$^{23}$Na/$^{51}$V-NMR study of $\alpha'$-NaV$_2$O$_5$

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Dedication

To those candles who burn themselves to enlighten my road, to my father, to my mother, my brothers, my sisters, my uncle, my wife, my cousins, my teachers, my friends, and to those who are looking forward to enrich their knowledge.

Husam Ahmad Hussein Mohammad
## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>Magnetic field (strictly the magnetic flux density or magnetic induction)</td>
</tr>
<tr>
<td>$B_0$</td>
<td>Static magnetic field of an NMR spectrometer</td>
</tr>
<tr>
<td>$B_0</td>
<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>Radiofrequency magnetic fields associated with frequencies</td>
</tr>
<tr>
<td>$B_{	ext{log}}$</td>
<td>Local magnetic field</td>
</tr>
<tr>
<td>$C$</td>
<td>Spin-rotation interaction tensor</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field strength</td>
</tr>
<tr>
<td>$\hat{H}$</td>
<td>Hamilton operator (in energy units)</td>
</tr>
<tr>
<td>$\hat{i}$</td>
<td>Nuclear spin operator</td>
</tr>
<tr>
<td>$I$</td>
<td>Nuclear spin quantum number</td>
</tr>
<tr>
<td>$M$</td>
<td>Magnetization (Magnetic moment density)</td>
</tr>
<tr>
<td>$M_0$</td>
<td>Equilibrium macroscopic magnetization per volume of a spin system in the presence of $B_0$</td>
</tr>
<tr>
<td>$M_X, M_Y, M_Z$</td>
<td>Components of macroscopic magnetization per volume.</td>
</tr>
<tr>
<td>$m_I$</td>
<td>Magnetic quantum number, Order of a spin transition</td>
</tr>
<tr>
<td>$N$</td>
<td>Total number of nuclei of a given type per volume in the sample</td>
</tr>
<tr>
<td>$q$</td>
<td>Electric field gradient tensor in units of the elementary charge</td>
</tr>
<tr>
<td>$Q$</td>
<td>$eQ$ is the nuclear quadrupole moment, where $e$ is the elementary charge</td>
</tr>
<tr>
<td>$T_c, T_0, T_{\pi}$</td>
<td>Transition temperature</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Spin-lattice (longitudinal) relaxation time</td>
</tr>
<tr>
<td>$T_2$</td>
<td>Spin-spin (transverse) relaxation time</td>
</tr>
<tr>
<td>$T_2^*$</td>
<td>Net dephasing time for $M_X$ or $M_Y$</td>
</tr>
<tr>
<td>$V$</td>
<td>Electric field gradient tensor. $V= eq$, where $e$ is the elementary charge</td>
</tr>
<tr>
<td>$V_{\alpha\beta}$</td>
<td>Elementary charge Elements of Cartesian electric field tensor</td>
</tr>
<tr>
<td>$W_0, W_1, W_2$</td>
<td>Relaxation rate constants (transition probabilities per time) between energy levels</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$W_{m\rightarrow m'}$</td>
<td>Transition probability</td>
</tr>
<tr>
<td>$a$</td>
<td>Nuclear spin wave function</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Spin-gap</td>
</tr>
<tr>
<td>$\eta$</td>
<td>The asymmetry parameter of the EFG tensor</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Plank's constant</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Magnetic susceptibility</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Magnetic moment</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>(i) Spectrometer operating frequency; (ii) Larmor precession frequency</td>
</tr>
<tr>
<td>$\nu_Q$</td>
<td>Quadrupole frequency</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Shielding tensor</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Time between two RF pulses</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>Correlation time</td>
</tr>
<tr>
<td>$\nu_L$</td>
<td>Larmor frequency</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>Angular velocity in rad.s$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{1/2}$</td>
<td>The line-width of an NMR signal at half-height</td>
</tr>
</tbody>
</table>
Abstract

In this work I present a $^{23}\text{Na}/^{51}\text{V}$-NMR study of sodium vanadate as pure compound, and the influence of very small amounts of Sodium substitution by Calcium and Lithium is reported and discussed. The measurements of spin-lattice relaxation for $^{23}\text{Na}$ and $^{51}\text{V}$ are also presented. The sodium vanadate is found to have a double phase transition. The two transitions are close together and take place around 34 K. Above the transition temperature there is one V site in the mixed oxidation state 4.5+ and there is one Na site. A consistency for a number of un-doped and very slightly doped samples of three vanadium valences is argued, confirming a charge ordering transition at transition temperature, in good qualitative agreement with Bernert’s model and as well in quantitative and qualitative agreement with Sawa’s monoclinic structure. Below the transition temperature sodium is found to have ten sites. The number of the Na site is continuously developed with decreasing the temperature below transition temperature. This continues development of the Na sites demonstrates that the second transition is continues.

The detailed spin-lattice relaxation rate for $^{23}\text{Na}$ in both, the pure and the doped samples, in transition region, provided evidence for a non-symmetric and complex transition peak structure which we relate to the onset of more than one transition occurring at slightly different temperatures. This scales with the transition temperature reduction provided by lithium and calcium doping. The two transitions (i.e. dimerization and charge ordering) are intimately related. We investigated the spin-gap by means of Vanadium and Sodium spin-lattice relaxation temperature dependence well below transition temperature. The analysis of the single crystal data reveals a significant anisotropy in the nature of the gap, which is sensitive to Calcium and Lithium doping, indicating that is constrained to the ladder plane.
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1 Introduction

1.1 Ladder materials and low dimensional magnetism

Quantum ladder systems attract a lot of interest [1,2]; the ladder systems are the first step from one-dimensional toward two-dimensional systems [3, 4, 5]. Many compounds have been experimentally realized with a ladder structure, such as SrCu$_2$O$_3$ [6, 7], (VO)$_2$P$_2$O$_7$ [8], Cu$_2$(C$_5$H$_{12}$N$_2$)$_2$C$_{14}$ [9], NaV$_2$O$_5$ [10]. The ladders are either built with an even or odd number of legs. The ladders with odd legs have properties similar to single chain compounds at low energies, and show gapless spin excitations. The antiferromagnetic spin systems are among the simplest many body systems which show strong quantum effects. Furthermore, the Antiferromagnetic spin ladders with an even number of legs are expected to have an excitation gap. Various works have treated the two-leg $S = 1/2$ spin ladder, confirming that they possess an excitation gap [11,12,13,14,15,16].

![Fig. 1.1.1: One planar layer of the crystal structure of α'-NaV$_2$O$_5$: only vanadium and oxygen atoms, which are situated in the same plane, are shown. The oxygen atoms at the top of the VO$_5$-pyramids are not seen in this projection as are the sodium atoms the Na atoms are offset from the plane of the ladders.](image)
The two-leg ladder is an intermediate between a 1D chain and a 2D plane. One of those ladders compounds that attracted more interest is $\alpha'$-NaV$_2$O$_5$. Its ladders are formed by layers of vanadium ions. Between the vanadium ions are oxygen ions along the rungs and along the legs of the ladders (Fig. 1.1.1). The V ions interact via super exchange through the oxygen ions along the rungs of the ladders; the hopping between vanadium ions along the rungs is stronger than along the legs of the ladders.

1.2 Vanadates

Vanadium can take various valence states from 2+ to 5+ and many of these valences exists in the binary V—O system in the form V$_n$O$_{2n-1}$ and V$_n$O$_{2n+1}$. Due to this variety of V-oxidation states, chemists and physicists are becoming more attracted and interested to such studies. Vanadium oxides form a variety of V-O coordination polyhedra, which vary from tetrahedron to trigonal pyramid, square pyramid, distorted octahedron and regular octahedron, and with oxidation state changes from +5 to +3 (Fig. 1.2.1). For the tetrahedral, the regular V—O distances range between

![Diagram of vanadium coordination polyhedra](image)

*Fig. 1.2.1: Metamorphosis of the vanadium coordination polyhedra. Vertical axis: coordination number; horizontal axis: oxidation state. [23]*
1.6 and 1.8 Å depending on the oxygen coordinates, and the oxidation state is always 5+. The trigonal bipyramid can be derived from the tetrahedra by adding a fifth oxygen atom opposite any face and simultaneously moving the vanadium atom to the centre of this face. The case of the inorganic square pyramid differs from the trigonal bipyramid in that four oxygen atoms lie coplanar or almost coplanar, whereas the fifth double-bonded oxygen occupies the square pyramid apex. Adding one more oxygen atom on the base converts the square pyramid into a distorted octahedron as shown in Fig. 1.2.1. All these coordination polyhedra are typical for vanadium with oxidation states from 5+ to 4+ (Table 1.2.1). The regular octahedron forms when moving to the lower oxidation states of 3+ and below.

A variety of vanadium compounds have been reported such as silver vanadate, $\text{Ag}_x\text{V}_4\text{O}_{11}$ and $\text{Ag}_x\text{V}_4\text{O}_{10}$ [17], tetramethylammonium $\text{V}_8\text{O}_{20}$ [18,19], sodium vanadate $\text{Na}_x\text{V}_2\text{O}_5$ [20], lithium vanadates $\text{Li}_x\text{V}_{3(1+n)}\text{O}_{8+7n}$ [21]. Zhang et al. [22] described a structure of $\text{V}_2\text{O}_5$ layers built with pairs of square pyramids and tetrahedra. Zavalij et al. [23] gave a topographical analysis and combinatorial deduction of the simplest structures for $\text{V}_6\text{O}_{14}$ layers constructed with zig-zag chains of edge-sharing square pyramids and tetrahedra. Galy [24] gave a general review of vanadium oxide phases with single and double $\text{M}_x\text{V}_2\text{O}_5$. Surely, vanadates are of industrial importance as catalyst materials, as antistatic coatings for photographic films, and as reversible cathodes in batteries [25,26].

<table>
<thead>
<tr>
<th>Table 1.2.1: The range of vanadium coordination, $V$—$O$ distances and the $V$ valences occurring in the $V$—$O$ binary system.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium coordination</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td>Tetrahedron</td>
</tr>
<tr>
<td>Trigonal bipyramid</td>
</tr>
<tr>
<td>Square pyramid</td>
</tr>
<tr>
<td>Distorted octahedron</td>
</tr>
<tr>
<td>Regular octahedron</td>
</tr>
</tbody>
</table>

There are number of compounds which are called sodium-vanadium bronzes. For one of them, $\text{Na}_x\text{V}_2\text{O}_5$, seven phases exist:
\( \alpha \) (0 \leq x \leq 0.02) has an orthorhombic structure identical with the \( \text{V}_2\text{O}_5 \) layer structure. \((Pmmn, a = 11.516 \text{ Å}, b = 3.565 \text{ Å}, c = 4.370 \text{ Å}).\)

\( \beta \) (0.21 \leq x \leq 0.35) has a monoclinic structure \((C2/m, a \sim 15.44 \text{ Å}, b \sim 3.61 \text{ Å}, c \sim 10.08 \text{ Å}, \beta = 109.6^\circ \) for \( x = 0.33 \)) [27].

