NMR line shapes and order-parameter determination in proton pseudo-spin-glasses

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The quadrupole-perturbed NMR line shape has been evaluated in the local approximation for an arbitrary static random-field distribution coexisting with Gaussian time-fluctuating random fields. The special case of a spin-glass-type static local random-field distribution is treated also. The results are compared with some recent experimental data for the deuteron glass $Rb_{1-x}(ND_4)_xD_2PO_4$. They show that by a comparison of experimental and theoretical line shapes in strongly disordered systems, not only the local random-field distribution but also the spin-glass order parameter can be determined.

I. INTRODUCTION

The usefulness of NMR for the study of phase transitions in nonrandom systems is based on the fact[1] that the NMR or nuclear quadrupole resonance (NQR) frequency is a function of the order parameter of the transition which is zero above T_c and nonzero below T_c. In strongly disordered systems[2] such as spin-glasses where there is an infinite number of order parameters the situation is radically different, as there is no long-range structural ordering and no sharp change in the NMR or NQR frequency at any temperature. The NMR technique is nevertheless capable[3] of providing useful information about strongly disordered systems, as here the quadrupole-perturbed NMR frequency of a given nucleus depends on the local random field h_i

$$\nu_i(t)=\nu_i(h_i(t)) \ , \tag{1}$$

and the NMR line shape reflects the distribution and dynamics of the local random fields. The $\nu=\nu(h)$ relation may be local or nonlocal. Here we shall treat the local case only. The local random field may be static ($h_{i,1}$) as in the case of substitutional impurities or time dependent ($h_{i,2}$) as in the case of the formation of short-range ordered dynamic clusters.

In this paper we present the relation between the random-field distribution and the quadrupole-perturbed NMR line shape for both first-order and second-order quadrupole-shifted nuclei.[3] Static as well as time-fluctuating random fields are considered. In Sec. II we evaluate the line shape for an arbitrary static random-field distribution $P(h)$ coexisting with Gaussian time-fluctuating random fields. In Sec. III we evaluate the NMR line shape for a spin-glass-type[4,5] static local random-field distribution. The obtained theoretical results are compared with the ^{87}Rb NMR spectra in the "deuteron" pseudo-spin-glass[2,6] $Rb_{1-x}ND_{4x}D_2PO_4$.

II. NMR LINE SHAPE

In the following we shall assume that the random field h_i creates a random local polarization

$$p_i=p_i(h_i) \tag{2}$$

and expand the electric field gradient (EFG) tensor at the site i in powers of this polarization:

$$\overleftrightarrow{T}=\overleftrightarrow{T}_0+\overleftrightarrow{T}_1p(t)+\overleftrightarrow{T}_2p^2(t)+\cdots \ . \tag{3}$$

As mentioned above, we shall here assume for sake of simplicity that the relation between $\overleftrightarrow{T}$ and p is a local one. For a random bond Ising model this relation is simply $p_i=\tanh[h_i/(kT)]$. In the high-temperature limit this can be approximated by $p_i=\gamma h_i$. The local approximation is exact for covalently bonded nuclei and a fair approximation for those ionic solids where the dimensions of the short-range ordered clusters are larger than the size of the region giving a dominant contribution to the EFG tensor. The extension to the nonlocal case will be treated later. We shall similarly restrict ourselves to the case where the local polarization induces a change in the quadrupolar transition frequencies. The case where the local polarization induces only a rotation in the principal axes of the EFG tensor without changing the principal values is reserved for a subsequent paper.

A. The static limit

If h (and p) are nonzero either due to the presence of static disorder $p_{i,1}\propto h_{i,1}=\Delta\neq 0$ or due to local ordering and breaking of ergodicity on the NMR time scale ($p_{i,2}\propto h_{i,2}\neq 0$), nuclei in differently polarized clusters have different resonance frequencies. The distribution of resonance frequencies $f(\omega)$ is simply related[2] to the spatial distribution of static random polarizations $g(p)$ [or static random fields $P(h)=g(p)dp/dh$]:

$$f(\omega)d\omega=g(p)dp \ , \tag{4a}$$

so that

$$f(\omega)=\frac{g(p)}{|d\omega/dp|} . \tag{4b}$$

If the relation $\omega=\omega(p)$ is known, a measurement of the NMR line shape allows for a direct determination of $g(p)$. Expanding the relation $\omega=\omega(p)$ into a Taylor series

$$\omega=\omega_0+\omega_1 p+\omega_2 p^2+\cdots , \tag{4c}$$

we see that different line shapes are predicted for the case where the relation between ω and p is linear ($\omega_1\neq 0$, $\omega_2=0$, i.e., $\omega_n=0$, $n>1$) and $d\omega/dp$ is always nonzero, or the case where ω is a general function of p and $d\omega/dp$ may be zero for some values of p.[3]

In the first of these two cases the NMR line shape will directly reflect $g(p)$ and will be thus always symmetric around ω_0. This case should be realized, for instance, in the *O-D—O* deuteron line shape as well as in the ^{87}Rb NMR line shape at those orientations where ω is linear in p.

In the second of the above two cases $f(\omega)$ may exhibit one or more singularities at those p (and ω) values where $d\omega/dp=0$. Such a situation seems to be, for instance, realized in the ^{87}Rb NMR in $Rb_{1-x}(NH_4)_xD_2PO_4$ where at some orientations of the crystal with respect to the external magnetic field the coefficient $\omega_1=0$ vanishes by symmetry. Here one finds

$$\omega=\omega_0+\omega_2 p^2 \tag{5a}$$

so that

$$f(\omega)=\frac{g(p)}{2\omega_2 p}\propto\frac{g(p)}{|\sqrt{(\omega-\omega_0)/\omega_2}|} \tag{5b}$$

resulting in a singularity at $p=0$ (or $\omega=\omega_0$) and an asymmetric line shape.

