NQR in Dipolar and Quadrupolar Glasses *

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It is shown that nuclear quadrupole resonance and quadrupole perturbed magnetic resonance represent a powerful technique to determine the local polarization distribution and its second moment, the Edwards-Anderson order parameter, in proton and deuteron glasses. For quadrupolar glasses the local orientational distribution function can be determined from the inhomogeneous NMR or NQR lineshape, thus allowing for a measurement of the quadrupolar Edwards-Anderson order parameter. The comparison of the temperature dependences of the thus obtained order parameters with theoretical predictions then allows for a discrimination between the different possible models of the glassy transition.

Key words: NQR, Glasses, Order parameters.

I. Introduction

A basic feature of the glassy state is its topological disorder which makes NQR and NMR in glasses a much more difficult task than comparative studies in non-random systems.

NQR and NMR are useful for the study of phase transitions in non-random systems because the NQR and NMR frequencies depend on the order parameter at the transition temperature T_c. Symmetry breaking at T_c and the appearance of a non-zero value of the order parameter thus result in a change or splitting of the NMR frequency. The temperature dependence of the NQR or NMR frequency allows for a determination of the temperature dependence of the order parameter while the temperature dependence of the spin-lattice relaxation rate T_1^{-1} allows for a determination of the Fourier transform of the local order parameter auto-correlation function at the Larmor frequency. The critical slowing down of the order parameter fluctuations at T_c ($\tau_{qc} \rightarrow \infty$ as $T \rightarrow T_c$) usually results in an anomaly in the spin-lattice relaxation rate and may also result in a linewidth anomaly.

In weakly disordered systems we still have below T_c local ordering in relatively large domains, and as far as NQR is concerned, the situation is not very different from the one found in non-random systems.

In strongly disordered systems, such as spin-glasses or structural glasses, the situation is radically different:

i) There is no long range ordering below T_c and there is no sharp change in the NMR or NQR frequency at any temperature. Similarly there is no sharp anomaly in T_1 at any temperature.

ii) The NQR frequency of a given nucleus i is, in the simplest case of covalent bonding, a function of the local polarization p_i,

$$\nu_i = \nu_i(p_i)\,, \tag{1 a}$$

which has the following properties:

$$\overline{p_i} = 0\,, \quad \overline{p_i^2} \neq 0\,, \tag{1 b}$$

i.e. the spatial average of the local polarization is zero while the spatial average of the square of the local polarization is non-zero.

iii) The NQR line is generally inhomogeneously broadened and reflects the distribution of resonance frequencies due to the spatial distribution of quasi-stationary local polarizations.

iv) The autocorrelation function of the local polarization is generally non-exponential and can in many cases be described by the stretched exponential law

$$G(t) = C\,\exp(-t/\tau)^{\alpha}\,, \tag{2}$$

where the parameters τ and α depend on the particular system and on external variables such as the temperature. The temperature and frequency dependence of the spin-lattice relaxation rate will therefore not be of the form proposed by Bloembergen, Purcell, and

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Pound. By measuring the frequency and temperature dependence of T_1, the parameters τ and α can be determined. It should be noted that (2) in fact describes a whole distribution of microscopic correlation times. The linewidth transition in random systems will therefore not be sharp as in pure systems but will be stretched over a large temperature interval.

Here we wish to show that NQR and quadrupole perturbed NMR is nevertheless capable of providing unique information about order parameters and the distribution and dynamics of the local polarizations in strongly disordered systems such as proton glasses, spin glasses, quadrupole glasses, incommensurate glasses and perhaps even structural glasses. It is also extremely useful for the study of weakly disordered systems with substitutional disorder.

II. NQR Lineshapes in Glasses

Glasses are aperiodic solids and contain a large number of topologically non-equivalent nuclear sites. In conventional glasses we always have a distribution of local deformations (e.g. bond angles and bond distances) resulting in a distribution of electric field gradient tensors. Instead of a few sharp lines as in periodic solids we thus expect to find in glasses an inhomogeneous broadening of the resonance lines, i.e. a frequency distribution $f(\nu)$ centered around the lines found in crystalline samples.

If we characterize the local deformations by a statistical distribution $\varrho(u)$ of the scalar displacement field u, we find the corresponding NQR frequency distribution $f(\nu)$ – describing the number of lines in the frequency interval $\mathrm{d}\nu$ – from

$$f(\nu)\,\mathrm{d}\nu = \varrho(u)\,\mathrm{d}u \tag{3a}$$

as

$$f(\nu) = \frac{\varrho(u)}{|\mathrm{d}\nu/\mathrm{d}u|}. \tag{3b}$$

The composite lineshape is a convolution of $f(\nu)$ with the homogeneous width $L(\nu-\nu_c)$ of a given line:

$$F(\nu) = \int L(\nu-\nu_c)\, f(\nu_c)\,\mathrm{d}\nu_c. \tag{3c}$$

If the relation between the NQR frequency and the local deformation u is linear,

$$\nu = \nu_0 + a_1 u, \tag{4}$$

the NQR lineshape $f(\nu)$ directly reflects the distribution of local deformations $\varrho(u)$.

