Doctoral Thesis

NMR studies of the low-temperature structure and dynamics of
the pseudo-spin glass D-RADP-X

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NMR STUDIES OF THE LOW-TEMPERATURE STRUCTURE AND DYNAMICS OF THE PSEUDO-SPIN GLASS D-RADP-X

A dissertation submitted to the
Swiss Federal Institute of Technology
Zürich
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presented by

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1999
Without an appreciation for grace and beauty, there's no pleasure in creating things and no pleasure in having them. Our lives are made drearier, rather than richer!

Bill Watterson

To my parents
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7 Summary

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Abstract

D-RADP-X is a solid solution of RbD₂PO₄ and ND₄D₂PO₄, which are representatives of the KDP (KH₂PO₄)-type structures. Phase transitions in the pure KDP-type systems are connected with ordering of protons or deuterons in the double well potential of the O-H···O bonds. Already in 1941 Slater was able to explain the transition from paraelectric (PE) KH₂PO₄ to the low temperature ferroelectric (FE) phase by stating that the PO₄ groups with two protons close (Slater groups, ²S) have a much lower energy than the groups with 0, 1, 3, or 4 protons close (Takagi groups, ⁰T, ¹T, ³T, ⁴T), respectively, and by assuming that the FE Slater groups have a slightly lower energy than the AFE Slater groups. This model predicts thus highly asymmetric O-H···O bonds, since the creation of a Takagi pair (²S +²S →¹T +³T) would result in an energetically highly unfavorable state.

The random substitution of NH₄ for rubidium introduces a competition between FE and AFE interactions and thus suppresses the long-range ordering of the O-H···O protons connecting the PO₄ groups, at low temperatures. It was an open question whether the low temperature structure of the KDP-type orientational glasses is given by a random freeze-out of the hydrogens on the O-H···O bonds or whether the Slater rules (ice rules) are fulfilled, resulting in a random or short-range ordered Slater lattice.

We could identify the six PO₄ Slater configurations in the measured ³¹P NMR rotation spectra and determine the corresponding chemical shift tensors. The fact that no signs of Takagi groups have been observed leads to the conclusion that for low temperatures (T ≈ 45 K) the structure of D-RADP-50 and probably also of the other mixed crystals of the KDP family is of the Slater type. Model calculations of the ⁸⁷Rb spin lattice relaxation (T₁) of D-RADP-50 show, that the measured temperature dependence of the T₁ distribution can be explained by assuming asymmetric O-D···O bonds.

Another problem addressed in this work is the O-D···O deuteron dynamics of D-RADP-50 in the temperature region between 50 K - 170 K. One question is whether the deuteron hopping between the two sites of the O-D···O bonds is partly correlated, since asymmetric bonds as the ice rules demand are not compatible with the high temperature PE structure. The latter is characterized by a time-averaged deuteron position being in the middle of the...
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O-D-O bonds. \(^2\)H and \(^{31}\)P NMR measurements of deuterated KDP (D-KDP) in the high temperature PE phase showed that the time averaged polarization \(p\) of the O-D-O bonds is zero on the NMR time scale [31, 9]. Thus the bias energy is zero for all bonds of the system, which is equivalent to symmetric bonds. This is in contradiction with the ice rules, which are certainly valid also in the PE phase. The only possibility to explain this discrepancy is to allow for bias fluctuations which symmetrize the O-D-O bonds in the long time limit.

A model is introduced to explain the \(^{87}\)Rb 2D exchange measurements and the observed line shape transition in the \(^{31}\)P spectra. In this model it is assumed that there are few unpaired Takagi groups (\(^1\)T, \(^3\)T) present in the Slater lattice which can move through the O-D-O network like quasi particles just by shifting hydrogens from one side of the bond to the other. Such a random motion symmetrizes all O-D-O bonds in the long time limit, thus it is very likely responsible for the behavior of the O-H-O bonds of the KDP type crystals in the high temperature PE phase.

We have observed a \(^{31}\)P line shape transition for \(T > 50\) K leading to a merging of the spectrum into a single line around 170 K. This transition could be of dynamic origin due to the motion of Takagi defects, leading to an exchange between the six different Slater configurations. Our analysis based on a dynamic line shape transition yields for the Takagi motion an autocorrelation time of 10 ms at 50 K.

\(^{31}\)P 2D exchange measurements at 50 K and 55 K however did not show any exchange on the expected time scale. The observed line shape transition is thus predominantly of static origin, due to a change of the "static" polarization distribution \(W(p)\) with temperature obtained from the random-bond-random-field model [14].

A further question is whether D-RADP-X forms a frozen glass state or whether it only appears static due to the very long correlation times exceeding normal measuring times. Dolinšek et al. detected a very slow intrabond exchange of the O-D-O deuterons in Rb\(_{0.68}(\text{ND}_4)\_0.32\text{D}_2\text{AsO}_4\) (D-RADA-32) with exchange times from 236 s to 14 s at temperatures between 24 K and 45 K [10]. From the observed behavior one can conclude that the O-D-O bonds are symmetric in the long time limit.

Although the \(^2\)H line shape is double-peaked in the temperature region \(T = 45 - 55\) K owing to the two deuteron sites of the O-D-O bond the deuterons are in the fast motion regime. The observed double-peaked line shape is due to the fact that the polarization distribution \(W(p)\) is double-peaked at these temperatures. We have performed \(^2\)H 2D exchange measurements to detect possible bias fluctuations of the bonds. No exchange peaks between the two sites could be observed for mixing times between 1 s and 10 s.

Since also for higher temperatures (\(T = 70 - 150\) K) the exchange rate \(\Gamma\) is much larger than the peak separation, the \(^2\)H NMR line reflects the time averaged polarization \(p\) of the O-
D···O bond. We have performed 2D exchange difference measurements with $T_1$ weighting to monitor fluctuations of $\rho$. The broader dynamic spectrum could clearly be distinguished from the static one indicating the presence of dynamic effects during the exchange times between 10 ms and several seconds. The fact that the width of the cross peaks was almost constant for different exchange times shows that the bias fluctuations must be faster than 10 ms. However it is not yet clear why the frequency difference between the diagonal and cross peaks is not larger than 4-5 kHz.

The dynamics of the KDP type crystals is thus not yet completely understood and it seems that the kind of the isomorphs (arsenates or phosphates) and possibly also the ammonium content $x = 0.01X$ strongly influences the nature and time scale of the motions involved.
Zusammenfassung

D-RADP-X ist eine Mischung von RbD₂PO₄ und ND₄D₂PO₄, welche beide Vertreter der KDP (KH₂PO₄) Struktur sind. Der Phasenübergang der reinen KDP Substanzen ist durch das Ordnung der Protonen, beziehungsweise der Deuteronen, im Doppelmuldenpotential der O-H-O Wasserstoffbrückenbindungen charakterisiert. Bereits 1941 gelang es Slater, den Phasenübergang von KH₂PO₄ von der paraelektrischen (PE) Hochtemperatur- zur ferroelektrischen (FE) Tieftemperaturphase zu erklären. Dabei wurde erstens den PO₄ Gruppen, die zwei nahe Protonen aufweisen (Slater Gruppen, ²S) eine viel tiefere Energie zugewiesen als denjenigen PO₄ Gruppen mit 0, 1, 3, 4 Protonen nahe (Takagi Gruppen, ⁰T, ¹T, ³T, ⁴T) und zweitens angenommen, dass die FE Slater Gruppen eine etwas kleinere Energie aufweisen als die AFE Slater Gruppen. Es ist klar, dass dieses Modell stark asymmetrische O-H-O Bindungen impliziert, da die Erzeugung eines Takagi Paars (²S +²S → ¹T +³T) einen energetisch ausgesprochen ungünstigen Zustand zur Folge hat.

Die statistische Verteilung von NH₄ Molekülen und Rubidium Atomen führt zu einander konkurrierenden AFE und FE Wechselwirkungen, so dass eine langreichweitige Ordnung der O-H-O Protonen, welche die PO₄ Moleküle miteinander verbinden, verhindert wird. Bis jetzt war unklar, ob die Tieftemperaturphase der Gläser vom KDP Typ durch ein statistisch zufälliges Einfrieren der Wasserstoffatome in den O-H-O Bindungen charakterisiert ist oder ob die Slater Regeln (Eis-Regeln) erfüllt sind, was äquivalent zu einem zufällig geordneten Slater Gitter ist.

Es war uns möglich, die sechs PO₄ Slater Konfigurationen in den gemessenen ³¹P Rotationspektren zu identifizieren und die zugehörigen Tensoren der Chemischen Verschiebung zu bestimmen. Aus der Tatsache, dass keine Anzeichen von Takagi Gruppen in den Spekten beobachtet werden konnten, schlossen wir, dass bei tiefen Temperaturen (T ≈ 45 K) die Struktur von D-RADP-50 und möglicherweise auch diejenige der anderen Mischkristalle des KDP Typs durch ein Slater Gitter gegeben ist. Modellrechnungen der ⁵⁷Rb Spin-Gitter Relaxation (T₁) von D-RADP-50 zeigen, dass sich die gemessene Temperaturabhängigkeit der T₁-Verteilung mit asymmetrischen O-D-O Bindungen erklären lässt.

Im weiteren war die Dynamik der O-D-O Deuteronen im Temperaturbereich von 50 K
bis 170 K Gegenstand der Untersuchungen dieser Arbeit. Insbesondere die Frage, ob die Deuteronen teilweise korrelierte Sprünge zwischen den beiden Minima der O-D-···O Bindungen vollführen, stand zur Diskussion, da die Forderung von asymmetrischen Bindungen durch die Slater Regeln nicht mit der PE Hochtemperaturstruktur verträglich ist. Diese besagt nämlich, dass im Zeitmittel die Deuteronen in der Mitte der O-D-···O Bindungen liegen. $^2$H und $^{31}$P NMR (Magnetische Kernresonanz) Untersuchungen von deuteriertem KDP (D-KDP) zeigten, dass im Zeitraumen der NMR die zeitlich gemittelte Polarisation $\rho$ der O-D-···O Bindungen in der PE Hochtemperaturphase gleich Null ist [31, 9]. Daraus folgt, dass auch die Energiedifferenz zwischen den beiden Bindungsminima verschwindet, gleichbedeutend mit symmetrischen Bindungen. Die einzige Möglichkeit die Diskrepanz zu den Eis-Regeln zu beseitigen liegt in der Vorstellung, dass sich die Energiedifferenz zwischen den Minima zeitlich derart ändert, dass die O-D-···O Bindungen im Zeitmittel symmetrisiert werden.

In dieser Arbeit wird ein Modell zur Erklärung der $^{87}$Rb 2D Austauschmessungen und der beobachteten Linienformumwandlung der $^{31}$P Spektren vorgeschlagen. Wir nehmen an, dass sich eine kleine Anzahl von ungepaarten Takagi-Gruppen ($^1$T, $^3$T) im Slater Gitter befindet. Diese können sich wie Quasi-Teilchen im O-D-···O Netzwerk praktisch frei bewegen, indem Wasserstoffatome auf ihren O-D-···O Bindungen verschoben werden. Eine derartige statistisch zufällige Bewegung wird alle O-D-···O Bindungen im Zeitmittel symmetrisieren und ist höchstwahrscheinlich auch für das Verhalten der Substanzen vom KDP Typ in der PE Hochtemperaturphase verantwortlich.

Wir haben eine Linienformumwandlung der $^{31}$P Spektren für Temperaturen oberhalb 50 K beobachtet, die dazu führt, dass bei etwa 170 K nur mehr eine einzelne Linie im Spektrum auftritt. Die Ursache dieser Umwandlung kann in der Bewegung der Takagi-Gruppen liegen, da diese einen Austausch zwischen den sechs verschiedenen Slater Konfigurationen bewirkt. Die Messresultate wurden somit unter der Annahme einer dynamischen Umwandlung analysiert, was eine Autokorrelationszeit von 10 ms bei 50 K lieferte.


Weiterhin herrscht Unklarheit darüber, ob sich D-RADP-X in einem eingefrorenen Glaszustand befindet oder ob der Zustand nur deswegen als statistisch erscheint, weil die Korrelationszeiten der Bewegungen so lange sind, dass sie übliche Messzeiten überschreiten. Dolinšek et al. beobachteten in Rb$_{0.68}$(ND$_4$)$_{0.32}$D$_2$AsO$_4$ (D-RADA-32) einen außerordentlich lang-

Auch bei höheren Temperaturen ($T = 70 – 150$ K) ist die Austauschrate $\Gamma$ viel grösser als die Aufspaltung der Linienmaxima, so dass die $^2$H NMR Frequenz ein Mass für die zeitlich gemittelte Polarisation $p$ der O-D...O Bindung ist. Es wurden $T_1$ gewichtete 2D Differenz-Austauschmessungen durchgeführt um Fluktuationen von $p$ zu beobachten. Das breitere dynamische Spektrum konnte klar vom statischen unterschieden werden, was auf eine Dynamik während der Austauschzeiten, die im Bereich 10 ms bis 1 s gewählt wurden, schliessen lässt. Die Tatsache, dass die Breite der Nebendiagonal-Signale nahezu unabhängig von den gewählten Austauschzeiten war, legt den Schluss nahe, dass die Fluktuationen von $p$ schneller als 10 ms sind. Ausserdem ist immer noch unklar, aus welchem Grund der Frequenzunterschied zwischen den Diagonal- und den Ausserdiagonal-Signalen den Wert von 4-5 kHz nicht übersteigt.

Somit ist die Dynamik der Kristalle des KDP Typs weiterhin nicht vollständig erklärbar. Es scheint, dass die Art und die Zeitskala der vorhandenen Bewegungen einerseits sehr stark von der Art der zueinander isomorphen Substanzen (Arsenat, Phosphat) und andererseits auch vom Ammoniumgehalt $x = 0.01X$ beeinflusst ist.
Chapter 1

Introduction

1.1 Motivation

Though the deuteron ordering in D-RADP-50 (Rb0.50(ND4)0.50D2PO4) is a cooperative phenomenon leading to a glassy phase state, it is not of long range type like ferroelectric (FE) D-RDP (RbD2PO4) or antiferroelectric (AFE) D-ADP (ND4D2PO4) because of the competing FE and AFE interactions. The aim of this work was to check whether the Pauling ice rules are valid also in the glass phase of D-RADP-50 and to investigate the mechanism responsible for the low temperature dynamics. For this purpose 31P chemical shift perturbed NMR was used.

In the thesis of Th. König slow motions of the O-D···O deuterons have been discovered with the help of 87Rb exchange difference NMR [20]. However their nature was then not yet understood. An aim of this thesis was thus the investigation of these slow motions with 31P and 2H NMR. Model calculations of the 87Rb 2D exchange spectra, as well as of the 87Rb line shape and spin-lattice relaxation, based on the point-charge model worked out in the thesis of N. Körner [19], were performed to support the investigation of the observed dynamic effects.

1.2 The mixed crystal D-RADP-X

Structure

RDP (RbH2PO4), ADP (NH4H2PO4) and their deuterated isomorphs D-RDP (RbD2PO4) and D-ADP (ND4D2PO4) are representatives of the KDP (KH2PO4)-type crystals. In these compounds the PO4 groups are linked by four O-H···O hydrogen bonds to the adjacent PO4 groups (Fig. 1.1); the O-H···O bonds form a double well potential for the hydrogens (deu-
terons). The rubidium atoms and/or the NH₄ molecules are situated in the middle between successive PO₄ in the c-direction.

**Phase diagram**

RDP undergoes a structural phase transition from the paraelectric (PE) to a ferroelectric state (FE) at $T_C = 147$ K, whereas ADP transforms at $T_C = 148$ K to an antiferroelectric (AFE) structure both characterized by a particular long range order of the hydrogens on the bonds. The fact that the corresponding phase transition temperatures are about 100 K higher for the deuterated compounds (D-RDP ($T_C = 220$ K) and D-ADP ($T_C = 240$ K)) shows the major role the hydrogen (deuterium) bonds play in the dynamics of the KDP-type structures.

D-RADP-ₓ (D-RADP-X, $X = 100x$) is a mixture of RbD₂PO₄ and ND₄D₂PO₄, where $x$ describes the content of ND₄D₂PO₄. Since both compounds have almost equal lattice parameters, excellent crystals for the whole composition range can be grown [46].

Fig. 1.2 shows the phase diagram of D-RADP-ₓ as a function of temperature and ammonium concentration $x$. Like in pure D-RDP, the compounds with a high rubidium concentration $x < 0.24$ undergo a ferroelectric phase transition (Fig. 6.16), which however does not occur at a sharp temperature but is rather smeared over a certain temperature range. In the same manner behave the mixed compounds with $x > 0.74$, but here the long range order is of an AFE type (Fig. 6.17 and 6.18) like for D-ADP.
In the intermediate range $0.24 \leq x \leq 0.74$ however the competition between ferro- and anti-ferroelectric interactions suppresses the transition to a long range ordered state. Only a short range (1-2 nm) correlation of the O-D-O bonds occurs, which is not a simple superposition of ferro- and antiferroelectric order. This can be seen in Fig. 1.3, which shows $^{87}$Rb rotation spectra of D-RADP-X for different temperatures and concentrations. Since the $^{87}$Rb NMR frequency depends on the arrangement of the nearest deuterons, it is possible to distinguish the different types of ordering: ferroelectric (Fig. 1.3 b), antiferroelectric (Fig. 1.3 f), and glass order (Fig. 1.3 d).

Since the deuterons on the bonds are reorientable electric dipoles and are thus considered as Ising pseudo-spins, we speak of a deuteron (DG) or pseudo-spin (PG) glass.

### The random-bond random-field model

The static properties of the pseudo-spin glass as a function of temperature is well described by the random-bond–random-field model, where the Hamiltonian includes a two-particle term, describing the interaction of the pseudospins as well as a single-particle term, which accounts for the interaction between the pseudospins and a field, introduced by the random
Figure 1.3: $^{87}$Rb line shape as a function of the angle for a rotation around the $a$-axis for various temperatures and ND$_4$ concentrations $x$ [19].
1.2. THE MIXED CRYSTAL D-RADP-X

distribution of ND4 molecules:

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - \sum_i f_i S_i^z$$

(1.1)

The random interactions $J_{ij}$ and random fields $f_i$ are assumed to be independently distributed according to their respective Gaussian probability densities with the widths $\sqrt{\Delta}$:

$$P(J_{ij}) = J^{-1}(2\pi)^{-1/2} \exp \left(-\frac{1}{2} \frac{J_{ij}^2}{J^2} \right)$$

(1.2)

$$P(f_i) = (2\pi\Delta)^{-1/2} \exp \left(-\frac{1}{2} \frac{f_i^2}{\Delta} \right)$$

(1.3)

The solution of this model using the replica formalism [8] yields for the replica symmetric phase a temperature dependent distribution of bond polarizations $W(p)$, with $p$ being the time averaged polarization of the bonds:

$$p = \frac{1}{T} \int_0^T p_i(t) \, dt, \quad p_i(t) = \pm 1$$

(1.4)

$$W(p) = \frac{1}{\tilde{\beta} \sqrt{2\pi(q+\Delta)^{1/2}} \left[1 - p^2 \right]} \exp \left(-\frac{1}{2} \frac{\arctan^2(p)}{\tilde{\beta}^2 J^2(q+\Delta)} \right)$$

(1.5)

where $\tilde{J} = J/\sqrt{N}$, $\tilde{\Delta} = \Delta/\tilde{J}^2$ and $N$ is the number of interacting pseudospins.

The Edwards-Anderson order parameter $q = q_{EA}$ is defined as the second moment of $W(p)$:

$$q_{EA} = \int_{-1}^{1} p^2 W(p) \, dp$$

(1.6)

and is given by a self-consistent relation

$$q = \frac{1}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \exp \left(-\frac{z^2}{2} \right) \tanh^2[\tilde{\beta}(q+\Delta)^{1/2}] \, dz$$

(1.7)

$p$ depends on the bias energy $E_B$ of the bond (Fig. 4.1), $p = \tanh(E_B/kT)$ as we shall see later on. For high temperatures $W(p)$ is centered around $p = 0$, corresponding to $E_B = 0$. For very low temperatures, $W(p)$ gets doubly peaked at $p = \pm 1$, meaning that the bonds are strongly polarized (Fig. 1.4). From the $^{87}$Rb NMR spectra $q_{EA}$ can be determined, yielding the values $\tilde{\Delta} = 0.35$ and the glass-transition temperature $T_G \equiv \tilde{J} = 90$ K [11].

**Experimental results**

The pure compounds D-RDP and D-ADP, which are in a long range ordered state for low temperatures, can be characterized by a single order parameter, which is the lattice dielectric
polarization for ferroelectric D-RDP or the sublattice polarization for antiferroelectric D-ADP. In ferroelectric D-RDP for example, the phase space consists of two minima in the free energy, separated by a large energy barrier, since all bond polarizations have to be reversed for a transition from one to the other state. In contrast to that the solid solution D-RADP-X, \(0.35 < x < 0.65, x = 0.01X\), is characterized only by a short range order. Here the order parameter is, in analogy to Eq. 1.6, defined as:

\[
q = \frac{1}{N} \sum_{i=1}^{N} \langle p_i^2 \rangle
\]  

(1.8)

The glass order parameter \(q\) is zero when all bonds are symmetric. Since the random substitution of \(\text{ND}_4\) for rubidium introduces a field acting on the polarizations \(p_i\), \(q\) is larger than zero for all temperatures. The phase state consists then of an infinitely large number of almost degenerate free energy minima, separated by low barriers, since much less polarizations \(p_i\) have to be reversed for a transition between two states.

Considering again the pure compounds, one realizes that the ergodicity is broken if for low temperatures the system assumes a long range ordered state. The high temperature space group is \(I42d\) which implies that the deuterons are in the middle of the O-D-\cdots-O bonds. It was shown by Bjorkstam that the deuterons jump fast between the two potential minima so that in the time average they are located in the middle of the bonds [31]. This also implies that the deuterons spend the same amount of time on either side of the bond. The question

Figure 1.4: Polarization distribution \(W(p)\) as a function of \(T/T_G\), where \(T_G\) is the glass transition temperature, \(T_G \equiv \tilde{T}\) (from Ref. [11]).
1.2. THE MIXED CRYSTAL D-RADP-X

is how this can be made compatible with the ice rules which were used by Slater to explain the phase transition from paraelectric (PE) to ferroelectric (FE) RDP. The ice rules say that the low energy state of the system is reached when two deuterons are close to the oxygens of each PO₄ group. These configurations are called Slater groups (D₂PO₄, denoted as ²S), see below. Slater attributed to the two FE H₂PO₄ groups a slightly smaller energy than to the four AFE H₂PO₄ groups. The states with 0, 1, 3 or 4 protons (⁰T, ¹T, ³T, or ⁴T, respectively) have according to the Slater theory a much higher energy, so that they are not important. From that point of view the phase transition to a long range ordered FE state can easily be understood. However the Slater rules imply that the O-H···O bonds must be asymmetric, since if one considers two linked Slater groups (²S→²S) and shifts the hydrogen of the linking bond to the other potential minima, two Takagi-defects (¹T→³T) are created, which is an energetically unfavorable state. Now, the asymmetric bond implies also that the hydrogen atoms spend more time in the lower potential minima than in the higher one. This is then a clear contradiction to the experimental results of Bjorkstam, as mentioned above. Asymmetric bonds imply that the high temperature is also not ergodic, since the time average of a single bond is not equal to the space average of all bonds, which is zero, since there is no macroscopic order parameter. This discrepancy can be removed if one assumes that the asymmetry of the bonds is time dependent so that the average is zero. In Ch. 2 a model is proposed which explains the time dependence of the bond asymmetries which on one hand is in accordance to the observation of Bjorkstam and on the other hand respects the Slater rules.

As already mentioned, the random-bond–random-field model describes very well the observed transition from an apparent single peaked (p = 0) distribution of local polarizations W(p) to a doubly peaked distribution (p = ±1) when the temperature is lowered.