\( \delta \) (0.55 \leq x \leq 0.57) monoclinic, \( C2/m, a = 11.663 \text{ Å}, b = 3.6532 \text{ Å}, c = 8.92 \text{ Å}, \beta = 90.91^\circ \) [28].

\( \tau \) (\( x = 0.64 \)) crystallizes in the monoclinic system \((C2/m, a = 11.674(9) \text{ Å}, b = 3.650(2) \text{ Å}, c = 8.905(5) \text{ Å}, \beta = 91.04^\circ \)) [19,29].

\( \alpha' \) (0.78 \leq x \leq 1.00) crystallizes in the orthorhombic system.

\( \eta \) (1.28 \leq x \leq 1.45),

\( \kappa \) (1.68 \leq x \leq 1.82).

The \( \beta \) phase has been studied intensively because of its quasi one-dimensional conducting properties [30, 31].

The \( \alpha'\)-\( \text{Na}_x\text{V}_2\text{O}_5 \) allows for a wide range of Na deficiency [32,33] (0.78 \leq x \leq 1.00). Isobe et al. have shown in magnetic susceptibility measurements done for powdered samples that the spin-Peierls like transition (see Sec. 1.3.3) is suppressed by Na deficiency and vanishes around \( x = 0.97 \), (Fig. 1.2.2).

---

**Fig. 1.2.2:** Temperature dependence of magnetic susceptibility of \( \alpha'\)-\( \text{Na}_x\text{V}_2\text{O}_5 \) (0.80 \leq x \leq 1.00). [32]
1.3 The problem of $\alpha'$-NaV$_2$O$_5$

1.3.1 High temperature phase

The $\alpha'$-NaV$_2$O$_5$ crystallizes in an orthorhombic structure with space group Pmmn [34,35,36,37]. The lattice parameters of the basic structure at 295 K are $a = 11.311$ Å, $b = 3.6105$ (6) Å, $c = 4.800(1)$ Å. The $\alpha'$-NaV$_2$O$_5$ is a ladder compound that consists of double chains of edge sharing VO$_5$ pyramids, which run along the orthorhombic $b$-axis. The sodium atoms are situated between the V—O planes where they form a chain along the $b$-axis (Fig. 1.3.1.1).

![Crystal structure of $\alpha'$-Na$_x$V$_2$O$_5$ at room temperature. V atoms are 5-fold coordinated by an oxygen pyramid. The Na atoms are located between the V—O planes.](image)

Sodium vanadate is an insulator. Its magnetic susceptibility has a temperature dependence which is similar to that of the Heisenberg spin-1/2 chain with the exchange constant $J \approx 560$ K, (Fig. 1.3.1.2) [38].
Recent years works, dealing with X-ray and NMR experiments, have stated that in this compound above $T_0 > 34$ K all vanadium are equivalent and have a mixed valence 4.5+, and there is a half d-electron per VOV rung [35,39]. Within the ladder, the V spins interact via the super exchange along the rung of the ladder through the O atoms [40] making V valence to 4.5+.

1.3.2 Low-temperature phase

At a temperature of $T_0 = 34$ K, sodium vanadate undergoes a phase transition, with consequence for the structure. The lattice periods along the ladders ($b$-direction) and parallel to the rungs in the ladder ($a$-direction) double, while the period in the direction perpendicular to the layers ($c$-direction) increases by a factor of four [41,43]. This exotic transition at 34 K was unexpected and triggered world wide investigations. Early studies suggested a spin-Peierls transition. Until then CuGeO$_3$ was the only known inorganic spin-Peierls compound [44]. My main goal is to shed light on the nature of the low-temperature phase of $\alpha'$-NaV$_2$O$_5$ by using $^{51}$V and $^{23}$Na-NMR as a local probe.

Early NMR experiments found that this compound undergoes a charge ordering transition to two inequivalent vanadium sites on cooling through $T_0$. Magnetic V$^{4+}$ and non-magnetic V$^{5+}$ have been attributed to the two NMR lines [45]. The $^{23}$Na-NMR spectrum of $\alpha'$-NaV$_2$O$_5$ single-crystalline sample has been measured by Ohama et. al. [46]. The authors have observed eight Na sites below $T_0$, and suggested a zig-zag charge ordering. Furthermore, the X-ray structure determination reported three non-equivalent V sites below $T_0$ [47,48]. The Anomalous X-ray-diffraction studies [49], on the other hand, show that the charge ordering in $\alpha'$-NaV$_2$O$_5$ is of zig-zag type in all vanadium ladders. The vanadium ladders are found to be modulated, and two different models of stacking of layers sequences along the $c$ direction coexist in the structure [49]. On one hand, the charge ordering in NaV$_2$O$_5$ is found to concern a small fraction of electrons, mainly the $d$-orbitals [50]. On the other hand, the numerical estimates for the microscopic coupling parameters [51], provide evidence for a substantial interladder spin-pseudospin interaction term in NaV$_2$O$_5$. This would allow simultaneously for the superantiferroelectric charge ordering and spin dimerization. Until our recent publications [52,53], this puzzle has been an open question in literature.
1.3.3 Nature of the low temperature transition(s): Spin-Peierls? Spin-gap?

$\alpha'$-NaV$_2$O$_5$ attracted much interest theoretically and experimentally, because of the evidence for a double phase transition around the transition temperature of $T_0 = 34$ K, attributed to a charge ordering and dimerization. This dimerization had first been interpreted as a spin-Peierls type. Isobe [38] claimed that the transition in this compound is of the spin-Peierls type, evidenced by magnetic susceptibility on powder sample of $\alpha'$-NaV$_2$O$_5$ in the temperature range 2 – 700 K in a 1 T field. Their measurement shows (Fig. 1.3.1.2) that $\chi$ has a broad maximum at room temperature, which is typical for low dimensional spin systems [38]. Furthermore, $\chi$ decreases rapidly below 34 K and, at the lowest temperature, shows an upturn. The overall behaviour is indicative for a non magnetic ground state (the upturn usually is attributed to impurity). Since the spin-Peierls compound CuGeO$_3$ shows the same decrease in $\chi$, Isobe claimed that this rapid decrease of $\chi$ below 34 K in $\alpha'$-NaV$_2$O$_5$ is an indicative that the transition is also spin-Peierls type.

Other investigations evidenced the more complex nature of the transition in $\alpha'$-NaV$_2$O$_5$; it is now clear that the transition is not a simple spin-Peierls transition:

1- Sodium vanadate does not show a strong suppression of $T_0$ by a magnetic field. The suppression of $T_0$ is characteristic for spin-Peierls systems. Heat capacity measurements, in magnetic fields of 0, 8, 16 T applied along $b$-axis (Fig. 1.3.2.1), show that the magnetic dependence of $T_0$ is only about 25% [54,55,56] of the value for standard spin-Peierls compounds [44, 57, 58].

![Fig. 1.3.2.1: Heat capacity of $\alpha'$-NaV$_2$O$_5$ measured in external fields $0 < B_0 < 16$ applied along $a$ and $b$ axis. [55]](image-url)
2- The specific heat shows that the entropy of the transition in $\alpha'$-NaV$_2$O$_5$ is considerably higher than the entropy of the spin-Peierls system [59,60].

3- The temperature dependence of the thermal conductivity in $\alpha'$-NaV$_2$O$_5$ has an anomaly below the transition temperature, where the thermal conductivity increases by a factor of 5 below $T_0$ (Fig. 1.3.2.2), which was not observed in the inorganic spin-Peierls material CuGeO$_3$ [61].

![Fig. 1.3.2.2: Temperature dependence of the thermal conductivity $\kappa$ (left) for $\alpha'$-NaV$_2$O$_5$ and (right) for CuGeO$_3$. [61]](image)

In addition to the phase transition below $T_0$, the opening of a spin-gap takes place and the size of the gap is about $\Delta \sim 100$ K, which gives a BCS ratio $2\Delta/k_BT_0 \approx 6$, and is much higher than for other organic or inorganic spin-Peierls materials (BCS-value of 3.5). The gap has been value determined by:

1) Elastic neutron scattering on a powder sample at 7 K by Fujii et al., yielding an excitation gap of 114 K [41].

2) The susceptibility measurement done by Ohama et al. determined a singlet to triplet gap with value of $\Delta \sim 98$ [62].

3) Ohama et al. also had reported a singlet to triplet spin-gap with value $\Delta \sim 108$ K measured by the spin lattice relaxation for V. The NMR measurement done on oriented powder sample where the magnetic field was applied parallel to the $c$-axis [45].

4) d.c. susceptibility done by Weiden et. al. result in a gap value $\Delta \sim 85 \pm 15$ K [63].
5) Electron spin resonance done in single crystal by Vasil’ev et al. reports a gap size about 92 K below $T_0$ [61]. Another electron spin resonance by Lohmann et al. on a single crystal was performed for $b$-axis perpendicular to the magnetic field. The study determined a singlet to triplet gap of $\sim 100 \pm 2$ K.

6) Submillimeter wave ESR observed a transition from singlet ground state to excited triplet states with an energy gap of value $\Delta \sim 8.13$ meV at zero field [64].

In conclusion, contemporary literature argues that $\alpha' \text{NaV}_2\text{O}_5$ possesses a spin-gap but no spin-Peierls transition. $T_0$ date, there is no consensus what the exact nature of the low-temperature phase is.

### 1.3.4 Double Phase Transition

In $\alpha' \text{NaV}_2\text{O}_5$ there are evidences for two phase transitions, this two transitions are separated by a few tenths of a Kelvin as it has been observed in:

1. The measurement of temperature dependence of the thermal expansion by Koppen et al. [54] shows one sharp peak-like transition, presumably of first order, at 33 K and another continuous step-like transition with the midpoint at 32.7 K and a width of about 3 K, (Fig. 1.3.3.1).

