Contribution to the statistical theory of the nuclear magnetic resonance line shape

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We propose a simple model capable of explaining the physical factors that determine the characteristic features of the nuclear magnetic resonance line shape in a solid. The model can be employed to investigate the line shape for the case of a rigid lattice as well as for the case of mobile nuclei. The actual calculations are made for single-crystal CaF$_2$, the traditional "trial" crystal in most studies of line shape. The results are in good agreement with experimental data.

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Starting with the classical paper by Bloembergen, Purcell, and Pound,[1] the theoretical interpretation and the calculation of the nuclear magnetic resonance (NMR) line shape has been the subject of dozens of investigations. It was assumed at first[1–5] that the NMR line should have a Lorentzian or Gaussian shape. The Lorentz lines should describe spectra in liquids or solids with strong exchange interaction between the spins, i.e., spectra produced in the presence of fast fluctuations of the local magnetic fields produced by the environment at a certain spin. The broadening of the resonance lines in solids can be due to a large number of physical factors. Very frequently, however, the decisive interaction causing the broadening is the dipole-dipole interaction between the magnetic moments of the nuclei. In this case the Gaussian lines should correspond to a distribution of dipole magnetic fields of the static type, which, as assumed, is realized in most solids.

Lowe and Norberg have subsequently shown[6] that the resonance line shape can be described in equivalent fashion with the aid of the Fourier transform of the correlation function of the transverse magnetization, which in turn corresponds to the free-precession signal (FPS) produced after a 90 degree radio-frequency pulse is applied to the spin system. It was shown in the same paper that the line shape in single-crystal CaF$_2$ is not Gaussian, since the FPS is a damped oscillating function of the time. This fact, as well as the recent rapid development of pulse methods in solid-state NMR,[7,8] in which the FPS curves are extensively used, has stimulated a new wave of studies devoted to the line shape of NMR[9–18] etc. Almost all these studies, however, deal with various methods of mathematically describing the FPS curve so as to obtain agreement with experiment, but hardly touch on the physical essence of the processes that shape the NMR line. A critical analysis of the theoretical papers[9–15] can be found in[19–21].

We note that pulse methods involve direct action on the spin-spin interactions in the crystal. Thus, for an adequate description of the physical processes that shape the resultant FPS line, it is necessary to be able to analyze in detail the behavior of the spin systems at times $t \lesssim T_2$, where T_2 is the spin-spin interaction time.

We propose here a simple model that makes it possible to calculate the principal parameters of the FPS curve and to explain the physical nature of the processes that govern its characteristic features, both for the case of a rigid lattice and in the presence of motion of the nuclei. Although the actual calculations were performed for single-crystal CaF$_2$—the "trial" crystal for most work on line shape, the method can be easily extended to include other crystals. In the early sixties, Abragam[2] has found empirically that FPS in single-crystal CaF$_2$ is well described by the trial function

$$\Gamma(t)=\frac{\sin(bt)}{bt}\exp\left(-\frac{a^2t^2}{2}\right). \tag{1}$$

The quantities a and b were chosen such that the absorption line had corrected second (M_2) and fourth (M_4) moments. Subsequently the experimental investigations of the asymptotic behavior of the FPS have shown[22] that at times $t \gtrsim T_2$ the signal takes the form

$$\Gamma(t)\sim\sin(bt)e^{-ct}/bt. \tag{2}$$

Despite the high reliability of the presented experimental facts, which have revealed interesting features, the problem of determining the physical causes of this character of the FPS has not been posed to this day, and there is no verification whatever of the empirical functions (1) and (2).

The F^{19} nuclei are the only nuclei in CaF$_2$ with a nonzero magnetic moment and form a primitive cubic lattice. In a constant magnetic field H_0 directed along the z axis, the crystal magnetic nuclear subsystem is described by the Hamiltonian

$$H=H_z+H_d^0; \tag{3}$$

where

$$H_d^0=\frac{\gamma^2\hbar^2}{2}\sum_{i\neq j}\frac{1-3\cos^2\theta_{ij}}{r_{ij}^3}\left(\frac{3}{2}S_{zi}S_{zj}-\frac{1}{2}\mathbf{S}_i\mathbf{S}_j\right), \tag{4}$$