The substitution of thallium atoms for rubidium followed by γ irradiation introduces an additional unpaired electron to make electronic paramagnetic resonance (EPR) measurements possible. Since the line splitting for the Ti²⁺ electron due to the different deuteron positions is much larger than for NMR measurements, the transition from the fast to the slow motion regime (see Sec. 1.3) occurs at higher temperatures. The aim of this study was to show whether the phase transition in RADP-X is only due to the temperature dependent distribution of bond asymmetries or whether the major role is played by the slowing down of the hydrogen motion. The interpretation of the data was only possible by taking into account static and dynamic features of the phase transition [32].

The question arises whether the glass state is an equilibrium state or a metastable state, appearing as static due to the long correlation times which exceed the measuring times of the experimental spectroscopic techniques. Measurements of the static field-cooled and zero-
field-cooled dielectric susceptibilities in D-RADP-60 show that for temperatures above 61 K both susceptibilities are equal and start to deviate below that temperature [41]. However, for lower temperatures, if $\chi_{FC}$ is not measured statically, no difference between $\chi_{FC}$ and $\chi_{ZFC}$ is observed, even for measuring frequencies as low as 0.001 Hz. The experimental time scale of a zero-field-cooled experiment $t_{exp}$ is determined by the longest time in which the polarization charge is allowed to build up after switching on the field, i.e. $t_{exp} \approx 3000$ s at low temperatures [42]. Thus it seems that the glass transition is a dynamic phenomenon with a tremendous slowing down of the correlation times at low temperatures.

A very important contribution to the solution of that problem is given in Ref. [10]. For different temperatures below 50 K, the 2D exchange spectrum of the O-D-\(\cdot\)-O deuterons in D-RADA-32 (Rb$_{0.68}$ND$_{4.32}$D$_2$As$_4$O$_{14}$) was measured. For long mixing times and a symmetric distribution of bond polarizations $W(p)$ centered at zero polarization $p = 0$, the ratio of cross to diagonal peaks can be related to the Edwards-Anderson order parameter $q_{EA}$ through:

$$q_{EA} = \frac{1 - R(t_{mix} \to \infty)}{1 + R(t_{mix} \to \infty)}$$

where $R(t_{mix}) = I_{cross}/I_{diag}$. $q_{EA}$ is always smaller than 1 and it can be shown theoretically that the value $R(t_{mix} \to \infty) = 1$ can only be achieved if all bonds are symmetric. The crucial point is that the evaluation of the data always yielded the value $R(\infty) = 1$ and that very long time constants such as $\tau_{exch} = 14.4$ s at $T = 45$ K and $\tau_{exch} = 236$ s at $T = 24$ K were found. This means that the order parameter is zero in the long time limit which is equivalent to the fact that all bonds are symmetric. This is in complete contradiction to the results of spin-lattice and line shape measurements and of course also to the random-bond–random-field model. Nevertheless these results gave a first hint, that there is a very slow motion in the glass state which averages the order parameter to zero for long times.

In this thesis a model for such a slow motion will be proposed which can describe some of the experimentally observed properties of D-RADP-50. Unfortunately, some observations cannot be explained by our model which may be too simple, since among other things the random distribution of Rb and ND$_4$ is not taken into account.

A further issue that will be addressed in this thesis is the conformation of the D$_2$PO$_4$ groups as a function of temperature. With the following assumptions concerning the arrangement of the hydrogen atoms, Slater was able to explain the transition to a ferroelectric long range order of KH$_2$PO$_4$ at the Curie temperature. The Slater rules, also denoted as ice rules, express the following behavior of the hydrogen atoms [24]:

1. The bonds connecting the oxygen atoms of the different PO$_4$ tetrahedra are occupied by exactly one hydrogen atom.
1.3. THE NMR TECHNIQUE

2. If one considers a particular PO₄ group, then two of the four hydrogens of the four bonds are close to the oxygens whereas the other two are far and are thus close to the oxygens of the neighboring PO₄ groups. The H₂PO₄ entities are called Slater groups.

3. The two polar Slater groups (two hydrogens close to the upper (lower) edge of the PO₄ tetrahedra) have a smaller energy than the four lateral Slater groups (one hydrogen close to the upper edge and one close to the lower edge).

The important question arising is whether the Slater rules are also maintained at high temperatures like ambient temperature, implying also that the O-H⋯O bonds can still be described by a double well and not a single well potential. A strong indication for that behavior comes from the important contribution of Bjorkstam [31], describing deuteron NMR measurements of KD₂PO₄ as a function of temperature. It was shown that the high temperature NMR spectrum of the O-D⋯O bonds propagating along the crystallographic a direction (called X bonds, see Fig. 5.8 page 51) consists of a single line which splits into two lines at the Curie temperature. He confirmed earlier predictions of Chiba [30], saying that the principal axis $V_{zz}$ of the EFG tensor points in direction of the O-D⋯O bond and that the $V_{yy}$ components from the two X bond deuteron sites make angles of ±35.5° with respect to the z-axis and hence deviate by 5° from being normal to P-O-D plane. The crucial point is that the high-temperature magnitudes and orientations of $V_{yy}$ and $V_{xx}$ agree within ≈ 1% with the average from the two possible deuteron positions in the bond at low temperature. This means that the deuterons spend the same amount of time on each side of the bond. Also high resolution neutron diffraction measurements determined a deuteron distribution that is clearly two-peaked in the tetragonal, para-electric phase at $T_c < 5$ K [34, 35].

In this thesis chemical shift perturbed $^{31}$P NMR measurements are presented. Since we assume that only the four deuterons attached to a PO₄ group influence the chemical shift of the $^{31}$P NMR frequency, we are able to determine the conformation of the PO₄ groups.

1.3 The NMR technique

In magnetic spin glasses, the application of an external magnetic field influences the behavior of the glass state. This is not the case with pseudo-spin glasses, which are susceptible to electric fields only, where the formation and the properties of the glass state can be monitored by nuclear magnetic resonance (NMR). Since several of the nuclei in D-RADP-X possess a nuclear spin $I > 0$, they can serve as probes with different properties to study the glass state. For instance, the NMR frequency of the rubidium atoms is sensitive to the arrangement of the deuterium atoms within a certain sphere, whereas the NMR frequency of deuterium
itself depends only on its position on the bond. Furthermore, the $^{31}\text{P}$ in the center of the \( \text{PO}_4 \) tetrahedra give us a powerful probe to monitor the arrangement of the deuterons attached to them.

The NMR technique itself is well suited to investigate various experimental time scales. First it is important to note that the inherent time integration of an NMR experiment lies in the region of 1-2 ms. That enables us, by measuring the NMR line shape, to monitor transitions from the fast motion regime \((\Gamma \gg 2\pi \Delta \nu)\) to the slow motion regime \((\Gamma \ll 2\pi \Delta \nu)\), where \(\Gamma\) is the exchange rate between two lines, separated by the frequency \(\Delta \nu\). This is not possible with other techniques like neutron or X-ray scattering, which only yield a superposition of instantaneous pictures of the situation because of the much shorter integration time.

Another important NMR technique is the spin-lattice relaxation measurement, where it is also possible to monitor dynamic processes, since \(T_1\) (the spin-lattice relaxation time) depends on the magnitude and frequency of the interactions between the nuclear spin under consideration and the other atoms in the crystal.

Two dimensional (2D) exchange measurements proved to be very successful in monitoring the time scale of very slow motions and what is of greater importance in enlightening the structure and conformational dynamics of molecules that is relevant in chemistry and biology. Nevertheless this method is also suited for solids, where in contrast to liquid samples the resonance lines can often not be resolved. In particular, the extension to 2D exchange difference experiments allows for a better discrimination between static and dynamic signals.

In contrast to 1D measurements (line shape, spin-lattice relaxation) where one is restricted to time scales of 1-2 ms, 2D measurements can span time scales as long as the spin lattice relaxation time \(T_1\) which can amount to hundreds of seconds and are thus able to monitor motions in the millihertz region.
Chapter 2

Model for the slow motion in D-RADP-X

In KDP (KH2PO4)-type structures there exist different types of thermally-induced motions. First of all, there are thermally activated motions of the hydrogen atoms between the two potential minima of the O-H···O bond (the proton intrabond hopping). Especially, in the KDP-type mixed crystal systems D-RADP-X, the partial substitution of ND4 molecules for Rb atoms introduces another source of thermally activated motions. It is known that the nitrogen atom occupies an off-center position, forming two short bonds and two long bonds to the nearest oxygen atoms of the four surrounding PO4 tetrahedra as can be seen in Fig. 2.1 [3, 7]. This induces a tilt in the double-well potentials of those O-H···O bonds, where one oxygen is N-H···O bonded, while the other neighbors on a Rb ion. This behavior can also explain the antiferroelectric ordering in NH4H2PO4 and ND4D2PO4, respectively. The T1 minimum of the ND4 deuteron spin-lattice relaxation occurs around T = 170 K and the activation energy determined from the slope of the high-temperature data amounts to 160 meV [7]. Since the ND4 groups either undergo reorientational motions as a whole or just change the nitrogen off-center position, also the mentioned tilt is time-dependent.

There is also an inherent bias, resulting from the Slater rules, which allow only two hydrogens to be near the oxygen atoms of every PO4 group (Slater groups) [24]. In the Slater theory, the two ferroelectric H2PO4 groups have a smaller energy than the four antiferroelectric H2PO4 groups. This model explains the ferroelectric phase transition in KH2PO4. Takagi extended this model by taking into account the defect states with an excess or lack of protons (HPO4 and H3PO4), which have, however, a considerably higher energy than the Slater groups [40]. In view of this theory, the explanation of the mentioned inherent bias is evident. Namely, if one considers two adjacent Slater groups (H2PO4-H2PO4) and shifts the hydrogen of the connecting O-H···O bond from one to the other potential minimum, an energetically highly unfavorable state (HPO4-H3PO4) is created. This is equivalent to an asymmetric two-minimum potential.
The crucial point is that we introduce an additional mechanism influencing the bias of the O-H-\cdot-O bonds in KDP type structures like D-RADP-X. First we think that the network of H$_2$PO$_4$ group forms a Slater lattice. However, it is reasonable to assume that a particular number of Takagi-defects are present in this Slater network. There is a small probability that the above mentioned process (H$_2$PO$_4$ + H$_2$PO$_4$ $\rightarrow$ HPO$_4$$^-$+H$_3$PO$_4$) happens simultaneously in three neighboring H$_2$PO$_4$ groups in such a way that we are left with a Slater group in the middle and two Takagi groups at the left and the right side (HPO$_4$$^-$ - H$_2$PO$_4$ - H$_3$PO$_4$) as shown in Fig. 2.2 (left).

Now the Takagi defects are separated and can move rather freely through the crystal, simply by shifting one deuteron from one side of the bond to the other as illustrated in Fig. 2.2 (right). In this figure it is shown that a Takagi group (D) with three protons close ($^3T$) may walk in the directions 1, 2, and 3 whereas direction 4 is forbidden since a H$_4$PO$_4$ group would be created at the position D. Depending on where $^3T$ was (A, B, or C) before it reached position D, the former Slater group at D will change its character (deuteron arrangement) when the Takagi group walks away from position D. Of course it is also possible that two complementary ($^1T$. $^3T$) Takagi defects annihilate again when they meet. If one neglects for a moment the bias introduced by the ND$_4$ groups, one expects that the three bonds (1, 2, and 3) are symmetric. This becomes clear if one considers for example in Fig. 2.2(right) the central Takagi group (D) and the adjacent Slater PO$_4$ group (A) at the left side. If we shift the deuteron on the bond (1) connecting these groups to the left, we again end up with a Slater-Takagi pair. Since this has the same energy as the former pair before the shift, one can conclude that the bond is symmetric.
Figure 2.2: Left: Creation of two unpaired Takagi defects, with the shifted hydrogens indicated by arrows. Right: Takagi group (D) surrounded by four Slater groups. The Takagi group can move in the directions 1, 2, and 3. Direction 4 is forbidden since a \( H_2PO_4 \) group would be created.

So far we didn’t make clear what is the influence of this Takagi defect motion on the bias of the bonds. This is best illustrated by the following figure (2.3). The left part of Fig. 2.3 shows a series of pictures of a part of the \( PO_4 \) network. In the first figure, a Takagi-defect is at the left side and is connected with two Slater groups. We are interested in the evolution of the bond, which belongs to the deuteron drawn as an open circle. Since it belongs to a Slater group in the first situation the bond is asymmetric whereas the left minimum is lower than the right one. If we now shift the deuteron which is indicated by an arrow we arrive to the situation as depicted in the second drawing. Since the Takagi group is now in the middle of the three \( PO_4 \) groups, the bond under consideration has become symmetric. It still remains symmetric as one shifts the deuteron (open circle) to the right to arrive at the third situation. In the last step the deuteron which is at the most-right is shifted to the right as indicated in the fourth drawing. Now we realize that the bond has got asymmetric again, with an asymmetry which is however opposite to the first situation.

In summary, one can state that this motion of a Takagi group changes the sign of the bias energy \( E_B \) of an O-D-\( \cdots \)O bond. However this process may be more complicated if we remember the additional bias introduced by the random substitution of ND\(_4\) molecules for Rb. Then the bias need not necessarily be inverted by a passing of a Takagi defect, but for sure the magnitude of the bias is changed.

This model of a Takagi-defect motion implies important consequences. If one starts with a randomly polarized Slater lattice and neglects the bias introduced by the ND\(_4\) groups, the existing Takagi defects will average the polarization of every O-D-\( \cdots \)O bond in the long time limit to zero, as long as the Takagi-defect density and mobility is sufficiently large.
Figure 2.3: Takagi defect motion. Right side: evolution of the bond with the deuteron drawn as an open circle.
This behavior has to be contrasted with the random-bond–random-field model which perfectly describes the static properties of the D-RADV-X system. This treatment is justified for the evaluation of line shape and $T_1$ data (at least for the Rb measurements, but not for the ESR $\text{Tl}^{2+}$ measurements, where the large splitting of the lines shifts the transition from the fast to the slow motion regime to higher temperatures).

As already outlined in Sec. 1.3 we speak of fast motion limit as long as the single particle autocorrelation time of the deuteron motion is much smaller than the inverse line splitting $(\Delta v)^{-1}$ of the NMR lines. The NMR experiment thus probes the real time average for the deuteron motion. That means if the time scale is so short that the bias energy is constant (no Takagi-defect motion), one is measuring the time-averaged local polarization:

$$p = \frac{1}{T} \int_0^T p(t) \, dt, \quad p(t) = \pm 1.$$  \hspace{1cm} (2.1)

$p$ is related to the bias energy $E_B$ of the bond through:

$$p = \tanh \left( \frac{E_B}{kT} \right)$$  \hspace{1cm} (2.2)

If however we go to temperatures and time scales where the motion becomes relevant we expect that the static theory does not suffice to describe the properties of the spin glass system D-RADV-X properly. This is for instance the case in the interpretation of the $\text{Tl}^{2+}$ ESR measurements, where static and dynamic features have to be included to explain the observed behavior.

These questions and discrepancies will be evaluated in the next sections, where experimental results will be presented to support the model of the Takagi-defect dynamics.
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Chapter 3

The point-charge model

In this chapter we derive an expression to calculate the EFG tensor elements at the Rb site for an arbitrary configuration of the surrounding hydrogen atoms. The calculation is based on the assumption of the rigid lattice model, which means that the arrangement of the hydrogen atoms does not influence the underlying crystal structure.

3.1 Quadrupole perturbed NMR

The electric quadrupole interaction describes the interaction of a nucleus with nuclear spin \( I > \frac{1}{2} \) with the gradient of the electric field at the position of the nucleus. The quadrupole Hamiltonian can be written as:

\[
\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} \sum_{\mu=-2}^{+2} F_{\mu} Q_{-\mu}
\]  

(3.1)

where \( F_0 Q = V_{zz}(3I_z^2 - \bar{I}) \), \( F_{-1} Q_{\pm 1} = (V_{zz} \pm iV_{xy})(I_z I_\mp + I_\pm I_z) \), \( F_{+2} Q_{\pm 2} = (1/2)(V_{xx} - V_{yy} \pm 2iV_{xy})I_z^2 \).

The total Hamiltonian is then given by the Zeeman plus the quadrupole term:

\[
\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_Q
\]  

(3.2)

In the high field case (\( \mathcal{H}_Z \gg \mathcal{H}_Q \)) for a spin \( I = \frac{3}{2} \) the transition between the \( m = \pm \frac{1}{2} \) levels is shifted from the Larmor frequency in second order by [18]:

\[
\Delta \nu = -\frac{v_Q^2}{12v_L} \left[ \frac{2(\bar{V}_{xx} + \bar{V}_{yy})}{(eq)^2} - \frac{(\bar{V}_{xx} - \bar{V}_{yy})^2}{4(eq)^2} - \frac{\bar{V}_{xy}^2}{(eq)^2} \right], \quad v_Q = \frac{3e^2qQ}{\hbar}
\]  

(3.3)

where \( \bar{V}_{ij} \) are the EFG tensor components in the Zeeman system with \( z \)-axis parallel to the external magnetic field, \( eq \equiv V_{zz} \) is the largest principal value of the EFG tensor, \( eQ \) is the electric quadrupole moment of the nucleus under consideration, and \( \hbar \) is the Planck constant.
The EFG tensor elements in the crystal system, $V_{ij}$, and in the Zeeman system, $\tilde{V}_{ij}$, are connected by an unitary transformation:

$$\tilde{V} = R(\alpha, \beta, \gamma) VR(\alpha, \beta, \gamma)^{-1} \quad (3.4)$$

If the external magnetic field $B_0$ is oriented parallel to the $z$-axis of the crystal we have

$$\tilde{V} = V \quad (3.5)$$

The terms in the square brackets in Eq. 3.3 are dimensionless quantities. If the factor $v_Q$ in front of Eq. 3.3 which is a frequency, is included in the square brackets, the tensor components $V_{ij}$ can then be expressed in frequency units. For our calculations we chose the units as MHz (Sec. 3.3).

$$\Delta v = \frac{1}{12v_L} \left[-2(V_{xx}^2 + V_{yy}^2) + \frac{1}{4}(V_{xx} - V_{yy})^2 + V_{zz}^2 \right], \quad [V_{ij}] = \text{MHz} \quad (3.6)$$

### 3.2 Symmetries of the Rb EFG tensor of D-RADP-X

#### 3.2.1 Rb EFG tensor for the long-range ordered AFE and FE states

X-ray and NMR-NQR measurements showed that the average structure of D-RADP-X is the same ($I\bar{4}2d$) for the whole composition range ($0 \leq x = 0.01X \leq 1$) at room temperature [21]. The average site symmetry at the Rb position is $\bar{4}z$. The average Rb EFG tensor is therefore given by:

$$V_0 = \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3.7)$$

Since the hydrogen atoms in the long range ordered phases are shifted out of the center position for only a small amount [47], we can perform a linear expansion of the EFG tensor components around their high temperature values:

$$V_{ij} = V_{ij}(0) + \Delta V_{ij} \quad (3.8)$$

In the long-range-ordered FE phase of D-RADP the space group is $F\bar{d}d2$ with two inequivalent Rb positions in the unit cell ($Z = 2$). The site symmetry at the Rb position is reduced to $2\bar{z}$ (see also Sec. 6.9) and the EFG tensor can be written as odd ($p_1$) and even functions ($p_1^2$) of the order parameter:

$$V^{FE} = V_0 + \begin{bmatrix} -\frac{\Delta V_n}{2} & \Delta V_{yy} & 0 \\ \Delta V_{yy} & \frac{\Delta V_n}{2} & 0 \\ 0 & 0 & 0 \end{bmatrix} p_1 + \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} p_1^2 + \ldots \quad (3.9)$$
3.2. SYMMETRIES OF THE Rb EFG TENSOR OF D-RADP-X

where \( V_n \equiv V_{xx} - V_{yy} \).

In the long-range-ordered AFE phase of D-ADP the space group is \( P2_12_12_1 \) with \( Z = 4 \) and there is no symmetry left at the ND\(_4 \) site:

\[
\mathbf{v}^{AFE} = \mathbf{V}_0 + \begin{bmatrix}
\frac{\Delta V_{yy}}{2} & \Delta V_{xy} & \Delta V_{xz} \\
\Delta V_{xy} & \frac{\Delta V_{zz}}{2} & \Delta V_{yz} \\
\Delta V_{xz} & \Delta V_{yz} & 0
\end{bmatrix} \begin{bmatrix}
-p_2 + \Delta V_{zz}^{(2)} \\
p_2 \\
0
\end{bmatrix}
\]

For the \( \alpha \)-rotation of the crystal for an angle \( \beta \), Eqs. 3.3 and 3.4 yield the following second-order frequency shifts for FE and AFE ordering. Note that we demand that \( p_i = \pm 1 \) which implies \( p_1 = p_2 \) and \( p_1^2 = p_2^2 \).

AFE ordering yields:

\[
\Delta v^{AFE}(\beta) = \Delta v^{FE}(\beta) + \frac{1}{12v_L} \left( \frac{3}{16} \Delta V_{yy} V_{zz} \left[ \frac{13}{4} - \cos(2\beta) - \frac{9}{4} \cos(4\beta) \right] p_1 \right.
\]

\[
\left. + \left\{ \frac{1}{2} \Delta V_{xy}^2 \left[ -1 + 3 \cos(2\beta) \right] + \frac{1}{32} \Delta V_{yy}^2 \left[ \frac{11}{4} + 3 \cos(2\beta) + \frac{9}{4} \cos(4\beta) \right] p_1^2 \right\} \right)
\]

and for FE ordering we find:

\[
\Delta v^{FE}(\beta) = \Delta v^{PE}(\beta) + \frac{1}{12v_L} \left( \frac{3}{8} \Delta V_{xy} V_{zz} \left[ -\sin(2\beta) + \frac{9}{2} \sin(4\beta) \right] p_2 \right.
\]

\[
\left. + \left\{ \frac{1}{2} \Delta V_{xy}^2 \left[ -1 + 3 \cos(2\beta) \right] + \frac{1}{8} \Delta V_{yy}^2 \left[ -7 - 9 \cos(4\beta) \right] \right\} p_2^2 \right)
\]

where \( \Delta v^{PE}(\beta) \) is the shift for the paraelectric case where \( p_1 = p_2 = 0 \).

If we consider only the case \( \beta = 0 \), we notice that for the FE case only the values \( \Delta V_{xy} \) and \( \Delta V_{yy} \) determine the frequency shift, whereas for the AFE case, the values \( \Delta V_{xz} \) and \( \Delta V_{yz} \) are important.

\[
\Delta v^{FE}(0) = \frac{1}{12v_L} \left[ \Delta V_{xy}^2 + \frac{1}{4} \Delta V_{yy}^2 \right] p_1^2
\]

\[
\Delta v^{AFE}(0) = \frac{1}{12v_L} \left[ -2(\Delta V_{xz}^2 + \Delta V_{yz}^2) \right] p_2^2
\]

3.2.2 Rb EFG tensor for the short-range ordered glass state

For low temperatures, DRADP-50 is in a glass state, characterized by short range order only. Like in the case of AFE ordering outlined in the former section there is no symmetry left at the Rb site for D-RADP-X. Thus we have to write the EFG tensor in the following form
(without an order parameter $p$):

$$V^{\text{Glass}} = V_0 + \begin{bmatrix} -\frac{\Delta v_1}{2} & \Delta V_{xy} & \Delta V_{xz} \\ \Delta V_{xy} & \frac{\Delta v_2}{2} & \Delta V_{yz} \\ \Delta V_{xz} & \Delta V_{yz} & 0 \end{bmatrix} + \Delta V_{zz} \begin{bmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \ldots$$  \hspace{1cm} (3.15)

The frequency shift for $\beta = 0$ (crystal principal $c$ axis parallel to the external field $B_0$) thus reads:

$$\Delta V^{\text{Glass}}(0) = \frac{1}{12\nu_L} \left[ -2(\Delta V_{xz}^2 + \Delta V_{yz}^2) + \frac{1}{4}(\Delta V_{xx} - \Delta V_{yy})^2 + \Delta V_{xy}^2 \right]$$  \hspace{1cm} (3.16)

$$[\Delta V_{ij}] = \text{MHz}$$

### 3.3 Comparison of measured and simulated EFG tensor values

The formula Eq. 3.16 which holds for $c||H_0$ is very useful for the determination of the EFG tensor, since only the deviations of the tensor elements $\Delta V_{ij}$ need to be calculated.