B. First-order quadrupole effects on the NMR line shapes —dynamic case

In the presence of time-dependent random fields the first-order quadrupolar frequency shift can be—in view of expansion (3)—written as

$$\omega(t)=\omega_0+\omega_1 p(t)+\omega_2 p^2(t)+\cdots . \tag{6}$$

To simplify the treatment we separate $p(t)$ into a slowly varying part p and a rapidly fluctuating part $\Delta p(t)$ so that

$$p(t)=p+\Delta p(t) . \tag{7}$$

Here p describes the contributions which are static or quasistatic on the NMR time scale. It is determined by the average

$$p=\frac{1}{t_0}\int_0^{t_0} p(t')dt' \tag{8}$$

over fluctuations which are fast as compared to the rigid lattice linewidth $t_0=\Delta\nu_0^{-1}$.

Inserting (7) into (6) one finds

$$\omega(t)=\omega_0+\omega_1 p+\omega_2 p^2+(\omega_1+2\omega_2 p)\Delta p(t)+\cdots . \tag{9}$$

The adiabatic NMR line shape $f(\omega)$ is now obtained from the Fourier transform of the autocorrelation function $G(t)$:

$$f(\omega)=\int G(t)e^{i\omega t}dt , \tag{10a}$$

where

$$G(t)=\langle e^{i\int_0^t\omega(t')dt'}\rangle \tag{10b}$$

and $\omega(t')$ is given by expression (9).

Assuming a Gaussian distribution of fluctuating random fields (and local polarizations) this now becomes

$$G(t)=e^{i\omega_0 t}\langle e^{i(\omega_1 p+\omega_2 p^2)t}e^{-(\omega_1+2\omega_2 p)^2\int_0^t(t-t')g(t')dt'}\rangle , \tag{11}$$

where

$$g(t')=\overline{\Delta p(0)\Delta p(t')} \tag{12}$$

and the brackets $\langle\ \rangle$ stand for the spatial average. Taking into account the spatial distribution of local random polarizations $g(p)$ we now find the first-order NMR line shape as

$$f(\omega)=\int\int g(p)e^{i(\omega_0-\omega)t}e^{i(\omega_1 p+\omega_2 p^2)t}e^{-(\omega_1+2\omega_2 p)^2\int_0^t(t-t')g(t')dt'}dp\,dt . \tag{13}$$

In order to get a more explicit expression for $f(\omega)$ we need to know the form of $g(t')$ and $g(p)$. Alternatively one can use Eq. (13) to obtain $g(p)$ and $g(t')$ from the experiments.

Spin-lattice relaxation time measurements[3] have shown that $g(t')$ can be in proton pseudo-spin-glasses described by a stretched exponential:[2]

$$g(t)=\overline{\Delta p^2}\exp[-(t/\tau)^\alpha] , \tag{14a}$$

where

$$\overline{\Delta p^2}=(1-\overline{p_1^2})\left[1-2x^2\int_0^x(x-x')\exp(-x'^\alpha)dx'\right],\quad x=t_0/\tau . \tag{14b}$$

Here $p_1=\gamma h_1$ represents the static part of the local polarization induced by substitutional impurities. The resulting line shapes have to be obtained by numerical techniques. The above expression for $\overline{\Delta p^2}$ is derived in Appendix A.

It should be noted that the total second moment of the NMR line shape reflecting the static or quasistatic part of $g(p)$

$$\overline{p^2}=\int_{-1}^{+1} g(p)p^2dp=1-\overline{\Delta p^2} \tag{14c}$$

increases with decreasing temperature as $\overline{\Delta p^2}\rightarrow 0$ according to (14b). At high temperatures, on the other hand, motional narrowing sets in, $\overline{\Delta p^2}=1-\overline{p_1^2}$ and $\overline{p^2}$ approaches its impurity induced static value $\overline{p_1^2}$ [Fig. 1(a)].