$$H_z=\sum_j\gamma\hbar H_0S_{zj}. \tag{5}$$

Here H_z is the Zeeman Hamiltonian, H_d^0 is the secular part of the dipole interaction[2], r_{ij} is the distance between the spins i and j; θ_{ij} is the angle between the direction of the constant magnetic field H_0 and the internuclear vector joining the spins i and j; γ is the gyromagnetic ratio. In the Hamiltonian H_d^0, in contrast to the total Hamiltonian H_d of the dipole-dipole interaction, the terms of the type $E \sim S_{+i} S_{zj}$ and $F \sim S_{+i} S_{+j}$ are neglected. The operators E and F mix states with different $S_z = \sum_j S_{zj}$, with a degree of mixing $\alpha \sim H_{\text{loc}}/H_0 \sim 10^{-4}$ (H_{loc} is the local field produced by the neighbors at the spin, $H_{\text{loc}} \sim 1$ Oe, $H_0 \sim 10^4$ Oe), and lead consequently to the appearance of weak satellites at frequencies that are multiples of the Larmor frequency ω_0.

The emf excited in a coil by the free precession of the spin[2] is determined by the x component of the total spin of the system (the analysis is carried out in a coordinate system rotating with frequency ω_0 about the z axis of the laboratory frame):

$$\langle S_x(t)\rangle = -\frac{\beta_l\hbar\omega_0}{\mathrm{Sp}(1)}\mathrm{Sp}\left\{\exp\left(\frac{i}{\hbar}H_d^0 t\right)S_x\exp\left(-\frac{i}{\hbar}H_d^0 t\right)S_x\right\} = -\frac{\beta_l\hbar\omega_0\,\mathrm{Sp}\{S_x^2\}}{\mathrm{Sp}\{1\}}\Gamma(t), \tag{6}$$

$$\langle A\rangle = \mathrm{Sp}\{A\rho\}, \quad \rho = (1-\beta_l\hbar\omega_0 S_x)/\mathrm{Sp}\{1\};$$

ρ is the density matrix of the system, β_l is the reciprocal lattice temperature,

$$\omega_0 = \gamma H_0, \quad S_x = \sum_j S_{xj}.$$

For the total spin we thus have

$$\frac{d}{dt}\langle S_x(t)\rangle = \frac{i}{\hbar}\langle [H_d^0, S_x]\rangle = \beta_l\frac{\omega_0}{\mathrm{Sp}(1)}\sum_j \mathrm{Sp}\left\{\exp\left(\frac{i}{\hbar}H_d^0 t\right)H_{zj}S_{yj}\exp\left(-\frac{i}{\hbar}H_d^0 t\right)S_x\right\}, \tag{7}$$

$$H_{zj} = \sum_{i\neq j}\frac{3}{2}\gamma\hbar\frac{1-3\cos^2\theta_{ij}}{r_{ij}^3}S_{zj} = \sum_{i\neq j}\frac{3}{2}b_{ij}S_{zj}.$$

Taking into account the structural equivalence of the spins, we get

$$\langle S_x(t)\rangle \sim \mathrm{Sp}\{S_x(t)S_x\} \sim N\langle S_{x0}(t)\rangle \sim N\,\mathrm{Sp}\{S_{x0}(t)S_x\}.$$

N is the number of spins in the sample. We obtain

$$\frac{d}{dt}\langle S_{x0}(t)\rangle = \beta_l\frac{\omega_0}{\mathrm{Sp}(1)}\mathrm{Sp}\left\{\exp\left(\frac{i}{\hbar}H_d^0 t\right)H_{z0}S_{y0}\exp\left(-\frac{i}{\hbar}H_d^0 t\right)S_x\right\}. \tag{8}$$

It is seen from the foregoing expressions that the rate of change of the x component of the average (summary: $\langle S_{x0}(t)\rangle = N^{-1}\langle S_x(t)\rangle$) spin is determined by the sum of the changes of the x components of the spins located at different sites of the crystal lattice, the change of $\langle S_{x0}(t)\rangle$ being in fact due to rotation of the individual spins in fields directed along the z axis. The latter is not surprising and is due to the axial symmetry of the Hamiltonian (4), owing to which $\langle S_{z0}(t)\rangle = \text{const}$. In spin systems with spherically symmetrical exchange interaction, e.g., the average spin is in fact stationary:

$$\langle S_{x0}(t)\rangle = \text{const}, \ \langle S_{y0}(t)\rangle = \text{const}, \ \langle S_{z0}(t)\rangle = \text{const}.$$