---

![Fig. 1.3.3.1: Coefficient of thermal expansion, for $B = 0$ T and $B = 8$ T, applied parallel to the $b$-axis. Note the step-like shift of data from $T_0$ to $T < T_0$ which overlaps with the sharp transition peak. [54]](image1)

![Fig. 1.3.3.2: Temperature dependence of the NMR line shift for $B_0 \parallel c$ $\text{Na}$, and $\text{V}$ in the vicinity of the double transition. [65]](image2)
2. Fagot-Revurat et al. [65] reported based on their $^{51}$V-NMR and $^{23}$Na-NMR measurements, that a charge ordering takes place before the opening of a suggested spin-gap, as shown in Fig. 1.3.3.2 These observations point out that at $T_{01}$ the charge ordering takes place, and then a spin-gap opens at $T_c (< T_0)$.

3. The sharp transition observed in the thermal expansion is observable clearly in specific heat measurements of Dischner et al. [66]. However, Bernert [67] showed that the specific heat capacity data of Dischner also show a clear jump in the logarithmic contribution [$\ln(1 - T/T_0)$] after the peak had been subtracted from the raw data (see Fig.s 1.3.3.3 and 1.3.3.4 [67]), the remaining ‘jump’ or step is attributed to the second phase transition.

Fig. 1.3.3.3: Specific heat contribution $C_p - m \ln(1 - T/T_c)$ with $m = 3.314$ μJ/mol K, so that the logarithmic peak is subtracted approximately. One observes a jump in specific heat.

Fig. 1.3.3.4: Specific heat $C_p$ vs. $\ln(1 - T/T_c)$ with $T_0 = 33.71$ K.

4. In dielectric measurement under pressure done by Yoshiaki, on pure compound, two transition temperatures were found [68]. These two transitions existed in the pressure region between 0.6 GPa and 6 GPa (Fig. 1.3.3.5), the pressure dependence of the two transition temperatures varies considerably.

Based on the unclear experimental evidence regarding the vanadium valences, and the nature of the apparent dimerization, further theoretical and structural studies have been conducted, which led to the development of a number of more sophisticated models of the low-temperature phase of $\alpha^\prime$-$\text{NaV}_2\text{O}_5$. 


Bernert et al. [69] have proposed a model with two slightly different vanadium layers, each consisting of two types of two-leg vanadium ladders. One of these ladders exhibits a zig-zag-type order for the magnetic (4.1+) and non-magnetic (4.6+) vanadium atoms $V_{21}$ and $V_{22}$. Two diagonally neighbouring $V_{21}$ atoms exhibit a dimerization with shifts in position of approximately 0.1 Å. In this model, the oxygen atoms are also slightly shifted but to a lesser degree than the V atoms. The second ladder contains site $V_1$ of nominal charge 4.5+. Regarding my $^{23}$Na-NMR studies (Sec. 4.1.3), it is important to note that Bernert’s model allows for six Na sites or even 12 Na sites if the very small differences of Na positions in the two layers are experimentally observable.

Sawa et al. [70] proposed a new low-temperature superstructure for $\alpha'$-NaV$_2$O$_5$ based on their X-ray diffraction experiments. The structure is monoclinic with the space group $A\bar{1}2$, $(a - b) \times 2b \times 4c$. The crystal structure consists of 8 non-equivalent V sites which are clearly separated into two groups (4+ like, 5+ like V), and of 8 Na sites.

On the other hand, van Smaalen et al. had ruled out the monoclinic distortion based on their X-ray diffraction data. Instead, they proposed that the low-temperature superstructure of $\alpha'$-NaV$_2$O$_5$ has Fmm2 orthorhombic $(2a \times 2b \times 4c)$ superlattice [71]. However, this conclusion was solely based on the old V-NMR result that there are only two vanadium valences present in the structure [45,65]. My present work proves that it is not so.
This brings the triclinic structure back in as a viable possibility for the true low-temperature structure of $\alpha'$-NaV$_2$O$_5$. In principle, the triclinic structure has an even lower symmetry than the monoclinic one, allowing for a larger number of Na and/or V sites. In van Smaalen’s model within the triclinic eight crystallographically independent vanadium atoms are present, but only four independent Na atoms appear. In this model there is a zig-zag charge ordering on all the ladders.

Worth noting that the relation between the two phase transitions has not been established until now. With the NMR measurements of the present work, I tried to clarify this relation by studying the spin lattice relaxation’s orientation and temperature dependence. I performed experiments on pure and on doped samples with different concentrations of Lithium and Calcium substituting Sodium. Lithium and Calcium suppress $T_0$ in qualitatively different ways. The Li had been chosen because it is close to Na in the same group in the periodic table so it has the same number of free electrons as Na. Ca adds an extra electron to the structure. We may expect qualitatively different influences for Ca and Li doping on the phase transitions. At any rate, both dopants reduce the bulk transition temperature, providing us with the means of a scale to probe the behaviour of the transitions.

The specific heat measurements of the samples [66] show that Li doping on Na sites shifts the charge transition temperature towards lower values with increasing concentration of Li in an almost linear manner in the studied concentration range. The peak in the specific heat is strongly suppressed with increasing the Li concentration up to 1 % (Fig. 1.3.3.7 [72]). In the case of Ca

![Graph showing specific heat vs. temperature of pure $\alpha'$-NaV$_2$O$_5$.](image)

*Fig. 1.3.3.6: Specific heat vs. temperature of the pure $\alpha'$-NaV$_2$O$_5$. [72]*
doping, the shift of the transition temperature with increasing Ca concentration happens in a sudden manner and is weak in comparison to the one for Li doping. The reduction of the specific heat anomaly at the transition temperature is strong. We expect that these different behaviours will help in the assignment of the various causes for the orientational dependence of $T_1$.

![Graph showing the specific heat vs. temperature for different doping percentages (x) of Li](image)

*Fig. 1.3.3.7: Specific heat vs. temperature for different doping percentages (x) of Li [72]. The suppression of and the shift in temperature of the transition are clearly visible.*

For such small dopings, one does not expect much effect on the line position and line-width in $^{23}$Na-NMR. For 1% Li nominal concentration (1/7% built in), much less than every hundreds Na atom is replaced by a Li atom. The electric field gradient (see Sec. 2.2.3) of the next neighboring Na atoms on both sides of the chain may be affected noticeably but not the further one’s, altering the line position for 2/7% of the Na. Such a small intensity can be expected to go undetected. With the matching of my results, with the important aspects of the recently proposed low-temperature models of $\alpha'$-NaV$_2$O$_5$, I intend to demonstrate the validity of my results and to clarify the nature of the low-temperature phase of $\alpha'$-NaV$_2$O$_5$.

All recent theoretical models which try to explain the large number of Na sites proven in NMR have to allow for more than two vanadium valences. So far, these had not been observed directly by microscopic methods. We present for the first time experimental evidence for three valences and at least four vanadium sites [53] (see Sec. 4.1).
My $^{23}\text{Na}$-NMR and $^{51}\text{V}$-NMR results are contradictory to those in the literature:

<table>
<thead>
<tr>
<th>Old NMR result</th>
<th>Our NMR investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 $\text{V}$ valences below $T_0$</td>
<td>3 $\text{V}$ valences below $T_0 + 1 \text{ V site}$</td>
</tr>
<tr>
<td>8 $\text{Na}$ sites below $T_0$</td>
<td>10 $\text{Na}$ sites below $T_0$</td>
</tr>
<tr>
<td>Single transition</td>
<td>Double transition</td>
</tr>
</tbody>
</table>

**Fig. 1.3.3.8:** Specific heat vs. temperature of $0.15\% \text{Ca}$ [72]. The suppression of the transition occurs at smaller concentrations for Ca than for Li.
2 Nuclear Magnetic Resonance Theory

2.1 Principles of NMR

In any NMR experiment, the important property of the nucleus is the nuclear spin, \( I \). And this spin generates a magnetic dipole. The intrinsic magnitude of this dipole is a fundamental nuclear property called the nuclear magnetic moment, \( \mu \). The symmetry of the charge distribution in the nucleus is a function of its internal structure; in the spherical case, the spin angular momentum number is \( I = 1/2 \), e.g. \(^{15}\text{N},^{19}\text{F},^{31}\text{P}\) etc. Nuclei which have a non-spherical charge distribution have higher spin numbers (e.g. \(^{10}\text{B},^{14}\text{N},^{23}\text{Na},^{51}\text{V}\) etc).

The magnetic quantum number \( m_I \) (where \( m_I \) takes values \( \pm I, \pm (I-1), \ldots, \pm 1/2 \) (half integer \( I \)) or 0 (integer \( I \)) restricts the component of the angular momentum parallel to the magnetic field \( I_z \) (and therefore \( \mu_z \)), but not the components perpendicular to the field. That means that the vectors \( I \) and \( \mu \) can take any orientation on a cone corresponding to a certain value of \( m_I \).

From a classical point of view, the magnetic field tries to align the magnetic moment parallel to the field. However, like a spinning top or the earth in the sun's gravitational field, the nucleus is subject to a force perpendicular to \( B_0 \) and \( \mu \) (Fig. 2.1.1):

\[
\frac{d\mu}{dt} = \gamma B_0 \times \mu
\]  

(2.1.1)

where \( \gamma \) is the magnetogyric ratio, a characteristic of the isotope, it is either positive or negative. \( B_0 \) is the magnetic field and it is along the z-axis of the laboratory coordinates.

As a result, the nucleus will not align parallel to the field but precess at an angle to the field. This is consistent with the quantum mechanical requirement of restricted values of the
z-component of the angular momentum, but no restriction of the x or y component. The angular velocity of the precession is obtained as

\[ \omega_0 = -\gamma B_0 \]  

or  

\[ \nu_0 = \frac{\gamma B_0}{2\pi} \]  

(2.1.2)

where \( \omega_0 \) is the angular velocity in rad s\(^{-1}\), whereas \( \nu_0 \) is the frequency measured in s\(^{-1}\) with \( \omega = 2\pi\nu \). The precession frequency \( \omega_0 \) is also called the Larmor frequency of a nucleus.

The Zeeman Hamiltonian for a spin with quantum number \( I \) in a magnetic field is given by

\[ \hat{H} = -\gamma \hbar \cdot \mathbf{I} \cdot B_0 \]  

(2.1.3)

The energy levels for a spin \( I \) under the influence of a fixed magnetic field split into \((2I + 1)\) sublevels, as shown in Fig. 2.1.2. The energy difference between neighbouring levels can be expressed by

\[ \Delta E_1 = -\gamma \hbar B_0 m_1 \]  

(2.1.4)

Zeeman energy levels are displaced by a constant value, \( \gamma \hbar B_0 \), which is generally called the Larmor frequency of the isotope in the field of \( B_0 \). This resonance frequency is found to vary in direct proportion to the applied field, thus the larger the magnetic field, the higher is the resonance frequency.
The presence of quadrupolar interaction (Sec. 2.2) shifts the energy levels for \( I > \frac{1}{2} \) such that a spectrum of more than one resonance line is obtained.