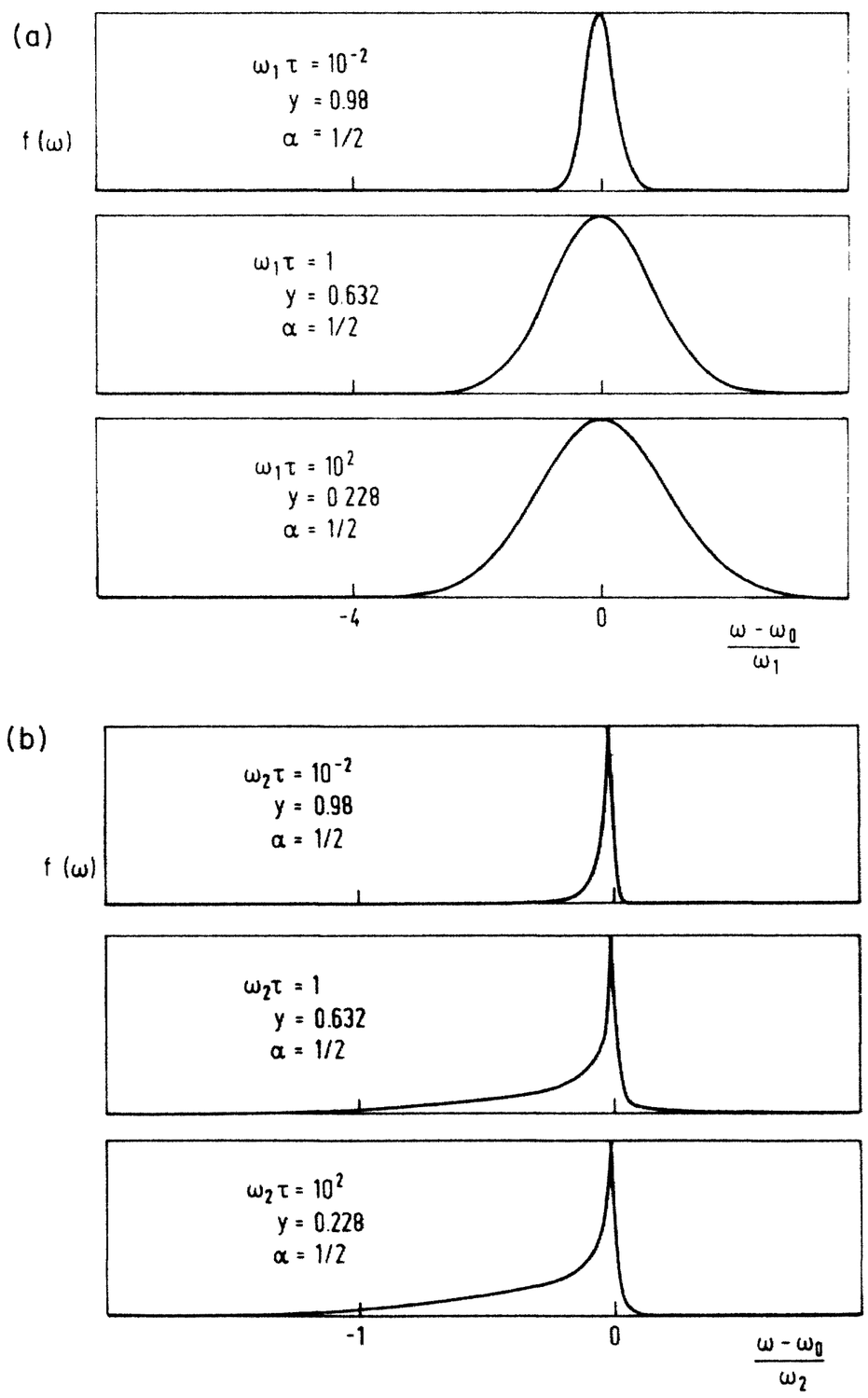

FIG. 1. (a) Effect of motion on the first-order quadrupole-perturbed NMR line shape $f(\omega)$ for the case where the linear term in p is dominant ($\omega_1\neq 0$, $\omega_2=0$). The line shape is evaluated according to Eqs. (13), (14a), and (14b) with $g(p)$ representing a Gaussian distribution (A10) and (A11) the variance of which is $1-y^2$. (b) Effect of motion on the second-order quadrupole-perturbed NMR line shape $f(\omega)$ for the case where the quadratic term in p is dominant ($\omega_1'=0$, $\omega_2'\neq 0$). The line shape is evaluated according to Eqs. (30), (14a) and (14b), and (A9)–(A12) with $g(p)$ representing a Gaussian distribution the variance of which is $1-y^2$.

In the linear case ($\omega_2=0$) the line shape $f(\omega)$ is symmetric and reflects the form of $g(p)$ whereas in the quadratic case ($\omega_1=0$) one finds generally an asymmetric line shape and a singularity as in the static case.

It should be noted that for very slow fluctuations [i.e., $\tau\rightarrow\infty$ in expression (14)] $f(\omega)$ reduces to the form $f(\omega)=g(p)/|d\omega/dp|$ found in the static limit. For very fast fluctuations ($\tau\rightarrow 0$), on the other hand, it becomes a convolution of $g(p)$ with a Lorentzian the width of which is determined by

$$\tau_c'=\int_0^{\infty} g(t')dt' \tag{15}$$

as

$$\exp\left[-\omega_1^2\int_0^t (t-t')g(t')dt'\right]\propto\exp(-\omega_1^2\tau_c' t) \tag{16}$$

thus simplifying expression (13). If expression (14) applies, one gets:

$$\tau_c'=\int_0^{\infty} e^{-(t'/\tau)^{\alpha}}dt' \ . \tag{17}$$

The line shape for the linear case in the limit of fast fluctuations now becomes

$$f(\omega)=\int g(p)\frac{2\omega_1^2\overline{\Delta p^2}\tau_c'}{(\omega_1^2\overline{\Delta p^2}\tau_c')^2+(\omega_0+\omega_1 p-\omega)^2}dp \tag{18}$$

leading to motional narrowing in the limit $\tau_c'\rightarrow 0$ [Fig. 1(a)].

C. Second-order effects on the line shape of the $\frac{1}{2}\rightarrow-\frac{1}{2}$ transition—dynamic case

The effect of molecular motion and fluctuating quadrupolar interactions on the second-order quadrupole shifts of the central $\frac{1}{2}\rightarrow-\frac{1}{2}$ transition have been determined by Bjorkstam and Villa.[7] Here we shall extend their approach to the study of NMR line shapes in the case of fluctuating random fields where the dominant second-order perturbation is quadratic in p and nonlocal in time.

The Hamiltonian of our problem is a sum of the Zeeman and the quadrupolar term

$$\mathcal{H}=\omega_L I_z+\mathcal{H}_{\text{int}} \ , \tag{19a}$$

where

$$\mathcal{H}_{\text{int}}=\sum_{l=-2}^{+2} A^{(l)}F^{(l)}=\sum_l \mathcal{H}^{(l)} \tag{19b}$$

with $A^{(l)}$ and $F^{(l)}$ describing the well-known spin and lattice operators of the quadrupolar Hamiltonian.[7] In the following let us assume that the quadrupolar term is small as compared to the Zeeman one.