In the general case one may expand the electric field gradient (EFG) tensor components $T^{(\mu)}(l)$ at site l in powers of nuclear displacements:

$$T^{(\mu)}(l) = T_0^{(\mu)}(l) + u_l \cdot T_{01}^{(\mu)}(l) + u^2\, T_{02}^{(\mu)}(l) + \ldots, \tag{5a}$$

where

$$T_{01}^{(\mu)}(l) = \sum_i \frac{\partial T_0^{(\mu)}(l)}{\partial \boldsymbol{u}_i}\,\frac{\boldsymbol{u}_i}{u_l} \tag{5b}$$

and

$$T_{02}^{(\mu)}(l) = \tfrac{1}{2}\sum_{i,j} \frac{\partial^2 T^{(\mu)}(l)}{\partial \boldsymbol{u}_i \cdot \partial \boldsymbol{u}_j}\,\frac{\boldsymbol{u}_i\,\boldsymbol{u}_j}{u_l^2}. \tag{5c}$$

Here the NQR frequency depends on the displacements of a large number of nuclei. The situation becomes simple if the radius of the region from which the main contributions to $T^{(\mu)}(l)$ come from is small enough, so that $u_i \approx u_j \approx u$ and we are in the local case. Here the frequency-displacement or frequency-local deformation relation is simply $\nu = \nu(u)$ and can be expanded in a Taylor series

$$\nu = \nu_0 + a_1 u + \tfrac{1}{2} a_2 u^2 + \ldots. \tag{6}$$

If the local site symmetry is high enough (e.g. if we have inversion symmetry) all odd terms in the expansion of $\nu=\nu(u)$ vanish and the leading term is quadratic in u:

$$\nu = \nu_0 + \tfrac{1}{2} a_2 u^2 + \ldots. \tag{7}$$

In the quadratic case, $\mathrm{d}\nu/\mathrm{d}u = a_2 u \propto \sqrt{\nu-\nu_0}$, $\nu-\nu_0>0$ and the lineshape $f(\nu)$ will be asymmetric (Fig. 1) in contrast to the linear case (4).

For conventional glasses the distribution of local deformations is Gaussian,

$$\varrho(u) = C\exp[-u^2/2\sigma^2], \tag{8a}$$

and the frequency distribution is in the linear case as well Gaussian

$$f(\nu) = \frac{C}{|a_1|}\cdot\exp[-(\nu-\nu_0)^2/(2a_1^2\sigma^2)]. \tag{8b}$$

In *spin glasses*, the local magnetization distribution $W(M)$ takes the place of the distribution of local deformations

$$U \to M, \quad \varrho(u) \to W(M). \tag{9a}$$

$W(M)$ is temperature dependent and changes from a single peaked form to a double peaked form at low temperatures.

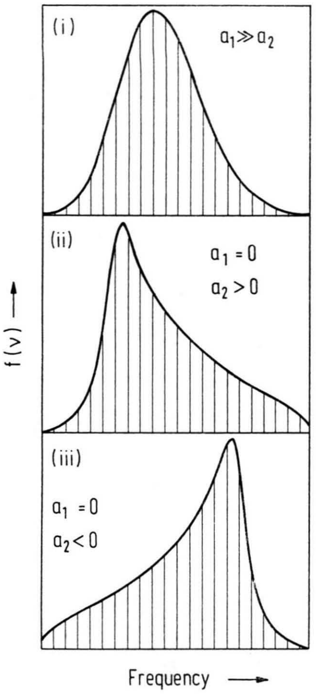

Fig. 1. Inhomogeneous NQR lineshapes in glasses: (i) Linear case, (ii) and (iii) quadratic cases.

In *proton* or *deuteron dipolar glasses* it is the local polarization distribution $W(p)$ which replaces $\varrho(u)$:

$$u \to p, \quad \varrho(u) \to W(p)\,. \tag{9b}$$

$W(p)$ is as well T-dependent and changes from a single peaked to a double peaked form.

In *quadrupolar glasses* it is the distribution of the orientations of e.g. the CN quadrupoles in the mixed alkalicyanides which replaces $\varrho(u)$:

$$u \to \langle Y_i^{\alpha} \rangle, \quad \varrho(u) \to W(\langle Y_i^{\alpha} \rangle)\,. \tag{9c}$$

$W(\langle Y_i^{\alpha} \rangle)$ is as well T-dependent and changes from a single peaked to a multiple peaked form at low T.

III. Effects of Impurities and Random Fields on Phase Transitions

Since substitutionally disordered mixed crystals provide for a link between perfect crystals and strongly disordered systems such as glasses, let us first review some properties of substitutionally disordered systems.

It is well known that impurities, substitutional and topological disorder as well as frustration and competing interactions may have drastic effects on the properties and phase transitions of solid state systems. Doping with non-symmetry breaking ions might produce two different effects: i) random changes in the interaction constants resulting in non-linear coupling to the order parameter, and ii) random fields resulting in linear coupling to the order parameter. While random interactions have only a subtle effect on the phae transition behaviour, the effects of random fields are rather drastic. Random fields destroy long range order for dimensionalities smaller than a critical dimensionality d_L where

$$\text{i)} \qquad d \leqq d_L = 2 \tag{10a}$$

for systems with a discrete symmetry (e.g. Ising-like Hamiltonians), while for systems with a continuous symmetry (incommensurate systems, Heisenberg-like Hamiltonians etc.) long range order is destroyed for

$$\text{ii)} \qquad d \leqq d_L = 4\,. \tag{10b}$$

Randomness thus increases the lower critical dimensionality from $d_L = 1$ to $d_L = 2$ for systems with a discrete symmetry, and from $d_L = 2$ to $d_L = 4$ for systems with a Hamiltonian with continuous symmetry. In strongly disordered systems spin-glass phases and percolation behaviour are found.