In most experiments on magnetic resonance, the thermal energy is large in comparison with the energy of the dipole-dipole interaction, so that the nuclear spin system is paramagnetic. In this situation, the local field $H_{z0}(t)$ acting on the spin can be represented in the form of a sum of two statistically independent contributions with principally different characters: $H_{z0}(t) = H_{z0}^{(1)}(t) + H_{z0}^{(2)}(t)$. The difference between $H_{z0}(t)$ and $H_{z0}^{(2)}(t)$ is connected, from the physical point of view, with the concept of the correlation and spin orientations. The presence of two fields is due to the presence in the crystal of two regions, in one of which the spin orientations and consequently the local fields produced by the spins are correlated with the selected orientation, and in the other they are not. We emphasize that we are dealing exclusively with temporal correlations and that a correlation between the field acting on the spin and the spin itself means that the change of the orientation of the selected spin involves a change of the effective field. Such an effect is impossible in the absence of correlations. Obviously, the correlation arises in the spin system only because (4) contains a scalar term, for otherwise when only the zz interaction remains, the z component of the local field is preserved, and consequently the motion of the selected spin cannot influence the field acting on it in any way. The action of the scalar term contained in (4) is realized in the spin system in the form of mutual spin flip flops (henceforth called *ff* processes), the probability of which[23,24]

$$W_{ij} = (8\sqrt{2})^{-1}\hbar^2\gamma^4 r_{ij}^{-6}\,(1-3\cos^2\theta_{ij})^2 T_2 \tag{9}$$

is a rapidly converging function of the distance between the flip-flopping spins. Furthermore, the correlation of a certain spin with the selected spin becomes weakened as a result of its interaction with its neighbors, and this weakening is larger the closer the neighbors. To estimate the correlation radius it is thus necessary to separate one spin and determine to the probability of its *ff* process with participation of each of the neighbors in accordance with (9).

The spins for which the *ff*-process probability is large correlate with the selected spin. Their number, however, cannot be too large, since $W \sim 1/r^6$, and consequently order of magnitude of the correlation radius does not exceed the lattice constant d. We shall henceforth use the term "cell" to designate a crystal with center at the selected spin and with radius equal to the correlation radius. Since the spins located outside the cell are not correlated with the selected spin, their effect on the motion of the selected spin can be described on the basis of the Anderson–Weiss statistical theory,[4] and only the influence of a relatively small number of spins contained in the cell can be investigated in greater detail. By using (9) to determine the correlation radius in CaF$_2$ with the field H_0 oriented along the three crystallographic directions, we obtain

$$[100] \leftrightarrow d, \quad [110] \leftrightarrow \sqrt{2}d, \quad [111] \leftrightarrow \sqrt{3}d.$$

The subsequent calculations confirm the correctness of this estimate.

A measure of the correlation of the spins in the cell, and consequently a measure of the deviation of the distribution of the local magnetic fields produced by them from a Gaussian distribution, can be the process $\varepsilon = M_4'/M_2'^2$, where M_2' and M_4' are the second and fourth moments of the distribution of the local magnetic fields produced by the cell at the selected spin. For a Gaussian function we have $\varepsilon = 3$, and for an isolated pair (fully determined motion) $\varepsilon = 1$.

The values of M_2' and M_4' were calculated with the aid of the Van Vleck formulas.[2] Whereas M_2' is the contribution made to the second moment only by the spins located inside the cell, for an adequate calculation of M_4' it does not suffice to take into account the interaction inside the cell only. It is necessary to take into account the interaction of each of the spins of the cell at least with those neighbors with which the interaction is strong enough. Consequently, when calculating M_4' we have retained in the lattice sums that enter in the corresponding Van Vleck formula the interaction of a fixed spin with the cell spins as well as the interaction of the latter with the spins of the cell whose centers each of them is in turn. The obtained values of ε are listed in Table I. It is seen that the values of ε do not differ greatly from the excess of the rectangular function for which $\varepsilon = 1.8$. We can thus expect the distribution of the effective local fields produced by the cell to be close to equiprobable in the interval $[-b, b]$. Knowing the contribution made to the second moment by the spins inside the cell, we can now determine b, since $M_2' = b^2/3$ for a rectangle. The results are listed in the table.