The change in the EFG tensor elements can be described by a linear expansion since the displacements ($\Delta \vec{r}$) of the deuterons out of the center of the bonds are small compared with the distance from the origin ($r$):

$$\Delta V_{jk} = \sum_{l=1}^{3} V_{jkl} \Delta x_l$$  \hspace{1cm} (3.17)

where the $\Delta x_l$ are the components of $\Delta \vec{r}_l$ and the $V_{jkl}$ are given by

$$V_{jkl} = Q \left( -\frac{15x_j x_k x_l}{r^7} + \delta_{jl} \frac{3x_k}{r^5} + \delta_{kl} \frac{3x_j}{r^5} + \delta_{jk} \frac{3x_l}{r^5} \right)$$  \hspace{1cm} (3.18)

The lattice sum of the contributions $V_{jkl}$ converges rather rapidly with $1/r^2$. In Ref. [21] $\Delta V_{jk}$ for a ferroelectric structure was calculated in the way described above, using 288 O-D-O bonds, what corresponds to 36 unit cells. The prefactor $Q$ of expression Eq. 3.18 was scaled to match the measured $\Delta V_{ij}$ values, taken from the difference of the EFG tensor above and below the phase transition. Knowing the value of $Q$ makes it possible to determine for every single hydrogen the contribution to the EFG tensor at the rubidium site. Since we used a linear expansion (Eq. 3.17) the contributions to the EFG tensor for a hydrogen on different sides of its bond differ by the factor $-1$. Thus if one knows the contribution of each individual hydrogen, it is possible to calculate the deviation of the EFG tensor elements for every configuration of all the hydrogens.
The model calculations yield for the deviations $\Delta V_{i,k}$ (Eq. 3.17) of the EFG tensors in the FE and AFE phases, respectively:

$$\Delta V^{\text{FE}} = \begin{bmatrix} \Delta V_{i,k}^{\text{FE}} \end{bmatrix}_{i,k=1..3} = \begin{bmatrix} -3.9 & 1.65 & 0 \\ 1.65 & 3.9 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$  \hspace{1cm} (3.19)$$

$$\Delta V^{\text{AFE}} = \begin{bmatrix} \Delta V_{i,k}^{\text{AFE}} \end{bmatrix}_{i,k=1..3} = \begin{bmatrix} 0 & 0 & -0.78 \\ 0 & 0 & -4.18 \\ -0.78 & -4.18 & 0 \end{bmatrix}$$  \hspace{1cm} (3.20)$$

If one takes into account only the 32 nearest deuterons to the central rubidium atom one gets:

$$\Delta V^{\text{FE}} = \begin{bmatrix} -3.81 & 1.62 & 0 \\ 1.62 & 3.81 & 0 \\ 0 & 0 & 0 \end{bmatrix} \hspace{1cm} \Delta V^{\text{AFE}} = \begin{bmatrix} 0 & 0 & -0.5 \\ 0 & 0 & -4.17 \\ -0.5 & -4.17 & 0 \end{bmatrix}$$  \hspace{1cm} (3.21)$$

which shows that the 32 nearest deuterons give the major contribution to the EFG tensor. By comparing the experimentally determined EFG tensors just above and below the phase transition one obtains

$$\Delta V^{\text{FE}} = \begin{bmatrix} -3.7 & 0.65 & 0 \\ 0.65 & 3.7 & 0 \\ 0 & 0 & 0 \end{bmatrix} \hspace{1cm} \Delta V^{\text{AFE}} = \begin{bmatrix} 0.55 & 0.68 & -2.3 \\ 0.68 & -0.55 & -4.2 \\ -2.3 & -4.2 & 0 \end{bmatrix}$$  \hspace{1cm} (3.22)$$

The point-charge model based on the assumption of a rigid lattice thus yields a fairly good approximation to the measured EFG tensor values.

### 3.4 Simulated 1D Slater spectrum

In this section we present a $^{87}\text{Rb}$ $\alpha$-rotation spectrum using the EFG tensor given by Eq. 3.15, where the deviations $\Delta V_{ij}$ (Eq. 3.17) were determined with the point charge model as described in the former section. To calculate the high temperature EFG tensor $V^{\text{Glass}}$ we used the value $\overline{V_{zz}} = e^2 q Q / h = 8$ MHz for D-RADP-50 [21].

As will be shown in Ch. 6 the low temperature structure of D-RADP-50 is a Slater lattice. With a Monte Carlo simulation as presented in Sec. 5.2.2, a random Slater lattice can be created and the EFG tensor resulting from the nearest 32 deuterons to a $^{87}\text{Rb}$ atom is calculated. This is done for a large number of Slater lattices and the corresponding frequencies stored in a 1D frequency histogram.
Figure 3.1: Left: Calculated AFE line positions for \( \alpha \)-rotation. Middle: Calculated FE line positions. Right: Simulated line positions for a random Slater lattice, original spectrum convoluted with Lorentzian of a line width of 10 kHz.

Figs. 3.1 show the calculated AFE, FE and Slater spectra, which were convoluted with a Lorentzian of a width of 2 kHz for the two former and 10 kHz for the latter. Since we were using the model as described in the former sections, the tensors for AFE and FE are the same as given by Eq. 3.21. If Figs. 3.1 are compared with Fig. 1.3 for \( x = 0.15, T = 142 \text{ K} \) (FE) and \( x = 0.95, T = 103 \text{ K} \) (AFE) one can see that the angular dependence of the lines for the long-range ordered AFE and FE phases is not equal, because of the deviations between measured and simulated EFG tensor values.

Only if the Slater spectra are convoluted with a Lorentzian of a rather large width, one gets a fairly smooth line shape, which compares quite well to the measured \(^{87}\text{Rb} \) line shape of the glass state of D-RADP-50. This shows that we deal with a distribution of local polarizations that do not assume the values \( p = \pm 1 \) only but are rather smeared over \( p = \pm (1 \pm \epsilon), \epsilon \ll 1 \).
Chapter 4

$^{87}\text{Rb} \ T_1$ measurements and simulations

4.1 Introduction

In this chapter we give a review of earlier spin lattice ($T_1$) measurements of $^{87}\text{Rb}$ and present simulations based on the results of the former chapter and an alternative explanation of the data. The rubidium nuclei are ionically bound in D-RADP. Since the nuclear spin is $I = 3/2$ the rubidium atoms are subject to the electric quadrupole interaction and are thus sensitive to the positions of the charges within a range of 1.5 nm, which thus equals the observation length of the rubidium nucleus. The quadrupole perturbed NMR line shape reflects the configuration of the deuterons on the O-D···O bonds and allows to discriminate between the various types of local deuteron order [21]. It is possible to identify unambiguously FE and AFE order. However, the line shape of the glass state is definitely not a superposition of FE and AFE lines as can be seen in Figs. 1.3.

Generally spin lattice relaxation ($T_1$) measurements are a means to study the dynamic properties of a material. In our particular case we assume that the main contribution to the $^{87}\text{Rb} \ T_1$-relaxation results from the motion of the hydrogen atoms on the O-D···O bonds. Whenever a deuterium changes its position, the value of the electric field gradient at the rubidium site changes also. The measurement of $T_1$ as a function of temperature allows us to reveal the dynamics of the local deuteron order.

In Sec. 4.2 we briefly introduce the results of earlier $T_1$ measurements of $^{87}\text{Rb}$ in D-RADP-50. In Sec. 4.3 the $T_1$ data of the former section are fitted with another model based on a distribution of correlation times due to a distribution of activation energies. Since we assume that the O-D···O bonds are asymmetric we further take into account that the mean square fluctuations and the autocorrelation times are reduced depending on the time averaged value of the polarization $p$. This enables us to determine a value for the bias energy $E_B$ (Eqs. 2.1 and 2.2).
In Sec. 4.5 a model is presented simulating the mean square fluctuations of the EFG tensor at the rubidium site for symmetric and asymmetric bonds. Using the results of these model calculations, in particular the value of $E_B$, we deduce in Sec. 4.6, that the O-D-O bonds are strongly biased already at temperatures around $T = 95$ K. This is in contrast to the random-bond–random-field model where the doubly peaked distribution of $W(p)$ only occurs at temperatures below $T = 50$ K [11].

### 4.2 $^{87}$Rb spin-lattice relaxation measurements

For a spin $I = \frac{3}{2}$ the recovery of the magnetization $M(t)$ towards the equilibrium value $M_0$ after an initial perturbation is biexponential and can be written as

$$M(t) = M_0 \left[ 1 - a \exp(-2W_1 t) + \exp(-2W_2 t) \right]$$

(4.1)

where the relaxation rates $W_1, W_2$ for the single quantum ($|\Delta m| = 1$) and the double quantum transitions ($|\Delta m| = 2$) are given by

$$W_1 = \frac{e^2 Q^2}{8I \hbar^2} \left[ \langle V_{ix}^2 \rangle + \langle V_{ix}^2 \rangle \right] J(\omega_L)$$

(4.2)

$$W_2 = \frac{e^2 Q^2}{8I \hbar^2} \left[ \frac{1}{4} \langle (V_{ix} - V_{ix})^2 \rangle + \langle V_{ix}^2 \rangle \right] J(2\omega_L)$$

(4.3)

It will be shown in Sec. 4.7, Eq. 4.43, that the mean square fluctuations of the EFG tensor elements $\langle V_{ij}^2 \rangle$ can be calculated as follows:

$$\langle V_{ij}^2 \rangle = \frac{1}{T} \int_0^T (V_{ij}(t) - \overline{V}_{ij})^2 dt$$

(4.4)

whereas $\overline{V}_{ij}$ denotes the time averaged value of the interaction.

$$\overline{V}_{ij} = \frac{1}{T} \left( \int_0^T V_{ij}(t) dt \right)$$

(4.5)

The spectral densities $J(\omega_L)$ and $J(2\omega_L)$ are the Fourier transforms of the normalized autocorrelation function $G(t)$ of the corresponding fluctuations

$$J(\omega) = \int_0^\infty G(t) 2 \cos(\omega t) dt$$

(4.6)

The simplest analytical form for $G(t)$ is an exponential function $\exp(-t/\tau_c)$. The temperature dependence of the autocorrelation time $\tau_c$ can be described by an Arrhenius law:

$$\tau_c = \tau_0 \exp \left( \frac{E_A}{kT} \right)$$

(4.7)
where $E_A$ is the barrier height and $\tau_\infty$ the inverse attempt frequency that is equal to the correlation time at infinite temperature.

In the case of correlated motions and a distribution of activation energies, the autocorrelation time can no longer be described by a mono-exponential decay, but for example by a stretched exponential:

$$G(t) = \exp(-t/\tau_c)^\alpha$$

where $\alpha$ is the stretched exponent ($0 < \alpha \leq 1$). The integration Eq. 4.6 can be performed analytically only in the extreme fast motion regime ($\omega\tau_c \ll 1$) and in the extreme slow motion regime ($\omega\tau_c \gg 1$). The Havriliak-Negami spectral density can mimic in some cases the spectral density of Eq. 4.8. Its analytical form is:

$$J_{HN}(\omega, \tau_c, \delta, \varepsilon) = \frac{2}{\omega} \sin \left[ \varepsilon \arctan \left( \frac{(\omega\tau_c)^\delta \sin(\delta \pi/2)}{1 + (\omega\tau_c)^\delta \cos(\delta \pi/2)} \right) \right]$$

$$\times \left[ 1 + 2(\omega\tau_c)^\delta \cos(\delta \pi/2) + (\omega\tau_c)^{2\delta} \right]^{-\varepsilon/2}$$

The Havriliak-Negami function has two free parameters: $\delta$ describes correlated motions and $\varepsilon$ a distribution of activation energies. For $\delta = \varepsilon = 1$ the Havriliak-Negami function reduces to

$$J(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2}$$

which is the Bloembergen-Purcell-Pound (BPP) spectral density for a single autocorrelation time which is described by $\exp(-t/\tau_c)$ [4].

In Ref. [19] the spin-lattice relaxation time of D-RADP-50 was measured for the orientation of the crystal $(c||H_0)$ as a function of temperature. The magnetization $M(t)$ was recorded with the inversion recovery method. Then the observed magnetization recovery was fitted by the function given in Eq. 4.1 and the obtained values of $\tau_1 = 1/2W_1$ and $\tau_2 = 1/2W_2$ plotted as a function of inverse temperature. The resulting curves were fitted with Eqs. 4.2, 4.3 taking into account the Arrhenius law for the autocorrelation time (Eq. 4.7) giving an activation energy $E_A = 81 \pm 5$ meV and $\tau_\infty = 0.56 \cdot 10^{-13}$ s. For the spectral density the Havriliak-Negami distribution was chosen, with $\varepsilon = 1$ and $\delta$ smoothly varied from 1 to 0.8 between 120 and 85 K.

### 4.3 Fit of $T_1$ data using the Davidson-Cole spectral density

From the chemical shift perturbed $^{31}$P NMR measurements (see Ch. 6) we conclude that the lattice consists of Slater groups, which means that always two deuterons are close and two
Figure 4.1: Schematic representation of an O-D-O double well potential. Solid line: symmetric potential, dashed line: asymmetric potential. $E_A$ is the activation energy which is the energy difference between the potential minimum and the maximum for symmetric bonds. $E_B$ is the bias energy which is one half of the energy difference between the left and the right potential minima.

are far. This also implies that the O-D-O bonds are strongly asymmetric, since a deuteron jump from the lower to the higher potential minimum results in a pair of two Takagi-defects (DPO$_4$-D$_3$PO$_4$) what is energetically highly unfavorable. The dwell time in the lower potential minimum ($\tau^-$) is considerably longer than in the higher one ($\tau^+$) for low temperatures and high bias energies $E_B$. The following equation holds for the ratio of the two dwell times:

$$\frac{\tau^-}{\tau^+} = \frac{1+|p|}{1-|p|}$$

(4.11)

where $p$ is the time averaged polarization (Eq.1.4).

The bias energy $E_B$ is half of the energy difference of the two potential minima as can be seen in Fig. 4.1. As already mentioned the following equation holds for the time averaged polarization:

$$p = \tanh \left( \frac{E_B}{kT} \right)$$

(4.12)

The autocorrelation time for a symmetric bond ($\tau_0$) is one half of the dwell time in one potential minimum.

$$\tau_+ = \tau_- = 2\tau_0$$

(4.13)

For an asymmetric bond however the autocorrelation time ($\tau_0$) is reduced compared to the
symmetric case, depending on the magnitude of $p$:

$$\tau_c = \frac{\tau^+ - \tau^-}{\tau^+ + \tau^-} = \tau_0 \sqrt{1 - p^2}$$  \hspace{1cm} (4.14)$$

We assume that for short time scales which are relevant for the spin-lattice relaxation no correlated motions of the deuterons take place. They perform just thermally activated jumps between the two potential minima, with a much longer dwell time in the lower minimum, however. The random substitution of Rb for ND$_4$ may be responsible for a distribution of activation energies for the single particle jumps. We thus tried to fit the $^{87}$Rb $T_1$ data with the Havriliak-Negami distribution for which $\delta$ was set to 1 which reduces then to the Davidson-Cole distribution [43] where $\varepsilon$, as already mentioned, describes the distribution of activation energies.

Generally the spectral density can be written as as distribution of BPP spectral densities [4, 43]:

$$J(\omega, x_1, x_2, \ldots) = \int_0^\infty \Lambda(\xi, x_1, x_2, \ldots) \frac{2\xi}{1 + \omega^2 \xi^2} d\xi$$  \hspace{1cm} (4.15)$$

Since the Fourier transform is a linear operation, $\Lambda$ gives the reduced correlation function as a distribution of exponential correlation times:

$$g(t, x_1, x_2, \ldots) = \int_0^\infty \Lambda(\xi, x_1, x_2, \ldots) \exp\left(-t/\xi\right) d\xi$$  \hspace{1cm} (4.16)$$

Most of the distributions are characterized by a particular correlation time $\tau$, which may be a cut-off $\xi$ or a mean $\xi$. In this case a dimensionless parameter $y = \xi/\tau$ can be defined. Further it is useful to introduce the parameter $z = \ln(\xi/\tau)$, yielding a distribution function $\Theta(z)$, defined by:

$$\Theta(z) dz = \Lambda(\xi) d\xi$$  \hspace{1cm} (4.17)$$

The Davidson-Cole distribution is given by:

$$\Theta(z, \varepsilon) = \begin{cases} \frac{\sin(\varepsilon\pi)}{\pi} \left(\frac{1}{\exp(-z) - 1}\right)^\varepsilon & \text{for } z < 0, \\ 0 & \text{for } z \geq 0 \end{cases}$$  \hspace{1cm} (4.18)$$

Since the distribution $\Theta(z, \varepsilon)$ is zero for $z = \ln(\xi/\tau) > 0$ it follows that $\tau$ is the upper cut-off frequency for the distribution of autocorrelation times. $\varepsilon$ describes the width of the distribution (Fig. 4.2).

As already mentioned, $W_1$ and $W_2$ are given by:

$$W_1 = \left[\left(V_{xx}\right)^2 + \left(V_{yy}\right)^2\right] J(\omega_L) = V_1^2 J(\omega_L)$$

$$W_2 = \left[\frac{1}{2}\left((V_{xx} - V_{yy})^2 + (V_{yy})^2\right) J(2\omega_L) = V_2^2 J(2\omega_L)$$
which are equivalent to Eqs. 4.2 and 4.3 if the $V_{1,2}$ are expressed in frequency units.

The asymmetry of the bond influences the relaxation rates in two ways. First one can show that for asymmetric bonds the mean square values of the fluctuating parts of the Hamiltonian are reduced by the factor $(1 - \rho^2)$ (see Sec. 4.5). The relaxation rates $W_1$ and $W_2$ thus depend on the temperature via $\rho$. Secondly, they also depend on the spectral densities $J(\omega_L)$ and $J(2\omega_L)$ which themselves depend on the temperature via the autocorrelation time $\tau_c$. The latter is reduced by the factor $\sqrt{1 - \rho^2}$ as shown above (Eq. 4.14).

We used the Davidson-Cole spectral density to fit the $\tau_i$ values. The mean square fluctuations for symmetric bonds $(V_{1,2}^2)$ were corrected with the factor $1 - \rho^2$, and the autocorrelation time for symmetric bonds $\tau_c$ was multiplied by $\sqrt{1 - \rho^2}$. Only data points from 45 to 200 K were included in the fit. The fit yielded for the activation energy $E_A = 1273 \text{ K} \cong 110 \text{ meV}$, and for the bias energy $E_B = 144 \text{ K} \cong 12.4 \text{ meV}$. The autocorrelation time and the mean square fluctuations which are defined for symmetric bonds were found to be $\tau_{\infty} = 0.43 \cdot 10^{-13} \text{ s}$, $V_1^2 = 6.86 \text{ MHz}^2$, and $V_2^2 = 2.56 \text{ MHz}^2$. The value $\varepsilon = 0.45$ for the Davidson-Cole distribution was found. Fig. 4.3 shows that the data is rather well described by the model with a distribution of activation energies yielding a value for $\varepsilon$ smaller than 1.
4.4 Fit of $T_1$ data using the BPP autocorrelation function

For comparison we fitted the $T_1$ data also with the BPP autocorrelation function (Eq. 4.10) where the reduction of the mean square fluctuations by $(1 - p^2)$ and the reduction of the autocorrelation time $\tau_c$ by $\sqrt{1 - p^2}$ was taken into account. The fit yielded a result comparable to the fit with the Davidson-Cole distribution. However the bias energy $E_B$ turned out to be zero, corresponding to symmetric bonds.

For the activation energy the fit yielded $E_A = 831 \text{ K} \cong 72 \text{ meV}$ and the autocorrelation time was $\tau_{\infty} = 1.2 \cdot 10^{-12} \text{ s}$. The mean square fluctuations were found to be $V_1^2 = 0.677 \text{ MHz}^2$ and $V_2^2 = 0.213 \text{ MHz}^2$.

4.5 Calculation of the mean square fluctuations

Using the point-charge model of Ch. 3 we want to simulate the mean square fluctuations of the EFG interaction for symmetric bonds to compare these values with the ones from the fits in Sec 4.3 and 4.4. The same simulation is performed for asymmetric bonds to confirm that the mean square fluctuations are reduced by the factor $\sqrt{1 - p^2}$ where $p$ is the time averaged polarization of the bond.
We assume that in the time scale of the $T_1$ relaxation (1-2 ms) the asymmetries of the bonds are static. The deuterons perform thermally activated jumps between the two potential minima. We take into account, that for asymmetric bonds, the dwell time in the lower minimum is much larger than in the higher one as expressed by Eq. 4.11.

We calculated the mean square fluctuations of the EFG tensor elements at the rubidium site, resulting from the motion of the nearest 32 deuterons to the Rb atom. Within a linear expansion like in Ch. 3 (Eq. 3.8) the contribution to the EFG tensor elements for a single deuteron $k$ can be written as

$$
(V_{ij})_k(t) = (V_{ij})_k(0) + p_k(t)(\Delta V_{ij})_k
$$

if the time dependence of $p_k$ is explicitly included. The prefactor $p_k$ of the deviations $(\Delta V_{ij})_k$, depends on which side of the bond the deuteron can be found ($p_k = \pm 1$). From Eq. 4.4 it is clear that the high temperature static values $(V_{ij}(0))_k$ need not to be considered for the calculation of the mean square values of the EFG tensor elements.

In the present model we took into account only the 32 nearest deuterons to the $^{87}$Rb giving the major contribution to the EFG tensor. The summation thus yields:

$$
V_{ij}(t) = \sum_{k=1}^{32} [(V_{ij})_k(0) + p_k(t)(\Delta V_{ij})_k] = V_{ij}(0) + \Delta V_{ij}(t)
$$

As stated above we only need to calculate $\Delta V_{ij}(t)$ which are the changes to the static EFG tensor values as a function of time, so only the dynamic part of Eq. 4.20 is considered:

$$
\Delta V_{ij}(t) = \sum_{k=1}^{32} p_k(t)(\Delta V_{ij})_k,
$$

where $ij$ denotes $xy, xz, yz, zz$ or $1(=xx-yy)$. $(\Delta V_{ij})_k$ are the individual contributions from the hydrogens to the total EFG tensor in first order and can be calculated using Eq. 3.18. $p_k(t)$ takes on the values $\pm 1$ and describes on which side of the bond the deuteron can be found as a function of time $t$.

Since we have to consider only the mean square fluctuations of $\Delta V_{ij}(t)$, we can define the mean square fluctuations $\langle V_{ij}^2 \rangle$ as the time average $\langle \ldots \rangle$ of $(\Delta V_{ij}(t) - \overline{\Delta V_{ij}})^2$:

$$
\langle V_{ij}^2 \rangle \equiv \langle (\Delta V_{ij}(t) - \overline{\Delta V_{ij}})^2 \rangle
$$

where $\overline{\Delta V_{ij}}$ is the time average of $\Delta V_{ij}$. Of course the following relation holds for the mean square fluctuations:

$$
\langle V_{ij}^2 \rangle = \langle (\Delta V_{ij}(t) - \overline{\Delta V_{ij}})^2 \rangle = \langle \Delta V_{ij}(t)^2 - 2\overline{\Delta V_{ij}}\Delta V_{ij} + \overline{\Delta V_{ij}}^2 \rangle
$$

$$
= \langle \Delta V_{ij}(t)^2 \rangle - 2\langle \Delta V_{ij}(t) \rangle \overline{\Delta V_{ij}} + \overline{\Delta V_{ij}}^2 = \langle \Delta V_{ij}(t)^2 \rangle - 2\overline{\Delta V_{ij}}^2 + \overline{\Delta V_{ij}}^2
$$

which can better be used for the calculations.
4.5. CALCULATION OF THE MEAN SQUARE FLUCTUATIONS

4.5.1 Mean square fluctuations for symmetric bonds

For the simulation the functions \( p_k(t) \) for the individual deuterons need to be determined which yield the corresponding total EFG tensor elements \( \Delta V_{ij}(t) \). As already mentioned the deuterons perform thermally activated jumps between the minima of the double well potential. The jumps are described as independent Poisson-random events with exponentially distributed waiting times similar to a radioactive decay. The waiting times are chosen such that the natural logarithm of a randomly distributed number in the half-open interval \([0,1)\) was taken which was then multiplied by the autocorrelation time \( \tau_c \). For the calculation we have set \( \tau_c = 1 \). Since we further assume that the bias of the bonds is zero, \( \tau_c \) is equal to half of the waiting time on one side of the bond.

