.

3. The model of a normal random process is based on an approximation of the free induction signal of an impurity spin, $g(t)$, by the first terms of a cumulant expansion:

$$g(t) = \left\langle I_- I_+ T\exp\left(-i \int_0^t \hat{\omega}_{loc}(\tau) d\tau \right) \right\rangle_0 / \langle I_- I_+ \rangle_0$$

$$\simeq \exp\left(- \int_0^t (t-\tau) K(\tau) d\tau \right), \quad K(\tau) = \langle \hat{\omega}_{loc}(\tau) \hat{\omega}_{loc} \rangle_0. \qquad (2)$$

In the calculation of $K(\tau)$, the effect of impurity spins on the host spins is ignored.[14,15] Under the assumption that the β-nucleus is at the origin of coordinates, the local field can be written in frequency units as follows:

$$\hat{\omega}_{\rm loc} = \sum_{A=F,L} \hat{\omega}_{\rm loc}^{(A)}, \quad \hat{\omega}_{\rm loc}^{(A)} = \frac{g_I g_A \beta_n^2}{\hbar a^3} \sum_i^A \frac{1-3\cos^2\vartheta_i}{\rho_i^3} A_i^z, \tag{3}$$

where A takes on the values F and L; the spins of the ^{19}F and ^{7}Li nuclei (with z components F_i^z and L_i^z) are $F=1/2$ and $L=3/2$, respectively; $g_I=0.8267$, $g_F=5.257$, and $g_L=2.171$ are the g-factors of the ^{8}Li, ^{19}F, and ^{7}Li nuclei; β_n is the nuclear magneton; $a=2.01$ Å is the distance between the nearest Li and F spins in the LiF crystal; $\rho_i=r_i/a$; $\mathbf{r}_i$ is the radius vector of a host spin; and ϑ_i is the angle between $\mathbf{r}_i$ and $\mathbf{H}_0$. The coordinate summation in (3) is carried out over all possible positions of the spin in the corresponding sublattice except $\mathbf{r}_i=0$. We then obviously have

$$K(t) = \sum_{A=F,L} K_A(t), \quad K_A(t) = \langle \hat{\omega}_{\rm loc}^{(A)}(t) \hat{\omega}_{\rm loc}^{(A)} \rangle_0, \tag{4}$$

and the calculation of $K_A(t)$ reduces to an analysis of the spin-diffusion propagators $G_{ij}^A(t) = \langle A_i^z(t) A_j^z \rangle_0 / \langle (A_i^z)^2 \rangle_0$, which obey the equation

$$\dot{G}_{ij}^A(t) = -\sum_k^A \int_0^t d\tau\, N_{ki}^A(t-\tau) [G_{ij}^A(\tau) - G_{kj}^A(\tau)]. \tag{5}$$

The latter equation can be derived by a standard projection technique. Below we use the following simple approximation for the kernels $N_{ij}^A(t)$:

$$N_{ij}^A(t) = N_{ij}^A g_{cA}(t), \quad N_{ij}^A = N_{ij}^A(t=0). \tag{6}$$

Here we choose $g_{cA}(t)$ in one of the three forms $\exp(-M_{2A}t^2)$, $\cosh^{-2}\sqrt{M_{2A}}t$, $(1+\frac{2}{3}M_{2A}t^2)^{-3/2}$. Here M_{2A} is the one-spin second moment of the host nuclei.[16] These expressions are exact at small values of $M_{2A}t^2$, and they give a qualitatively correct description of the decay of $g_{cA}(t \to \infty)$. The spin diffusion coefficient calculated from these expressions for the CaF_2 crystal agree satisfactorily with experiment.[18] In practice, however, far simpler and more convenient expressions, rather than the exact solution of Eqs. (5) and (6), were used:

$$K_A(t) = \tilde{K}_A(t_{\rm eff}) = M_{2IA}\left((1-\gamma_a)\exp\left(-\frac{\alpha_A t_{\rm eff}^A}{\tau_{cA}} \right) + \frac{\gamma_A}{(1+\beta_A t_{\rm eff}^A/\tau_{cA})^{3/2}} \right), \tag{7}$$

$$M_{2IA} = \langle (\omega_{\rm loc}^{(A)})^2 \rangle, \quad \tau_{cA}^{-1} = \sum_i^A N_{ik}^A T_{2A}, \tag{8}$$

$$t_{\rm eff}^A = \int_0^t (t-\tau) g_{cA}(\tau) \frac{d\tau}{T_{2A}}, \quad T_{2A} = \int_0^\infty g_{cA}(\tau) d\tau. \tag{9}$$

The coefficients α_A, β_A, and γ_A are determined from the requirement that the values of $\partial \tilde{K}_A(t)/\partial t|_{t=0}$ and $\int_0^\infty dt K_A(t)$ and the asymptotic behavior $\tilde{K}_A(t \to \infty)$, calculated from expressions (7)–(9) and (3)–(6), be the same at $\tau_{cA} \gg T_{2A}$ (Table I).

TABLE I. Values of the numerical coefficients $\alpha_{F(L)}$, $\beta_{F(L)}$, and $\gamma_{F(L)}$ used in Eq. (8).