An analysis of an isolated cell was carried out with a computer for the [100] orientation; this called for the solution of a seven-spin problem. In the calculations we disregarded the interaction of the cell spins with their neighbors outside the cell. One can expect, however, the neglect of the cell environment at high temperatures not to influence too greatly the results of the calculation, since on the average the random character of the orientations of the spins in the environment weakens their effect on the cell. Calculation of the contribution made to the FPS by the isolated cell should lead primarily to a weakening of its damping in comparison with the exact calculation. The correctness of this assumption is confirmed by our calculation of the excess of the expression (8) for an isolated cell with orientation [100], namely $\varepsilon = 1.6$. The obtained value of ε is close to the excess of a rectangle and reflects an insufficient damping of the FPS. The results of the rigorous calculation of $\langle S_{x0}(t)\rangle$ are shown in Fig. 1. The insufficient damping of the curve is due to the fact that the cell is isolated. At the same time, the oscillation frequency is close to that observed in experiment. For [110] and [111] the cell contains 19 and 21 spins, respectively, and the analysis becomes difficult.

It remains for us to investigate the contribution made to the local field at the selected spin by the spins that are not contained in the cell. Since these spins are not correlated, their contribution is the sum of a large number of small independent quantities, and consequently the distribution function of the local fields from these spins is Gaussian. For a complete determination of a Gaussian function it suffices to calculate its second moment. We have calculated the contribution made to the second moment relative to the selected spin from the spins not contained in the cell. The results for a, which are listed in the table, are in good agreement with experiment.

According to the statistical theory of line shapes, the correlation function in a rigid lattice takes the form[2]

$$\Gamma(t) = \int_{\omega} e^{i\omega t} P(\omega)\, d\omega, \tag{10}$$

where $P(\omega)$ is the distribution function of the local fields. In the case of CaF_2, recognizing that the field at the spin is the sum of two statistically independent contributions with Gaussian and rectangular distributions, we obtain

$$\Gamma(t) = \int_{\Delta} d\Delta \int_{\omega} d\omega\, e^{i(\omega+\Delta)t} P_1(\omega) P_2(\Delta)$$
$$= \int_{-b}^{b} e^{i\omega t}\, d\omega \int_{-\infty}^{\infty} d\Delta\, e^{i\Delta t} \exp\left(-\frac{\Delta^2}{2a^2}\right) = \frac{\sin bt}{bt} \exp\left(-\frac{a^2 t^2}{2}\right). \tag{11}$$

This expression, however, does not take into account the influence of the flip flops of the uncorrelated spins on the Gaussian component of the FPS. The local field produced by the remote spins at the selected spin is a Gaussian random function of the time, since it is a sum of a large number of small independent and independently varying contributions. A Gaussian random process is uniquely defined by its correlation function,[2,23] and the Gaussian component of the FPS takes the form

$$G(t) = \exp\left\{-a^2 \int_0^t (t-\tau) k(\tau)\, d\tau\right\}, \tag{12}$$

a^2 is the already calculated second moment of the Gaussian function,

$$k(t) = \frac{1}{a^2} \operatorname{Sp}\left\{\exp\left(\frac{i}{\hbar} H_d^0 t\right) H_{z0}' \exp\left(-\frac{i}{\hbar} H_d^0 t\right) H_{z0}'\right\}, \tag{13}$$
$$H_{z0}' = \sum_{j\neq 0} \frac{3}{2} b_{0j} S_{zj}.$$

The prime on H_{z0} denotes that the summation does in-

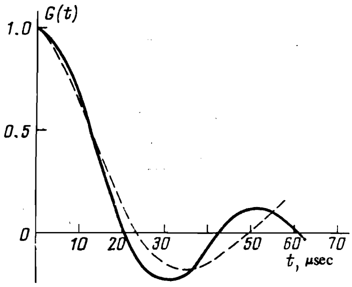

FIG. 1. Free-precession signal component due to the correlations in the spin system: solid curve—$\sin(bt)/bt$; dashed—result of the exact quantum-mechanical calculation of $\langle S_{x0}(t)\rangle$ for the cell with the aid of (8).

clude the spins contained in the cell.