Fig. 2.1.2: The nuclear energy level splits into \((2I + 1)\) sublevels under the influence of a magnetic field. The cases for \(^{23}\text{Na}\) \((I = 3/2)\) and \(^{51}\text{V}\) \((I = 7/2)\), which are important for this work, are illustrated.

2.1.1 Radio Frequency Pulse and Free Induction Decay (FID)

When the nuclei are placed in an external magnetic field, these nuclei will precess about an axis in the direction of the external field. The component of the magnetization vector, \( M \), in the longitudinal axis \( z \) is \( M_z \) with maximum magnitude. The component of \( M \) in the transverse plane \( M_{xy} \) is zero, as shown in Fig. 2.1.3a. When an external force in the form of Radio Frequency pulse, RF, imposes a magnetic field, \( B_1 \), on the system perpendicular to \( B_0 \), \( M \) moves away from its equilibrium, as shown in Fig. 2.1.3b.

We can make the oscillating \( B_1 \) field a static one by performing a coordinate transformation into a rotating frame using the following equations

\[
\begin{align*}
  x' &= x \cos(\omega t) + y \sin(\omega t) \\
  y' &= -x \sin(\omega t) + y \cos(\omega t) \\
  z' &= z
\end{align*}
\]  

(2.1.5)
If the rotating set of coordinates is chosen to rotate at the same speed and in the same direction as the nuclear precession, \((\omega = \omega_0)\), then each individual nuclear magnetic moment appears static in that frame. As there is apparently no precession, and the cause of the precession is the external field, \(B_0\), this external field effectively disappears in the rotating frame (Fig. 2.1.4). The net magnetization looks just the same, though, along the \(z\)-axis as before.

Fig. 2.1.4: In the Laboratory frame, the oscillating RF field \((B_1)\) consists of two counter-rotating vectors. Switching to the rotating frame makes \(B_1\) static, and simplifies the physical picture.

If a 90° RF pulse is applied to the system, then \(M\) is projected into the transverse plane \(x, y\) and \(M(t) = M_{xy}\). Applying instead a 180° RF pulse to \(M\), the \(M\) along +\(z\)-axis is entirely inverted into the –\(z\)-axis where it has undergone full saturation. After absorbing the energy, the nuclei release
this energy and return to their initial state of equilibrium. This produces an observable rotating magnetic field at the Larmor frequency. If a coil of wire is wound around the sample, an alternating potential will be induced in the coil. As the magnitude of the transverse magnetization decreases, so does the magnitude of the voltage induced in the receiver coil. The induction signal is transient and called the free induction decay, FID, signal, and is also the source of information for all NMR experiments and images. Fig. 2.1.5 shows the FID signal in the time domain. The FID decays due to three distinct effects:

1. The field of the magnet is not perfectly uniform so that the nuclei in different parts of the sample precess at slightly different frequencies and get out of phase with one another, thereby gradually decreasing the net magnetization of the sample. This effect is always dominant.

2. Nuclei in any given substance are generally located in several different lattice environments in each of which the precession frequency will be perturbed by a slightly different amount by local magnetic dipole interactions. As in 1) the result is a gradual loss of phase coherence and a decay of the resultant magnetization.

3. Electromagnetic interactions between the nuclei and the surrounding particles cause transitions between the spin up and spin down states whose coherent combination is manifested as magnetization rotating in the xy-plane. The result is a gradual decay of these coherent combinations and a return to the state of thermal equilibrium in which the magnetization is in the z direction and therefore cannot be detected by the coil.

![Fig. 2.1.5: The received FID after application of a RF pulse.](image-url)
2.1.2 Bloch equations and relaxation

When the sample is inserted into the magnetic field $B_0$, the Boltzmann distribution of spin states occurs among the energy levels. This equilibrium is established by means of specific relaxation processes and gives rise to a small excess of nuclei in the lower state. We can apply an oscillating field, $B_1$, perpendicular to the $B_0$ axis, to manipulate this spin system. After $B_1$ is removed, there are two different mechanisms that allow spins to return to equilibrium of the longitudinal and transverse components. The spin-lattice relaxation is a process whereby non-radiative energy transfer takes place from “excited” spins to the surrounding of the nucleus. These relaxation processes can be described by the Bloch equations

\[
\frac{dM_z}{dt} = -\gamma (M \times H)_z + (M_0 - M_z)/T_1
\]
\[
\frac{dM_x}{dt} = \gamma (M \times H)_x - M_x/T_2
\]
\[
\frac{dM_y}{dt} = \gamma (M \times H)_y - M_y/T_2
\]

(2.1.6)

where $T_1$ is the spin-lattice relaxation time or longitudinal relaxation, and $T_2$ is the spin-spin relaxation time [73]. The spin lattice relaxation time is the time describing how $M_z$ returns to its equilibrium value. Fig. 2.1.6 shows the $T_1$ recovery curve after a 90° pulse has been applied to the system.

![Fig. 2.1.6: The $T_1$ recovery curve for spin $\frac{1}{2}$.](image)

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Chapter 2

The general equation for spin lattice relaxation time has been calculated by Andrew et al. for the central transition and for general $I$ is

$$\frac{1}{T_1} = \frac{(2I+3)}{5I(2I-1)}(W_1 + 4W_2) \quad (2.1.7)$$

where $W_1 = W_{3/2 \rightarrow 1/2} = W_{1/2 \rightarrow -3/2}$ and $W_2 = W_{3/2 \rightarrow -1/2} = W_{1/2 \rightarrow 3/2}$. $W_{m \rightarrow m'}$ is the transition probability per unit time between the levels $m$ and $n$, the transition probability can be written as

$$W_{m \rightarrow m-1} = W(I+m)(I-m+1) \quad (2.1.8)$$

[74,75]. The recovery of the central line for $I=3/2$ is given by

$$a_{1/2}(t) = 1 - \frac{2}{5}e^{-2Wt} - \frac{5}{5}e^{-12Wt} \quad (2.1.9)$$

where $a_m(t) = [n_m(t) - n_{m-1}(t)]$, and $n_m(t) = [N_m(t) - N_m^0]/\sum_m N_m^0$, $N$ the population of the $m^{th}$ state at time $t$ and $N_m^0$ is corresponding thermal equilibrium population.

Albert Narath has derived expressions for the relaxation behaviour for the central transition $\pm 1/2 \leftrightarrow \mp 1/2$ for nuclear spin with higher spin. For our case, in general we need the formula that describe relaxation for $I = 7/2$ which is given in general by

$$a_{1/2}(t) = \alpha_{1/2,-5/2}e^{-2Wt} + \alpha_{1/2,-1/2}e^{-12Wt} + \alpha_{1/2,3/2}e^{-30Wt} + \alpha_{1/2,7/2}e^{-56Wt} \quad (2.1.10)$$

where $\alpha_{m \rightarrow m} = C_{m \rightarrow m} \sum_{m'}(C^{-1})_{m' \rightarrow m}a_{m'}(0)$, the $C$ the matrix element are given in Albert Narath paper [76]. If, however, the transitions are well separated in the spectrum, as is the case for vanadium in chapter 4, a simplified exponential function may suffice.

There are additional relaxation processes that adiabatically redistribute any absorbed energy among the many nuclei in a particular spin system without the spin system as a whole losing energy. Therefore, the lifetime for any particular nucleus in the higher energy state may be decreased, but the total number of nuclei in that state will be unchanged. This also occurs exponentially and is associated with a second time constant, $T_2$, the spin-spin relaxation time.
Under some circumstances, the line-width of an NMR signal at half-height, $\omega_{1/2}$, can be related to $T_2$ by

$$\omega_{1/2} = \frac{1}{\pi T_2} \quad (2.1.11)$$

The $T_2$ processes determine the disappearance of the $M_{xy}$ components of the magnetization and, hence, the observability of the NMR signals.

This can be envisioned in the following way: In addition to the rotation, the net magnetization starts to dephase because each of the spins is experiencing a slightly different magnetic field due to local variations and thermal vibrations and consequently rotates at its own Larmor frequency. The longer the elapsed time the greater the phase difference and the smaller the remaining macroscopic magnetization $M$. The spin-spin relaxation time $T_2$ is the time constant which describes the return to equilibrium of the transverse magnetization, $M_{xy}$

$$M_{xy} = M_{xy0} e^{-t/T_2} \quad (2.1.12)$$

$T_2$ is always less than or equal to $T_1$. The net magnetization in the $XY$-plane goes to zero and while the longitudinal magnetization grows until we have $M$ along $Z$. Both processes, spin-spin relaxation and spin-lattice relaxation, occur simultaneously, only that $T_2$ is less than or equal to $T_1$.

There are two factors which contribute to the decay of transverse magnetization:
1) The molecular interactions.
2) The inhomogeneity of the magnetic field $B_0$.

The combination of these two factors is what actually shows as the FID. The effect of the inhomogeneity is in most cases unwanted, which is why one uses the spin-echo technique (see Sec. 3.2) where its effect is cancelled out. The combined time constant is called $T_2^*$.

The relaxation processes occur by interaction of the nuclear spin with magnetic fields, produced by magnetic dipoles (e.g., other nuclei, paramagnetic ions), which are fluctuating due to random spin tumbling. The nature and the rate of the spins tumbling affect (the tumbling rate shown graphically in Fig. 2.1.7) the $T_1$ and $T_2$ relaxation times. Spin tumbling that occurs at a rate comparable to the resonance frequency $\nu_0$ for the nucleus is most effective in promoting spin-lattice relaxation, i.e., yield the lowest values for $T_1$. $T_2$ values can be decreased even further
as the spin tumbling becomes slower than $\nu_0$, but $T_1$ values will begin to increase. These relationships can be expressed generally as follows:

$$\frac{1}{T_1} = \gamma^2 B^2_{\text{loc}} \left( \frac{\tau_c}{1 + (2\pi \nu_0 \tau_c)^2} \right)$$

$$\frac{1}{T_2} = \gamma^2 B^2_{\text{loc}} \left( \tau_c + \frac{\tau_c}{1 + (2\pi \nu_0 \tau_c)^2} \right)$$

where $B^2_{\text{loc}}$ is the mean-square average of the local magnetic fields, i.e., a measure of the strength of the interaction between the nuclear spin and the fluctuating magnetic fields, and $\tau_c$ is the correlation time. The correlation time is a quantitative measure of the rate of spin tumbling [77].

\[Fig. 2.1.7: \text{The tumbling rate shown graphically.}\]

### 2.2 Spin interactions

#### 2.2.1 Chemical shift

Chemical shift is modification of the magnetic field at the nucleus due to the surrounding electrons and indirect spin–spin coupling interaction of magnetic moments mediated by intermediate electron spins. Causes shift of the resonance frequency of atoms. In atoms, the nuclei see a magnetic field $\Delta B$ in addition to the applied field $B_0$. The chemical shift is due to the orbital motion of electrons. The diamagnetic current flow in an orbital produces an extra magnetic field, which reduces the resonance frequency $\omega = \gamma (B_0 + \Delta B)$. The additional field is proportional to the applied field $\Delta B \propto B_0$. Thus, the chemical shift may be written as $\Delta B = -\sigma B_0$ with the field independent value $\sigma \ (\sigma > 0)$. 