The temporal evolution of the 32 nearest deuterons was calculated with a Monte Carlo simulation yielding a series of data points \((t_n, \Delta V_{ij}(t_n))\), where \( t_n \) is the time when a deuteron jumps and \( \Delta V_{ij}(t_n) \) is defined as in Eq. 4.21. 3200 data points were calculated in this way, corresponding to about 100 jumps for each of the 32 deuterons.

One finds that the autocorrelation function for \( \Delta V_{ij} \) is again an exponentially decaying function with the same time constant \( \tau_c \) as for the single particle jumps.

As shown in Eq. 4.23 the summation can be made in the following way:

\[
\langle V_{ij}^2 \rangle = \frac{1}{N} \sum_{n=1}^{N} \Delta V_{ij}(t_n)^2 \Delta t_n - \overline{\Delta V_{ij}^2}
\]  

(4.24)

where \( N = 3200 \) and the time increments \( \Delta t_n \) are defined as

\[
\Delta t_n = \begin{cases} 
  t_n - t_{n-1} & \text{for } n \geq 2 \\
  t_1 - 0 = t_1 & \text{for } n = 1
\end{cases}
\]

(4.25)

and \( \overline{\Delta V_{ij}} \) can be calculated by

\[
\overline{\Delta V_{ij}} = \frac{1}{N} \sum_{n=1}^{N} \Delta V_{ij}(t_n) \Delta t_n
\]

(4.26)

since the space average is equal to the time average.

Several hundred simulations were performed as described above and the averaged values for the mean square fluctuations were calculated, yielding the values given in Table 4.1.

We get thus for \( V_1^2 \) and \( V_2^2 \):

\[
V_1^2 = \langle V_{xz}^2 \rangle + \langle V_{xy}^2 \rangle = 5.31 \text{ MHz}^2
\]

(4.27)

\[
V_2^2 = \frac{1}{4} \left( \langle V_{xy}^2 \rangle + \langle V_{yx}^2 \rangle \right) = 7.37 \text{ MHz}^2
\]

(4.28)
| \langle V^2_{zz} \rangle^{1/2} | 2.64 MHz |
| \langle V^2_{yy} \rangle^{1/2} | 4.85 MHz |
| \langle V^2_{xx} \rangle^{1/2} | 1.22 MHz |
| \langle V^2_{x} \rangle^{1/2} | 1.63 MHz |
| \langle V^2_{z} \rangle^{1/2} | 1.63 MHz |

Table 4.1: Simulated mean square EFG tensor values for symmetric bonds.

### 4.5.2 Mean square fluctuations for asymmetric bonds

It is easy to show analytically that for a single or for two bonds the mean square fluctuations are reduced by the factor \(1 - p^2\). For 32 deuterons in asymmetric bonds we performed a similar simulation as in the former section. However, in this case the dwell times which are equal \(2\tau_c\) for symmetric bonds have to be corrected because of the asymmetry:

\[
\tau_+ = 2\tau_c \sqrt{\frac{1 - |p|}{1 + |p|}} \quad (4.29)
\]

\[
\tau_- = 2\tau_c \sqrt{\frac{1 + |p|}{1 - |p|}} \quad (4.30)
\]

where \(\tau_+\) is the dwell time in the upper potential minimum, and \(\tau_-\) the dwell time in the lower one, respectively. The simulated values for the mean square fluctuations for biased bonds were exactly reduced by the factor \(1 - p^2\) compared to the values \(V_{zz}^2, V_{yy}^2\) for symmetric bonds determined in the former section.

### 4.6 Conclusions

From Eq. 3.13 and 3.14 we find that \(V_{zz}^2\) corresponds to the ferroelectric fluctuations and \(V_{yy}^2\) is related to the antiferroelectric ones. The simulated value for \(V_{zz}^2\) is 5.31 MHz\(^2\) and the value from the fit is 6.86 MHz\(^2\). However, the simulated value for \(V_{yy}^2\) is 7.37 MHz\(^2\) whereas that from the fit is 2.56 MHz\(^2\).

If however one compares the mean square fluctuations from the BPP model with the simulated ones, one observes that the former are about a factor of 10 smaller than the latter.

The fact that the point-charge model itself yields a fairly good approximation to the deviations (see Sec. 3.3) and the finding that the mean square fluctuations from the fit with the Davidson-Cole function are of the same order of magnitude supports the assumption that in the case of D-RADP-50 we deal with a biased Slater lattice.

For the Davidson-Cole fit we got for the activation energy \(E_A = 110\) meV corresponding to the cut-off energy on the high energy side of the distribution of activation energies. The
Figure 4.4: Solid line: time averaged polarization \( p \) as a function of temperature depending on the bias energy \( E_B = 12.4 \text{ meV} = 144 \text{ K} \) determined from the fit of the Davidson-Cole function to the \( T_1 \) data. Dotted line: \( (1-p^2) \); reduction factor for the mean square fluctuations. Dashed line: \( \sqrt{1-p^2} \); reduction factor for the autocorrelation time.

corresponding \( \tau_{\infty} \) was determined as \( 0.43 \cdot 10^{-13} \text{ s} \). The value \( \varepsilon = 0.45 < 1 \) shows that we deal with a distribution of activation energies. The integration

\[
\bar{E} = \int_0^{E_C} E f(E) dE
\]

yields the mean energy \( \bar{E} \) of the distribution. The definition of the distribution \( f(E) \) implies a temperature dependence for \( f(E) \) and thus also for \( \bar{E} \) which decreases from 103 meV for 50 K to 77 meV for 250 K.

Since \( \xi = \tau_{\infty} \exp(E_C/kT) \) where \( E_C \) is the cut-off energy of the distribution of activation energies \( E \) and \( \tau = \tau_{\infty} \exp(E/kT) \) we can perform the integration of \( \xi \Theta(\zeta) \) analytically, where \( \Theta(\zeta) \) is the distribution of \( \zeta = \ln(\xi/\tau) \). One finds then \( \bar{E} = -1.64 \) which yields the relation

\[
\bar{E} = E_C - 1.64 kT
\]

Fig. 4.4 shows the time averaged polarization as a function of temperature. Already for temperatures below 100 K, \( p \) is larger than 0.9 what is in accordance with our assumption of a strongly biased Slater lattice. The question arises how can this model be related to the random-bond-random field model which predicts the distribution of the polarization \( W(p) \) to be centered around zero for high and moderate temperatures. Only at temperatures \( T < 50 \text{ K} \) the function \( W(p) \) becomes doubly peaked at \( p = \pm 1 \) meaning that the bonds are strongly
biased and the order parameter $q_{EA}$ is close to 1 (see Fig. 1.4). A possible solution for this discrepancy may come from the following argument. The parameters of the random-bond–random-field model are determined from the second moment of the $^{87}$Rb $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ NMR spectra in D-RADP-44 in the temperature region 80 to 370 K [11]. If our assumption that Takagi-defects are present in the lattice is correct, then the correlation time of their motion is smaller than the integration time of the line shape measurements for temperatures above 100 K. Whenever a Takagi-defect passes through a Slater lattice, the polarization of the involved bonds change the sign (as long as one neglects the random distribution of ND$_4$ which also contributes to the bias). On a long time scale every bond is subject to a large number of Takagi defect passes, so that the polarization of the bond is zero, corresponding to the distribution of $W(p)$ centered around zero which is predicted by the random-bond–random-field model in this temperature region.

4.7 Appendix

4.7.1 General relaxation theory

The theory for the relaxation of a spin system with the states $m$ under the influence of a small perturbative interaction $H'_1$ can be found in standard textbooks [25, 26]. The density matrix formalism together with second order perturbation theory yields the following expression for calculating the occupation of the states $m$ as a function of time:

$$\frac{d}{dt} (m | \rho | m) = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} g_{mk}(\tau) \exp(-i(\omega_m - \omega_k)\tau) d\tau = W_{km} = \frac{j_{mk}(\omega_m - \omega_k)}{\hbar^2}$$  \hspace{1cm} (4.33)

where $\omega_m = E_m / \hbar$, $\omega_k = E_k / \hbar$ and $g_{mk}(\tau)$ is the correlation function of the perturbation $H'_1$:

$$g_{mk}(\tau) = \overline{\langle m | H'_1(t) | k \rangle | k | H'_1(t + \tau) | m \rangle}$$  \hspace{1cm} (4.34)

The bar in Eq. 4.34 expresses the ensemble average. In Ref. [26] it was shown that for the case of a fluctuating field ($H = (H_1(t), H_2(t), H_3(t))$) under the assumption that $H_q(t)$ takes on two values $\pm h_0$, the following relation holds:

$$\overline{H_q(t)H_q(t + \tau)} = \hbar^2 \exp(-\tau/\tau_0)$$  \hspace{1cm} (4.35)

where $\tau_0$ is the correlation time of the fluctuations between $\pm h_0$.

$$\frac{1}{\tau_0} = 2W$$  \hspace{1cm} (4.36)

In practice the interaction not only assumes two values but many more, as for instance for the case of the rubidium spin-lattice relaxation, where the perturbative Hamiltonian depends
on the positions of the surrounding $N$ deuterons, so that we have $2^N$ possibilities for the interaction. Nevertheless a similar expression as Eq. 4.35 can be found also for such situations as will be shown in the following.

### 4.7.2 Relaxation due to quadrupolar interaction

In Ref. [45] the following expression is given for the calculation of the transition rate between the states $m$ and $k$ if a perturbative quadrupole interaction is present:

$$W_{mk} = \left| \frac{\mathcal{H}_{mk}(0)}{\hbar} \right|^2 j_{mk}(\omega_{mk})$$

(4.37)

where $\mathcal{H}_{mk}$ is the matrix element of the perturbation Hamiltonian and $j_{mk}(\omega_{mk})$ the spectral density of $g_{mk}$.

$$j_{mk}(\omega) = \int_{-\infty}^{\infty} g_{mk}(\tau) \exp(-i\omega\tau) d\tau$$

(4.38)

Eq. 4.37 holds when the correlation time for the dependence of $\mathcal{H}_{mk}$ is much less than $W_{km}^{-1}$ (weak collision approach) which is fulfilled unless the fluctuations are extremely slow.

The transition probabilities $W_1(|\Delta m| = 1)$ and $W_2(|\Delta m| = 2)$ can then be written

$$W_1 = \frac{e^2 Q^2}{8\hbar^2} J_1(\omega)$$

(4.39)

$$W_2 = \frac{e^2 Q^2}{8\hbar^2} J_2(2\omega)$$

(4.40)

where $J_{1,2}$ are the spectral densities of the lattice functions $V_{\pm 1} = V_x \pm iV_y$ and $V_{\pm 2} = (1/2)(V_{xx} - V_{yy}) \pm iV_{xy}$:

$$J_{1,2}(\omega) = \langle V_{1,2}^2 \rangle \cdot 2 \int_0^\infty g(t) \exp(-i\omega t) dt$$

(4.41)

$g(t)$ denotes the reduced correlation function for the lattice functions $V_{\pm 1}$ and $V_{\pm 2}$:

$$g_{1,2}(\tau) = \langle V_{1,2}^2 \rangle g(\tau)$$

(4.42)

$\langle V_{1,2}^2 \rangle$ is given by

$$\langle V_{1,2}^2 \rangle = \langle \overline{V_{1,2}^2} \rangle - (\langle V_{1,2} \rangle)^2$$

(4.43)

where the bar again denotes the space average. Thus we find for the relaxation rates:

$$W_1 = \frac{e^2 Q^2}{8\hbar^2} \left[ \langle V_{1,2}^2 \rangle + \langle V_{2,2}^2 \rangle \right] \cdot 2 \int_0^\infty g(t) \exp(-i\omega t) dt$$

(4.44)

$$W_2 = \frac{e^2 Q^2}{8\hbar^2} \left[ \frac{1}{4}(V_{xx} - V_{yy})^2 \right] \cdot 2 \int_0^\infty g(t) \exp(-i2\omega t) dt$$

(4.45)

To calculate the relaxation rates $W_{1,2}$, the mean square fluctuations $\langle V_{1,2}^2 \rangle$, which result from a space average need to be determined. Assuming that the crystal is in an ergodic state, the space average can be replaced by a time average as described in Eq. 4.23.
4.7.3 Relaxation due to chemical shift interaction

In this section we calculate the fluctuations of the chemical shielding to study its influence on the spin lattice relaxation of $^{31}$P in D-RADP-50. For the calculations we use the chemical shift tensor values which are presented in Ch. 6. Again we assume that the relaxation is due to the motion of Takagi defects which change the deuteron configuration for the PO$_4$ group of the phosphorus atom under consideration.

In Ref. [1] it was shown that the high temperature $T_1$ minimum at $T \approx 170$ K of D-RADP-X is due to the reorientational motion of the ND$_4$ groups. The low-temperature $T_1$ minimum at $T \approx 77$ K that is only present for the mixed crystals but not for the pure compounds RbD$_2$PO$_4$ and ND$_4$D$_2$PO$_4$, is attributed to the O-D···O deuteron motion.

Of course there are two parts contributing to the relaxation. One is the single particle hopping of the deuterons, the other is the bias fluctuations of the O-D···O bonds.

In this simulation we only consider the influence of the bias fluctuation themselves without taking into account the microscopic process which in fact involves the Takagi defect states. This treatment is justified to determine the relaxation rates approximately, since the chemical shift tensors of the Takagi states are of the same order of magnitude as the Slater CS tensors as shown in Sec. 6.5.

The rate for the transition between nuclear spin energy levels $(1/2) \leftrightarrow -(1/2)$ can be calculated as follows. The perturbative Hamiltonian is given by:

$$\mathcal{H}_\text{I} = \hbar \gamma \sigma \vec{B} \cdot \vec{I}$$

(4.46)

where $\vec{I} = (I_x, I_y, I_z)$ and $I_x, I_y, I_z$ are the Pauli matrices. One thus finds for the correlation function, similar to the former section:

$$g_{12}(\tau) = \langle |\mathcal{H}_\text{I}(t)|^2 |\mathcal{H}_\text{I}(t+\tau)|^2 \rangle = \frac{1}{4} \hbar^2 \gamma^2 I_0^2 \left( \langle \sigma^2_{x} \rangle + \langle \sigma^2_{y} \rangle \right) g(\tau)$$

(4.47)

The transition rate can then be written:

$$W_{12} = \frac{1}{4} \left( \langle \sigma^2_{x} \rangle + \langle \sigma^2_{y} \rangle \right) \cdot 2 \int_0^\infty g(t) \exp(-i\omega t) dt$$

(4.48)

if the mean square fluctuations are expressed in frequency units. The aim of the simulation was to calculate the value $\langle \sigma^2_{x} \rangle + \langle \sigma^2_{y} \rangle$ to estimate the maximal relaxation rate. The $T_1$ minimum is given by $\omega_c \tau_c \approx 1$ which yields for the spectral density, for which the BPP function Eq. 4.10 was assumed, the value $J(\omega) = \tau_c = 1/\omega_L$. For the $T_1$ minimum we find thus:

$$\frac{1}{T_1} = \frac{1}{4} \left( \langle \sigma^2_{x} \rangle + \langle \sigma^2_{y} \rangle \right) \frac{1}{\omega_L}$$

(4.49)
Figure 4.5: Mean square fluctuations $\langle \sigma_{xz}^2 \rangle + \langle \sigma_{yz}^2 \rangle$ in units of kHz$^2$ of the chemical shift interaction for the $a$-rotation (left) and $c$-rotation (right).

Fig. 4.5 shows the mean square fluctuations $\langle \sigma_{xz}^2 \rangle + \langle \sigma_{yz}^2 \rangle$ in units of kHz$^2$ as a function of the angle for the rotation around the $a$ and $c$ axis. One can see that the mean square fluctuations depend on the $^3$P site (A, B, C, D, Figs. 6.16-6.18) and also on the angle. Eq. 4.49 yields thus $T_1$ values which are of the order of 100 s to 500 s, whereas the measured value for the orientation $a \perp H_0$, $\langle c.H_0 \rangle = 40^\circ$ amounts to 27 s at $T = 77$ K. This shows that the mean square fluctuations are larger by a factor 4 to 20, corresponding to approximately 2 to 4.5 higher $\sigma$ tensor values. In Sec. 6.5 we estimate the chemical shift tensor values for the Takagi groups and find that these are of the same magnitude as those for the AFE and FE Slater groups. One possibility to explain this discrepancy is of course that the microscopic nature of the relaxation has to be taken into account. That means that also Takagi groups with zero or four deuterons close should occur for the relaxation process, since we assume that their chemical shift tensor elements are larger than those of the Takagi groups with one or three deuterons close.
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Chapter 5

2D measurements and simulations

In contrast to line shape and spin-lattice relaxation measurements, the observation time of which is of the order of the inhomogeneous spin-spin relaxation time \( T_2^* \approx 10^{-4} \) s, this time scale can be extended to several hundreds of seconds with two dimensional (2D) exchange measurements. In this experiments it is possible to correlate a spin state for two particular points in time, the difference of which is called mixing time. Thus it is possible to monitor motions with frequencies which are of the order of the inverse mixing time and which can be so small as the inverse spin-lattice relaxation time \( T_1^{-1} \).

In this chapter we introduce first the technique of the 2D exchange measurements. Then we turn to \(^{87}\text{Rb} 2\text{D exchange measurements. We have seen in Ch. 3 and 4 that the rubidium NMR line shape is strongly influenced by the positions of the deuterons within a range of 1.5 nm. With 2D exchange measurements it should be possible to monitor the deuteron motions as a function of temperature and time. Here we will present a model to simulate the measured \(^{87}\text{Rb} 2\text{D exchange spectra, with which we try to explain the dynamics of the deuterons around the rubidium atom.}\)

Then we report on \(^2\text{H} 2\text{D exchange measurements. The major difference to the rubidium atoms is that the deuteron atoms are not ionically but covalently bound. This implies then that the EFG tensor at the deuterium site depends only on its actual position on the bond. All surrounding deuterons do not influence the EFG tensor at the deuteron site under consideration. Its largest component \( V_{zz} \) points along the O-D-O axis and \( V_{yy} \) makes angles \( \pm 35^\circ \) with respect to the \( z \) axis, which makes the two sites physically inequivalent and gives rise to resolved lines in the spectrum [30].\)

The measurements are performed in the temperature range from 45 - 150 K, where the deuterons are in the fast motion regime. Thus in a \(^2\text{H} 2\text{D experiment the time-averaged polarizations for two distinct points in time are compared. Since the time averaged polarization is directly connected to the bias of the bond, we are able to tell, whether and how fast the bias changes during the mixing time.} \)
5.1 The 2D exchange technique

5.1.1 Basic pulse sequence

In Fig. 5.1 the basic pulse sequence for a 2D exchange experiment is sketched. The three main parts of the pulse sequence are the preparation and detection period before and after the mixing period, whereas the latter is much longer than the two former. The spin states before and after the mixing time must be correlated to reveal the dynamics of the spin system during that time. For the sake of simplicity let's assume that we are dealing with a spin system which can have only two different Larmor frequencies $\omega_0^{(1)}$ and $\omega_0^{(2)}$. This may be due to different spatial positions of the spin itself like in the case of $^2$H or because of the different surroundings like in the case of rubidium. We are interested in monitoring transitions between the two different states. Let's take a look at the group of spins which are at the beginning of the experiment in state 1 with the Larmor frequency $\omega_0^{(1)}$. The first pulse ($P_1$) takes the magnetization to the $x,y$ plane, where it begins to precess according to its Larmor frequency $\omega_0^{(1)}$. The higher $\omega_0^{(1)}$ the larger the precession angle during the evolution time $t_1$. The second pulse ($P_2$) takes the $y$-component of the rotated magnetization back to the $z$-direction. Thus the information about the Larmor frequency $\omega_0^{(1)}$ is now stored in the magnitude of the magnetization. The spins which change their Larmor frequency during the mixing time precess after the last pulse ($P_3$) with $\omega_0^{(2)}$. A series of experiments is carried out with $t_1$ being incremented making possible a Fourier transformation in $t_1$ and $t_2$ direction. If some of the spins have changed their Larmor frequency from $\omega_0^{(1)}$ to $\omega_0^{(2)}$, a signal called cross peak appears in the 2D frequency spectrum at the position $(\omega_0^{(1)}, \omega_0^{(2)})$. The signal of the other spins which did not undergo a net change during the mixing time, for example from $\omega_0^{(1)}$ to $\omega_0^{(2)}$ and back to $\omega_0^{(1)}$, appear on the diagonal at the position $(\omega_0^{(1)}, \omega_0^{(1)})$.

If the mixing time $t_{mix}$ is varied, the time dependence of the transition between the two states can be monitored. The described method is very useful as long as the resonance lines in the 1D spectrum are resolved, since in the 2D spectrum the cross peaks do not overlap either. Therefore this method is successful in NMR of liquids, since the fast rotation of the molecules averages out all anisotropic interactions which leads to sharp lines with a width of a few Hz [27].

In the solid state, however, the dipole-dipole interaction induces a broadening of the resonance lines which can amount to more than 100 kHz. In this case the cross peaks overlap, but more important is the fact, that the cross peaks overlap with the diagonal peak, which makes the distinction between dynamic and static signals impossible. The NMR lines are many times also strongly inhomogeneously broadened, representing a continuous distribution of
resonances. In such a case, the cross peaks will also be continuous and will overlap among themselves and with the diagonal peaks. A solution for this problem is provided by the 2D exchange difference pulse sequence as will be discussed in the next section.

![Diagram of exchange pulse sequence](image)

Figure 5.1: Basic exchange pulse sequence. The echo is formed at the position $t_2 = t_1$.

### 5.1.2 Application to unresolved spectra

Fig. 5.2 shows the same pulse sequence twice, where however the time intervals $t_w$ and $t_{mix}$ differ. Let’s neglect the part denoted as “$T_1$-weighting” for a moment. Then the pulse sequence corresponds basically to the 2D exchange experiment as outlined in the former section but with an additional echo pulse $(P_0, P_{12})$, which however is not important in this context. The experiment is performed in such a way, that in addition to the normal 2D experiment with a particular mixing time $t_{mix1}$ a second experiment with a much shorter mixing time $t_{mix2}$ is made. Since $t_{mix2}$, still being larger than the preparation and detection time, is chosen so short, that no motion can take place in this period, this experiment in fact corresponds to a static picture of the system. The static spectrum is then subtracted from the dynamic one with the long mixing time $t_{mix1}$. Since the width of the dynamic spectrum is larger than that of the static one and the integral intensity for both is identical, the resulting difference spectrum shows positive cross peaks and negative diagonal peaks. The cross peak in fact corresponds to those spins that underwent a net motion during the mixing time and can, due to the different sign, very well be discriminated from the diagonal peak.

So far we did not mention the $T_1$-weighting time prior to the 2D exchange sequence. This additional pulse sequence corrects for the differently relaxed $z$-magnetizations during the mixing times $t_{mix1}$ and $t_{mix2}$. The first two pulses $(P_1(7), P_2(8))$ take the magnetization to the $(−z)$ direction and it relaxes during the weighting times $t_{w1}$, $t_{w2}$ because of the spin lattice ($T_1$) relaxation. Since the weighting times are chosen in such a way that

$$t_{w1} + t_{mix1} = t_{w2} + t_{mix2}$$  \hspace{1cm} (5.1)
the amount of relaxed magnetization is identical in both experiments which allows for a
direct comparison of the spectra.

2D exchange difference NMR with the so called $T_1$-weighting is thus a useful method for
monitoring slow motions in systems with overlapping resonance lines.

![Diagram of 2D exchange difference pulse sequence with $T_1$-weighting.](image)

Figure 5.2: 2D exchange difference pulse sequence with $T_1$-weighting. The echo pulse $P_{6(12)}$ shifts
the echo to the position $t_2 = t_1$, where it is well separated from the last pulse.