It is clear from physical considerations that the correlation time of the local fields is of the order of magnitude of T_2. More accurately, this time can be calculated as

$$T_2^* = (M_2^*)^{-1/2}, \quad M_2^* = \frac{d^2}{dt^2} k(t)\big|_{t=0}. \tag{14}$$

It is thus easy to obtain $T_2^* \approx 3T_2$. Using expression (12), we find that at $t < T_2^*$ we have

$$G(t) = \exp(-a^2t^2/2), \tag{15}$$

and at $t \gtrsim T_2^*$

$$G(t) = \exp(-a^2T_2^*t) = \exp(-ct); \tag{16}$$

such an asymptotic behavior was observed experimentally in[22] after the appearance of the second zero in the FPS. The time T_2^* corresponds to the midpoint of the interval between the first and the second zeros. The calculated values of c agree well with experiment (see the table).

The NMR line shape of a number of crystals containing relatively isolated spin groups was investigated theoretically and experimentally in the later forties and early fifties (see the papers by Pake[26] and by others), with the dipole interactions within the group taken into account exactly (in some cases, an exact solution of three- and four-spin problems is possible). The interaction between the groups was taken into account by broadening the spectrum components by Gaussian lines. This approach gave good agreement with experiment. It is easily seen that the calculations performed in[26] agree with the scheme described above, inasmuch as in this situation the cell is chosen to be an isolated group.

One of the most remarkable features of NMR absorption lines is their high sensitivity to nuclear motion. The motion of the atoms produces a time variation of the local fields at the nuclei, and this indeed is the cause of the transformation of the line shape. In particular, in liquids the line becomes narrow and Lorentzian. The influence of the motion on the NMR line shape should be taken into account successively on the basis of the foregoing. The random-field method has been used so far to consider a number of problems, such as destruction of the fine structure of spectra consisting of very narrow lines in high-resolution spectroscopy, the destruction of the spectra of crystal hydrates,[27] in which NMR lines also have a fine structure, and the alteration of Gaussian lines by the motion.[4,5]

TABLE I. Parameters of free-precession signal in single-crystal CaF_2.

	Experiment[2,22]			Theory			
	a, Oe	b, Oe	c, μsec^{-1}	a, Oe	b, Oe	c, μsec^{-1}	ε
[100]	1.11	5.85	0.05	1.11	5.85	0.035	2.0
[110]	0.972	3.5	0.041	0.972	3.5	0.03	2.11
[111]	0.715	2.32	0.031	0.675	2.23	0.0246	2.3

The problem of transformation of spectra in the presence of motion was considered in the most general form in[25,28]. Within the framework of the concepts described above, however, using the random-field theory, this problem can be solved quite simply and in a physically lucid form. With respect to the motion we assume that the change of the frequency takes place jumpwise and the time of the jump is much shorter than the lifetime of the spin at the lattice site. Both assumptions correspond to the case of diffusion. In this situation it is natural to expect that the local fields before and after the jump are not connected in any way, and the probability that the spin will land in a definite field is determined completely by the distribution of the fields in the rigid lattice. The motion of this type is well approximated by a Poisson random process. It now remains to trace all the possible trajectories of spin motion, including 1, 2, ... jumps, recognizing at the same time that the local field at the spin is a sum of two statistically independent contributions.

The transverse component, which acquires a spin having a frequency $\omega + \Delta$ with a time t, is equal to

$$\begin{aligned} S_{x0}(t) \sim \Big\{ & \exp\Big[\Big(i\omega - \frac{1}{\tau}\Big)t\Big] + \int\limits_{\omega_1} d\omega_1 \int\limits_0^t g_1(\omega_1) \exp\Big(i\omega_1 t - \frac{t_1}{\tau}\Big)\frac{dt_1}{\tau} \\ & \times \exp\Big(-\frac{t-t_1}{\tau}\Big) \exp[i\omega(t-\tau)] + \ldots\Big\}\Big\{\exp\Big[\Big(i\Delta - \frac{1}{\tau}\Big)t \\ & + \int\limits_{\Delta_1} d\Delta_1 \int\limits_0^t g_2(\Delta_1) \exp\Big(i\Delta_1 t_1 - \frac{t_1}{\tau}\Big)\frac{dt_1}{\tau} \exp\Big(-\frac{t-t_1}{\tau}\Big) \exp[i\Delta(t-\tau)] + \ldots\Big\}. \end{aligned} \tag{17}$$

Here $g_1(\omega)$ and $g_2(\Delta)$ are the distribution functions of the contributions made to the local field in the rigid lattice, while $1/\tau$ is the average frequency of the jumps.