IV. Substitutionally Disordered Ferroelectric and Antiferroelectric Systems: $Rb_{1-x}(ND_4)_xD_2AsO_4$

It has been recently shown [1, 2] that substitutionally disordered mixed crystals $Rb_{1-x}(ND_4)_xD_2AsO_4$ – henceforth designated as RADA – of ferroelectric RbD_2AsO_4 and antiferroelectric $ND_4D_2AsO_4$ represent a frustrated H-bonded system with randomly competing interactions [3]. For pure RbD_2AsO_4 the ferroelectric transition takes place at $T_c = 178$ K whereas the antiferroelectric transition in pure $ND_4D_2AsO_4$ occurs at $T_c = 304$ K. For small x the system shows a paraelectric-ferroelectric and for large x a paraelectric-antiferroelectric transition. For intermediate x-values no long range ordering takes place and the system forms at low temperatures a "proton" or "deuteron" dipolar glass [4, 5]. In contrast to isomorphous $Rb_{1-x}(ND_4)_xD_2PO_4$ [4, 5] the phase diagram is not symmetric [2] as the paraelectric-antiferroelectric transition temperature is much higher than the paraelectric-ferroelectric one.

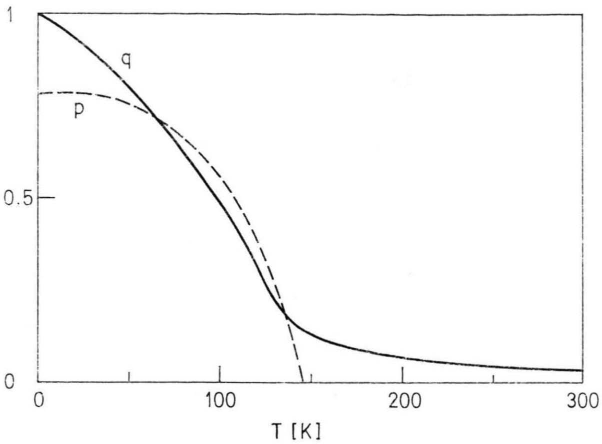

Fig. 2. Temperature dependences of the glassy order parameter q ($\triangleq q_{\mathrm{EA}}$) and the long range order parameter p according to (8a, b) for $\tilde{J}_0 = 160$ K, $\tilde{J} = 90$ K, and $\Delta/\tilde{J}^2 = 0.3$.

The phase diagram of the RADA system can be described by the random bond Ising model [3]

$$\mathscr{H} = -\tfrac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z , \tag{11}$$

where the pseudo-spin variable $S^z = \pm 1$ describes the two possible deuteron sites in the O–D···O bonds and the random interactions J_{ij} are distributed according to a Gaussian probability density:

$$P(J_{ij}) = \left(\frac{1}{2\pi J^2}\right)^{-1/2} \exp\left[-(J_{ij} - J_0)^2/(2J^2)\right]. \tag{12}$$

The J_{ij} are assumed [3] to be infinitely ranged with a mean $J_0 = \tilde{J}_0/N$ and a variance $J = \tilde{J}/N^{1/2}$. Here N is the number of pseudo-spin sites. $\tilde{J}_0$ and $\tilde{J}$ are both concentration dependent:

$$\tilde{J}_0(x) = -\tilde{J}_0^{\mathrm{AFE}} \cdot x + \tilde{J}_0^{\mathrm{FE}}(1-x) \tag{13}$$

and

$$\tilde{J}(x) = 2\,[x(1-x)]^{1/2}\, \tilde{J}_{0.5} . \tag{14}$$

Here $\tilde{J}_0^{\mathrm{AFE}} > 0$ and $\tilde{J}_0^{\mathrm{FE}} > 0$ are parameters appropriate for pure $ND_4D_2AsO_4$ and RbD_2AsO_4, where $\tilde{J}_{0.5}$ characterizes the 50% RDA-ADA mixture.

For $|\tilde{J}_0| > \tilde{J}$ a transition from a paraelectric into a ferroelectric ($\tilde{J}_0 > 0$) or antiferroelectric ($\tilde{J}_0 < 0$) phase appears, whereas for $\tilde{J} \geqq |\tilde{J}_0|$ the transition is from a paraelectric into a pseudo-spin glass phase with zero long range order $p = \frac{1}{N} \sum_i \langle S_i^z \rangle$ but non-zero Edwards-Anderson glassy order parameter $q_{\mathrm{EA}} = \frac{1}{N} \sum_i \langle S_i^z \rangle^2$.

If $|\tilde{J}_0| > \tilde{J}$ and $\tilde{J}_0 < 0$ as expected for $Rb_{0.40}(ND_4)_{0.60}D_2AsO_4$, we should have a para-electric-antiferroelectric transition with non-zero long range order (i.e. "staggered polarization" $p \neq 0$) below T_c. This should exist in addition to the pseudo-spin glass order represented by q_{EA}.

In analogy to $Rb_{1-x}(ND_4)_xD_2PO_4$ (RADP) we now add to (11) a random field term $-\sum_i S_i^z f_i$. The random fields f_i are as well distributed according to a Gaussian probability density with a variance Δ and zero mean value.