Orientation	α_F	β_F	γ_F	α_L	β_L	γ_L
[001]$\parallel$$\mathbf{H}_0$	0.87	1.52	0.04	0.69	0.75	0.17
[011]$\parallel$$\mathbf{H}_0$	0.70	1.2	0.19	0.80	0.82	0.24
[111]$\parallel$$\mathbf{H}_0$	0.69	0.13	0.03	0.86	0.50	0.09

4. The results of the calculations are shown in Fig. 1 along with experimental data. For the first time, a good agreement with experiment over a $g(\omega)$ range of four or five orders of magnitude has been achieved without the use of adjustable parameters. This agreement can be taken as strong evidence for the validity of modeling the behavior of the local field of the host by a normal random process.

When various trial functions are used for $g_{cA}(\tau)$, we find essentially indistinguishable curves of the NMR lineshape function of ^{8}Li, as shown in Fig. 1. The high-frequency asymptotic behavior $g(\omega \to \infty)$ corresponding to these functions is exponential, differing in numerical parameters from one function to another. However, these functions were not reached in our experiments; i.e., the pre-asymptotic terms were important. We might note in this connection that Zobov's theory[7] gives a fairly good description of the slopes of the wings of $g(\omega)$ in semilogarithmic scale, but it is not suitable for a quantitative description of experimental data (the discrepancy between theory and experiment is more than an order of magnitude), because of specifically these important pre-asymptotic terms.

A distinctive feature of this problem is that the spectrum of the Hamiltonian is not known, and the temporal pattern is the primary one. In practice, only the first few derivatives of the correlation functions of interest at $t=0$ are known. Under these conditions, we can point out at least three important and general *a priori* principles which constitute the advantage of using the model of a normal random process over the memory-function method:[14] 1) In the limit of slow fluctuations, the model of a normal random process yields a Gaussian line, in very good agreement with the exact solution. The same is true of the instantaneous distribution of the local field. Obtaining corresponding results by the memory-function method requires much more intricate constructions. 2) The model of a normal random process is the simplest generalization of a normal static distribution of local magnetic fields using a physically transparent hypothesis regarding the nature of the motion of these fields. There is no corresponding clear model in the memory-function method. 3) In an analysis of the model of a normal random process itself by the memory-function method, in lowest-order perturbation theory in the spin–field interaction, with realistic expressions for the local-field correlation functions as in (7), we obtain incorrect asymptotic results on $g(\omega)$ at both high and low frequencies. We also obtain incorrect results on $\langle I_+(t \to \infty) I_- \rangle_0$.

The results of the present study extend these arguments to arbitrary frequencies. These results show that the hypothesis of normal fluctuations of the local field, combined with the general principles of the theory of irreversible processes, leads to a good

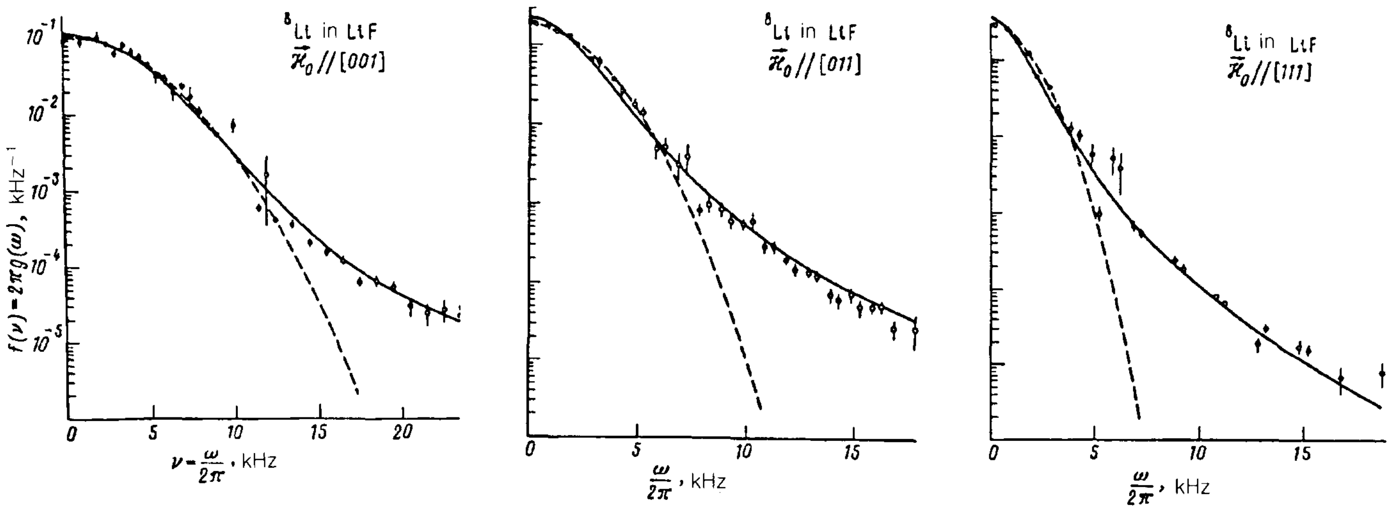

FIG. 1. Shape functions of the NMR of β-active ^{8}Li nuclei in LiF crystals versus the frequency of the scanning rf field for various orientations of the crystals in a magnetic field H_0. Solid curves—Result of a theoretical calculation of $g(\omega)$; dashed curves—gaussians with theoretical second moments.

and also comparatively simple description of the phase relaxation of impurity nuclei. This description is extremely convenient for interpreting experimental data. The approach developed here is essentially insensitive to details introduced in a model-dependent fashion.

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