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2.2.2 Knight shift

In materials containing conduction electrons these can interact strongly with the nuclear spin via a contact interaction that produces relaxation and a change in resonance frequency termed the Knight shift, observed for the first time in 1949 by Walter D. Knight [78]. The Knight shift (KS) given by $KS = \frac{\Delta \omega}{\omega} = \frac{\Delta B}{B}$. The Knight shift is feature of metals and superconductors, for simple metal it is positive. It is (almost) independent of the static field, and temperature. $KS$ increases in general with increasing nuclear charge $Z$, and is identical for different isotopes. The Knight shift is an order of magnitude stronger than typical values of the chemical shift in non-metals. Knight shift is not caused by the spatial average of the magnetization of the conduction electrons.

2.2.3 Electric quadrupole effect

A nucleus having the nuclear spin $I$ carries an electric quadrupole moment $eQ$ when the nuclear spin quantum number $I$ is greater than $l/2$ (like in the case of $^{23}\text{Na}$ and $^{51}\text{V}$). These nuclei in any sample are surrounded by inner-shell electrons, valence-shell electrons and various other atoms or ions. The electric charges on these particles produce an electric potential $V$ at the position of the quadrupolar nucleus in question and, when the charge distribution around the nucleus is not spherically symmetric; the electric field gradient (EFG) at the quadrupolar nucleus can be described by a symmetric traceless tensor, which can also be diagonalized:

$$V = \begin{pmatrix} V_{XX} & V_{XY} & V_{XZ} \\ V_{YX} & V_{YY} & V_{YZ} \\ V_{ZX} & V_{ZY} & V_{ZZ} \end{pmatrix}$$

$$V^{\text{PAS}} = \begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix}$$

$PAS$: principal axis system.
The EFG interacts with the nuclear electric quadrupole moment, the Hamiltonian of this interaction in the principal axis system of the EFG tensor being given by

\[ \hat{H}_Q = \left[ e^2 Q q / 4I(2I-1) \right] \left[ (3I_z^2 - I) + \eta(I_x^2 - I_y^2) \right] \] (2.2.2)

In Cartesian coordinates \((x, y, z)\) in such a way that

\[ |V_{zz}| \geq |V_{xx}| \geq |V_{yy}| \] (2.2.3)

where

\[ V_{zz} = eq \] (2.2.4)

And \(\eta\) is the asymmetry parameter of the EFG tensor defined by

\[ \eta = (V_{xx} - V_{yy}) / V_{zz} \] (2.2.5)

where \(0 \leq \eta \leq 1\). The asymmetry parameter is a measure of deviation from cylindrical symmetry. For example, the spherically symmetric EFG (i.e., \(V_{zz} = 0\), therefore no quadrupolar interaction) occurs in sites of high symmetry such as perfectly octahedral lattice sites. Whereas an axially symmetric EFG has \(\eta = 0\) (i.e., \(V_{xx} = V_{yy} = V_{zz}\)), and occurs in sites of relatively high symmetry like distorted octahedra or the base centre position in pyramidal coordinations. The EFG axes do not necessarily coincide with the main crystallographic axes.

The measure of the magnitude of the quadrupolar interaction is the nuclear quadrupole frequency, \(\nu_Q\), which is given by

\[ \frac{\partial^2 V}{\partial x^2} \]
\[ \frac{\partial^2 V}{\partial y^2} \]
\[ \frac{\partial^2 V}{\partial z^2} \] (2.2.1)
\[ \nu_0 = 3 \frac{e^2 Q q}{[2I(2I-1)]} \]  

(2.2.6)

The effect of the quadrupolar interaction, as a sum of first \( (\hat{H}_Q^{(1)}) \) and second order \( (\hat{H}_Q^{(2)}) \) interactions, is shown in Fig. 2.2.1.

Fig. 2.2.1: First-order and second-order quadrupolar interactions, with the influences of each of these interactions on the energy levels of \( I = 3/2 \) quadrupolar nucleus for \( \eta = 0 \).

Starting from the unperturbed Zeeman interactions in the left part of the figure with equal levels spacing, the first order quadrupolar perturbation splits the spectrum into a triplet, leaving the \( \pm 1/2 \leftrightarrow \mp 1/2 \) transition unchanged. The second order alters the spectrum of the central transition too.

The magnitude of the first-order quadrupolar interaction is proportional to \( 2I(2I-1)/3 \) and is much greater than that of the second-order quadrupolar interaction (proportional to \( e^2 Q q[2I(2I-1)]/3 \)). The central transition of a quadrupolar half-integer nucleus (i.e., \( \pm 1/2 \leftrightarrow \mp 1/2 \) transition) is not affected by the first-order contributions, since the energy levels of the +1/2 and -1/2 spin states are shifted by the same amount in the same direction. In the Fig. 2.2.2, we show an example of a NMR spectrum for a quadrupolar nucleus with \( I = 3/2 \). The
spectrum is a powder pattern. In case of a single crystalline sample, like in our spectra presented below in chapter 4, the singularities at $v_0$ and $v_0 \pm v_Q/2$ build sharp, separated lines. If one applies the external magnetic field along another axis than the main EFG axis, the singularities form in different positions of the powder pattern envelope.

*Fig. 2.2.2:* NMR single crystal spectrum of a quadrupolar $I = 3/2$ nucleus with a small nuclear quadrupolar interaction.
3 Experimental

All the experimental results that presented here were performed in a commercial Bruker MSL 300 in 7-Tesla field. The data were processed and analyzed using Bruker 1D-WINNMR and Microcal Origin 6 software.

All the experimental data presented here have been carried out with single crystals of $\alpha'$-NaV$_2$O$_5$, $\alpha'$-Na$_{0.9966}$Li$_{0.0034}$V$_2$O$_5$, $\alpha'$-Na$_{0.9989}$Li$_{0.0011}$V$_2$O$_5$ and $\alpha'$-Na$_{0.9985}$Ca$_{0.0015}$V$_2$O$_5$ for $^{23}$Na and $^{51}$V. Both are quadrupolar nuclei (Table 3.1).

In general, vanadium can obtain different oxidation states: 5+, 4+, 3+, 2+ and 0+. The vanadium has the electron configuration [Ar]3d$^3$4s$^2$. V$^{5+}$ is nonmagnetic with configuration [Ar]3d$^0$ and the V$^{4+}$ is magnetic with configuration [Ar]3d$^1$.

For the pure sample the transition temperature is $T_0 \sim 34$ K. For lithium doping of 0.34 % the transition temperature is reduced to $\sim 32$ K and for Ca doping of 0.15% to $\sim 32.5$ K, as has been shown by the specific heat measurement for our single crystals [72] (see Fig.s 1.3.3.6 to 8 in the introduction).

<table>
<thead>
<tr>
<th>Table 3.1: Some physical properties of the $^{23}$Na and $^{51}$V.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Isotope</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>$^{23}$Na</td>
</tr>
<tr>
<td>$^{51}$V</td>
</tr>
</tbody>
</table>
The single crystals were prepared from a NaVO₃ flux. In the first step, Na₂CO₃ and V₂O₅ are mixed and then heated up to 550 °C in air to form NaVO₃. In the second step, the NaVO₃ is mixed with VO₂ in the ratio of 8 : 1 and then heated up to 800 °C in an evacuated quartz tube and then cooled down at a rate of 1 K/h. The excess NaVO₃ was dissolved in water. The lithium-doped sample was produced by substituting partially in the first step Na₂CO₃ with Li₂CO₃ [38]. Dischner did grow several samples with different Li concentrations (1% - 10%) and Ca concentrations. However, due to the low distribution coefficient during the flux growth process, the real amount of Li-content in the sample is much lower than the nominal one by a factor of 7.5. The real Li concentration was determined for the two Li-doped samples (5 % Li and 10 % Li), using inductive coupled plasma for the V content and atomic absorption spectroscopy for the Li and Na. For the other Li-doped samples the Li concentration was scaled accordingly. The Li sample was investigated using X-ray powder diffraction. There was no effect on the lattice parameter, only at the high Li-content (> 0.9), a small decrease of the c lattice parameter was observed (see Table 3.2) [79]. The Ca-doped sample was grown by substituting partially in the first step Na₂CO₃ with CaCO₃. The chemical composition of the samples has been determined using energy dispersive X-ray fluorescence microprobe measurements. The results showed that the real Ca content of some samples were smaller than the nominal one by a factor of 0.75 [80], the sample that we use here had the nominal content. The typical crystal size is (7 mm × 0.5 mm × 0.07 mm), the weight for Li sample 7.1 mg and Ca is 6.3 mg and for the pure is 6.6 mg. The shape is like a needle and the colour is black.

| Table 3.2: Composition and lattice parameter of some Li-doped samples. |
|-------------------|-------------------|--------|--------|--------|
| Normal Li-content % | Resulting Li-content % | a (Å) | b (Å) | c (Å) |
| 0 | 0 | 11.312(3) | 3.6106(9) | 4.8031(10) |
| 2.4 | 0.34 | 11.312(1) | 3.6112(11) | 4.8012(3) |
| 7 | 0.9 | 11.312(3) | 3.6096(11) | 4.7974(7) |

3.1 Finding the 90° pulse

Finding the correct 90° pulse is important for measuring the spin lattice relaxation. It can be found by two ways: by changing the power of the pulse or the pulse period (i.e. how long the RF is applied). The first method is to fix the pulse period and then start to change the power step by
step. In the second method the power is fixed and the period of the pulse is varied. After applying FT to the signal, we plot the intensity of the FT signal against the pulse length or against the power of the pulse. The resulting plot is a sin-wave and the first maximum of the sin-wave is 90° pulse. The 180° pulse is twice the 90° pulse.