The order parameters p and q_{EA} are determined by the coupled self-consistent equations:

$$p = \int_{-\infty}^{+\infty} \frac{dz}{\sqrt{2\pi}}\, e^{-z^2/2} \tanh\left[\beta(\tilde{J}\sqrt{Q})\, z + (|\tilde{J}_0|\, p)\right], \tag{15a}$$

$$q_{\mathrm{EA}} = \int_{-\infty}^{+\infty} \frac{dz}{\sqrt{2\pi}}\, e^{-z^2/2} \tanh^2\left[\beta(\tilde{J}\sqrt{Q})\, z + (|\tilde{J}_0|\, p)\right]. \tag{15b}$$

Here $\beta = 1/(kT)$ and $Q = q + \Delta/\tilde{J}^2$. The temperature dependences of p and q_{EA} expected on the basis of (15a–b) are schematically shown in Figure 2. We see that q_{EA} is – for $\Delta \neq 0$ – different from zero at all temperatures whereas p is non-zero only below T_c. It should be noted that the temperature dependence of q_{EA} is below T_c strongly affected by the temperature dependence of p.

The relation between the NQR frequency ν_i at a given Rb site and the local O–D··· O bond polarization $p_i = \langle S_i^z \rangle$ can be written as

$$\nu_i = \nu_0 + \sum_j C_{ij} \langle S_j^z \rangle . \tag{16}$$

The presence of glassy disorder will result in an inhomogeneous broadening of the Rb-NQR-line. The second moment of the inhomogeneously broadened line is above T_c proportional to q_{EA}:

$$\begin{aligned} M_2 &= \int f(\nu)\,(\nu - \nu_0)^2\, d\nu \\ &= \frac{1}{N_{\mathrm{Rb}}} \sum_i \sum_{jk} \left[C_{ij} C_{ik} \langle S_j^z \rangle \langle S_k^z \rangle\right]_{\mathrm{AV}} = C\, q_{\mathrm{EA}}, \quad T > T_c, \end{aligned} \tag{17}$$

where

$$C = \frac{1}{N_{\mathrm{Rb}}} \sum_i \sum_j \sigma_{ij}^2 .$$

Here $[\ldots]_{\mathrm{AV}}$ denotes the disorder average, i.e. the simultaneous average over random bonds and random fields.

The centre of gravity, $\bar{\nu}=\int f(\nu)\,\nu\,\mathrm{d}\nu$ of the NQR line is in this case proportional to the long range order parameter p:

$$\bar{\nu}=\nu_0, \qquad T>T_c \quad (p=0); \tag{18a}$$

$$\bar{\nu}=\nu_0+\nu_1 p, \quad T<T_c \quad (p\neq 0). \tag{18b}$$

If higher order terms are added to the expansion (16), one sees that above T_c the centre of gravity of the NMR line $\bar{\nu}$ is proportional to q_{EA} and is thus not really T-independent as predicted by (18a).

The above predictions are fully supported by recent ^{87}Rb experiments in $Rb_{1-x}(ND_4)_xD_2AsO_4$ and $Rb_{1-x}(ND_4)_xD_2PO_4$.

V. Proton and Deuteron Glasses

For $\tilde{J}>\tilde{J}_0$ the paraelectric-ferroelectric respectively paraelectric-antiferroelectric transition is suppressed and the model discussed above predicts a transition to a pseudo-spin glass phase.

The existence of a phase transition [6] in real spin glasses is still one of the great open problems in condensed matter physics. This is also true for proton or deuteron pseudo-spin glasses which are characterized by the random freeze-out [7, 8] of the hydrogen ions between the two possible positions in the $O-H\cdots O$ bonds in mixed solid solutions of hydrogen bonded ferroelectric and antiferroelectric crystals. In spite of many investigations it is still not clear what is the nature of the observed freeze-out. Do we have a pseudo-spin glass transition of the Ising type [6–8] driven by randomly frustrated competing interactions and occurring at a non-zero transition temperature T_G, or just a strong random field type single particle freezing?

The problem which makes experimental studies of spin glasses as well as proton and deuteron glasses so difficult is that the Edwards-Anderson order parameter q_{EA} characterizing the deuteron glass as well as magnetic spin glasses, has no macroscopic conjugate field and is therefore hard to measure directly. Here we show that quadrupole perturbed NMR allows a direct experimental determination of the average local polarization distribution function $W(p)$ and its second moment, the Edwards-Anderson order parameter q_{EA}, in proton and deuteron glasses. This is so as the site averaged distribution of NMR frequencies is a direct measure of the average distribution of the local $O-D\cdots O$ deuteron polarization.

The average probability distribution of the local polarization p is defined as

$$W(p)=\frac{1}{N}\sum_i \delta(p-\langle S_i^z\rangle)=[\delta(p-\langle S_i^z\rangle)]_{AV}, \tag{19}$$

where N is the number of lattice sites, $\langle\ldots\rangle$ represents the thermal average while $[\ldots]_{AV}$ denotes the disorder average, i.e. the simultaneous average over random bonds and random fields. $W(p)$ for the Ising pseudo-spin model with infinitely ranged random interactions and quenched random field [8] is for the replica symmetric phase obtained [9] as

$$W(p)=\frac{1}{\beta\tilde{J}\sqrt{2\pi(q+\tilde{\Delta})}}\,\frac{1}{(1-p^2)} \cdot\exp\left(-\frac{1}{2}\,\frac{\operatorname{arctanh}^2(p)}{\beta^2\tilde{J}^2(q+\tilde{\Delta})}\right). \tag{20}$$