Using the Magnus expansion[7] up to second-order terms one find the evolution operator as

$$E(t)=\exp\left[-i\int_0^t dt'[\mathcal{H}^{(0)}(t')+\mathcal{H}'(t')]\right] \tag{20a}$$

with

$$\mathcal{H}'(t)=\sum_{l=1,2}[A^{(l)},A^{(-l)}] \times\int_0^t dt''F^{(l)}(t')F^{(-l)}(t'')\sin[l\omega_L(t'-t'')]\ . \tag{20b}$$

As shown in Appendix B, the effect of nonsecular terms omitted in expression (20) is negligible. The time evolution of I_x is now given by

$$I_x(t)=E(t)I_xE^*(t)=e^{i\int_0^t\Delta\omega(t')dt'}I_x\ , \tag{21a}$$

where

$$\Delta\omega=\langle m+1\,|\,\mathcal{H}^{(0)}+\mathcal{H}'\,|\,m+1\rangle-\langle m\,|\,\mathcal{H}^{(0)}+\mathcal{H}'\,|\,m\rangle =\sum_{l=1,2}C_m^{(l)}\int_0^{t'}dt''F^{(l)}(t')F^{(-l)}(t'')\sin[l\omega_L(t'-t'')]\ , \tag{21b}$$

and $C_m^{(l)}$ are the corresponding matrix elements.

Because of the "quadratic" nature of the second-order shift we can omit higher-order terms and make the approximation

$$F^{(l)}=f_0^{(l)}+f^{(l)}p(t)\ , \tag{22}$$

where $p(t)$ stands for the local cluster polarization. This leads to

$$\Delta\omega=\sum_{l=1,2}C_m^{(l)}\int_0^t[f_0^{(l)}f_0^{(-l)}+f^{(l)}f_0^{(-l)}p(t')+f_0^{(l)}f^{(-l)}p(t'')+f^{(l)}f^{(-l)}p(t')p(t')]\sin[l\omega_L(t'-t'')]dt''\ . \tag{23}$$

Let us in the following concentrate on fluctuations which are slower than the nuclear Larmor frequency, $\omega_L\tau>1$. This is not a serious limitation for glasses and pseudo-spin-glasses.[2]

Here we can make the approximation

$$\int_0^{t'}p(t'')\sin[l\omega_L(t'-t'')]dt''\approx p(0)\frac{1-\cos l\omega_L t'}{l\omega_L}\ . \tag{24}$$

Neglecting terms which oscillate fast compared to the Larmor frequency one gets

$$I_x(t)=I_x\exp\left[i\sum_{l=1,2}C_m^{(l)}f^{(l)}f_0^{(-l)}p(0)t+i\sum_{l=1,2}C_m^{(l)}\frac{f^{(l)}f^{(-l)}}{l\omega_L}\int_0^t p(0)p(t')dt'\right]\ . \tag{25}$$

This expression is still too complicated for an analytical determination of the NMR line shape. Using the separation of $p(t)$ into slowly and quickly fluctuating parts (expression 7) one can make—when treating second-order terms—the approximation

$$p(0)p(t')\approx p(p+\Delta p(t')),\quad p(0)\approx p \tag{26}$$

leading to

$$I_x(t)=I_x\exp\left[i\left[\sum_{l=1,2}C_m^l f^{(l)}f_0^{(-l)}pt+\sum_{l=1,2}C_m^{(l)}\frac{f^{(l)}f^{(-l)}}{l\omega_L}p\right]\int_0^t\Delta p(t')dt'+i\sum_{l=1,2}C_m^{(l)}\frac{f^{(l)}f^{(-l)}}{l\omega_L}p^2\right]\ . \tag{27}$$

Introducing $\omega_1'=\sum_{l=1,2}C_m^{(l)}f^{(l)}f_0^{(-l)}$ and

$$\omega_2'=\sum_{l=1,2}C_m^{(l)}\frac{f^{(l)}f^{(-l)}}{l\omega_L}\ , \tag{28}$$

one finally obtains the autocorrelation function $G(t)$ as

$$G(t)=\left\langle\exp(i\omega_0 t)\exp[i(\omega_1'p+\omega_2'p^2)t]\exp\left[-i\omega_2'p\int_0^t\Delta p(t')dt'\right]\right\rangle\ . \tag{29}$$

For fluctuating Gaussian random fields one now obtains the NMR line shape as

$$f(\omega)=\int\int g(p)\exp i(\omega_0-\omega)t\exp i(\omega_1'p+\omega_2'p^2)t\exp\left[-(\omega_2'p)^2\int_0^t(t-t')\overline{\Delta p(0)\Delta p(t')}dt'\right]dp\,dt\ . \tag{30}$$

The result here is quite analogous to the first-order case, except that due to the special structure of Eq. (30) fluctuating random fields do not affect the line shape if $\omega_2'=0$. This is important as it allows for a discrimination between static and dynamic line broadening mechanisms by varying the crystal orientation thus changing the relative magnitude of ω_2' and ω_1'.

The similarity between expressions (30) and (13) is due to the approximation (26) where quadratic terms in $\Delta p(t)$ are neglected. In the general case (25) we have to rely on

numerical methods.

The above result (30) again represents a kind of a convolution of $g(p)$ with a motionally narrowed line-shape function and reduces to Eq. (4b) for $\tau \rightarrow \infty$. For $\overline{p^2} > \overline{\Delta p^2}$ the motional averaging effects are small irrespective of τ and show up only in the tails [Fig. 1(b)].

The experimental line shape $F(\nu)$ is obtained after a convolution of $f(\omega)$ with the homogeneous line-shape function which is normally a Gaussian.