### 5.2 $^{87}$Rb 2D exchange difference measurements

As already stated the Rb atoms in D-RADP-X are ionically bound. Because of the qua-
drupole interaction the Rb NMR frequency is sensitive to the arrangement of the deuterons
on their bonds in a range of 1-2 nm. We have seen in Fig. 1.3 that the Rb line shape (1D)
measurements can distinguish between various local correlations of the deuterons. On the
other hand, 2D measurements should allow for a determination of the dynamics of the local
deuteron order.

In Ch. 6 we will see that at temperatures smaller than 50 K, D-RADP-50 forms a Slater
lattice, that means that two deuterons are close to a PO$_4$ group and two are far.

We are interested in whether the local structure changes with time, what the time constants
are, and whether there is a particular size of structure that changes as a whole, or whether
the changes are only local. Provided that the low temperature structure is a Slater lattice and
the dynamics can be described by the motion of Takagi-defects, only single O-D···O bonds
are affected and we cannot expect correlated changes of large structures.

In Ref. [20] 2D exchange difference measurements of $^{87}$Rb in D-RADP-50 are reported in the
temperature region between 40 K and 50 K to monitor the motion of the deuterons in the glass
state. For $T = 50$ K the mixing time was set to values between 20 ms and 700 ms. Dynamic
5.2. \(^{87}\text{Rb}\) 2D EXCHANGE DIFFERENCE MEASUREMENTS

Figure 5.3: \(^{87}\text{Rb}\) 2D exchange measurements of D-RADP-50. Left: \(T = 50\ \text{K}, t_{\text{mix}} = 10\ \text{ms}, t_w = 500\ \mu\text{s}\). Right: \(T = 40\ \text{K}, t_{\text{mix}} = 1\ \text{s}, t_w = 1\ \text{ms}\). [20] Note that both spectra show the same Rb line, but for the spectrum on the left hand side, the upper mirror copy was chosen for display.

effects could be unambiguously detected for these mixing times, however the frequency jumps did amount only to 1-2 kHz although the total 1D spectrum extends over a much larger frequency range as shown in Figs. 5.3. Basically the same observation was made for \(T = 45\ \text{K}\) and \(T = 40\ \text{K}\) for mixing times between 10 ms and 1 s.

The following model based on the point-charge model as outlined in Ch. 3 was investigated to explain the measured spectra. In this model the random distribution of \(^{87}\text{Rb}\) and \(\text{ND}_4\) is not taken into account.

5.2.1 Model with independent deuteron jumps

We have seen in Eq. 3.16 that for the orientation \(c||H_0\) the shift of the \(^{87}\text{Rb}\) Larmor frequency due to the quadrupole interaction can be written as a function of \(\Delta V_{ij}\) only, which can be calculated using a point-charge model (Ch. 3). In this way it is possible to calculate the \(^{87}\text{Rb}\) NMR frequency for every particular deuteron configuration of its nearest 8 deuterons, which give the major contribution to the EFG tensor at the Rb site. The easiest model is to assume that during the mixing time of a 2D experiment a particular deuteron configuration can achieve any of the \(2^8\) possible configurations with equal probability by independent jumps of the deuterons. With a Monte Carlo simulation a starting configuration \((p_1, p_2, \ldots, p_8)\) with \(p_i = \pm 1\) is created which yields the corresponding frequency \(v_{\text{initial}}\). In the same way the frequency \(v_{\text{final}}\) for another configuration after the mixing time is calculated. Obviously, the frequency pair \((v_{\text{initial}}, v_{\text{final}})\) corresponds to a cross peak in the 2D exchange spectrum.
This procedure is repeated several times for random initial and final configurations and the corresponding frequency pairs stored in a two-dimensional histogram. As can be seen in Figs. 5.3 and 5.4, the simulated spectrum does not reproduce the measured one, since a considerable amount of cross peaks are too far away from the diagonal. This discrepancy can not be removed even if one restricts to a jump of only one of the 8 deuterons as it is shown in Fig. 5.4. Also if one demands that all 8 deuterons jump simultaneously the cross peaks are farther away from the diagonal than observed experimentally.

This shows unambiguously that the jumps of the 8 nearest deuterons are not independent. It should be noted that according to $T_1$ measurements the motion is so fast that during the mixing time more than one deuteron changes its position. Only a selected combination of several deuteron jumps leads to the observed small frequency shifts.

In a new model we try to introduce a restriction for the deuteron motion to improve the calculated 2D exchange spectrum.

### 5.2.2 Model with restricted jumps

The 32 nearest deuterons were included to calculate the EFG tensor to provide a much smoother frequency distribution. In this model a large number of PO$_4$ groups around the central rubidium atom was taken into account, namely all PO$_4$ groups within 6 lattice constants in $x$- and $y$-direction and 8 in $z$-direction. To account for the restricted motion of the deuterons, we imagine that the lattice consists of Slater groups (D$_2$PO$_4$) and that a deuteron can only change its position when it is passed by a Takagi defect (DPO$_4$ or D$_3$PO$_4$) which
is also present in the lattice as described in Ch. 2. The restriction was fulfilled in the following way. First, the PO₄ lattice was set to an antiferroelectric deuteron configuration. Then one of the AFE PO₄ groups was changed to a FE configuration. It is easy to see that this can be achieved when two deuterons of the selected PO₄ group are shifted, one is added to the PO₄ group and one removed. This process yields thus a FE PO₄ group and two Takagi defects (DPO₄ and D₃PO₄), being adjacent to the FE Slater group. With a Monte Carlo simulation, these Takagi groups are shifted randomly through the crystal, for instance a D₃PO₄ defect can move in the direction of one out of three bonds where the deuterons are close, just by shifting the corresponding deuteron from near to far. The fourth direction however is forbidden in our model, since a D₄PO₄ group with 4 deuterons would be created, which is an energetically highly unfavorable state. Clearly, the two Takagi defects can annihilate, in this case again two new defects are created in our model. For all these calculations periodic boundary conditions were used.

This procedure maintains the Slater configuration of all PO₄ groups, except for the fact that two Takagi defects are present, of course. To achieve a random Slater lattice, which is the initial configuration for the simulation, the Takagi defects have to perform a large number (≈ 10⁷) of moves. It is obvious that the positions of the 32 nearest deuterons change in a restricted way, when the Takagi defects pass through the corresponding PO₄ groups.

This model can thus be used to calculate the 1D line shape, just by storing the different NMR frequencies due to the various deuteron configurations which are created because of the motion of the Takagi defects. In Fig. 3.1, Sec. 3.4 the comparison between simulated and measured line shape is shown.

For the calculation of the 2D exchange spectrum we proceeded in a similar manner as for the model with the eight nearest deuterons in the previous chapter. Again we started with a deuteron configuration with frequency ν_initial, then the Takagi defect can move for a particular number N of steps and the frequency ν_final of the achieved configuration is calculated. The pair (ν_initial, ν_final) is again stored in a 2D frequency histogram. Obviously the number N can be related to the velocity of the Takagi defects.

Fig. 5.5 shows the simulated 2D spectra for two different values of N, which is the number of Takagi steps before calculating the new frequency. The points on the diagonal were set to zero. The width of the cross peaks for 16 steps (left figure) is rather narrow, like in the measured spectra (Fig. 5.3). The simulation with 4096 steps shows much broader cross peaks like in the former simulation with independent deuteron jumps. If one assumes that the total number of steps is related to the length of the mixing time, we should observe for long mixing times a spectrum comparable to the figure with 4096 steps.

In Fig. 5.6 the integrated intensity as a function of the difference from the diagonal is plotted
Figure 5.5: Contour plot of simulated $^{87}$Rb 2D exchange spectra with the diagonal peak set to zero. Left: 16 Takagi steps between the calculation of the initial and the final frequency. Right: 4096 Takagi steps.

Figure 5.6: Simulation of a 2D exchange spectrum with 16 Takagi steps (solid line) and 4096 Takagi steps (dotted line). Intensity as a function of frequency difference from the diagonal of the cross peaks. Both plots are area-normalized.
for 16 and 4096 Takagi steps. Since both plots are area-normalized, one observes that for
16 steps most of the off-diagonal intensity is within ±4 kHz of the diagonal. For 4096 steps
we find that the intensity is also predominantly in that region but still a part can be found
at larger distances from the diagonal. Experimentally, one observes at long mixing times,
for example for $t_{\text{mix}} = 1\, \text{s}$ at $T = 40\, \text{K}$, still only narrow cross peaks. This is in contrast to
our model where we expect large frequency jumps, when the Takagi groups perform a large
number of steps to achieve a new configuration.

This discrepancy may reside in the oversimplified Takagi defect model. In reality not only
two but a considerable number of defects are present in the crystal, therefore it may be that
the motion of deuterons is even more restricted, since one can imagine that a larger amount
of Takagi defects could lead to a reduction of their mobility. For example if a Takagi group of
a certain kind, for example with 3 deuterons close, moves along a chain of O-D-…O bonds,
then the same way for an equivalent Takagi group is forbidden. Only a Takagi group with
one deuteron can go in the same direction or a Takagi group with 3 deuterons can go in the
opposite direction.

This problem could be attacked in a further model, but then a more sophisticated algorithm
for the Takagi-defect motion should be found. Of course also the random distribution of Rb
and ND$_4$ should be included in the model. Since the ND$_4$ molecule occupies an off-center
position, the two closest O-D-…O deuterons are repelled (see Fig. 2.1). That means that the
asymmetry of the bonds in the lattice which in our model is dependent on the arrangement
of the deuterons also experiences an amplification or a reduction depending on the off-center
position of the ND$_4$ molecule.

One can thus imagine that in the case of a larger asymmetry, the corresponding freedom of
motion of a Takagi group is canceled. On the other hand, if the bias due to the ice rules and
that due to the ND$_4$ position are of opposite sign, the corresponding bond becomes nearly
symmetric provided that both asymmetries are of the same order of magnitude. This effect
enhances then the creation probability of a Takagi pair (see Fig. 2.2).

Clearly the bias introduced by the ND$_4$ molecule can also fluctuate as long as the temperature
is high enough to allow reorientational motions of the whole ND$_4$ molecule. This is fulfilled
for temperatures above 110 K. In Refs. [3, 6] the activation energy of the ND$_4$ motion was
determined as 160 meV and the $T_1$ minimum of the ND$_4$ deuteron spin-lattice relaxation is
at 160 K. If one assumes $\tau_c(\omega_c) \approx 1$ for this temperature and takes into account the Arrhenius
law for $\tau_c$, one finds for $\tau_{\text{cav}}$ the value $3.8 \times 10^{-9}\, \text{s}$. For $T = 90\, \text{K}$ the autocorrelation time $\tau_c$
of the ND$_4$ motion thus amounts to 3.4 s which shows that the ND$_4$ reorientational motion
is completely frozen in below these temperature. Although the reorientational motion of the
whole ND$_4$ molecule is frozen in, meaning that the N-D-O bonds are fixed, it is still possible
that the off-center position of the nitrogen atom may fluctuate since it is natural to assume that a much lower energy barrier is present for that motion.

From that point of view, the bias energy of the O-D-···O bonds consists of a contribution due to the ice rules and due to the different nitrogen off-center positions.

As a summary one can say that the comparison of the experiment with the model of independent deuteron jumps shows that the motion of the deuterons must be restricted. This restriction can be modeled by a Slater lattice, the bias energies of which are changed by a motion of Takagi-defects. For a better description of the experiments the random field and a larger number of Takagi defects should be taken into account.

5.2.3 Model with small polarization fluctuations

In this section an alternative model is presented which could simulate the observed 2D exchange difference spectra. Again we assume that the PO₄ network forms a Slater lattice, where 2 deuterons are close and two are far, so that we are dealing with strongly polarized bonds. We assume that the polarization can be expressed as a sum of a large time independent polarization and a small varying fluctuation:

\[ p(t) = p_0 + \Delta p(t) \]  

(5.2)

For instance, \( p_0 = 0.9 \) and \( \Delta p(t) \) assumes values in the interval \([-0.1,0.1]\) so that the total polarization lies in \([0.8,1]\). In Fig. 5.7 two simulated 2D exchange spectra are displayed for \( p_0 = \pm 0.9, \Delta p(t) \in [-0.1, 0.1] \) (left) and \( p_0 = \pm 0.75, \Delta p(t) \in [-0.25, 0.25] \) (right). One can see that the spectrum along the diagonal (\( \nu_1 = \nu_2 \)), which corresponds to the 1D spectrum, is narrower for the latter case than for the former, which is not physical.

However one could imagine, that there are regions in the crystal having strongly polarized bonds \( p = \pm 1 \), which do not undergo any polarization changes, yielding thus a total width like in the normal 1D spectrum. Additionally, there are regions, where the polarization can fluctuate as described above and thus lead to cross peaks in the spectra, the diagonal width of them being smaller than the width of the 1D spectrum. Thus this interpretation could also explain the observations in the 2D exchange difference spectra as displayed in Figs. 5.3.

5.3 \(^2\text{H} \) 2D exchange difference measurements at 70-150 K

In the temperature region 70 - 150 K, the D-RADP-50 crystal is in the fast motion regime. In Sec. 4.3 the activation energy \( E_A = 1273 \) K, the single particle autocorrelation time at infinite temperatures \( \tau_\infty \) and the bias energy \( E_B = 144 \) K have been determined from the \( T_1 \)
5.3. $^2$H 2D EXCHANGE DIFFERENCE MEASUREMENTS AT 70-150 K

![Graphs](image)

Figure 5.7: Simulated $^{87}$Rb 2D exchange spectra, under the assumption that the polarization fluctuates, so that $p_0 = \pm 0.9$, $\Delta p(t) \in [-0.1, 0.1]$ (left) and $p_0 = \pm 0.75$, $\Delta p(t) \in [-0.25, 0.25]$ (right) data. Since for the autocorrelation time of the deuteron motion the following equation holds:

$$\tau_c = \sqrt{1 - p^2} \tau_e \exp \left( \frac{E_A}{kT} \right)$$

(5.3)

where the time averaged polarization is given by

$$p = \tanh \left( \frac{E_B}{kT} \right)$$

(5.4)

one finds $\tau_c = 0.2 \, \mu s$ at 70 K and $\tau_c = 0.15 \, \text{ns}$ at 150 K. These results show that the deuteron jumps are much faster than the integration time of NMR which is of the order of 1-2 ms. The $^2$H NMR line reflects then the time averaged polarization $p$ of the O-D- O bond. Since we expect that the Takagi motion is responsible for slow fluctuations of the bias energy $E_B$ and thus also of $p$ we performed 2D exchange difference measurements to observe these motions.

In D-RADA-32 (Rb$_{0.68}$(ND$_4$)$_{0.32}$D$_2$AsO$_4$) a very slow deuteron motion has been discovered below 50 K [10]. It could be shown in a 2D experiment that the deuterons jump between the potential minima. The observation that the cross peak and the diagonal peak have the same intensity for long mixing times leads to the important result that all O-D- O bonds are symmetric in the long time limit. The extrapolation of the measured exchange times to higher temperatures yields $\tau_c = 3 \, \text{s}$ at 70 K.

As outlined in Ch. 2 we imagine that there exist Takagi-groups in the crystal, defects with one or three deuterons close (ice rules violated) that can move like quasiparticles through the crystal. It is quite clear that a deuteron changes its position when it is reached by such a
defect. We further demand that defects with zero or four deuterons close can not be created because of the high energy needed.

If we assume that we have a jump of a deuteron on a bond that connects two Slater groups (D$_2$PO$_4$, D$_3$PO$_4$), then this jump creates two unpaired Takagi groups (D$_3$PO$_4$, DPO$_4$), that means one with three and the other with only one deuteron close. These Takagi groups can walk away or they annihilate when the proton jumps back.

It is quite reasonable to assume that the creation and annihilation process of unpaired Takagi groups is very fast, since we are dealing with an unequilibrium state. But there is also a small probability that the Takagi groups move away from each other, and we have a process that is changing the bias of the bonds in a rather slow manner (see Fig. 2.3). This process should be visible in our experiment but not the fast creation-annihilation process.

It is important to mention again, that during the preparation time of the 2D exchange measurement, we measure the time averaged polarization. The system evolves during the mixing time, and in the detection time also the time averaged polarization is measured. Since in this experiment we are able to correlate these two polarizations, we should be able to reveal slow polarization fluctuations during the long mixing time.

5.3.1 1D spectrum and rotation pattern

In an external magnetic field the Zeeman interaction induces a splitting of the energy levels of the nuclear spin. For $^2$H with nuclear spin $I = 1$ one gets thus three equidistant energy levels, yielding only one resonance line with frequency $\omega_L$ for the two allowed transitions $(m = 1) \leftrightarrow (m = 0)$ and $(m = 0) \leftrightarrow (m = -1)$.

The deuterons are further subject to the electric quadrupole interaction, which in the case of a high magnetic field can be treated as a small perturbation to the Zeeman interaction. The energy levels are shifted by an amount proportional to the square of the magnetic quantum number $m$, thus the single resonance line splits into two lines still centered around $\omega_L$. Thus for every deuteron a pair of lines exist. In Fig. 5.8(a) the $c$-projection of the D-RADP-X structure is shown, the projection of the O-D-...O bonds onto the $(a,b)$ plane is parallel either to the $x$ or $y$ direction, the corresponding bonds are thus denoted as X and Y bonds. In Fig. 5.8(b) the distinction between $X_+$ and $X_-$ bonds is made, because of the angle of 0.5° between these bonds and the $(a,b)$ plane. $X_+$ and $X_-$ refer to the direction the upper part of the bonds point to. Since the deuteron sites A and A' are connected by the symmetry element 2$_{1v}$ of the space group, the EFG tensor is equivalent, and the sites A and A' can thus not be distinguished in the NMR spectrum. Obviously the same holds for the sites B and B'. In Refs. [28, 29] the O-D-...O deuteron spectrum for KD$_2$PO$_4$ was measured, where the crystal
Figure 5.8: Figs. a) and b) show the c-projection of the D-RADP-X structure. Inside the squares displaying the PO₄ tetrahedra, their z-coordinate in units of the unit cell length is given. (b) X⁺ and X⁻ bonds with the possible deuteron positions A, A', B and B'.
was cooled below the Curie point while an electric field parallel to the c-axis was applied. Depending on the direction of the field only the lines owing to A,A' or B,B' appear in the spectra, whereas all four lines are present without an external electric field during cooling, since oppositely polarized domains were formed in the crystal.

Fig. 5.9 shows the $^2$H rotation spectra around the $a$-axis ($a \perp H_0$) at room temperature for a repetition rate of 120 s. At this temperature the $T_1$ time for the O-D...O deuterons amounts to about 200 s, whereas that of the ND$_4$ deuterons is around 100 ms [6]. The latter give rise to only two lines since the fast reorientation of the ND$_4$ molecule leads to a rotationally averaged EFG tensor [3]. The splitting of the ND$_4$ lines has a maximum of about 5 kHz at $c \parallel H_0$ what can be used for a proper orientation of the crystal c-axis. The other four lines belong to the X and Y bonds. The former show only a weak angular dependence because of the small angle between them and the rotation axis. On the other hand the $Y_+$ and $Y_-$ bonds show the expected $\cos^2(\beta)$ dependence.

In Fig. 5.10 the one-dimensional $^2$H spectrum at $T = 69$ K for the orientation $a \perp H_0$, $<c, H_0> = 33^\circ$ is displayed. Since the irradiation frequency (46.112 MHz) was not chosen in the center of the spectrum but was shifted by $\Delta = 44$ kHz, the intensity distribution is not
symmetric around the Larmor frequency $\omega_L = 46.068$ MHz. If one compares this to Fig. 5.9 one can see that the lines at $v = -44$ kHz correspond to the O-D...O Y bonds which are well separated from the lines of the X-bonds located at $v \approx -90$ kHz and $v \approx 0$ kHz. Since the ND$_4$ system is in contrast to Fig. 5.9 in the slow motion regime, the quadrupole interaction is no more averaged to a rotationally symmetric tensor, leading to the resonance lines at 25 kHz and $-110$ kHz.

### 5.3.2 Separation experiment

In a first step we did a separation experiment to discriminate between the homogeneous and the inhomogeneous line width [12]. If the latter is large with respect to the former it follows that we are dealing with a spatial distribution of bond asymmetries which is then the prerequisite for a 2D exchange experiment to monitor temporal fluctuations of the asymmetry.

The separation pulse experiment consists of a pulse sequence

$$90_\chi - \frac{t_1}{2} - 90_\chi - \frac{t_1}{2} - t_2$$

where $t_1$ is incremented like in the 2D experiments which allows then for a Fourier transformation of the signal as a function of $t_1$ and the acquisition time $t_2$. The amplitude of the echo signal is reduced because of the homogeneous or $T_2$ spin-spin relaxation. The projection of the 2D frequency spectrum onto the $\omega_1$ axis shows the homogeneously broadened
spectrum, whereas the projection onto the $\omega_2$ axis displays just the normal spectrum which is inhomogeneously broadened. As already mentioned the EFG tensor of $^2$H depends only on the position where the deuteron is located. Since in the fast motion regime the EFG tensor reflects the time averaged polarization of the bond, the inhomogeneous broadening is due to different bias energies of the O-D-·-O bonds.

We found the inhomogeneous broadening to be 17.4 times larger than the homogeneous one, what means that we are dealing with a distribution of asymmetric bonds.

### 5.3.3 Measurements

We performed thus 2D exchange difference measurements in the fast motion regime (70-150 K). Because of the fast intrabond exchange in this temperature range, the deuteron sites A and B' (Fig. 5.8(b)) can not be discriminated. However, as stated above, the line shape of the O-D-·-O lines reflects the time-averaged polarization distribution. The 2D experiments should reveal whether slow motions of the bias energies are present or not.

For the orientation $a \perp H_0$, $< (c, H_0) = 33^\circ$ as displayed in Fig. 5.10, the investigated X bond at 0 kHz is well separated from the other O-D-·-O Y and the ND$_4$ lines to exclude spin diffusion, which is the exchange of magnetization due to mutual spin flips of the corresponding spins [49, 50].

In Sec. 5.1.1 it was shown that the data processing requires the Fourier transform in $t_1$ and $t_2$ direction. The NMR signal as a function of $t_2$ can always be represented as a complex signal $f(t_1, t_2)$ because of the $\pi/2$ shift between the two receiver channels, what makes possible a complex Fourier transformation, giving the so called "interferogram" $f(t_1, \omega_2)$. For the Fourier transformation in $t_1$ direction, only the real part of $f(t_1, \omega_2)$ is used. The 2D spectrum thus consists of two mirror copies in the $(+|\omega_1|, \omega_2)$ and the $(−|\omega_1|, \omega_2)$ plane. Since we are only interested in the exchange spectrum visible in the X bond, the irradiation frequency was set in the middle between the X bond and the Y bond, so that the mentioned mirror copies do not overlap.

The experiments were performed using the 6-pulse sequence, i.e. $T_1$-weighting plus the four pulse exchange sequence, or the 5-pulse sequence, where the last echo pulse was skipped (see Sec. 5.5). The flip angle of all pulses was cycled between $\pm 90^\circ$ and the respective signals added or subtracted to eliminate all unwanted coherences. The 5-pulse sequence is advantageous over the 6-pulse sequence, since only $2^5$ instead of $2^6$ experiments have to be performed in a given phase cycling scheme. Also for the latter, for $t_1$ larger than $2\Delta$, the first echo appears in the acquisition time, $2\Delta$ before the proper echo. Nevertheless, if $\Delta$ is chosen large enough, both echoes are well separated and the unwanted echo can be cut out.
5.3. $^2$H 2D EXCHANGE DIFFERENCE MEASUREMENTS AT 70-150 K

Figure 5.11: 3D plot of $^2$H 2D exchange spectra at $T = 70$ K. Left: Dynamic signal $S_1$, $t_{m1} = 400 \mu s$, $t_{mix1} = 1000$ ms. Right: Static signal $S_2$, $t_{m2} = 1000$ ms, $t_{mix2} = 400 \mu s$.

The application of the 5-pulse sequence gives also a better resolution, since the signal was always larger than for the 6-pulse sequence because of the homogeneous $T_2$ relaxation. The 5-pulse sequence has the drawback, that for small values of $t_1$, the signal interferes with the last pulse $P_3$.