It is trivial to verify that the first moment of the distribution $W(p)$ is the total polarization P, which is zero in the absence of a homogeneous external electric field, while its second moment is just the proton glass order parameter

$$q_{EA}=\int \mathrm{d}p\, p^2\, W(p). \tag{21}$$

In Fig. 3, the distribution function $W(p)$ is plotted for $\Delta=0.35$ and several values of the reduced temperature $T/\tilde{J}$. For $T<T_G=\tilde{J}$, $W(p)$ exhibits a two-peak structure with maxima near $p=\pm 1$. However, $W(p)=0$ at $p=\pm 1$. At $T\approx T_G$, $W(p)$ flattens out, and for $T>T_G$ becomes a bell-shaped distribution with a maximum at $p=0$. On increasing the temperature the width of $W(p)$ decreases, and for extremely high temperatures it behaves asymptotically as

$$T\xrightarrow{\lim}\infty\colon\quad W(p)\to\delta(p), \tag{22}$$

which can easily be derived from (20). Similarly, one can show that in the absence of random fields, i.e., for $\Delta\to 0$ one has $p_{EA}=0$ for $T>T_G$ and again $W(p)=\delta(p)$ for all temperatures $T>T_G$.

The relation between the Larmor frequency of a deuteron positioned at the i-th hydrogen bond in a mixed RADP crystal and the pseudo-spin polarization $\langle S_i^z\rangle$ of this bond can be in the simplest case written as

$$\nu_i=\nu_0+\nu_1\langle S_i^z\rangle. \tag{23a}$$

If the local polarization $p_i=\langle S_i^z\rangle$ is non-zero due to the presence of random fields or random bond interactions leading to a glass ordering and making the

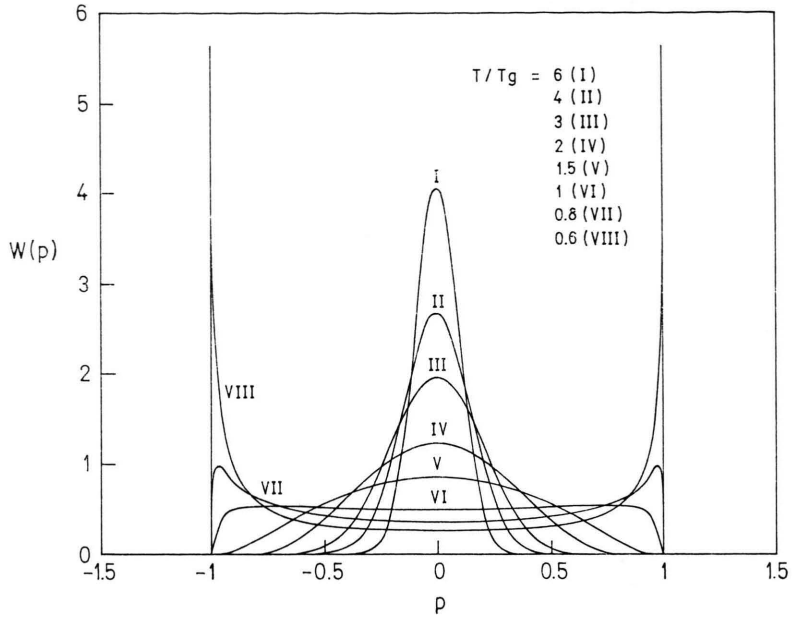

Fig. 3. Temperature dependence of the average local polarization distribution function $W(p)$ for $\tilde{\Delta}=0.35$ [9].

O–D···O potential asymmetric, quadrupolar nuclei like O–D···O deuterons with different p_i will have different NMR and NQR frequencies. This will result in an inhomogeneous broadening of the NMR or NQR lines.

The inhomogeneous deuteron NMR lineshape is here characterized by the average frequency distribution function

$$f(\nu)=\frac{1}{N}\sum_i \delta(\nu-\nu_i)=[\delta(\nu-\nu_i)]_{\mathrm{AV}}\,, \tag{23b}$$

where self-averaging has again been assumed.

From (19) and (23) we immediately find the inhomogeneous deuteron frequency distribution $f(\nu)$ as

$$f(\nu)=W(p)/\nu_1\,. \tag{24}$$

If higher order terms are present in the relation between the O–D···O NQR frequency and the pseudo-spin polarization of this bond, (24) is generalized to

$$f(\nu)=W(p)/|\mathrm{d}\nu/\mathrm{d}p|\,. \tag{25}$$

An experimental determination of $f(\nu)$ thus immediately yields $W(p)$ and its second moment q_{EA} [9] as described by (21).

If the nuclear spin is situated at a position i other than the pseudo-spin site, its resonance frequency is generally perturbed by a group of pseudo-spins rather than by a single one as described by (23a). In this case the second moment of $f(\nu)$ will be still proportional to q_{EA} [9].

All above considerations are valid if the local dipole moment fluctuations are fast compared to the rigid lattice quadrupolar splittings.

At low temperatures in the slow motion regime we have to take into account the additional broadening due to the slowing down of the fluctuations by convoluting $W(p)$ with the lineshape $I(\omega, p)$ for chemical exchange [10] in an asymmetric two-site potential

$$I(\omega)=\int_{-1}^{+1} I(\omega,p)\,W(p)\,\mathrm{d}p\,. \tag{26}$$

$I(\omega)$ reduces to $f(\nu)$ in the fast motion limit. For the O–D···O case we have [10] in particular

$$I(\omega,p)=\frac{4\delta^2\Omega_0}{(\delta^2-\omega^2)^2+4\Omega_0^2[\omega\cosh(\mathrm{artgh}\,p)-\delta\sinh(\mathrm{artgh}\,p)]^2} \tag{27}$$

where δ is the frequency separation between the two O–D···O deuteron sites in the H-bond and $\Omega_0=1/\tau$ is the frequency of exchange between the two sites which is thermally activated and can be derived from the T_1 data [7]. It is the ratio between Ω_0 and δ which determines the cross-over between the fast and the slow motion regimes.