A comparison between the room-temperature experimental and theoretical $^{87}\mathrm{Rb}\frac{1}{2} \rightarrow -\frac{1}{2}$ quadrupole perturbed NMR line shapes[3] in $Rb_{1-x}(ND_4)_xD_2PO_4$ at different orientations of the crystal with respect to the external magnetic field is shown in Fig. 2. The increase in the linewidth at orientations different from $\mathbf{c}\|\mathbf{H}_0$ is due to the presence of terms linear in p which are forbidden at $\mathbf{c}\|\mathbf{H}_0$. In the linear case ($\omega_2=0$)—$\sphericalangle(\mathbf{c},\mathbf{H}_0)=70°$—the line shape is symmetrical and reflects the form of $g(p)$, whereas in the purely quadratic case ($\omega_1=0$) the line shape is asymmetrical and exhibits a singularity at $p=0$. At this temperature the experimentally determined form of $g(p)$—and $P(h)$— is Gaussian.

It is interesting to note that at room temperature $\omega_2' p^2 \Delta p^2 \tau_c' < 1$ so that the time-fluctuating part of the random field is averaged out and the NMR line shape is determined by the static part of the random field.[3]

III. THE STATIC LOCAL RANDOM-FIELD DISTRIBUTION AND ORDER PARAMETER DETERMINATION FOR A PSEUDO-SPIN-GLASS

In Sec. II we have seen that NMR line-shape data allow for a quantitative determination of that part of the local random polarization—or field—distribution $g(p)$ which is static on the NMR time scale. Let us now evaluate the NMR line shape for the static local random field—and polarization—distribution which is specific for spin glasses.[4,5] Our goal is to find out whether NMR allows not only for a determination of the random local fields but also for a determination of the Edwards-Anderson spin-glass order parameter

$$q = \frac{1}{N} \sum_i \langle S_i^z \rangle^2 .$$

The local random-field distribution at any site i is here defined as[4,5]

$$P_i(h) = \langle \delta(h - h_i) \rangle , \tag{31}$$

where $\langle\ \rangle$ refers to a thermal average. The random average of h_i, i.e., the average over the distributions $P_i(h)$ is of course zero,

$$\overline{\langle h_i \rangle} = 0 , \tag{32}$$

in strongly disordered systems because of lack of long-range order whereas $\overline{\langle h_i \rangle}^2 \neq 0$. The NMR line shape in a disordered system will normally reflect the spatial average

$$P(h) = N^{-1} \sum_i P_i(h) . \tag{33}$$

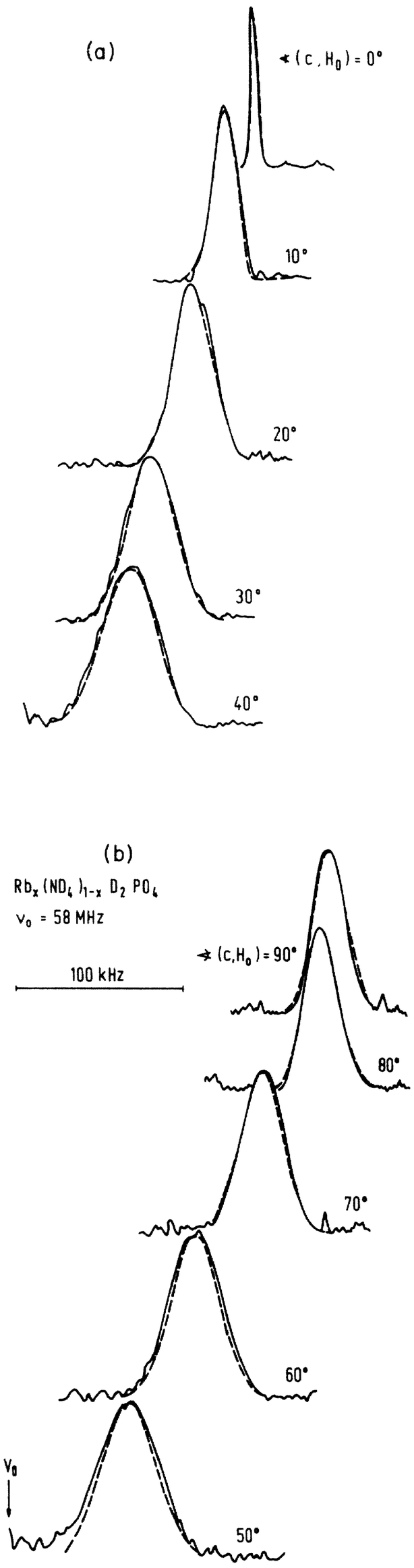

FIG. 2. Comparison between the experimental and theoretical $^{87}\mathrm{Rb}$ $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line shapes in $Rb_{1-x}(ND_4)_xD_2PO_4$ ($x=0.5$) for different crystal orientations where the ratio between ω_1 and ω_2 varies between the pure quadratic case ($\omega_1=0$, $\omega_2 \neq 0$) and the pure linear case ($\omega_1 \neq 0$, $\omega_2=0$). The comparison is made for room temperature. Here we have 0°: $\omega_1'=0$, $\omega_2'=-10$; 10°: $\omega_1'=20$, $\omega_2'=-8$; 20°: $\omega_1'=32$, $\omega_2'=-5$; 30°: $\omega_1'=40$, $\omega_2'=-4$; 40°: $\omega_1'=46$, $\omega_2'=-3$; 50°: $\omega_1'=48$, $\omega_2'=-3$; 60°: $\omega_1'=42$ $\omega_2'=-3$; 70°: $\omega_1'=35$, $\omega_2'=0$; 80°: $\omega_1'=28$, $\omega_2'=3$; 90°: $\omega_1'=27$, $\omega_2'=4$. The units are arbitrary.