As already mentioned, the $t_1$ time had to be incremented. The first value was chosen to be $3 \mu s$, the increment was $4$ or $5 \mu s$, yielding a broad enough frequency range. The $t_2$ increment was $1$ or $2 \mu s$.

5.3.4 Processing of the files

Figs. 5.11 and 5.12 show plots of 2D exchange spectra at $T = 70$ K for a mixing time $t_{mix} = 1000$ ms. One can observe that the width of the dynamic signal ($t_{mix} = 1000$ ms) is larger than that of the static one ($t_{mix} = 400 \mu s$). This proves that the deuterons undergo motions during the mixing time, but the frequency changes are still restricted to a small range of about $2$ kHz.

Fig. 5.13 shows the difference of the dynamic ($S_1$) and the static ($S_2$) spectra. The cross peaks resulting from the deuteron bonds, which changed the bias during the mixing time, are well separated from the diagonal. The width of the cross peaks is determined by the length of the squares as shown in the figure. One has to pay attention to choose the proper contour level so that the noise amplitude is still smaller than the cross peak.

2D exchange difference spectra were measured as a function of the mixing time and temperature. The determination of the cross peak width was done in the following way. First the intensity of the 2D difference spectra $I_{(S_1-S_2)}(v_1,v_2)$ as a function of the mixing time was
Figure 5.12: $^2$H 2D exchange spectra at $T = 70$ K. Left: Dynamic signal $S_1$, $t_{w1} = 400 \mu$s, $t_{mix1} = 1000$ ms. Right: Static signal $S_2$, $t_{w2} = 1000$ ms, $t_{mix2} = 400 \mu$s.

Figure 5.13: $^2$H 2D exchange difference spectra at $T = 70$ K, dynamic - static signal ($S_1 - S_2$, Fig. 5.12), $t_{mix} = 1000$ ms.
normalized to one. For all spectra of a particular temperature, the contour plots (Fig. 5.13) of the 2D difference spectra were plotted where the contour levels \( I_{s_1-s_2} = \pm \alpha \) were chosen so that the length of the diagonal peak was identical. This is necessary to compare the width of the cross peaks for different mixing times. However, since the length of the diagonal peak was not equal for different temperatures, the widths of the cross peaks for different temperatures cannot be compared directly. For instance, the contour levels were chosen in the range [0.014, 0.03] for 70K, [0.02, 0.075] for 130K, and [0.011, 0.014] for 150K.

The width of the cross peaks was determined in the following way. As shown in Fig. 5.13, a square was drawn in the 2D spectra with the left-lower corner \((v, v)\) at the diagonal and the right-upper corner \((v + \Delta v, v + \Delta v)\) so that the right-lower corner \((v, v + \Delta v)\) touches the contour of the cross-peak. The same was done for the other contour above the diagonal. The absolute value \(\Delta v\) was determined at different points \(v_1\) of the diagonal and the mean value was calculated, which was then plotted as a function of the mixing time \(t_{\text{mix}}\) (Fig. 5.14).

The first and most important thing to notice is that although the total width of the line is about 18 kHz, the largest frequency jumps are only a few (4-5) kHz.

The second important observation is the fact that the width of the cross peaks in the 2D spectra does not rise slowly with increasing mixing time but is almost constant for all measured mixing times which shows that the bias fluctuations must be faster than 10 ms.
CHAPTER 5. 2D MEASUREMENTS AND SIMULATIONS

Figure 5.15: $^2$H 2D exchange spectra at $T = 45$ K. Left: Dynamic signal $S_1$, $t_{\text{mix}} = 1$ s. Right: Dynamic signal $S_1$, $t_{\text{mix}} = 10$ s. O-D⋯O deuteron peaks at $v = 15$ kHz and $v = 23$ kHz, indicated by fat arrows, pointing down. ND$_4$ peak at $v = 37$ kHz indicated as thin arrow, pointing up.

The width of the cross peaks strongly depends on the choice of the contour level as can be seen in Fig. 5.14.

5.4 $^2$H 2D exchange measurements at 45-55 K

At temperatures around 50 K, the deuterons are still in the fast motion regime, that means that the time scale of their motion is smaller than the integration time of NMR. In spite of that the deuteron line shape is double-peaked here, because also the polarization distribution $W(p)$ is double-peaked at these temperatures. We thus performed normal 2D exchange measurements at these temperatures to see whether cross peaks at the intersection of the two O-D⋯O frequencies appear, which can be assigned to bias fluctuations of the O-D⋯O bonds.

Fig. 5.15 shows the dynamic signal ($S_1$) for the mixing times 1 s and 10 s. No cross peaks are visible at the intersection of the two O-D⋯O deuteron peaks, the frequency of which is indicated by fat arrows. Only for $t_{\text{mix}} = 10$ s a broadening of the lines takes place and some intensity between the two O-D⋯O peaks is visible. This did not get more pronounced even if we increased the mixing time to 30 s.

The spectrum for 10 s however shows that there is an exchange between the ND$_4$ peak (thin arrow) and the neighboring O-D⋯O peak. We assigned that to spin diffusion. This is supported by the fact, that the spectrum in the O-D⋯O – ND$_4$ region did not change substantially when increasing the temperature to 50 and 55 K for the same mixing time of 10 s.
5.5 Appendix

Here we present calculations of the signal for the 2D exchange pulse sequence without the waiting period. The basic scheme is the three pulse sequence. An echo pulse $P_6$ may be added to separate the signal from the $P_3$ pulse for small $t_1$ values.

For the calculation we used the formulas describing the effects of $x$ and $y$ pulses on a spin $I = 1$ system and further the evolution of the density matrix $\rho$ due to the first-order quadrupole coupling, described in Ref. [33].

![Image](image.png)

Figure 5.16: 2D exchange sequence with four pulses.

5.5.1 Four pulse sequence

Fig. 5.16 shows the same pulse sequence as in Fig. 5.2 without $T_1$-weighting. Starting with pure $z$-magnetization, the calculation of the pulse sequence as depicted yields the density operator

$$\rho = I_z [\cos(\omega_1 t_1 + \omega_2 t_2) + \cos(\omega_1 t_1 - \omega_2 t_2)]$$

(5.5)

provided that the double quantum coherences are decayed after the mixing period. $\omega_1$, $\omega_2$ are the resonance frequencies during the preparation ($t_1$) and detection ($t_2$) period, respectively. If we set $\omega_1 = \omega_2$, the arguments of the cosine terms of Eq. 5.5 are zero and two echo signals are formed at the time $t_2 = \pm t_1$. The first one is called virtual echo, since it appears earlier as $t_1$ is increased. This was never observed in the $^2$H experiments. However a more intense signal was observed which appeared before the real echo at $t_2 = t_1 - 2\Delta$. This is attributed to the signal which would occur if only a three pulse sequence was used as will be outlined in the next section (Sec. 5.5.2). It turned out that this echo always has the same phase as the desired echo and can thus not be eliminated by the phase cycling.

An advantage of the four pulse sequence is that all echo signals are separated from the last pulse and thus never lie in the dead time of the spectrometer.
5.5.2 Three pulse sequence

This pulse sequence (Fig. 5.17) is the same as the one above, but the echo pulse is skipped. With the same assumptions as for the four pulse sequence, we find the density operator:

$$\rho = I_y [\cos(\omega_1 t_1 + \omega_2 t_2) + \cos(\omega_1 t_1 - \omega_2 t_2)]$$  \hspace{1cm} (5.6)

Again two echoes form, separated by $2t_1$, before (virtual echo) and after $P_5$, whereas only the latter was observed experimentally.

The advantages of this pulse sequence are that it is less time consuming since less pulses have to be cycled which is crucial when the $T_1$ relaxation time is very long. Of course it is in this case important that the signal-to-noise ratio is good enough for one sweep only. Compared to the four pulse sequence a larger signal amplitude is measured which enhances thus the resolution.

The disadvantage is that the signals for the first experiments (small $t_1$) interfere with the dead time of the last pulse.
Chapter 6

Chemical shift perturbed NMR of $^{31}$P in D-RADP-X

$^{31}$P spin lattice relaxation ($T_1$) measurements are a good means to reveal the dynamic and structural properties of the spin glass system D-RADP-X. The use of a spin 1/2 nucleus over quadrupolar nuclei has the advantage that it has only one transition, so that it is easier to separate effects due to a distribution of correlation times from multilevel quadrupolar effects. It is expected that the $^{31}$P spin-lattice relaxation depends on the nearest hydrogens, which can be the "acid" (O-H···O) hydrogens as well as the hydrogens of the NH$_4$ groups. In Ref. [1], for ADP (NH$_4$H$_2$PO$_4$) and D-ADP (ND$_4$D$_2$PO$_4$) a single Bloembergen-Purcell-Pound [4] (BPP)-type $T_1$ minimum is observed. The $T_1$ minima appear at $T = 180$ K and $T = 168$ K for pure D-ADP and ADP, corresponding to a single activation energy of $E_A = 165$ meV and 186 meV, respectively. The similarity of the activation energies as well as the temperatures for the $T_1$ minima obtained from $^{31}$P and ND$_4$ deuteron data, suggest that the same mechanism (ND$_4$ reorientation) is responsible for the relaxation [2, 6, 3]. Therefore the single $T_1$ minimum can be attributed to NH$_4$ reorientations and the effects of the O-H···O motion on the $^{31}$P relaxation in the pure compounds D-ADP and ADP can be ruled out. This is also confirmed by $^{31}$P measurements on a pure RDP single crystal which yielded no $T_1$ minimum over the temperature range 180-77 K. Since for NH$_4$H$_2$PO$_4$ and ND$_4$D$_2$PO$_4$ no further $T_1$ minimum has been observed at lower temperatures, this means that either $\omega_k \tau_c = 1$ is not satisfied for the motion of the acid hydrogens or the mean square fluctuations of the interaction are too small to induce relaxation (Sec. 4.5).

The measurement of $T_1$ as a function of temperature for the mixed crystals D-RADP-X with $0.01X = x \approx 0.22 - 0.78$ yields a high-temperature ($T = 180$ K) $T_1$ minimum similar to the pure compounds. However at $T = 77$ K a second $T_1$ minimum appears. Since this tempera-
ture is very close to that at which the \( T_1 \) minima for \(^{87}\text{Rb} \) and O-D-\( \cdots \)O were observed, it is also attributed to the slowing down of the O-D-\( \cdots \)O deuteron motion.

Concerning the dependence of the pseudo-spin glass state formation on ammonium concentration, one finds that the low-temperature peak of the \( T_1 \) minimum for the \( x = 0.78 \) crystal is significantly flattened out, indicating that this ammonium concentration \( x \) may correspond to the borderline concentration for a pseudo-spin glass state [1].

These results show that it is possible to probe the occurrence of the pseudo-spin glass state via the \(^{31}\text{P} \) spin-lattice relaxation measurements. One can unambiguously show the crucial role of the hydrogens in the formation of the pseudo-spin glass. To further investigate the dynamics of the glass state we performed line shape measurements to monitor the microscopic features of the glass state formation (Sec. 6.6).

In Ch. 5 we used the model of a Takagi defect, which passes through a Slater lattice and thus changes the bond asymmetries to simulate the 2D exchange spectra of \(^{87}\text{Rb} \). In Sec. 6.7 we interpret our measurements of the chemical shift perturbed \(^{31}\text{P} \) NMR spectra in terms of this model.

We show that at low temperatures only the six Slater groups (\( \text{D}_2\text{PO}_4 \)) are visible in the spectra what implies that D-RADP-50 in fact forms a Slater lattice.

We assume that the observed line shape transition at higher temperatures is due to transitions between the Slater groups, giving us the possibility to determine an activation energy and an inverse attempt frequency.

Further we perform \(^{31}\text{P} \) 2D exchange measurements to see whether transition between the Slater groups appear. These results can then be compared with the exchange times determined from the observed line shape transition.

### 6.1 Introduction

The spin Hamiltonian of a nucleus with spin quantum number \( I = 1/2 \) can be written as:

\[
\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{CS} + \mathcal{H}_D
\]  

(6.1)

The Zeeman-interaction \( \mathcal{H}_Z \) is much larger than the dipolar interaction \( \mathcal{H}_D \), which is usually again larger than the chemical shift interaction \( \mathcal{H}_{CS} \). There are still two possibilities to make visible the chemical shift interaction \( \mathcal{H}_{CS} \). One is the use of multi-pulse techniques developed by Waugh. Huber and Haeberlen by averaging out the spin part of the truncated dipolar Hamiltonian \( \mathcal{H}_D \). The other is the use of strong magnetic fields, which enhance the magnitude of the chemical shift interaction, since it is proportional to the applied magnetic field.
6.1. INTRODUCTION

The chemical shift interaction $\mathcal{H}_{CS}$ describes the shift of the Larmor frequency due to the screening of the external magnetic field $B_{\text{ext}}$ by the electrons in the atomic orbitals. Since the electron density is orientation dependent it is described by a second rank tensor, which is called the chemical shift tensor.

The effective magnetic field at the nucleus site can be written as:

$$B_{\text{eff}} = B_{\text{ext}} + \Delta B = B_{\text{ext}} + \sigma B_{\text{ext}} = (1 + \sigma)B_{\text{ext}}$$

(6.2)

The shift of the Larmor frequency is usually very small, thus the values of the chemical shift tensor are usually expressed in parts per million (ppm).

In Ref. [9] the ferroelectric transition of KD$_2$PO$_4$ was monitored by $^{31}$P chemical-shift perturbed NMR. The chemical shift tensor for temperatures above the phase transition temperature is given by a single tensor which is axially symmetric whereas below $T_c$ four different sigma tensors corresponding to the two FE domains and the two inequivalent $^{31}$P sites exist, connected by the symmetry elements. The space group of the low temperature phase is $F\overline{d}d2$ (Sec. 6.2). These results are given in Tables 6.1 and 6.2.

Table 6.1: Chemical shift tensors for KD$_2$PO$_4$ at $T > T_c$

$$\sigma [\text{ppm}] = \begin{bmatrix} 12 & 0 & 0 \\ 0 & -15 & 0 \\ 0 & 0 & -15 \end{bmatrix}$$

Table 6.2: Chemical shift tensors for KD$_2$PO$_4$ at $T < T_c$

$$\sigma_{1,4} [\text{ppm}] = \begin{bmatrix} 30 & \mp 52 & 0 \\ \mp 52 & -15 & 0 \\ 0 & 0 & -15 \end{bmatrix}, \quad \sigma_{2,3} [\text{ppm}] = \begin{bmatrix} -15 & \pm 52 & 0 \\ \pm 52 & 30 & 0 \\ 0 & 0 & -15 \end{bmatrix}$$

The phosphorus atoms in KDP (KH$_2$PO$_4$) type structures are in the center of a tetrahedron of oxygen atoms. Since the PO$_4$ tetrahedra are connected via hydrogen bonds which form a double well potential, the chemical shift tensor at the $^{31}$P site depends on which side of the bond the hydrogen atoms can be found.

We assume that the four hydrogen atoms that belong to the four oxygen atoms around the phosphorus atom give the major contribution to its chemical shift (CS) tensor. Thus chemical shift perturbed NMR of $^{31}$P is a powerful tool to monitor the conformation of the deuterons of a D$_2$PO$_4$ group in D-RADP-X. It is necessary to measure rotation spectra around the
main axes of the crystal which then allow for the determination of the chemical shift tensor elements.

In Sec. 6.2 the angular functions of the chemical shift perturbed line-positions are developed by taking into account the symmetry elements of the crystal. Then in Sec. 6.3 the rotation pattern for antiferroelectric D-RADP-95 is shown and the corresponding chemical shift tensor is determined. The $a$- and $c$-rotation patterns of D-RADP-50 for a few temperatures between 45 K and 168 K are shown in Sec. 6.4. For particular orientations the line shape as a function of temperature recorded with much smaller temperature steps is presented. In Sec. 6.7 the line shape is calculated theoretically as a function of the exchange rate for a six-site exchange, which is then compared to the experimental one to determine the exchange rates as a function of temperature (Sec. 6.7.3).

6.2 General

The chemical shift tensor in the crystal eigenframe can be written as a sum of an isotropic and an anisotropic part,

$$\sigma = \sigma_{\text{isotropic}} + \sigma_{\text{anisotropic}} = \begin{bmatrix} \sigma_{\text{iso}} & 0 & 0 \\ 0 & \sigma_{\text{iso}} & 0 \\ 0 & 0 & \sigma_{\text{iso}} \end{bmatrix} + \begin{bmatrix} \sigma_{xy} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \quad (6.3)$$

where we have assumed that the latter is symmetric [17]. By definition the trace of the anisotropic part is zero.

$$\text{tr}(\sigma) = 0 \iff \sigma_{xx} + \sigma_{yy} + \sigma_{zz} = 0 \quad (6.4)$$

In the following we denote the anisotropic part of the chemical shift tensor as $\sigma_a$. To calculate the chemical shift tensor $\sigma'_a$ in the laboratory frame, we have to perform an orthogonal transformation $R$:

$$\sigma'_a = R\sigma_a R^{-1} \quad (6.5)$$

where $R$ is the transformation from the crystal to the laboratory frame.

The frequency shift ($\nu_L \to \nu_L + \Delta\nu$) can then be calculated using the following relation:

$$\frac{\Delta\nu}{\nu_L} = \frac{\Delta B_z}{B_z} = \sigma'_{zz} \quad (6.6)$$

6.2.1 Angular functions for the $a$-rotation

Let's suppose that the crystal is oriented in such a way, that the $a$, $b$ and $c$ axes are parallel to the laboratory frame given by $(x,y,z)$. For the $a$-rotation by the angle $\beta$ the orthogonal
transformation $R$ is given by

$$R = R_{11}(\beta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \beta & \sin \beta \\ 0 & -\sin \beta & \cos \beta \end{bmatrix}$$  \hspace{1cm} (6.7)

and we find for $\sigma_{zz}$ as a function of the rotation angle $\beta$:

$$\sigma'_{zz} = -\frac{1}{2} \sigma_{xx} + \frac{1}{2} (\sigma_{zz} - \sigma_{yy}) \cos(2\beta) + \sigma_{yz} \sin(2\beta)$$  \hspace{1cm} (6.8)

### 6.2.1.1 Antiferroelectric lines for the $a$-rotation

The symmetry group of antiferroelectric ND$_4$D$_2$PO$_4$ is $P2_12_12_1$. $2_{1x}$ connects two PO$_4$ groups (A-B and C-D) in the direction of the rotation axis (See Fig. 6.17). We see from Eqs. 6.8 and 6.30 that these two groups have the same chemical shift. However $2_{1y}$ connects two PO$_4$ groups (A-D and B-C) in the direction orthogonal to the rotation axis. The sine-part of the chemical shift has positive and negative sign for the two groups, respectively. This gives us a means to identify some of the lines in the rotation spectra.

For temperatures below $T = 240$ K \cite{22} the symmetry group $P2_12_12_1$ for antiferroelectric ND$_4$D$_2$PO$_4$ is a subgroup of $I\bar{4}2d$ which is the space group of the paraelectric high temperature phase. The four different AFE domains (1, 2, 3, 4) are thus connected by the symmetry elements belonging to $I\bar{4}2d$ but not to the subgroup $P2_12_12_1$. These are for example $4_z$ and $2_c$. A further hint to discriminate between lines of the four different domains comes thus from the lost symmetry elements. From the symmetry element $4_z^2 = 2_z$ and Eq. 6.32 we find that two domains (1 and 2 of Fig. 6.17) have the same cosine but alternating sine terms.

The symmetry element $4_z$ (Eq. 6.33) gives the connection between AFE domains 1 and 3 (Fig. 6.17, 6.18), which results in a different amplitude of the cosine term and also for the sine term as can be seen from Eqs. 6.8 and 6.33.

The following table (Table 6.3) summarizes the angular dependence of the frequency for the different domains (1, 2, 3, and 4) and the PO$_4$ sites (A, B, C, and D), see Fig. 6.17.

### 6.2.1.2 Ferroelectric lines for the $a$-rotation

The symmetry group for ferroelectric RbD$_2$PO$_4$ is $Fdd2$. The symmetry element $d$ denotes a diamond glide plane, given by a mirror operation $m_{xy}$ or $m_{yx}$ followed by a translation. $m_{xy}$ connects neighboring (i.e. A-B, B-C) PO$_4$ groups. On the other hand, $2_z$ makes the connection between two PO$_4$ groups (A-C and B-D), that are not directly linked. It is clear that twice the operation $d$ can substitute for $2_{1z}$. Since $d$ is given by Eq. 6.35 and therefore $d^2 = 1$ we find with Eq. 6.32 that $\sigma_{xz} = \sigma_{yz} = 0$. 
<table>
<thead>
<tr>
<th></th>
<th>AFE 1</th>
<th>AFE 2</th>
<th>AFE 3</th>
<th>AFE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>cs</td>
<td>c-s</td>
<td>CS</td>
<td>C-S</td>
</tr>
<tr>
<td>Site B</td>
<td>cs</td>
<td>c-s</td>
<td>CS</td>
<td>C-S</td>
</tr>
<tr>
<td>Site C</td>
<td>c-s</td>
<td>cs</td>
<td>C-S</td>
<td>CS</td>
</tr>
<tr>
<td>Site D</td>
<td>c-s</td>
<td>cs</td>
<td>C-S</td>
<td>CS</td>
</tr>
</tbody>
</table>

\[ c = \frac{1}{2}(\sigma_{xx} - \sigma_{yy}) \cos(2\beta) \]

\[ C = \frac{1}{2}(\sigma_{xx} - \sigma_{yy}) \cos(2\beta) \]

\[ s = \sigma_{zz} \sin(2\beta) \]

\[ d = \sigma_{zz} \sin(2\beta) \]

Table 6.3: Angular dependence for the AFE lines for \( \alpha \)-rotation. For example the symbol c-s stands for the angular dependence \( \frac{1}{2}(\sigma_{xx} - \sigma_{yy}) \cos(2\beta) - \sigma_{zz} \sin(2\beta) \).

The operation \( d (m_{xy}) \) interchanges \( \sigma_{xx} \) and \( \sigma_{yy} \) which means that we have different amplitudes for the cosine part for linked PO\(_4\) groups. The lost symmetry element \( A_x \) (Eq. 6.33) also leads to a change in amplitude. Table 6.4 gives an overview over the angular functions for the domains 1 and 2 and the four sites (A, B, C, and D). Although the sites A, C and B, D are equivalent, all four functions are given for the sake of simplicity.

<table>
<thead>
<tr>
<th></th>
<th>FE 1</th>
<th>FE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>c</td>
<td>C</td>
</tr>
<tr>
<td>Site B</td>
<td>C</td>
<td>c</td>
</tr>
<tr>
<td>Site C</td>
<td>c</td>
<td>C</td>
</tr>
<tr>
<td>Site D</td>
<td>C</td>
<td>c</td>
</tr>
</tbody>
</table>

\[ c = \frac{1}{2}(\sigma_{xx} - \sigma_{yy}) \cos(2\beta) \]

\[ C = \frac{1}{2}(\sigma_{xx} - \sigma_{yy}) \cos(2\beta) \]

Table 6.4: Angular dependence for the FE lines for \( \alpha \)-rotation.

### 6.2.2 Angular functions for the c-rotation

Here the angular functions for the rotation of the crystal around the \( c \)-axis (\( c \perp H_0 \)) are developed. For the calculation, we have to perform a rotation about the \( \alpha \)-axis by an angle of
\[ R = R_\gamma(\beta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\beta & \sin\beta \\ 0 & -\sin\beta & \cos\beta \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \]

In this case we get for the \(zz\)-component of the chemical shift tensor in the laboratory frame:

\[ \sigma'_{zz} = -\frac{1}{2}\sigma_{zz} + \frac{1}{2}(\sigma_{xx} - \sigma_{yy})\cos(2\beta) + \sigma_{xy}\sin(2\beta) \]

### 6.2.2.1 Antiferroelectric lines for \(c\)-rotation

We have seen already that \(2_1x\) connects two PO\(_4\) groups in \(x\)-direction (A-B and C-D) and \(2_1y\) connects two PO\(_4\) groups in \(y\)-direction (A-D and B-C). From Eqs. 6.30 and 6.31 we see that these transformations change the sign of \(\sigma_{xy}\). Thus for the line positions as a function of the angle we conclude that the cosine part is equal, but the sine part has opposite sign for two PO\(_4\) groups that are directly connected.