The second method was used in my measurement to find the 90° pulse for $^{23}\text{Na}$ and $^{51}\text{V}$. For sodium the 90° pulse was 2 $\mu$s and for vanadium it was 1.5 $\mu$s. 1.5 $\mu$s corresponds to an excitation width of 700 kHz. With this pulse width it was not possible to measure all V satellites in one shot, because they are spaced over $\sim$2 MHz. In order to find all the V satellites, a frequency scan was carried out and then the spectra were matched together (Fig. 4.1.1). This can lead to non-comparable intensity ratios between the different scans.

### 3.2 Spin echo

The $^{23}\text{Na} / ^{51}\text{V}$-NMR measurements were carried out by the spin-echo method. The spin echo is used to eliminate the effect of inhomogeneity of the applied field [81]. The spin echo consists of two FID’s back to back, hence, using the spin echo we can get better signal to noise ratio. In this method, two RF pulses are applied: The first pulse is a 90° pulse which flips the magnetization into the xy-plane. During the free precessional period, the spins precess about the z direction and

![Spin Echo Diagram](image)

**Fig. 3.1:** The spin echo sequence, (above) pulse train scheme, (below) (a) a 90° pulse puts $M$ into the xy-plane (b) the spins start to dephase, (c) a 180° pulse interchanges the slow and fast spins at time $\tau$ (d) refocusing occurs, (e) the echo at time $2\tau$. 


because each spin precesses at a slightly different frequency, they begin to dephase. Before the spins are completely dephased, a second RF pulse (180° pulse) is applied at a time ($\tau$) after the first pulse and flips the spin packets through 180° within the xy-plane. During the final free precessional period the spins again precess in the xy-plane, but now the spin with higher precessional frequencies are behind those with lower frequencies and will therefore catch up. Eventually, after a time $\tau$, equivalent to the separation between the pulses, the spins will again line up and a net magnetization will result. This recovery of the initial magnetization is termed a spin echo.

In our NMR measurement the signal has been recorded in a fixed magnetic field of 7 Tesla, where the magnetic field has been applied approximately parallel to the crystallographic $a$-, $b$-, $c$-axes, in the temperature range 5 – 100 K. Note, that the crystallographic axes are tilted with respect to the EFG axes ($xyz$) by nearly 5° (see the rotation pattern in Appendix).

### 3.3 Saturation recovery

There are two principle methods for measuring the spin lattice relaxation time: inversion and saturation recovery. The inversion recovery employs a 180 – 90° pulse sequence; it starts by inverting the magnetization ($M_{Z0} = -M_{Z0}$) by 180° pulse, and then monitoring the recovery at various delay times by a 90° pulse or, optionally, by a spin-echo sequence. The saturation recovery uses a train of 90° pulses which destroy $M_z$, followed by a single 90° pulse or a spin-echo train to monitor $M_{xy}$ after a variable delay time.

![Diagram of saturation recovery pulse sequence](image)

Fig. 3.2: The saturation recovery pulse sequence: $t$ pulse spacing during saturation comb ($T_2^* < t < T_1$), and $\tau$: magnetization recovery time. First the comb sequence destroys all the magnetization; after $\tau$ one measures with 90° pulse how much of the magnetization is already restored.
The saturation recovery was used in my measurement for finding the spin-lattice relaxation time for $^{23}\text{Na}$ and $^{51}\text{V}$. It was chosen, because destroying the magnetization is more effective than inverting it to the $-M_0$ for broad lines, where $T_2 < T_1$ and yields better defined initial conditions. In the saturation recovery we need to find the best delay time list, which will allow monitoring the magnetization recovery. To do that, preliminary experiment on the sample was carried out to establish the dynamic range of the recovery. Measuring $T_1$ is time intensive. In the saturation recovery method, varying the delay time $\tau$ will allow us to map the relaxation time of the sample. The values of $\tau$ for our samples were between 1 ms and 20 s, i.e. it varied over four orders of magnitude.

### 3.4 Phase correction

In NMR experiments, the response of the sample to the coherent radiation is detected by a synchronous detector. There is a need to set the detector phase, so that it will be set to the absorption mode for all lines in the spectrum (Fig. 3.3). Due to improper setting of the detector for the absorption mode, the percentage of dispersion-like character increases with the frequency offset. When the response plotted in phase with the excitation vs. frequency is called dispersion spectrum, the plot of the response which lags the excitation by $\pi/2$ is called absorption spectrum. After Fourier Transform is applied to the FID, the imaginary part of the FT is indicated as the dispersion spectrum, and the real part is indicated as the absorption spectrum. If the initiation of data collection is delayed, the effective phase shift at different frequencies becomes larger as the frequency becomes larger. The receiver system may also introduce phase shifts. The most basic

![Fig. 3.3: Absorption and dispersion spectrum.](image)
cause for frequency dependent phase shifts, though, is that a finite $B_1$ rotates magnetizations at different offsets by different amounts. All of these phase shifts are approximately linear in frequency for moderate frequency deviations. Therefore, a linear phase correction of the form $\Delta \phi = (A \omega / 2\pi) + B$ is quite effective [82,83] (compare Sec. 4.1.3).

The absorption from dispersion spectra in principle can separate by applying the phase corrections to the spectrum. There are two types of phase correction performed on the signal after Fourier Transform had been applied on it: zero order correction, which is frequency independent and first order phase correction, which has linear frequency dependence. The zero and first order phase corrections are varied until the real part of the spectrum is pure absorption and the imaginary part is pure dispersion. This process is more complicated if the initial phase is not a multiple of $\pi/2$ and if the spectrum consists of overlapping peaks. Then the baseline of the frequency domain spectrum will show some curvature. There is also a limit to the range where linearity in frequency is given for the phase offset. As will be discussed in Sec. 4.1.3, this limit is reached for our Na satellite spectra.

### 3.5 The rotation pattern

The tensor nature of the quadrupole interaction leads to an angular dependence of line positions, depending on the direction in which the external magnetic field $B_0$ is applied to the crystallographic axes of a single crystal sample. The tensor can be mapped out by recording the rotation pattern. For the rotation pattern measurement we used a special rotator and stator which contains the coil. It has 12 holes (see Fig. 3.4) spaced at 30°. We have developed this rotator for my experiments. A pin is used to fixate the rotator. The rotator has three holes, which enhances the precision to 10° with error of 2° for sample mounting. The sample is mounted on the flat surface of the rotator as in Fig. 3.4.

![Fig. 3.4: The rotator and the stator that were used for precise positioning during the measurement of the rotation pattern.](image)
4 Results and Discussions

In this chapter, the NMR result for $^{23}\text{Na}/^{51}\text{V}$ in the pure $\alpha'\text{-NaV}_2\text{O}_5$ and in the Calcium and Lithium-doped samples will be discussed here. First, the influence of the temperature on Vanadium and the number of Vanadium sites in the low-temperature phase and the dependence on orientations are investigated (Sec. 4.1.1.1, 4.1.1.2, 4.1.1.6, 4.1.1.7). Then the experimental result will be compared with the theoretical model for the low-temperature phase (Sec. 4.1.1.3). The influence of the Calcium and Lithium doping on the number of the Vanadium sites were investigated by NMR experiment (Sec. 4.1.2). In the second section (Sec. 4.1.3), the influence of the temperature and directional dependence of the number of Sodium sites, below the transition temperature and their dependence on the Lithium and Calcium doping, will be discussed. In the final experimental section, the spin lattice relaxation measurement is presented for Sodium in the pure sample and in the Lithium and Calcium sample below and above the transition. From the Sodium spin lattice relaxation rate, it is shown that there is more than one transition in this compound and evidence for the opening of a spin-gap is given. The Vanadium spin-lattice relaxation is presented too and the gap is fitted and compared to the gap deduced from Sodium spin-lattice relaxation.

4.1 $^{23}\text{Na}/^{51}\text{V}$-NMR line splitting and Number of Na/V sites in $\alpha'\text{-NaV}_2\text{O}_5$

In this section I will present the first NMR evidence for charge ordering into three Vanadium valences with four V sites and ten sodium sites in the low-temperature phase, below $T_0$, of sodium vanadate ($\alpha'\text{NaV}_2\text{O}_5$).
4.1.1 $^{51}$V-NMR in the pure $\alpha'$-NaV$_2$O$_5$

First, I will discuss the number of the Vanadium sites and their valences in the pure sample for $B_0 \parallel a, b$ and $c$. Then I will compare my result with the old $^{23}$Na/$^{51}$V-NMR measurement and with the theoretical models which were known until the writing of this thesis.

4.1.1.1 Influence of valence on $^{51}$V-NMR spectrum

$^{51}$V has a spin $I = 7/2$, therefore, seven transitions resulting in a spectrum of seven lines. First, for the pure sample, I will discuss the $\pm \frac{1}{2} \leftrightarrow \mp \frac{1}{2}$ transition only. For the pure sample of $\alpha'\text{-NaV}_2\text{O}_5$ for $B_0 \parallel a$, we observe above $T_0$ as expected one Vanadium line (Fig. 4.1.1). This line is attributed to one Vanadium site in the average oxidation state 4.5+. On cooling through the transition temperature, this V line splits into three lines (labeled 1, 2, 3 in Fig. 4.1.1). These three lines have different intensities. The separation between line number 1 and 2 is 45 kHz and between 2 and 3 is 90 kHz.

![Fig. 4.1.1: The $^{51}$V ($\frac{1}{2} ; \frac{1}{2}$) spectrum of $\alpha'$-NaV$_2$O$_5$ for $B_0 \parallel a$ at various temperatures. In the low temperature phase and below $T_0$ three different vanadium valences appear due to charge ordering (sites 1, 2, and 3).]
The three V lines are due to three inequivalent V in the low-temperature phase. The domineering contribution for the line position relative to the Larmor frequency is the EFG, which consists of contributions of the V valence and of the distribution of electric charge about the V by the lattice [84]. In the low-temperature phase, the latter is influenced by the small differences of the V and O positions due to the dimerization of some of the V ions. It is assumed in the literature that the influence of the valence is dominating. Hence, three V lines prove three valences.