This average is in the thermodynamic limit equal to the average over the spatial disorder $\overline{\langle\ \rangle}$ as $P(h)$ is self-averaging.[4]

The local random field h_i consists[5] for Ising-type spin-glasses or pseudo-spin-glasses like $Rb_{1-x}(ND_4)_xD_2PO_4$ where

$$\mathcal{H}=-\sum_{i,j}J_{ij}S_i^zS_j^z-\sum_i\Delta_iS_i^z\ , \tag{34}$$

—and where J_{ij} and Δ_i are random variables—of two different contributions:

$$h_i=\Delta_i+\sum_i J_{ij}S_i^z=h_{i,1}+h_{i,2}\ . \tag{35}$$

Here $h_{i,1}=\Delta_i$ represents a temperature-independent local random external field. In $Rb_{1-x}(ND_4)_xD_2PO_4$ such a field is induced by the random substitution of NH_4 ions for the Rb ions.[5] It can be represented by a Gaussian distribution

$$P(\Delta_i)=\frac{1}{\sqrt{2\pi\Delta^2}}\exp(-\tfrac{1}{2}\Delta_i^2/\Delta^2) \tag{36}$$

of variance Δ^2 and zero mean.

The nonzero value of $h_{i,2}=\sum_i J_{ij}S_i^z$ is due to ergodicity breaking on the NMR time scale. The random distribution of coupling constants in a spin or pseudo-spin-glass $P(J_{ij})$ is as well usually taken as Gaussian

$$P(J_{ij})=\frac{1}{\sqrt{2\pi J^2}}\exp[-(J_{ij}-J_0)^2/2J^2]\ . \tag{37}$$

We shall discuss only systems where $J_0=0$.

In contrast to $P(\Delta_i)$ the averaged static local field distribution $P(h_{i,2})=P(\sum_j J_{ij}S_j^z)$ will be temperature dependent both above and below the spin-glass temperature T_G.[4] At high temperatures $P(h)$ approaches a Gaussian distribution with a variance $\tilde{J}^2+\Delta^2$ which is a sum of the variances of the local random-field distribution and the random exchange distribution. Above T_G, the distribution will be single peaked for $\Delta^2=0$. Below T_G, it will be double peaked for the symmetric Sherrington-Kirkpatrick (SK) spin-glass model thus exhibiting a zero field dip.[4] In the presence of an external random field, $\Delta^2\neq0$, the transition is smeared[5] and $P(h)$ may be double peaked even above T_G.

The "external" random field Δ_i, the Edwards-Anderson spin-glass order parameter $q=\langle S^z\rangle^2$, and the local field distribution $P(h)$ are here related[4,5] by two coupled equations:

$$q=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}dz\,e^{-z^2/2}th^2[\beta\tilde{J}z(q+\tilde{\Delta}^2)^{1/2}]\ , \tag{38}$$

$$P(h)=\frac{1}{2\pi\tilde{J}\sqrt{1-q}}e^{-\beta^2\tilde{J}^2(1-q)/2}\int_{-\infty}^{+\infty}dz\,e^{-z^2/2}\frac{ch(\beta h)}{ch\beta z\tilde{J}\sqrt{q+\tilde{\Delta}^2}}\exp-\left[\frac{(h-z\tilde{J}\sqrt{q+\tilde{\Delta}^2})^2}{2\tilde{J}^2(1-q)}\right]\ . \tag{39}$$

Here $\tilde{J}=J\sqrt{N}$ and $\tilde{\Delta}^2=\Delta^2/\tilde{J}^2$.

The local random-field distributions[5] $P(h)$ for $\tilde{\Delta}^2=0$ and $T/T_G=1.2, 1.1$ and 1.0, 0.9, and 0.8 are presented in Fig. 3(a), whereas in Fig. 3(b) $P(h)$ is shown for $\tilde{\Delta}^2=0.5$. For $\Delta\neq0$, q is different from zero even above $T_G=\tilde{J}/k$. It should be noted that the above treatment is static and that motional narrowing effects are neglected. For proton pseudo-spin-glasses this is not too bad of a approximation as the amplitude of the fluctuating part of the random field is small in comparison with the static one. This is a result of the fact that the transition is smeared out by the presence of static random fields—induced by substitutional disorder—resulting in a finite value of the Edwards-Anderson order parameter far above the nominal transition temperature T_G.

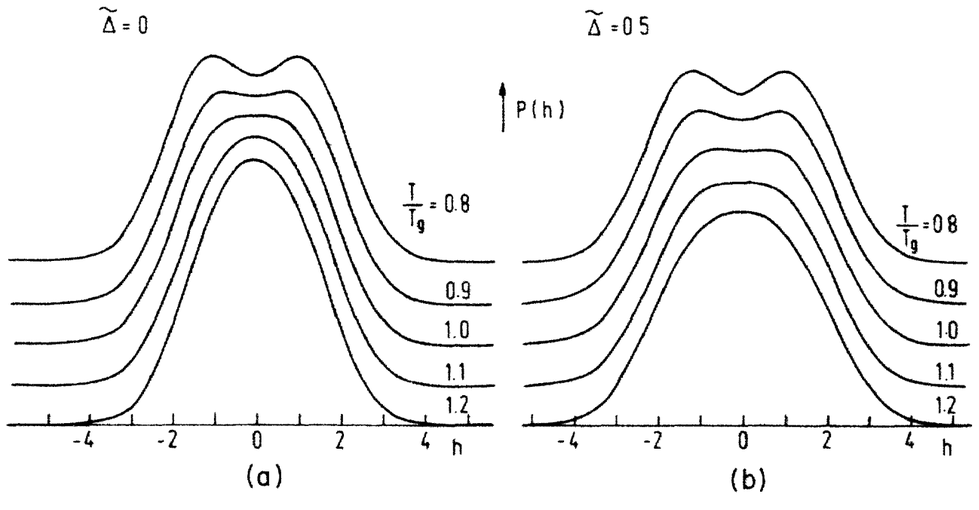

FIG. 3. Comparison between the spin-glass-type (Ref. 5) local-field distributions $P(h)$ for different temperatures for (a) $\tilde{\Delta}=0$ and (b) $\tilde{\Delta}=0.5$.