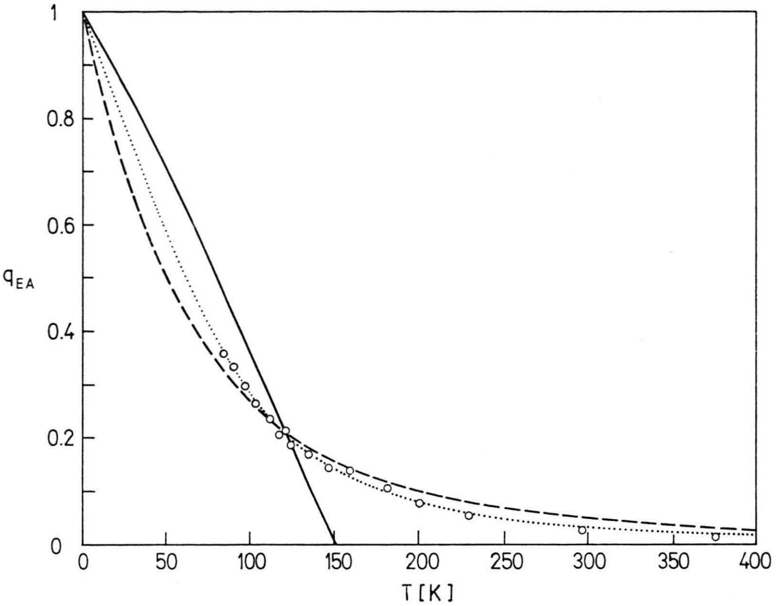

Fig. 4. Temperature dependence of the Edwards-Anderson order parameter q_{EA} as determined [9] from the second moment of the ^{87}Rb 1/2 → −1/2 NMR spectra in $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$. The dotted line represents the calculated temperature dependence for $\tilde{\Delta} = 0.35$, $T_g = \tilde{J} = 90$ K, whereas the dashed line represents the best fit for the pure random field model $T_g = 0$, $\sqrt{\tilde{\Delta}} = 68$ K and the solid line the curve for the pure random bond model with $T_g = 151$ K and $\tilde{\Delta} = 0$.

The $O-D\cdots O$ deuteron and ^{87}Rb 1/2 → −1/2 quadrupole perturbed NMR spectra have been measured for RADP single crystals with $x = 0.44$ at an orientation where the relation between v and p is close to being linear. The inhomogeneous broadening of the spectra has been found to be much larger than the homogeneous linewidth measured by the Hahn echo.

The temperature dependence of q_{EA} obtained from the second moment of the ^{87}Rb 1/2 → −1/2 lineshapes – after subtracting the contribution due to the homogeneous linewidth – are shown in Figure 4. The data taken in the fast motion regime cannot be fitted [9] by a pure glass transition model ($\tilde{J}^2 \neq 0$, $\Delta = 0$) nor by a pure random field model ($\tilde{J}^2 = 0$, $\Delta \neq 0$) for any value of $\tilde{J}$ or Δ. A perfect fit can be however again obtained [9] for $\tilde{J}^2 \neq 0$ and $\Delta \neq 0$. This demonstrates a random field smearing of the Ising pseudo-spin glass transition in RADP as predicted [8]. The $O-D\cdots O$ deuteron spectra indeed show the predicted change from a single peaked structure at high temperatures to a double peaked structure at low temperatures (Figure 5). The observed frequency distribution can be quantitatively described [9] by (24)–(27) using the q_{EA} value derived from the ^{87}Rb second moment data (Fig. 4), i.e. for $\tilde{\Delta} = 0.35$ and $T_G = \tilde{J}/k = 90$ K. NMR and NQR can be thus used to determine $W(p)$ and q_{EA}.

The cross-over between the fast and the slow motion regime occurs – for this orientation – at 47 K. The dynamic corrections (26)–(27) for the $O-D\cdots O$ deuteron lineshape again do not involve any free parameters as the correlation frequency $\Omega_0 = 1/\tau$ can be obtained from the $O-D\cdots O$ deuteron and ^{87}Rb spin-lattice relaxation time data [7].

It shold be noted that in the slow motion regime the second moment of the lineshape is *not* proportional to q_{EA}, but approaches a constant value at low T.

It should be stressed that the technique described here is quite general and not at all restricted to proton glasses. An analogous relation between the local magnetization distribution function, the NMR-NQR frequency distribution function and the Edwards-Anderson order parameter can be also derived for magnetic spin glasses though in that case magnetic resonance experiments are more difficult in view of the effect of the magnetic field on the spin glass transition.