For $B_0 \parallel a$ line number 3 has the biggest relative intensity, it increases strongly with decreasing temperature. This increase, however, does not reflect a change in the true site occupancies. In principle, there are two possibilities to explain the observed differences in relative intensities of the three lines. The cause can be due to relaxation behaviour or correlation time (the correlation time ($\tau_c$) is the time needed to effectively couple the NMR excitation to the spins. The coupling is influenced by the rate of spin-tumbling, $\tau_c$ is a measure of the frequency of the field fluctuation, see equation (2.1.1.3)). Concerning the temperature dependence of the spin lattice relaxation for the three V sites, my measurement shows that there is no evidence for relaxation effects on the V sites. An influence of the correlation time proposes a fluctuation of the spins, which belong to sites 1 and 2. Indeed no NMR signal can be detected for a large number of those spins. These spins will not contribute to the lines intensity. For this case, one concludes that lines number 1 and 2 correspond to V$^{4+}$-like spins. $4+\text{-like}$ means magnetic vanadium. But there is no macroscopic magnetism. Therefore, the moments are fluctuating. If they fluctuate at a rate which is not accessible for NMR (because of the correlation time –see Redfield theory in Slichter [77]), the spins that tumble at those rates cannot be observed. Not all spins will be invisible, because some spins will accidentally be tumbling at speeds which are observable. For the measurement, I used the spin echo experiment. The extreme of the correlation time is given by the minimal observation time, which is around 10 micro seconds. Spins, which tumble much faster than that won’t be observed. Such fast tumbling is not unusual; in fact the majority of quantum events take place at much faster time scales than micro seconds.

My conclusion about the assignment of the valences of the V lines, agrees well with what we found, from the experiments on vanadium reference compounds with well known valences $3+$, $4+$, $5+$:

(a) the line position of $V^{3+}$ in $V_2O_3$, $V^{4+}$ in $VO_2$, and $V^{5+}$ in $V_2O_5$ has been determined experimentally (square symbols in Fig. 4.1.2). These provide information about, which valence can be expected to be found on the low
frequency side, and it sets an approximate reference for the range of spread, which can occur for valence changes from 4+ to 5+.

(b) The magnitude of the EFG is proportional to $1/R^3$ (where $R$ is the in-plane V—O distance of the oxygen coordination). I plotted $1/R^3$ vs. the V valence for the three compounds. This approximation assumes that the in-plane terms dominate the EFG at the vanadium site, although, clearly, from the valence point of view, out-of-plane influences are influencing the valence of vanadium too. It is striking how well the NMR frequency scales with this crude, leading-order analysis for a number of compounds, for which vanadium ranges from +3 to +5 valences. Within the limits of this approximation, we may extract the valence of given vanadium from the line position (frequency). The method may be over simplified; it is still the only way published to directly measure the valences for $\alpha$-NaV$_2$O$_5$. Valences are calculated in models and fitted in X-ray data, but there is always an extra dimension of uncertainty in such indirect proceedings.

Fig. 4.1.2: The valences of the V on the left in the three different reference compounds vs. the frequency (filled squares) and the $1/R^3$ (where $R$ is the average distance between the V at the centre and the O (R) in the corners of the pyramid base) (open circles).
Table 4.1.1: In-plane V–O distances and vanadium valence for some vanadium oxides used in Fig. 4.1.2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>V—O (Å) (at room temperature)</th>
<th>V (valence)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂O₃</td>
<td>1.965</td>
<td>3+</td>
</tr>
<tr>
<td>VO₂</td>
<td>1.927</td>
<td>4+</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>1.838</td>
<td>5+</td>
</tr>
<tr>
<td>α⁺NaV₂O₅</td>
<td>1.916</td>
<td>4.5+</td>
</tr>
</tbody>
</table>

In Fig. 4.1.1, line 2 is separated by approximately 40 kHz from lines 1 and 3. Considering that the true quadrupolar frequency is probably larger than 600 kHz, because of a small non-collinearity of the EFG main axes with the crystallographic axes (use 1 MHz for calculation). A calculated second order quadrupolar shift of about 20 kHz [85] for $^{51}I_L = 78.864$ MHz indicates that indeed the line positions can be dominated by the quadrupolar shift. From now on, I will assume, for my further analysis, that the scaling of the NMR line shift with valence (Fig. 4.1.2) results predominantly from the quadrupolar interaction, but it is possible that secondary causes play a role in the line shift too.

At this point it is advisable to remember that despite the similarities in their V—O coordination, the three reference compounds are of a quite different nature: V₂O₃ is metallic, VO₂ magnetic and V₂O₅ diamagnetic. In my leading order analysis, I start by assuming, that changes in the line position due to hyperfine fields or Knight shifts are not the dominant sources of the actual vanadium line positions.

From 34K down to 30 K, the relative intensities of the lines appear to be close to the true intensity, since the charge ordering will disappear and all vanadium will be 4.5+ above $T_0$. The spins have to ‘get ready’ to lock into 4.5+, which will happen through a slowing down of the tumbling. Eventually, the tumbling gets slow enough, so that we will see the full NMR intensity again. That happens at about 30 K, above this temperature, the relative intensities of the V lines stop changing (apart from the unavoidable Boltzmann factor). In this sense, the true relative intensity ratio of the lines is; line 1: line 2: line 3 is like 1 : 1 : 4. An explanation for this relative intensity difference would be due to the site occupancy. Then line 3 represents site 3 of V, which has four times the number of V ions than sites 1 or 2 (Fig. 4.1.1).
**4.1.1.2 Influence of the structure on $^{51}$V-NMR spectrum**

My experimental results on the pure sample for $B_0 \parallel a$ done for all V satellites (Fig. 4.1.3), show that the (5/2;7/2) and satellite splits into two satellites. This splitting is due to a fourth V site in the low-temperature phase, which possesses the same valence as the 5+ like V, but has a slightly changed neighbourhood resulting in an altered EFG. The spectrum is well fitted by two quadrupole frequencies, $\nu_{Q1} \parallel a = 570 \text{ kHz}$ and $\nu_{Q2} \parallel a = 600 \text{ kHz}$ with $\eta = 0.47$. This slight difference in the quadrupole frequency will be most prominent for (5/2;7/2) transitions, but it is visible as a shoulder on the (3/2;5/2) satellites (Fig. 4.1.3). The observation of the line splitting for the outer satellite only can be easily understood: the difference between the two quadrupole frequencies, $\Delta \nu_Q$, adds one $\Delta \nu_Q$ to the first satellite pair, which is too small to be observed within the line-width. It adds up to $2\Delta \nu_Q$ for the second satellite pair, which appears as a shoulder to the line. For the last satellite pair it is three times $\Delta \nu_Q$ and therefore it becomes the most visible. The same splitting could in principle be present for the other two V lines, line 1 and 2; however, it is not observed and this is due to the lines small intensities - for the following interpretation, we assume that this splitting does not occur.

![Graph showing the splitting of V lines](image)

*Fig. 4.1.3: The $^{51}$V spectrum of $\alpha'$-NaV$_2$O$_5$ at 10 K for $B_0 \parallel a$: The (5/2;7/2) satellites are split due to two slightly in equivalent crystallographic vanadium sites. The small peaks between the lines of the main spectrum arise because of vanadium with different valences.*
Within this “4-site scenario” one can explain the relative intensity differences of lines 1, 2, and 3. Line 3 (Fig. 4.1.1) consists of 2 lines, which have the same line-width (∼ 22 kHz) and the same shift and valence. This implies that there are four V sites in the low-temperature structure instead of three. The four site scenario reduces the differences in relative intensities to $1:1:2:(2)$. Thus, one would look for a model that asks for three valences, one of which (the 5+-like) has two slightly different positions.

### 4.1.1.3 Low temperature models

#### 4.1.1.3.1 Bernert’s model:

Bernert et al.\cite{69} reported a structure determination by synchrotron X-ray diffraction for the low-temperature phase of $\alpha'$-$\text{NaV}_2\text{O}_5$. It is based on their structure data; they performed a bond-valence calculation for the V sites in the low-temperature phase. In this model, there are two slightly different types of vanadium layers; each consists of two types of two-leg vanadium ladders. One of these ladders exhibits a zig-zag-type modulation for the $V^{4.1+}$ and $V^{4.6+}$ vanadium atoms $V_{21}$ and $V_{22}$, and a dimerization between the magnetic V ions. The other ladder contains site $V_1$ of nominal charge 4.5+. The crystallographic position in the two layers are similar (Fig. 4.1.4), and the two different layers are labeled by the subscripts a and b for the vanadium sites. Apart from the slightly different magnitude of the shifts, the main qualitative difference is, that in layer a the V1a site shift in b direction towards the V21a site, while in layer b, the V1b site

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**Fig. 4.1.4:** Bernert et al.\cite{69} theoretical model of low-temperature structure of $\alpha'$-$\text{NaV}_2\text{O}_5$.  

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is shifted away in b-direction from the V21b site. In this model, the abundance of the $V^{4.5+}$ is twice of that of any of the others sites. Within Bernert’s model, one can expect 3 vanadium lines, and due to the small difference between the two layers, one can expect up to a further three V lines within each layer in the NMR spectrum, if one can resolvable this small difference with the broad V line. In this model also, they found a shift in the oxygen ions position, where the oxygen is off from the rung of the ladder in the low-temperature phase. This will affect the EFG of the V and of the Na ions. The result for three V valences in my NMR measurements agrees qualitatively with this model in the low-temperature phase. Within this model, the observed fourth line would be correspondent to another $V^{5+}$ like position.

If we assume, that line 1 and 2 are split too and we do not resolve that, then we count their valences intensities raised by a factor of two, relative to the other where we do resolve it. Then, the relative intensities are not 1 : 1 : 2 but 1 : 1 : 4, which is harder to explain by the model. And if the 1 : 1 : 4 is the true result, then maybe not every other ladder is $4+/5+$, but only every third ladder is. Ladder 1 has then one 4+ and one 5+ and ladder 2 and 3 have four 4.5+ in relation. In Bernert’s model we would, according to my valence assignments, expect the strong line in the middle position (Fig. 4.1.5).

![Graph](image)

**Fig. 4.1.5:** Vanadium valences of Bernert’s model convert through Fig. 4.1.2 into theoretical vanadium line positions for the low-temperature phase, with the experimental line-widths, predicts three valences with intensity ratios of 1:2:1.
4.1.1.3.2 The monoclinic model:

Sawa et al. [70] proposed, based on the X-ray diffraction experiment, a new low-temperature superstructure for $\alpha^2$NaV$_2$O$_5$, which is a monoclinic crystal structure with the space group $A\overline{1}2$, $(a-b) \times 2b \times 4c$. The crystal structure consists of eight inequivalent V sites. The valence of each V site was calculated by the bond valence sum (BVS) method [86,87]. Fig. 4.1.6 shows the calculation results by the BVS method for the eight V sites in the low-temperature phase. These sites are clearly separated into two groups. Sawa et al. conclude that the 1c, 1d, 2a, and 2d sites are V$^{4+}$ like and the 1a, 1b, 2b, and 2c sites are V$^{5+}$ like. Within the resolution of the NMR experiment it seems possible to distinguish between three or four V, as given by the observed line-width (Fig. 4.1.7).