Introducing $G_0(t)$ and $\Gamma_0(t)$, which are the correlation functions in the rigid lattice and are connected[2] by a Fourier cosine transformation with $g_1(\omega)$ and $g_2(\omega)$, and summing over all the spins, we obtain

$$\begin{aligned} S_x(t) \sim \Gamma(t) = & \Big\{G_0(t)e^{-t/\tau} + \frac{1}{\tau}\int\limits_0^t dt_1 G_0(t_1) G_0(t-t_1) e^{-t/\tau} + \ldots\Big\} \\ & \times \Big\{\Gamma_0(t)e^{-t/\tau} + \frac{1}{\tau}\int\limits_0^t dt_1 \Gamma_0(t_1)\Gamma_0(t-t_1)e^{-t/\tau} + \ldots\Big\}. \end{aligned} \tag{18}$$

To sum the series we take the Laplace transforms of both parts of (18). After obvious intermediate operations we obtain

$$F(s) = \int\limits_0^\infty \Gamma(t)e^{-st}dt = \frac{1}{2\pi i}\int\limits_{\lambda-i\infty}^{\lambda+i\infty} F_1(z)F_2(s-z)\,dz, \tag{19}$$

where

$$F_1(s) = \frac{\varphi_1(s+2/\tau)}{1-\tau^{-1}\varphi_1(s+2/\tau)}, \quad F_2(s) = \frac{\varphi_2(s)}{1-\tau^{-1}\varphi_2(s)}. \tag{20}$$

Here $\varphi_1(s)$ and $\varphi_2(s)$ are the Laplace transforms of the functions $G_0(t)$ and $\Gamma_0(t)$. Taking the inverse transform of (19) we get

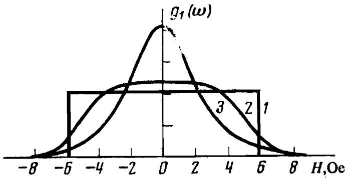

FIG. 2. Transformation of the rectangular component of the line shape in CaF_2 as a function of τ: 1) $1/\tau=0$, 2) $1/\tau=4\times10^3$ Hz, 3) $1/\tau=2\times10^4$ Hz (for F^{19} nuclei, 1 Oe $=4\times10^3$ Hz).

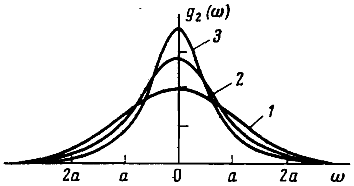

FIG. 3. Transformation of Gaussian component of the line shape in CaF_2 as a function of τ: 1) $1/\tau=0$, 2) $1/\tau=0.5$, $a\sqrt{2}$, 3) $1/\tau=a\sqrt{2}$; a^2 is the second moment of the Gaussian function.

$$\Gamma(t)=G_1(t)\Gamma_1(t). \tag{21}$$

$G_1(t)$ and $\Gamma_1(t)$ are the results of the inverse Laplace transformation. Since the numerical methods of finding the originals from the known transforms have been well developed,[29] we can use (19) directly for the actual calculations or, by tracing the deformation of each of the contributions separately, obtain the convolution of the results.

We now investigate the behavior of the CaF_2 in the case of strong heating. Denoting by $g_1(\omega)$ the deformed rectangular distribution and by $g_2(\omega)$ the deformed Gaussian distribution, we obtain

$$\begin{gathered}
g_1(\omega)=\operatorname{Re}\left\{\frac{1}{b}\operatorname{Arctg}\frac{b}{i\omega+1/\tau}\middle/\left[1-\frac{1}{b\tau}\operatorname{Arctg}\frac{b}{i\omega+1/\tau}\right]\right\},\\
g_2(\omega)=\operatorname{Re}\left\{\frac{1}{a}\sqrt{\frac{\pi}{2}}\,w(z)\middle/\left[1-\frac{1}{a\tau}w(z)\right]\right\},\\
z=\frac{i/\tau-\omega}{\sqrt{2}\,a}\\
w(z)=\frac{2}{\sqrt{\pi}}e^{-z^2}\int_z^{i\infty}e^{y^2}dy;
\end{gathered} \tag{22}$$

$w(z)$ is the tabulated[30] error function in the complex plane.

The results of the calculation by formulas (22) are shown in Figs. 2 and 3. It is seen that with increasing temperature (with decreasing τ) both components, and consequently also their convolution, become close to Lorentzian.

Thus, the described approach, from both points of view, makes it possible to handle spectra both in a rigid lattice and in the presence of motion of the nuclei.

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