VI. Quadrupolar Glasses

Quadrupolar (or "orientational") glasses [11] may form a conceptual link between spin glasses – where for certain models exact solutions exist demonstrating a phase transition to a new thermodynamic state – and conventional glasses which are much less understood and are generally considered to be metastable states. The quadrupolar glass is characterized by a

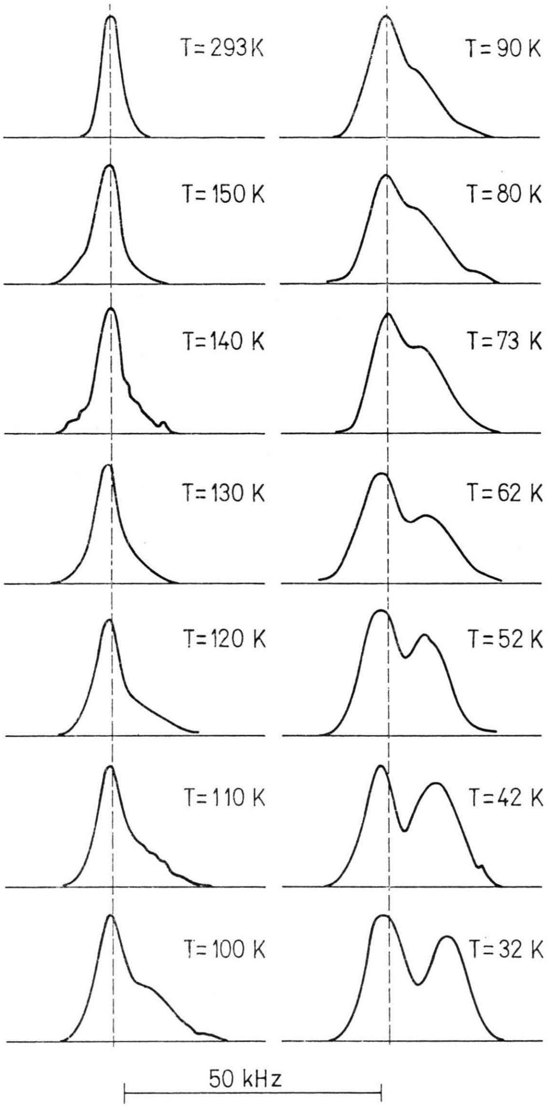

Fig. 5. $Rb_{0.56}(ND_4)_{0.44}D_2PO_4$. Temperature dependence of the O–D···O deuteron NMR lineshape for $x = 0.44$ and $a \perp B_0$, $\sphericalangle\, b, B_0 = 45°$ showing [9] the predicted change from a single peaked $f(\nu)$ – and $W(p)$ – to a double peaked $f(\nu)$ and $W(p)$. At this orientation the relation between ν and p is $\nu - \nu_0 = \nu_1 p + \nu_2 p^2$ with $\nu_1 = 5.2$ kHz and $\nu_2 = 3.3$ kHz resulting in an asymmetric lineshape [9].

random orientational freeze-out of the molecular quadrupoles (e.g. the dumbbell shaped CN groups [11] in mixed cyanides) without any head-tail (i.e. dipolar) ordering. This is to be compared with the random head-tail freeze-out of the Ising spins in a classical spin glass. In both cases the freeze-out is driven by randomly frustrated competing interactions.

In spite of many investigations it is still not clear from the experimental side whether we have in the mixed cyanides [12] such as $Na(CN)_xCl_{1-x}$ and $Na_xK_{1-x}CN$ a true collective transition to a quadrupolar glass state driven by a random bond Hamiltonian or just a strong random field type single ion freezing with the local random fields determining the alignment of the orientational degrees of freedom. The Edwards-Anderson order parameter q characterizing the spin glass as well as the quadrupolar glass state can be hardly measured directly by macroscopic techniques because the conjugate macroscopic field is experimentally not available. The quadrupolar q_{EA} can be, however, again directly measured by NMR or NQR [11].

The Hamiltonian for a set of quadrupoles with randomly quenched and frustrated pairwise interactions can be for the mixed cyanides expressed [11] in terms of the symmetry adapted spherical harmonics Y^α of E_g ($\alpha = 1, 2$) and T_{2g} ($\alpha = 3, 4, 5$) symmetry as

$$\mathcal{H} = -\sum_{i,j} \sum_{\alpha,\alpha'=1}^{5} J_{ij}^{\alpha,\alpha'}\, Y_i^\alpha\, Y_j^{\alpha'} - \sum_i \sum_{\alpha=1}^{5} f^\alpha{}_i\, Y_i^\alpha . \qquad (28)$$

Here the five components of the symmetric traceless Cartesian quadrupole tensor of rank 2 and dimension 3 are replaced by the five orientational coordinates Y_i^α; the f_i^α represent the random strain fields at site i and the coupling constants $J_{ij}^{\alpha;\alpha'}$ account for both the direct and the lattice mediated CN-CN quadrupole interactions [12]. The lattice coordinates which are bilinearly coupled to the Y_i^α have been already eliminated from the Hamiltonian (28). The random interactions J_{ij} and the random fields f_i are independently distributed according to their Gaussian probability densities

$$P(J_{ij}) \propto \exp[-(J_{ij} - J_0)^2/(2J^2)] , \qquad (29\,a)$$

$$P(f_i) \propto \exp[-f_i^2/(2\Delta)] \qquad (29\,b)$$

with J_0, J, and Δ being concentration dependent. For a given domain in the orthorhombic phase of both the pure and the mixed cyanides, for one Y^α of T_{2g} symmetry the relation $\overline{\langle Y^\alpha \rangle} = N^{-1} \sum_i \langle Y_i^\alpha \rangle \neq 0$ holds ($\langle\ \rangle$ denotes thermal averaging). The monoclinic and rhombohedral phases, on the other hand, are characterized [12] by the condensation of two, respectively three $\langle Y^\alpha \rangle$ ($\alpha = 3, 4, 5$). In the glass phase $\overline{\langle Y^\alpha \rangle} = 0$, q_{EA}, however, is non-zero and can be expressed as

$$q = \sum_{\alpha=1}^{5} q_\alpha = N^{-1} \sum_{\alpha=1}^{5} \sum_i \langle Y_i^\alpha \rangle^2 . \qquad (30)$$