In the general case, however, the full dynamic spin-glass problem has to be solved or one has to rely on the methods developed in Sec. II and determine the quasistatic $g(p)$ and the fluctuating $\Delta p(t)^2$ from the experiment.

A comparison between the experimental and theoretical ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line shapes[3] in $Rb_{1-x}(ND_4)_xD_2PO_4$ for $x=0.5$ at an orientation where the linear term is dominant is shown in Fig. 4. Whereas the line shape which reflects $g(p)=P(h)(dp/dh)^{-1}$ shows a single peak at 121 K, it shows a double peak at 57 K. The agreement between the theoretical static line shape and the experimental one is satisfactory.

A comparison between the experimental and the static theoretical ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line shapes at $\mathbf{c}\|\mathbf{H}_0$ where the linear term is zero and the quadratic term is dominant is shown in Fig. 5. The line shape shows the typical singularity and can be fitted with $T_G=\tilde{J}/k=90$ K, $\Delta^2=0.5\tilde{J}^2$, and a nonzero Edwards-Anderson order parameter q which varies from 0.14 at $T=165$ K $>T_G$ to $q=0.74$ at 33 K $<T_G=90$ K.

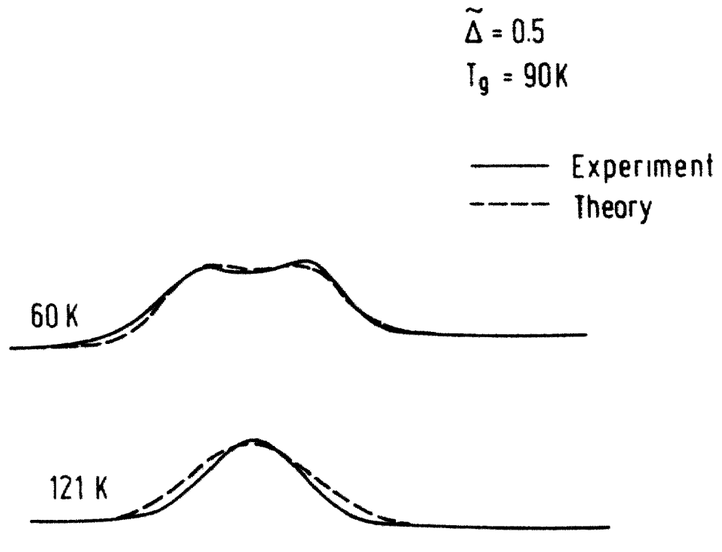

FIG. 4. Comparison between the experimental and theoretical $^{87}Rb\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line shapes in $Rb_{1-x}(ND_4)_xD_2PO_4$ ($x=0.5$) for an orientation where the term linear in p is dominant and $T=57\ K<T_G$ as well as $T=121\ K>T_G$.

The determination of the quadrupole perturbed NMR line shape[3,8,9] in strongly disordered systems like spin glasses or pseudo-spin-glasses thus allows not only for a determination of the local random-field distribution $g(p)$, respectively, $P(h)$ but also a determination of the Edwards-Anderson spin-glass order parameter q.

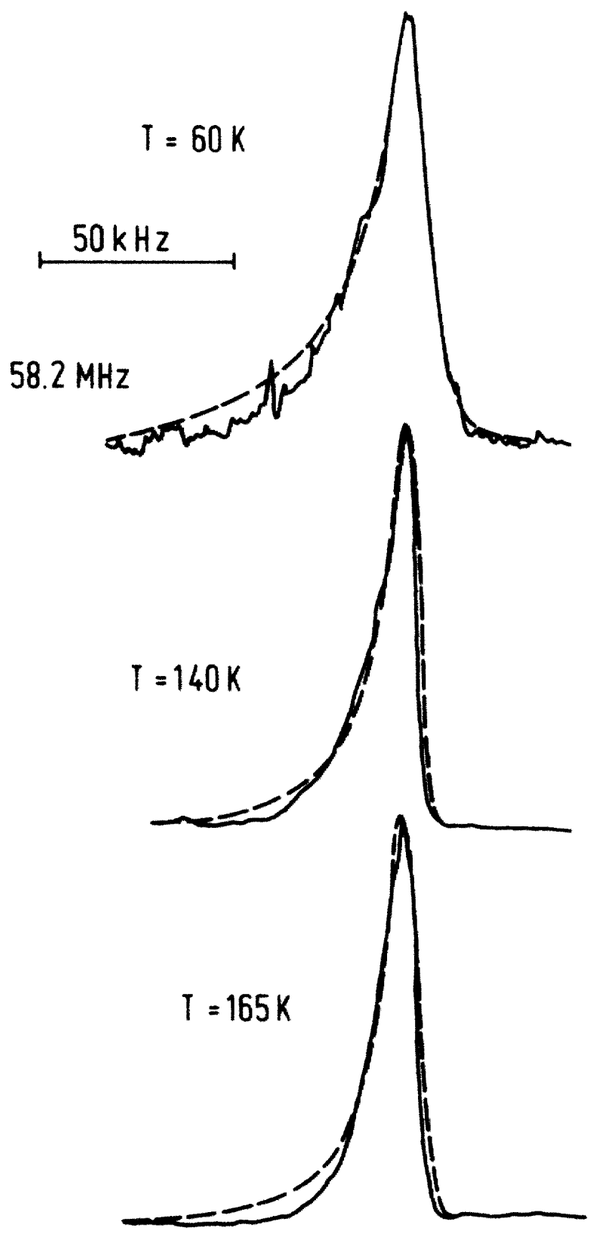

FIG. 5. Comparison between the experimental and theoretical ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line shapes in $Rb_{1-x}(ND_4)_xD_2PO_4$ ($x=0.5$) for an orientation ($\mathbf{c}\|\mathbf{H}_0$) where the term quadratic in p is dominant and different temperatures above and below T_G. The pseudo-spin-glass transition is smeared out because of the presence of the static random field $\tilde{\Delta}=0.5$. Here we have $q=0.14$ at $T=165$ K, $q=0.19$ at $T=140$ K, and $q=0.55$ at $T=60$ K, whereas T_G is 90 K.