By making use of the lost symmetry elements we can draw the following conclusions. \(4_z\) connects domains 1 and 2. That transformation (Eq. 6.32) changes neither \(\sigma_{xy}\) nor the terms \(\sigma_{xx}\) and \(\sigma_{yy}\), thus these two domains yield the same frequencies in the \(c\)-rotation. Obviously the same holds for domains 3 and 4.

\(4_z\) relates domains 1 and 3, i.e. from Eq. 6.33 it follows that the sign of \(\sigma_{xy}\) is changed, furthermore we see that \(\sigma_{xx}\) and \(\sigma_{yy}\) are exchanged. So we find that the sign of both the cosine and the sine part change when going from domains 1 or 2 to domains 3 or 4. These results are summarized in Table 6.5.

<table>
<thead>
<tr>
<th></th>
<th>AFE 1</th>
<th>AFE 2</th>
<th>AFE 3</th>
<th>AFE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>(c-s)</td>
<td>(c-s)</td>
<td>(-c-s)</td>
<td>(-c-s)</td>
</tr>
<tr>
<td>Site B</td>
<td>(c-s)</td>
<td>(c-s)</td>
<td>(-c-s)</td>
<td>(-c-s)</td>
</tr>
<tr>
<td>Site C</td>
<td>(c-s)</td>
<td>(c-s)</td>
<td>(-c-s)</td>
<td>(-c-s)</td>
</tr>
<tr>
<td>Site D</td>
<td>(c-s)</td>
<td>(c-s)</td>
<td>(-c-s)</td>
<td>(-c-s)</td>
</tr>
</tbody>
</table>

\[ c = \frac{1}{2}(\sigma_{xx} - \sigma_{yy})\cos(2\beta) \]

\[ s = \sigma_{xy}\sin(2\beta) \]

Table 6.5: Angular dependence for the AFE lines for \(c\)-rotation.
6.2.2.2 Ferroelectric lines in c-rotation

The operation $d(m_{xy}, m_{yx})$ interchanges $\sigma_{xx}$ and $\sigma_{yy}$, therefore the cosine part has opposite sign for connected PO$_4$ groups.

The operation $\bar{4}_c$ is again a lost symmetry element, connecting the two ferroelectric domains. From Eq. 6.32 we find that both the cosine and the sine part have opposite signs for the two domains as is shown also in Table 6.6.

<table>
<thead>
<tr>
<th>Site</th>
<th>$\sigma_{xy}$</th>
<th>$\sigma_{yx}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>cs</td>
<td>-c-s</td>
</tr>
<tr>
<td>B</td>
<td>-cs</td>
<td>c-s</td>
</tr>
<tr>
<td>C</td>
<td>cs</td>
<td>-c-s</td>
</tr>
<tr>
<td>D</td>
<td>-cs</td>
<td>c-s</td>
</tr>
</tbody>
</table>

$$c = \frac{1}{2}(\sigma_{xx} - \sigma_{yy})\cos(2\beta)$$

$$s = \sigma_{xy}\sin(2\beta)$$

Table 6.6: Angular dependence for the FE lines for c-rotation.

6.3 Chemical shift tensor of $^{31}P$ in D-RADP-95

By lowering the temperature D-RADP-95 undergoes an antiferroelectric phase transition at $T = 225$ K. The c-rotation was performed at $T = 89$ K. Only a single line was observable in the spectrum showing no angular dependence of the resonance frequency. Thus we can conclude from Eq. 6.10 that $\sigma_{xy}$ is zero and that $\sigma_{xx}$ and $\sigma_{yy}$ are equal.

For the $a$-rotation the temperature was set to $T = 195$ K. The $a$-rotation shows two strong resonance lines with a large splitting and two very weak lines with only a small splitting. These belong to the four AFE domains in the following manner. Since $\sigma_{xx} = \sigma_{yy}$ we find from Table 6.3 that the cosine term for all lines is identical, but the amplitude of the sine-term for the AFE domains 1 and 2 ($\sigma_{xy}$) is different from that of domains 3 and 4 ($\sigma_{xy}$). Provided that the resulting signal from all four domains is equal in intensity the different line-intensities would imply that the volume fractions of domains 1 and 2 is different from that of domains 3 and 4.

To find the elements of the chemical shift tensor we fitted two pairs of Gaussians (equal amplitude and width for the same pair) to the different spectra to find the peak positions as a function of the rotation angle. The peak positions for all four lines were then fitted simulta-
Figure 6.1: Left: Rotation spectrum for D-RADP-95 around a-axis at $T = 195$ K. The inner lines are not visible in this scale. Right: Calculated lines with fitted chemical shift tensor elements.

neously with the functions in Table 6.3 yielding the following values for the anisotropic part of the chemical shift tensor:

\[ \sigma_{\text{AFE}}[\text{kHz}] = \begin{bmatrix} 2.01 & 0 & 1.98 \\ 0 & 2.01 & 6.29 \\ 1.98 & 6.29 & -4.02 \end{bmatrix} \]

\[ \sigma_{\text{AFE}}[\text{ppm}] = \begin{bmatrix} 16.5 & 0 & 16.3 \\ 0 & 16.5 & 51.8 \\ 16.3 & 51.8 & -33.0 \end{bmatrix} \]

\[ \sigma_{\text{isotropic}}[\text{kHz}] = 0.027 \quad \sigma_{\text{isotropic}}[\text{ppm}] = 0.22 \]

### 6.4 Chemical shift tensor of $^{31}$P in D-RADP-50

#### 6.4.1 Determination of the chemical shift tensor elements at low temperatures

For low temperatures D-RADP-50 forms a pseudo-spin glass which is in contrast to the mixtures with low (0% $\leq X \leq 30$%) and high (68% $\leq X \leq 100$%) ammonium content (x = $0.01X$) characterized only by a short range order of Slater groups. We should therefore be able to observe and discriminate the six different types of Slater D$_2$PO$_4$ groups (four AFE and two FE) via the different chemical shift of the $^{31}$P Larmor frequency.

We recorded rotation spectra around the crystal principal axes $a$ and $c$ between 0° and 180° with 5° steps. Due to the very long $T_1$ relaxation time, the repetition time was set to 3600 s and only one sweep for every phase was measured.

For the evaluation of the rotation spectra we assumed that only the AFE and FE groups (the
six Slater groups) should be visible in the rotation spectra. We used the following iterative procedure for the analysis of the rotation spectra. In a first step the line shape spectra for every rotation angle was fitted to a sum of gaussians with equal amplitude and width for the AFE and also for the FE lines. The line positions found in this way were plotted as a function of the rotation angle and the angular functions (Table 6.3, 6.4, 6.5, 6.6) were fit to find the values of the chemical shift tensor. As stated above we made use of the symmetry elements to fit all the lines at the same time. The fitted line positions were used then as starting values for the next fit of the line shapes and so on, until a stable solution is found. It is clear that the values for the \(a\)- and \(e\)-rotation were combined to find the proper values of the \(\sigma\)-tensor. Concerning the \(\alpha\)-rotation we have to mention that the crystal was oriented in a way that the rotation axis was not parallel to the \(a\) axis but laid in the \(a, b\) plane. This may be due to a misorientation of the crystal or to a wrong cut of the crystal faces. We determined a value of \(7.3^\circ\) for the angle between the \(\alpha\)-axis and the rotation axis. Fig. 6.2 shows that this misorientation has only minor influence on the AFE lines, whereas the splitting of the FE lines is rather prominent.

The AFE chemical shift is:

\[
\sigma_{\text{AFE}}[\text{kHz}] = \begin{bmatrix} 1.54 & 0 & 2.21 \\ 0 & 1.54 & 6.23 \\ 2.21 & 6.23 & -3.08 \end{bmatrix}, \quad \sigma_{\text{AFE}}[\text{ppm}] = \begin{bmatrix} 12.7 & 0 & 18.2 \\ 0 & 12.7 & 51.3 \\ 18.2 & 51.3 & -25.4 \end{bmatrix}
\]

\[\sigma_{\text{isotropic}}[\text{kHz}] = 1.09\]

For the FE tensor we find:

\[
\sigma_{\text{FE}}[\text{kHz}] = \begin{bmatrix} -1.68 & 6.04 & 0 \\ 6.04 & 3.04 & 0 \\ 0 & 0 & -1.36 \end{bmatrix}, \quad \sigma_{\text{FE}}[\text{ppm}] = \begin{bmatrix} -13.8 & 49.7 & 0 \\ 49.7 & 25.0 & 0 \\ 0 & 0 & -11.2 \end{bmatrix}
\]

\[\sigma_{\text{isotropic}}[\text{kHz}] = 1.40\]

\[\sigma_{\text{isotropic}}[\text{ppm}] = 11.5\]
6.4. CHEMICAL SHIFT TENSOR OF $^{31}P$ IN D-RADP-50

Figure 6.2: Left: Rotation spectrum of D-RADP-50 around axis $a'$ in the ($a, b$) plane at $T = 46$ K ($\langle a, a' \rangle = 7.3$ deg). Right: Calculated lines with fitted chemical shift tensor elements. Full lines = AFE lines, dashed lines = FE lines. For this orientation the two low-field and the two high-field FE lines are the two pairs, which are split due to the misorientation.

Figure 6.3: Left: Rotation spectrum of D-RADP-50 around $c$-axis at $T = 45$ K Right: Calculated lines with fitted chemical shift tensor elements. Full line = AFE lines, dashed lines = FE lines.
6.5 Calculation of chemical shift tensors for Takagi groups

We have seen in the former sections that the low temperature spectra at 45 K or 46 K can be fitted well by assuming that the lattice is of the Slater type. We took into account the symmetry elements of the space group which connect the CS tensors for the PO₄ groups in the same domain and the lost symmetry elements which connect the PO₄ groups of the different domains.

The fact that the spectra could be very well described in this way is a strong evidence that the D₂PO₄ groups in fact form a Slater lattice at low temperatures. This is a very important result since it is the first time that the microscopic structure of D-RADP-50 at low temperatures could be monitored.

In this section we want to give another argument that supports the above result. We try to calculate the CS tensors for the Takagi groups with only one deuteron close (¹T) from the experimentally determined AFE and FE CS tensors.

Then we show the rotation pattern of the ¹T Takagi groups and of the ³T (3 deuterons close) Takagi groups, the CS tensor of which can be described by a sum of the ¹T CS tensors.

6.5.1 Linear combination

The general form for the CS tensor of a ¹T Takagi group is

\[
¹T = \begin{bmatrix}
a & d & e \\
d & b & f \\
e & f & c \\
\end{bmatrix}
\]

Of course the four different ¹T Takagi groups (³T₁, ³T₂, ³T₃, ³T₄) which exist for each site (A,B,C or D, see Table 6.3 and Fig. 6.17) are connected by the lost symmetry elements 4₂, 2₂, 4₃. The total (anisotropic and isotropic) CS tensor of an AFE group is thus written as a sum of ¹T₁ and ¹T₂ if we assume that ¹T₂ = 4₂(¹T₁)(4₂)⁻¹.

\[
\sigma_{AFE}[kHz] = \begin{bmatrix}
2.63 & 0 & 2.21 \\
0 & 2.63 & 6.23 \\
2.21 & 6.23 & -1.36 \\
\end{bmatrix}
\]

\[
= \begin{bmatrix}
a & d & e \\
d & b & f \\
e & f & c \\
\end{bmatrix} + \begin{bmatrix}
b & -d & -f \\
-d & a & e \\
-f & e & c \\
\end{bmatrix} = \begin{bmatrix}
a+b & 0 & e-f \\
0 & a+b & e+f \\
e-f & e+f & 2c \\
\end{bmatrix}
\]
It is necessary to introduce a small correction term to the CS tensor of the Takagi groups for a superposition which yields the CS tensor of the FE group.

\[
\tilde{T}_1 = \begin{pmatrix}
a & d & e \\
d & b & f \\
e & f & c
\end{pmatrix}
+ \begin{pmatrix}
x & 0 & 0 \\
0 & x & 0 \\
0 & 0 & y
\end{pmatrix}
\]

(6.13)

The correction is rotation-symmetric. A ferroelectric Slater group can then be written as \( \tilde{T}_1 + \tilde{T}_3 \) or \( \tilde{T}_2 + \tilde{T}_4 \).

We further assume that the Takagi groups with three deuterons close (\(^3T\)) can be either written as a superposition of three \( \tilde{T} \) groups (e.g. \( \tilde{T}_1 + \tilde{T}_2 + \tilde{T}_3 \)) or as a superposition of two \( \tilde{T} \) groups and one \( I \) group (e.g. \( \tilde{T}_1 + \tilde{T}_2 + \tilde{T}_3 \)).

The total FE CS tensor can then be written

\[
\sigma_{FE}[\text{kHz}] = \begin{pmatrix}
-0.28 & 6.04 & 0 \\
6.04 & 4.44 & 0 \\
0 & 0 & 0.04
\end{pmatrix}
= \begin{pmatrix}
a + x & d & e \\
d & b + x & f \\
e & f & c + y
\end{pmatrix}
+ \begin{pmatrix}
a + x & d & -e \\
d & b + x & -f \\
-e & -f & c + y
\end{pmatrix}
\]

(6.14)

Now one can solve the equations which follow from Eq. 6.12

\[
a + b = 2.63
\]

(6.15)

\[
e - f = 2.21
\]

(6.16)

\[
e + f = 6.23
\]

(6.17)

\[
2c = -1.99
\]

(6.18)

and those from Eq. 6.14

\[
2a + 2x = -0.28
\]

(6.19)

\[
2b + 2x = 4.44
\]

(6.20)

\[
2c + 2y = 0.04
\]

(6.21)

\[
2d = 6.04
\]

(6.22)
One finds then for the CS tensors in units of kHz:

\[
\begin{bmatrix}
0.135 & 3.02 & 4.22 \\
3.02 & 2.495 & 2.01 \\
4.22 & 2.01 & -0.995
\end{bmatrix}
\]

\[\mathbf{T}_1 = \begin{bmatrix}
0.135 & 3.02 & 4.22 \\
3.02 & 2.495 & 2.01 \\
4.22 & 2.01 & -0.995
\end{bmatrix}\]

\[\mathbf{\tilde{T}}_1 = \begin{bmatrix}
-0.14 & 3.02 & 4.22 \\
3.02 & 2.22 & 2.01 \\
4.22 & 2.01 & 2.01
\end{bmatrix}\]

One can observe that there is only a small difference between the CS tensors \(\mathbf{T}_1\) and \(\mathbf{\tilde{T}}_1\).

### 6.5.2 Superposition spectra for the a-rotation

We first plot the spectra obtained with the superposition of the Takagi groups giving the Slater groups. The comparison with Table 6.3 and 6.4 shows that the four possible AFE superpositions \((1^T_1 + 1^T_2, 1^T_2 + 1^T_3, 1^T_3 + 1^T_4, 1^T_1 + 1^T_4)\) and the two possible FE superpositions \((1^T_1 + 1^T_3, 1^T_2 + 1^T_4)\) already correspond to all possible lines in the \(a\)-rotation spectra.

Figs. 6.4 show the \(a\)-rotation spectra for the AFE and FE Slater groups (top), for the \(1^T_1\) and \(1^T_1\) Takagi groups (middle), and for the \(3^T_1\) and \(3^T_1\) Takagi groups (bottom). The first thing to notice is that the small correction term introduced for the description of the FE Slater groups does not lead to large shifts of the lines. However, the large difference between the Takagi spectra and the AFE-FE spectra confirms that the observed lines can be unambiguously assigned to the AFE-FE Slater groups. This is also seen in the \(c\)-rotation spectra as will be shown below.

### 6.5.3 Superposition spectra for the c-rotation

Table 6.5 shows that the four domains for site A describe only two lines visible in the rotation spectrum. Thus the symmetry element \(2\) has to be applied to the CS tensor of site A to get that of site B. This tensor describes then the other two lines.

Again, the AFE-FE lines (top), \(1^T_1\) and \(1^T_1\) Takagi lines (middle), and the \(3^T_1\) and \(3^T_1\) Takagi lines (bottom) for the rotation around the \(c\)-axis are displayed (Fig. 6.5). Similar to the case of the \(a\)-rotation the calculated Takagi line positions differ strongly from the observed AFE-FE ones.

We can thus conclude that for low temperatures around 45 K, either the density of the Takagi groups is so small that they are not visible, or the density of Takagi groups is considerable but they are moving so fast that only a time averaged polarization is visible.
Figure 6.4: Measured and calculated line positions for the rotation around $\alpha$-axis. Top: Measured line positions of AFE and FE Slater groups described as a superposition of $\tilde{1}T$ and $\tilde{3}T$ Takagi groups. Middle: Calculated line positions of $\tilde{1}T$ ($T1-1$, $\ldots$, $T1-4$) and $\tilde{3}T$ ($T1-5$, $\ldots$, $T1-8$) Takagi groups. Bottom: Calculated line positions of $\tilde{3}T$ ($T3-1$, $\ldots$, $T3-4$) and $\tilde{5}T$ ($T3-5$, $\ldots$, $T3-8$) Takagi groups.
Figure 6.5: Measured and calculated line positions for the rotation around c-axis. Top: Measured line positions of AFE and FE Slater groups described as a superposition of $^1T$ and $^1\tilde{T}$ Takagi groups. Middle: Calculated line positions of $^1T$ (T1-1A, …, T1-2B) and $^1\tilde{T}$ (T1-5A, …, T1-6B) Takagi groups. Bottom: Calculated line positions of $^3T$ (T3-1A, …, T3-2B) and $^3\tilde{T}$ (T3-5A, …, T3-6B) Takagi groups.
6.6 Rotation spectra for temperatures 45-168 K

We noticed that in the rotation spectra at $T = 46 \text{ K}$ all six Slater groups are visible. That means that during the observation time, which is for NMR of the order of the inhomogeneous transverse relaxation time ($T_2 = 10^{-4} \text{ s}$), the configuration of the PO$_4$ groups remains nearly unchanged. This is in contrast to the single particle autocorrelation time, which is in this temperature region of the order of $10^{-5} - 10^{-4} \text{ s}$ (Sec. 4.6).

This can be explained as follows. During the integration time of the NMR experiment, the hydrogen atoms perform many uncorrelated jumps in a strongly biased Slater lattice. For low temperatures we expect this bias to be constant during the measuring time. The $^{31}\text{P}$ measurement thus experiences a time averaged static D$_2$PO$_4$ group.

Within our Takagi-defect model we expect for higher temperatures that an exchange between the six Slater groups takes place. The question is whether this model persists also at very high temperatures where the bonds are possibly not asymmetric like in the random-bond–random-field model. This model predicts a large amount of symmetric bonds at high temperatures. This could be interpreted in terms of a long time limit with a large enough number of passes of Takagi defects through a D$_2$PO$_4$ group.

Fig. 6.6 shows that for increasing temperatures the exchange between the six Slater groups gets faster. The lines shift towards the center of gravity, so that for $T = 168 \text{ K}$ only a single line is visible in the spectrum. If our model is correct, this shows clearly the thermally activated Takagi motion symmetrizing the O-D–O bonds in the long time scale.

This observation can clearly be distinguished from an uncorrelated thermally activated hopping. As long as the bonds remain asymmetric even between moderate and high temperatures, the dwell time in the higher potential minimum ($\tau^+$) is always much shorter than in the lower one ($\tau^-$), which implies that the time averaged polarization is always different from zero. This follows from the expression for the dwell times in an asymmetric potential (Eq. 4.30).

From the fits of the Davidson-Cole spectral density together with the assumption that the bonds are asymmetric we determined in Sec. 4.3 a bias energy of $E_B = 12.4 \text{ meV} \cong 144 \text{ K}$. Fig. 4.4 shows that $p$ is about 0.9 for $T = 95 \text{ K}$ and 0.7 for $T = 170 \text{ K}$ ($\tau^+ / \tau^- = 0.17$). This shows that also for higher temperatures the polarization is still rather high.

The same observation as for the $\alpha$-rotation was made also for the $c$-rotation of the crystal as shown in Fig. 6.7. In these spectra it is easier to discriminate FE and AFE groups, since the latter show no angular dependence. Refer to Table 6.6 to assign the lines to the different domains and sites.

To observe the line shape transition more thoroughly a sequence of spectra for a fixed orien-
Figure 6.6: $^{31}\text{P}$ $\alpha$-rotation spectra of D-RADP-50 for different temperatures.
Figure 6.7: $^{31}$P c-rotation spectra of D-RADP-50 for different temperatures.
ation with smaller temperature increments was recorded (Fig. 6.8). These spectra were then compared with theoretically calculated line shapes, the theory of which will be developed in the next section.

![Figure 6.8: Left: Spectra at $\alpha' \perp H_0, \angle(c, H_0) = 40^\circ$ and at right: $\epsilon' \perp H_0, \angle(a, H_0) = 45^\circ$ for different temperatures. Note that the baseline indicates the temperature on the y-axis.](image)

### 6.7 Theoretical line shape for an exchange process

#### 6.7.1 General

In Ch. 2 it was already shown that the passing of a Takagi-defect through a bond changes its polarization. In the previous section (Sec. 6.6) we discussed that the $^{31}$P line shape measures the (short-) time averaged polarization of the four nearest O-D···O bonds. Since in our model the lattice is of a Slater type, one can observe transitions between the six different Slater groups which can be distinguished by their different time-averaged polarizations. Thus we are dealing basically with a six-site exchange, since a PO$_4$ group can be in one of the four AFE or two FE states. This point will we discussed in a more detailed manner in the following. Generally, the theoretical line shape $I(\omega)$ for a multi-site exchange process can be calculated using the standard theory [25]:

$$I(\omega) = \text{Re} \left( \vec{p} \cdot A^{-1} \cdot \vec{1} \right)$$  \hspace{1cm} (6.24)

$$A = i(\Omega - \omega \cdot \vec{1}) + \Pi$$  \hspace{1cm} (6.25)

where $\vec{p} = (p_1, p_2, \ldots, p_6)$ describes the population of the six Slater groups. $\vec{1}$ is the unity vector $(1, 1, \ldots, 1)$. 
Figure 6.9: Schematic c-projection of the six Slater groups. The order is shown as used for the calculations of Eqs. 6.24-6.27. a-d are the antiferroelectric Slater groups, e-f are the ferroelectric Slater groups.

The matrix $\omega$ contains the six $^{31}$P resonance frequencies:

$$
\Omega = \begin{bmatrix}
\omega_1 & 0 & 0 & 0 & 0 & 0 \\
0 & \omega_2 & 0 & 0 & 0 & 0 \\
0 & 0 & \omega_3 & 0 & 0 & 0 \\
0 & 0 & 0 & \omega_4 & 0 & 0 \\
0 & 0 & 0 & 0 & \omega_5 & 0 \\
0 & 0 & 0 & 0 & 0 & \omega_6 \\
\end{bmatrix}
$$

(6.26)

$I$ is the identity matrix and $\Pi$ describes the transition rates between the six states, the order of which is shown in Fig. 6.9.

$$
\Pi = 2 \cdot \begin{bmatrix}
-2(k_1 + k_2) & k_1 & 0 & k_1 & k_2 & k_2 \\
k_1 & -2(k_1 + k_2) & k_1 & 0 & k_2 & k_2 \\
0 & k_1 & -2(k_1 + k_2) & k_1 & k_2 & k_2 \\
k_1 & 0 & k_1 & -2(k_1 + k_2) & k_2 & k_2 \\
k_2 & k_2 & k_2 & k_2 & -4k_2 & 0 \\
k_2 & k_2 & k_2 & k_2 & 0 & -4k_2 \\
\end{bmatrix}
$$

(6.27)

The transition matrix $\Pi$ describes the possible direct transitions between the six Slater groups, that means processes where only two hydrogen atoms have to be shifted, one is removed and the other added. The transition between the two kinds of FE groups for example is only possible when four hydrogens shift, the same holds for some transitions between the AFE groups. A direct transition from one to the other Slater group, requiring therefore two hydrogen moves, can be assigned to the passing through of one Takagi defect, a PO$_4$ group where three hydrogens or only one hydrogen is close to the oxygen atoms (Fig. 6.10). $k_1$ is the transition probability per second for a transition between two AFE Slater groups under the assumption that exactly two hydrogen atoms are involved in this process. $k_2$ is the exchange rate constant for the transition between an AFE group and a FE group. The diagonal values of the transition matrix $\Pi$ express the fact that the populations of the six
Slater groups are time independent. They can be calculated as

$$\Pi_{ii} = -\sum_{k=1}^{6} \Pi_{ik}. \quad (6.28)$$

The prefactor 2 in front of the transition matrix comes from the fact that there are always two paths to achieve a new configuration, depending on whether in the first step a hydrogen is added or removed (Fig. 6.10). If one deals for instance with a Takagi group with one proton in excess ($D_3PO_4$) causing the polarization change then a hydrogen is first added and another removed afterwards.