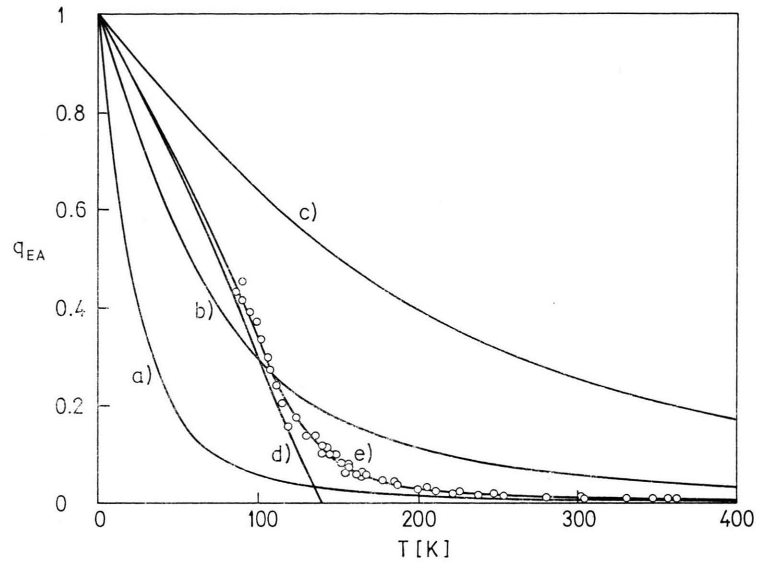

Fig. 6. $Na(CN)_{0.65}Cl_{0.35}$. Comparison between the temperature dependences of the quadrupolar Edwards-Anderson order parameter q_{EA} determined from the second moment data (circles) and the predictions of the various theoretical models [11]. Curves a, b, c: Pure random field models. Curve d: Pure random bond model. Curve e: Fit to the random bond–random field model. The same q_{EA} values were obtained from the ^{23}Na and ^{35}Cl data.

According to

$$q_\alpha = \int p^2\, G_\alpha(p)\, \mathrm{d}p, \tag{31a}$$

the q_α are the second moments of the orientational distribution functions G_α for the CN quadrupoles

$$G_\alpha(p) = N^{-1} \sum_i \delta(p - p_{i,\alpha}) \tag{31b}$$

with $p_{i,\alpha} = \langle Y_i^\alpha \rangle$.

In the local case the EFG tensor elements V_i^{mn} at a given CN ion are linear functions of the five $p_{i,\alpha}$ of this quadrupole:

$$V_i^{mn} = \sum_\alpha A_\alpha^{i,mn}\, p_{i,\alpha}\,. \tag{32}$$

The distribution of resonance frequencies $f(v)$ is then related to the spatial distribution G_α of the frozen-out orientations of the CN quadrupoles

$$f(v) = \int \cdots \int G_1(p_1) \ldots G_5(p_5) \cdot \delta[v - v(p_1, \ldots, p_5)]\, \mathrm{d}p_1 \ldots \mathrm{d}p_5\,. \tag{33}$$

For quadrupolar glasses $G_\alpha(p)$ thus plays the same role as $W(p)$ for proton glasses and the local magnetization distribution function for spin glasses. Measurements of $f(v)$ and its moments thus yield information about the G_α and their moments. If particularly only one $p_{i,\alpha}$ is important, (33) reduces to $f(v) = G_\alpha(p_\alpha)/(\mathrm{d}v/\mathrm{d}p_\alpha)$. Thus, if the relation between v_i and this $p_{i,\alpha}$ is known, a measurement of the inhomogeneous NMR lineshape allows for a direct determination of G_α. If, on the other hand, the relation between v_i and the five $p_{i,\alpha}$ is linear, the second moment is

$$M_2[f(v)] = v_0^2 + \sum_\alpha v_\alpha^2\, q_\alpha\,. \tag{34}$$

For the case of mixed cyanides only one q_α is important. A measurement of the temperature dependence of the squared width of the satellite distributions yields the temperature dependence of q. The shape of the $q(T)$ curves then allows a discrimination between a random field type single ion freezing and a collective glass transition.

The systems studied [11] were $Na(CN)_xCl_{1-x}$ and $Na_xK_{1-x}CN$. For the $Na(CN)_xCl_{1-x}$ system with $x = 0.65$ we find $T_g = 140$ K and a rather small value $\Delta/J^2 = 0.03$ [11]. The data for $x = 0.45$ can be now fitted with the same value of Δ/J^2 and $T_g = 146$ K. This is exactly what is expected if the system behaves as an ideal solution so that $\Delta \propto x(1-x)$ and $J = k_B T_g \propto [x(1-x)]^{1/2}$. Very good fits can be as well obtained [11] for the $Na_xK_{1-x}CN$ data (Fig. 6) with the parameters $T_g = 276$ K, $\Delta/J^2 = 0.06$ for $x = 0.57$; $T_g = 250$ K, $\Delta/J^2 = 0.06$ for $x = 0.70$; $T_g = 223$ K, $\Delta/J^2 = 0.08$ for $x = 0.77$. As expected, Δ/J^2 is nearly concentration independent, but the value is larger than in the $Na(CN)_xCl_{1-x}$ system so that the ergodic–nonergodic transition line [8] is significantly below $T_g = J/k_B$.

The above data clearly show that we deal in the mixed cyanides with a random field smearing of a glass transition and not with a “single ion” freezing in random fields or with a “straight” spin-glass like glass transition.

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