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APPENDIX A

Let us now derive expression (14b) using the fact that the absolute value of the random variable p is 1 and that $p=p_1+p_2$ where p_1 stands for the static impurity-induced part and p_2 for the time-fluctuating part due to pseudo-spin-interactions. Taking into account expressions (7) and (8) and $p(t)^2=1$, we can write

$$\overline{\Delta p(t)^2}=1-\overline{p^2} \tag{A1}$$

and

$$\overline{\Delta p(t)^2}=1-\overline{\left[\frac{1}{t_0}\int_0^{t_0}p(t')dt'\right]^2}\ . \tag{A2}$$

Introducing

$$g_p(t)=\overline{p(0)p(t)}\ , \tag{A3}$$

we can rewrite (A2) as

$$\overline{\Delta p(t)^2}=1-\frac{2}{t_0^2}\int_0^{t_0}\int_0^{t'}g_p(t')dt'dt\ . \tag{A4}$$

Integrating per parts one finds

$$\overline{\Delta p(t)^2}=1-\frac{2}{t_0}\int_0^{t_0}(t_0-t)g_p(t)dt\ . \tag{A5}$$

Assuming that $g_p(t)$ can be well described by a stretched exponential[2] form of the autocorrelation function:

$$g_p(t)=\overline{p_1^2}+\overline{p_2^2}\exp[-(t/\tau)^\alpha]$$
$$=\overline{p_1^2}+(1-\overline{p_1^2})e^{-(t/\tau)^\alpha} \tag{A6}$$

expression (A5) becomes

$$\overline{\Delta p(t)^2}=[1-2(\tau/t_0)^2u(t_0/\tau)](1-\overline{p_1^2})\ , \tag{A7}$$

where

$$u(x)=\int_0^x(x-x')\exp(-x'^\alpha)dx'\ . \tag{A8}$$

Expression (30) can be now, e.g., for $\omega_1'=0$ rewritten as

$$f(\omega)=\int\int g(p)e^{-i\omega t}e^{i\omega_2'p^2t}e^{-\omega_2'^2p^2y^2z(t)}dp\,dt\ , \tag{A9}$$

where

$$g(p)=\frac{1}{2\pi}\exp\left[-\frac{p^2}{2(1-y^2)}\right]\ , \tag{A10}$$

$$y^2=\left[1-\int_0^1(1-x)e^{-(x/\tau\omega_2')^\alpha}dx\right](1-\overline{p_1^2})\ , \tag{A11}$$

$$z(t)=\int_0^t(t-t')e^{-(t'/\tau)^\alpha}dt'\ . \tag{A12}$$

APPENDIX B

Here we would like to estimate the direct effect of the nonsecular terms $\mathcal{H}''_{\rm int}(t)=\sum_{l\neq 0}\mathcal{H}^{(l)}$ which were neglected in the evolution operator $E(t)$ given by expression (20a). Introducing the interaction representation $\tilde{\mathcal{H}}''_{\rm int}(t)$ and

$$E''(t)=\exp\left[-i\int_0^t dt'\tilde{\mathcal{H}}''_{\rm int}(t')\right], \tag{B1}$$

one finds

$$E''(t)=\exp\left[-\sum_{l=\pm 1,2}\mathcal{H}^{(l)}(t)(1-e^{il\omega_L t})/l\omega_L\right]. \tag{B2}$$

Neglecting terms oscillating at the Larmor frequency one gets

$$E''(t)\simeq 1-\sum_{l=\pm 1,\pm 2}\mathcal{H}^{(l)}(t)/l\omega_L\ . \tag{B3}$$

The resulting correction thus adds to the previously calculated spectrum only a small part which covers the frequency range of fluctuations of $\Delta p(t)$. It is in comparison to the main part reduced by the ratio between the quadrupolar and Zeeman frequencies $\omega_q/\omega_L \ll 1$.

To stress the difference between the effect of E'' and E and to show when the effect of E is observable, it is worthwhile to make an estimate of the exponential factor in the expression (25) which was previously obtained from (21a):

$$\exp\left[i\int_0^t\Delta\omega(t')dt'\right]\simeq\exp\left[i\frac{\omega_q^2}{\omega_L}\int_0^t p(0)p(t')dt'\right]. \tag{B4}$$

In the very slow motion regime $\omega_2^2\tau/\omega_L>1$ and Eq. (B4) reduces to

$$\exp\left[i\frac{\omega_q^2}{\omega_L}p^2t\right] \tag{B5}$$

resulting in a frequency shift $(\omega_q^2/\omega_L)p^2$. As soon as the motion becomes faster and $1>\omega_2^2\tau/\omega_L$ the approximation (B5) is valid only for $t\ll\tau$. For $t\gg\tau$ one can approximate (B4) by a time-independent constant

$$\exp\left[i\frac{\omega_q^2}{\omega_L}\tau\right], \tag{B6}$$

and for even faster fluctuations $\omega_q\tau\sim 1$ by

$$1+i\frac{\omega_q^2}{\omega_L}\tau\ . \tag{B7}$$

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