### 6.7.2 Simulation

The aim of our calculations is to compare the calculated spectra with the measured ones to determine the rate constants $k_1$ and $k_2$ as a function of temperature. In detail we proceeded the following way for the simulation. In the D-RADP-crystal there exist four inequivalent $^{31}P$ sites that are connected by the symmetry elements of the corresponding space group ($P2_12_12_1$ or $Fdd2$). To each of the four inequivalent sites belong 6 Larmor frequencies due to the different chemical shift tensor for the various $D_2PO_4$ groups. For a particular site however, the four chemical shift tensors due to the four AFE domains and the two of the FE domains are connected by the symmetry elements that are lost for the transition from the high-temperature $I42d$ structure to the low-temperature antiferroelectric ($P2_12_12_1$) and ferroelectric ($Fdd2$) structure, respectively.

The six frequencies for a particular site need not necessarily be different what can be seen in Tables 6.3 and 6.4 for the $a$-rotation and Tables 6.5 and 6.6 for the $c$-rotation.

The exchange spectrum for each of the four inequivalent $^{31}P$ sites is then calculated separately according to Eq. 6.24 and then superimposed. To account for the dipolar broadening the calculated spectrum was convoluted with a Gaussian.

It is very important to mention the following: From Table 6.4 it becomes clear that the FE chemical shift of site $A$/domain 1 and of site $B$/domain 2 are identical. The same holds also
6.7. THEORETICAL LINE SHAPE FOR AN EXCHANGE PROCESS

for site A/domain 2 and site B/domain 1. It follows that only two FE lines appear in the spectra, thus it is of course irrelevant which of the two FE tensors (σ_{xx} and σ_{yy} interchanged) one assigns to the site A and which to B.

This changes dramatically for the situation when the crystal is not properly oriented like in our experiment, where we rotate around an axis a' in the (a, b) plane, with γ the angle between a and a'. In this case σ'_{zz} has the following angular dependence (under the assumption that σ_{xz} = σ_{yz} = 0 for the FE case):

\[ \sigma'_{zz} = \text{const} + \left( -\sigma_{xx} \sin^2 \gamma - \sigma_{yy} \cos^2 \gamma + \sigma_{xx} - \sigma_{yy} \sin 2\gamma \cos 2\beta \right) \]  

(6.29)

The lost symmetry element \( \bar{4}_z \) connects two FE domains. From Eq. 6.33 we know that \( \sigma_{xx} \) and \( \sigma_{yy} \) are interchanged and also that \( \sigma_{yy} \) changes the sign. The latter point is only relevant when \( \gamma \neq 0 \), as can be seen from Eq. 6.29, and thus leads to a splitting of the two FE lines.

The frequency difference between a particular AFE group and the two EE groups can assume only two values corresponding to the FE domains 1 and 2. However, 4 lines appear in the spectrum, it is important, which FE tensor is assigned to the site A and which to the site B for the numerical calculation of the exchange spectra.

However in our experiments we were not able to distinguish between these two cases (Fig. 6.13), but it should be possible with the use of stronger magnetic fields leading to a larger splitting of the lines.

6.7.3 Determination of the parameters for the thermally activated process

In this section we want to determine the transition rate constants \( k_1 \) and \( k_2 \) as a function of temperature. We will see that the process involved seems to be thermally activated with an activation energy \( E_A = 27 \text{ meV} \). The process is much slower (\( \tau = 2.1 \cdot 10^{-5} \text{ s} \)) than the single particle autocorrelation time determined from spin-lattice relaxation measurements (Sec. 4.3, see also Fig. 6.14).

For particular orientations of the crystal, the exchange spectrum is calculated for several values of \( k_1 \) and \( k_2 \). The fraction (number of FE groups/number of AFE groups) which determines the population vector \( \hat{p} \) (Eq. 6.24) of the six Slater groups was also adapted for the calculation. Since the exchange spectra can not be expressed as analytical functions, it was not possible to fit the spectra automatically, however we tried to find the best visible correlation between measured and calculated spectrum.

Fig. 6.11 and 6.12 show a series of fitted spectra for two different orientations. Only the spectra between \( T = 44.7 \text{ K} \) and \( T = 83 \text{ K} \) were fitted. The rate constants were set so that
Figure 6.11: Comparison of simulated (solid line) and measured spectra (dotted line) for different temperatures, at the orientation $a \perp H_0$, $\langle c, H_0 \rangle = 40^\circ$. The rate constant $k_1$ is displayed.
Figure 6.12: Comparison of simulated (solid line) and measured spectra (dotted line) for different temperatures, at the orientation $c \perp H_0$, $<a,H_0> = 45^\circ$. The rate constant $k_1$ is displayed.
$k_2 = 1.5 \, k_1$. The ratio between FE and AFE groups and also the width of the convoluted Gaussian was adapted to find a better match between measured and simulated spectra. The FE ratio varied from 48% FE for the lowest to 68% FE for the highest temperatures. These values are reasonable since the integral area of the AFE and the FE lines for the low temperature spectra at 45 K and 46 K were equal. This implies then that there are more FE Slater groups (50%) than one would expect (33%).

For temperatures up to $T = 65$ K the fits correspond to the measured spectra but deviates from them at higher temperatures but still the behavior is reproduced fairly well.

Fig. 6.13 shows the temperature dependence of the rate constant $k_1$. One can see that the simulated values for $k_1$ can be approximated by an exponential with \( k_\infty \approx 4.7 \cdot 10^4 \) rad s$^{-1}$ and an activation energy of 27 meV $\approx 315$ K. The inverse attempt frequency at infinite temperatures is \( \tau_\infty = 1/k_\infty = 2.1 \cdot 10^{-5}$ s. This fit could possibly be improved by fitting a distribution of correlation times. A linear plot of the inverse attempt frequency as a function of the inverse temperature in Fig. 6.14 shows that we are dealing with a much slower motion compared with the single particle autocorrelation time. The model of a Takagi defect motion yields values for the auto correlation time which are 1 ms at $T = 83$ K and rise to 10 ms for lowering the temperature to $T = 45$ K. The time scale of the Takagi-defect motion is several orders of magnitude longer than the single particle autocorrelation time and can thus clearly be distinguished from the thermally activated hopping (Fig. 6.14). The spectra in this
6.7. THEORETICAL LINE SHAPE FOR AN EXCHANGE PROCESS

Theoretical line shape for an exchange process can be well simulated by the line shape function calculated for a six site exchange, corresponding to transitions between the six Slater PO₄ groups. If our model of the Takagi-defect motion is correct, the fact that the ³¹P lines merge into a single one at temperatures larger than 170 K implies that the motion is symmetrizing the O-D-O-O bonds on a long time scale.

It is not clear whether the autocorrelation time still remains finite even at much lower temperatures. This would imply that the glass state of D-RADP-X is not a frozen-in non-ergodic state but the ergodicity is restored by the observed motion. As already mentioned in the introduction, a symmetry restoring motion is observed for ²H 2D exchange measurements in D-RADA-32 [10].

For higher temperatures the lines shift towards the center of gravity of the spectrum and finally merge into one single line at temperatures around $T = 170$ K. It is possible that in this temperature region both the effects of Takagi-defect motion and the diminished time-averaged polarization (Fig. 4.4) contribute to the averaging of the exchange spectrum.

The use of higher magnetic fields could enhance the chemical shift interaction by a factor 2-3 thus leading to a larger splitting of the observed lines. The transition from the slow-motion to the fast-motion regime occurs around 140 K for a

---

**Figure 6.14:** Simulated $\tau_c$ values as a function of $1000 / T$ fitted with an Arrhenius function (dotted line) with $E_A = 27$ meV and $\tau_m = 2.1 \cdot 10^{-5}$ s. The solid lines result from the fits of the $^{87}$Rb $T_1$ data with the BPP function $E_A = 81 \pm 5$ meV. The dashed-dotted line is the autocorrelation time for deuteron jumps in an asymmetric potential ($E_B = 12.7$ meV) for an (upper cut-off) activation energy of 104 meV resulting from the fit of the $T_1$ data using the Davidson-Cole spectral density.
7 T magnet where the exchange rate $\Gamma$ is related to the line splitting which is about $\Delta = \pm 2\pi \cdot 5 \text{ kHz}$ by

$$\frac{4\Delta}{\Gamma} \approx 1$$

However it is masked by the broadening due to the dipolar interaction. In a 21 T (14 T) magnet one can estimate that the transition temperature should be about 133 K (62 K) higher.

### 6.8 2D exchange measurements of $^{31}P$ at low temperatures

Although the data can be quite well fitted with the dynamic model, one might argue however that the observed transition is not of dynamic origin but is purely static, analogous to the results of the random-bond-random-field model where the distribution of the time averaged polarization $p$ is doubly peaked at $p = \pm 1$ for low temperatures and becomes centered around zero for high temperatures (Fig. 1.4). In our case the Potts model for the 6 Slater states should be used, which describes the random interactions of the Slater groups with each other and with the random field [48].

In order to confirm or to rule out our model we performed $^{31}P$ 2D exchange measurements. For the experiments we chose the orientation $\theta |H_0, \phi |H_0) = 45^\circ$ where the splitting of the lines is the largest (Fig. 6.8).

For the 2D experiments we used the pulse sequence

$$90^\circ_{x} - t_1 - 90^\circ_{x,\pm} - t_m - 90^\circ_{x,\mp} - t_2$$

where $t_1$ is the evolution time which is incremented to allow for a Fourier transform in $t_1$. $t_m$ is the mixing time and the acquisition is made during $t_2$. As usual the irradiation frequency was set outside of the spectral lines to prevent an overlap of the two mirror copies in the 2D frequency spectrum. The pulses were cycled between $\pm \nu$ to remove all unwanted signals but the stimulated echo.

From the simulation of the exchange process (Sec. 6.7.3) due to the motion of Takagi defects, we conclude that the autocorrelation time of the Takagi defects is of the order of 1 ms at 50 K. We thus performed an experiment at 50 K for a mixing time of 20 ms. As can be seen in the contour plot (Fig. 6.15, left spectrum of top row), only diagonal peaks at the positions (in kHz) $(\omega_{FE}, \omega_{FE}) = (3, 3)$ and $(16, 16)$ and $(\omega_{AFE}, \omega_{AFE}) = (12, 12)$ show up in the spectrum, although the mixing time is so long that cross peaks are expected at the intersections between the three frequencies.

If the mixing time is increased to 200 ms one observes a broadening of the cross peaks which is attributed to spin diffusion (Fig. 6.15, top row, right). Spin diffusion is an exchange
6.8. 2D EXCHANGE MEASUREMENTS OF $^{31}$P AT LOW TEMPERATURES

of magnetization between nuclei which results from the dipolar interaction [51]. Since it is not effective when the frequencies of the interacting spin differ strongly ($\tau^{-1} \propto \Delta \nu^{-4}$) there is only intensity near the diagonal peaks.

Only at a very long mixing time of 800 ms cross peaks between the AFE and the FE lines appear, which however are not very well separated from the diagonal peaks as can be seen for the peaks at (15.22), and (22.15) (kHz) in Fig. 6.15, middle row, left.

The temperature was increased to 55 K for the same mixing time (800 ms) where the spin lattice relaxation time of $T_1$ is smaller allowing for a reduction of the repetition time from 20 to 10 minutes. The number of sweeps could be thus increased from 1 to 2 leading to a better resolution. However one does not expect that the exchange time increases drastically. This is shown in Fig. 6.15 where the cross peaks are better visible. The distortions in the spectra along the $v_1$ axis may result from $T_1$ independent signals which are not completely canceled by the pulse sequence.

We also performed experiments at 77 K, where the lines have still not yet merged as can be seen in Fig. 6.8. In Fig. 6.15 (bottom row, left, $t_{mix} = 200$ ms) one can observe that the diagonal peaks can not be distinguished in the 2D contour plot what may be because the irradiation frequency was chosen too far away from the lines. The experiment for 800 ms with an irradiation frequency closer to the lines shows again the three diagonal peaks. Surprisingly no cross peaks appear like at lower temperatures, only a broadening of the diagonal is observed when the mixing time is increased from 200 ms to 800 ms. At present we do not have an explanation of that behavior. Additional measurements at temperatures around 65 K would be needed.

The other point which is unclear is that for 50 K and 55 K only at very long mixing times like 800 ms cross peaks occur. This time scale is about two orders of magnitude longer than that determined from the simulation of the line shape transition. This may be because there is a distribution of correlation times for the Takagi defect motion. In a 2D exchange experiment only those Takagi defects with correlation times shorter than the mixing time but longer than the $T_2$ relaxation time can be monitored as cross peaks. If the distribution is very broad, than the cross peaks may be much weaker than the diagonal peak so that they are not visible.
Figure 6.15: Contour plots of the 2D exchange spectra of $^{31}$P at temperatures 50 K, 55 K and 77 K for mixing times between 20 ms and 800 ms. The spectra are normalized to 1 and the contour levels are 0.05, 0.1, 0.2, ..., 0.8. Since the irradiation frequency was not kept constant for all experiments, the spectra are shifted along the diagonal $\omega_1 = \omega_2$. 

CHAPTER 6. CHEMICAL SHIFT PERTURBED NMR OF $^{31}$P IN D-RADP-X
6.9 Appendix

6.9.1 FE and AFE domains

In Fig. 6.16 the $z$-projections of the deuteron configuration for the two FE domains are shown. Figs. 6.17 and 6.18 show the four AFE configurations.

![Diagram of ferroelectric and antiferroelectric domains](image)

Figure 6.16: $z$-projection of the ferroelectric domains FE 1 (left side) and FE 2 (right side), the $x$-axis is horizontal and the $y$-axis vertical. The $^{31}$P sites A,C are physically equivalent. The same holds for B,C.

6.9.2 Symmetry elements

6.9.2.1 High temperature paraelectric phase: space group $I4_2d$

Symmetry elements of the point group: $1, 4_2^x, 4_2^y, 2_z, 2_y, m_{xy}, m_{x\bar{y}}$

6.9.2.2 Low temperature antiferroelectric phase: space group $P2_12_12_1$

Symmetry elements of the point group: $1, 2_x, 2_y, 2_z$

6.9.2.3 Low temperature ferroelectric phase: space group Fdd2

Symmetry elements of the point group: $1, 2_z, m_{xy}, m_{x\bar{y}}$
Figure 6.17: \( z \)-projection of the antiferroelectric domains AFE 1 (left side) and AFE 2 (right side), the \( x \)-axis is horizontal and the \( y \)-axis vertical. The four inequivalent \( ^{31}\text{P} \) sites are denoted as A, B, C, and D.

Figure 6.18: \( z \)-projection of the antiferroelectric domains AFE 3 (left side) and AFE 4 (right side), the \( x \)-axis is horizontal and the \( y \)-axis vertical. The four inequivalent \( ^{31}\text{P} \) sites are denoted as A, B, C, and D.
6.9.3 Transformations of the chemical shift tensor

In this section we list the symmetry operations of the AFE and FE symmetry group and the
lost symmetry elements from the high temperature phase which were used to calculate the
chemical shift tensor elements in Sec. 6.2.

The AFE symmetry operations are $2_1 v$, $2_1 i$, $2_1 z$ [23]. The transformation of the (anisotropic)
chemical shift tensor in the crystal eigenframe ($\sigma$) to the laboratory system ($\sigma'$) yield:

$$\sigma' = 2_t \sigma 2_t^{-1} = \begin{bmatrix}
\sigma_{xx} & -\sigma_{xy} & -\sigma_{xz} \\
-\sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\
-\sigma_{xz} & \sigma_{yz} & \sigma_{zz}
\end{bmatrix}$$  (6.30)

$$\sigma' = 2_v \sigma 2_v^{-1} = \begin{bmatrix}
\sigma_{xx} & -\sigma_{xy} & \sigma_{xz} \\
-\sigma_{xy} & \sigma_{yy} & -\sigma_{yz} \\
\sigma_{xz} & -\sigma_{yz} & \sigma_{zz}
\end{bmatrix}$$  (6.31)

$$\sigma' = 2_z \sigma 2_z^{-1} = \begin{bmatrix}
\sigma_{xx} & \sigma_{xy} & -\sigma_{xz} \\
\sigma_{xy} & \sigma_{yy} & -\sigma_{yz} \\
-\sigma_{xz} & -\sigma_{yz} & \sigma_{zz}
\end{bmatrix}$$  (6.32)

The lost symmetry elements for a transition from the paraelectric case ($I\bar{4}2d$) to $P2_12_12_1$
are e.g. $4_2 \bar{2}$, $4_2 z$, $m_{xy}$, $m_{x\bar{x}}$. They connect the four different AFE configurations. We get for
example:

$$\sigma' = 4_z \sigma 4_z^{-1} = \begin{bmatrix}
\sigma_{xy} & -\sigma_{xy} & -\sigma_{yz} \\
-\sigma_{xy} & \sigma_{xx} & \sigma_{xz} \\
-\sigma_{yz} & \sigma_{xz} & \sigma_{zz}
\end{bmatrix}$$  (6.33)

$$\sigma' = m_{xy} \sigma m_{xy}^{-1} = \begin{bmatrix}
\sigma_{xy} & \sigma_{xy} & -\sigma_{yz} \\
\sigma_{xy} & \sigma_{xx} & -\sigma_{xz} \\
-\sigma_{yz} & -\sigma_{xz} & \sigma_{zz}
\end{bmatrix}$$  (6.34)

where $m_{xy}$ is given by

$$m_{xy} = \begin{bmatrix}
0 & -1 & 0 \\
-1 & 0 & 0 \\
0 & 0 & 1
\end{bmatrix}$$  (6.35)

The symmetry group for ferroelectric D-RDP is $Fdd2$. The FE symmetry operations are $2_1 z$
and a diamond glide plane $d$, which is given by a mirror plane parallel to $c$ ($m_{xy}$ or $m_{x\bar{x}}$) and
a translation in $a$ or $b$ direction.
Chapter 7

Summary

Chemical shift perturbed NMR of $^{31}$P has proved to be a powerful tool to monitor the local order of the deuterons. It could be confirmed that the low-temperature structure of D-RADP-50 is given by a Slater lattice, where two deuterons are close to each PO$_4$ group. The Slater or ice rules are thus not only fulfilled in the long-range ordered crystals D-RDP and D-ADP, but also in the glass state of D-RADP-50 and possibly also in the other mixed crystals of the KDP-type.

The observed line-shape transition of the $^{31}$P spectrum at higher temperatures leads to the conclusion that the deuteron bonds are symmetric. This can be explained by fluctuations of the bias energies which symmetrize the bond asymmetries in the long time limit. These fluctuations which seem to be thermally activated are due to a motion which is much slower than the single particle overbarrier hopping of the deuterons. The slow motion is possibly the motion of unpaired Takagi defects in a Slater lattice although it could not be monitored directly in the 2D exchange spectra of $^{31}$P. It is reasonable to assume that we do not deal with a single correlation time for the Takagi motion but that there is a distribution of correlation times. This may be the reason why we do not observe the Takagi defects directly since if we assume the distribution to be very broad, then there will be only a small fraction of Takagi groups that can be observed in the time-window of the 2D NMR measurements.

In the thesis of Th. König [20] $^{87}$Rb 2D exchange spectra have been calculated based on the point-charge model introduced in the thesis of N. Körner [19] and described in Ref. [21]. The calculated spectra show that the deuterons do not move independently. In the present thesis we introduced the model of unpaired Takagi defects in a Slater lattice. Again the point-charge model was used to calculate the $^{87}$Rb EFG tensor depending on the positions of the nearest 32 deuterons on their bonds. The deuteron arrangement changes in a restricted way when Takagi defects move through the lattice. The calculated 2D exchange spectra show that the cross peaks are close to the diagonal like in the measured spectra of Th. König.
However the role of the random distribution of Rb and ND$_4$ was not taken into account in the model. We think that the nitrogen motion between the different off-center positions is also a source which can influence the dynamic behavior of D-RADP-X. That dynamics may be even slower than that of the Takagi defect motion.

The point-charge model was also used to calculate the $^{87}$Rb line shape for the long-range ordered phases and for the glassy region of D-RADP-50, for which we have taken into account that the structure is given by a randomly ordered Slater lattice. The point-charge model, based on the assumption of a rigid lattice, gives a rather good approximation to the measured EFG tensor values. However there are still small deviations which are the reason why the calculated line positions do not show exactly the same orientational dependence as the measured lines. Nevertheless, the calculated line shape for the glassy phase shows that the assumption of a Slater lattice together with a distribution of polarizations around $\pm 1$ can mimic the measured spectra in the glassy regime.

In this thesis a new approach was used to fit the $T_1$ data described in the thesis of N. Körner. The new fit is based on the assumption that the bonds are asymmetric with a fixed bias energy and a distribution of activation energies. The determined mean square fluctuations of the EFG tensor elements compare well to those calculated with the point-charge model, which supports our assumption of asymmetric bonds. However, the single bias energy used to describe the reduction of the mean square fluctuations and the autocorrelation time should be replaced by a distribution of bias energies.

Since $^{31}$P chemical shift perturbed NMR is a powerful tool to monitor the local order of the deuterons in D-RADP-50, it could thus also be used to explore other concentration regimes of the phase diagram. First it would be interesting to investigate other concentration ranges in the glass state ($0.35 \leq x \leq 0.65$) to determine the parameters of the $^{31}$P line shape transition as in D-RADP-50.

It is known from $^{87}$Rb line shape measurements [19, 21] and from X-ray scattering [38] that for the concentration range close to the AFE boundary D-RADP-X forms AFE domains. In the thesis of Th. König it was shown that on the ferroelectric side of the phase diagram it exists a coexistence region of FE clusters and glass state. For a low ammonium content of 25% and 30% a phase segregation into a FE and a glassy region was discovered using $^{87}$Rb line shape analysis. With $^{31}$P line shape analysis for different temperatures it should be possible to monitor the formation and the dynamics of the AFE or FE domains. Possibly the $^{31}$P line shape consists of a superposition of two spectra, one for the domains and the other for the disordered interdomain region, which may have different correlation times. In this case the effects of a static line shape transition, due to a temperature dependence of the bond asymmetries, and of a dynamic line shape transition, due to the motion of Takagi defects, can be studied simultaneously.
Experimental

All the experiments presented in this thesis were made in a magnetic field of 7 Tesla using one of the two home-built double-conversion spectrometers with two intermediate frequencies (IF$_1$, IF$_2$). Except for the low temperature $^2$H 2D exchange measurements (Sec. 5.4) which were performed on a spectrometer with IF$_1 = 390$ MHz, IF$_2 = 20$ MHz, the spectrometer with IF$_1 = 145$ MHz, IF$_2 = 15$ MHz was used. The local oscillator (LO) frequency was produced with an Adret 740A UHF Generator or a Rhode & Schwarz Signal Generator. The signals were recorded and averaged in a LeCroy 9310 Dual 300 MHz digital oscilloscope. All the data was transferred to an Apple Computer, where the processing was done using MATLAB.

The pulse programmer was an Interface Technology RS-670 Digital Word Generator. A Kalmus LP-1000 high power transmitter was used for the excitation of the probes. The crystals were mounted in a home-built probe head, which was placed inside a Helium gas flow cryostat. The temperature stability was usually better than ±0.1 K.
References


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REFERENCES


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Zürich, July 19, 1999

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