![Figure 4.1.6: The valences of the eight V sites estimated by the BVS method [70].](image)

We arrived at Fig. 4.1.7 by taking the model valences and transformed them into NMR frequencies, based on Fig. 4.1.2 using the experimental line-widths on them. The separation between line 1 and line 3 (Fig. 4.1.1) used to represent the difference between the lowest V valence and the highest one from the BVS method, where the position of line 1 and line 3 is as the position of the lowest valences and the highest valences, respectively. Then we calculated the position of the valences in between according to Fig. 4.1.2. This allows us to decide whether a resolution of these lines would be expected in the NMR experiment; from this figure we see that
the 5+ like V 1b, 1a, 2c and 2b would appear as one experimental line, yielding a relative intensity of four times the single line. 4+ like V 1c and 2a should result in a second NMR line. Mixed valences V 1d and 2d may either both be resolved or not, and they form at least a third V peak. This leads to an intensity ratio of 1 : 1 : 2, if the last mentioned set is not resolved. The monoclinic system is also able to explain relative intensities of 1 : 1 : 2, which Bernert’s model cannot do.

![Graph](image)

\[ ^{51}V \text{ line position relative to } ^{23}Na \ (kHz) \]

*Fig. 4.1.7: Vanadium valences of Sawa’s model convert through Fig. 4.1.2 into theoretical vanadium line positions for the low-temperature phase, with the experimental line-widths, requires at least three experimentally resolved NMR lines with intensity ratios 1:1:2.*

### 4.1.1.4 Experimental V valences

To estimate the valence of the V sites from the NMR line position, assuming that the line positions of the V are dominated by the valence of the ions. We find the ratio of the separation of line 1 and line 2 to the separation of line 2 and line 3, is like 1:2. This implies that the ratio of the charge difference between line 1 and line 2 ($\varepsilon_{\text{NMR}}$) to the charge difference between line 2 and line 3 ($\delta$) is like 1 : 2, if we ignore the non-linearity of Fig. 4.1.3. Then the valence of line 1 is equal to $(4.5 - \varepsilon)^+$ and line 3 is equal to $(4.5 + \delta)^+$. We will now estimate the values of $\varepsilon$ and $\delta$ by subsequently testing experimental separation $\varepsilon$ and calculating $\delta$ for the two models. First, within Bernert’s model ($V^{4.1+}$, $V^{5+}$, $V^{4.6+}$) the $\varepsilon_B = 0.4$ and $\delta_B = 0.1$. If my $\varepsilon_{\text{NMR}}$ is set to 0.4 then $\delta_{\text{calculated}} = 0.8$, or, if $\delta_{\text{NMR}} = 0.1$ then $\varepsilon_{\text{calculated}} = 0.05$. On the other hand, the monoclinic structure by using the valences 4.15+, 4.3+ and 4.8+ of the BVS yields the values for $\varepsilon_{\text{ms}} = 0.15$ and $\delta_{\text{ms}} = 0.5$. In this case, if $\varepsilon_{\text{NMR}} = 0.15$ then $\delta_{\text{cal}} = 0.3$, or if $\delta_{\text{NMR}} = 0.5$ then $\varepsilon_{\text{cal}} = 0.25$. 
Only the third set \((\varepsilon = 0.15, \delta = 0.3)\) can be satisfactorily matched to the real line positions. Within the assumption mentioned above for the calculation of \(\delta\) and \(\varepsilon\), the experimental ratio of \(\delta: \varepsilon\) compared with the \(\delta\) and \(\varepsilon\) of the two models suggests that, the monoclinic structure is more consistent with the experimental results than Bernert’s model for the low-temperature phase crystal structure of \(\alpha’\)-NaV\(_2\)O\(_5\).

### 4.1.1.5 Summary

This is the first microscopic evidence for more than two V valences in the low-temperature phase of \(\alpha’\)-NaV\(_2\)O\(_5\), where we found four V sites with three valences in the low-temperature phase. The three valences are fit in the valence range 4+ to 5+. My NMR result supports the monoclinic structure with a layer like arrangement. Later I will examine my conclusion for vanadium with \(^{23}\text{Na}\)-NMR.

### 4.1.1.6 \(^{51}\text{V}\)-NMR in \(\alpha’\)-NaV\(_2\)O\(_5\) for \(B_0 \parallel c\)

Next, I will discuss the spectrum when the magnetic field applied parallel to the \(c\)-axis \((B_0 \parallel c)\). For \(B_0 \parallel c\) as it was for \(B_0 \parallel a\), above \(T_0\) there is one V site. Below \(T_0\), I find three V lines and these lines have different intensity as it was in the case of \(B_0 \parallel a\). The relative intensities of the three lines do not show the same behaviour as it was for \(B_0 \parallel a\). In the temperature region 30 – 34 K the relative intensity ratio for \(B_0 \parallel a\) was 1 : 1 : 4, but for \(B_0 \parallel c\) I found no difference between the relative intensity ratio in the temperature region 30-34 K and the ratio found below 30 K. Considering my argument for the cause of the change in relative intensities for \(B_0 \parallel a\), I conclude that for \(B_0 \parallel c\) the fluctuations persist to closer to the charge ordering transition than for \(B_0 \parallel a\). Fluctuations, which affect the \(c\)-direction spectrum, occur in the \(c\) direction which is perpendicular to the ladder plane. Whereas fluctuations have already slowed down significantly in the \(a-b\) plane for 30 – 34 K. Note, that in the case of relaxation effects, the fluctuations perpendicular to the applied field direction matter, whereas here for the spectrum effects parallel to the field have influence.

This observation leads us to believe that the charge ordering establishes itself first within the ladder plane, and then expands beyond it, i.e. it is low dimensional or anisotropic in nature. This view is confirmed by the point made in the following paragraph. In Sec. 4.1.3 I will complement
this result with the view that Na takes on the charge order onset, and we will be able to give a limit for the spatial extent or outreach of the transition within the low dimensional structure.

Another difference in the spectrum for $B_0 || c$ is the line-width of 40 kHz, which is almost twice the line-width in the case $B_0 || a$. One can expect either of two causes being responsible for this: 1) Broadening of the lines in this direction could be an indication that, all lines observed for $B_0 || a$ consist of two lines, hence two sites causing them, and the quadrupolar tensor allows for a larger separation in $B_0 || c$ than for $B_0 || a$ (compare to Sec. 4.1.3: Na NMR), or, 2) A faster spin-spin relaxation for $B_0 || c$ than for $B_0 || a$ (compare equation 2.1.11). Faster $T_2$ relaxation for $B_0 || c$ means structurally a more efficient relaxation mechanism in the $b-a$ plane, the ladders plane. Indeed, it is reasonable to assume that $T_2$ would be shorter for directions of short un-interrupted V—V distances. Different peaks i.e. different valences have, due to the nature of the valence change, the dimerization, different distances, hence should have different line-widths. Further experimental evidence is needed to decide the true cause for the line broadening with change of direction. It should, however, be noted (that point 2) is in compliance with my conclusion in the last paragraph, that for $B_0 || c$ spin tumbling is still probed when it is not for $B_0 || a$. 

**Fig. 4.1.8:** The $^{51}V$ spectrum of $\alpha'-$NaV$_2$O$_5$ for $B_0 || c$ below and above $T_0$: The co-existence of three vanadium valences below $T_0$. 

\[\begin{align*}
\alpha'-\text{NaV}_2\text{O}_5 \\
B_0 \parallel c \\
B_0 = 7 \text{T}
\end{align*}\]
For $B_0 \parallel c$ line 3 has again the biggest relative intensity, indicating that the sequence of valence-frequency has not changed with the change of direction. For $B_0 \parallel c$, I observe a relaxation effect (Fig. 4.1.9) enhancing line number 3 relative to the two other lines. Peak 3 has the longer $T_1$, because it still grows from 5 ms to 100 ms to 600 ms evolution time in the pulse train (Sec. 3.3), whereas the other peaks stop growing around 40 ms. This is another confirmation of my assignment, that line 3 is most 5+ like and line 1 and line 2 are 4+-like lines, because 4+ should have a short $T_1$ due to the magnetic relaxation channel, which is not present for 5+-like V.

![Fig. 4.1.9: The relaxation effect for 3 V sites for $B_0 \parallel c$.](image)

For $B_0 \parallel c$, the lines are shifted toward higher frequency with decreasing the temperature. In Fig. 4.1.10, the NMR shift is plotted relative to $\nu_L$ for line #1, 2, 3 below $T_0$. The shift is bigger than for $B_0 \parallel a$, the absolute amount of the shift during the transition differs by about a factor of 8. For $B_0 \parallel a$ and below $T_0$, there is no NMR line shift, but for $B_0 \parallel c$ there is still noticeable temperature dependence. This leads us to believe, that the shift for $B_0 \parallel c$ is coupled to the continuous change due to the dimerization (compare Sec. 4.1.3, Fig.s 4.1.3.1 and 4.1.3.5b: appearance of new Na lines), whereas the shift for $B_0 \parallel a$ sees only the charge ordering.

The spacing between line 1 and line 2 for $B_0 \parallel c$ is 70 kHz and between line 2 and line 3 is 110 kHz. This spacing does not change with decreasing the temperature. The difference in the spacing between the line in the case of $B_0 \parallel a$ and $B_0 \parallel c$, is due to the tensorial nature of the quadrupole frequency. The quadrupole frequency for $B_0 \parallel c$ ($\nu_Q \parallel c = 700$ kHz) is larger than the quadrupole frequency in $B_0 \parallel a$ ($\nu_Q \parallel a = 570$ kHz). The frequency position of the three lines fit in the range of the frequency position of valence range 4+ – 5+ (Fig. 4.1.2).
Assigning the valences to line positions for $B_0 \parallel c$ by the same method as for $B_0 \parallel a$, we obtain the same result as before: Only the third set ($\varepsilon = 0.15$, $\delta = 0.24$) representing the monoclinic system agrees with the data. Note that these quantities show some directional dependence, but my reference data are orientation-averaged, therefore we get some systematic error.

4.1.1.7 $^{51}$V-NMR in $\alpha'$-NaV$_2$O$_5$ for $B_0 \parallel b$

In the pure sample for $B_0 \parallel b$, I present the main line of V with its six satellites (Fig. 4.1.11). Below $T_0$, the $(5/2; 7/2)$ splits into two satellites, as well as the $(3/2; 5/2)$, these new two satellites are of equal intensity. The splitting of the quadrupole satellite is probably due to two different values of $\nu_Q$, i.e. to two crystallographically distinct sites. The spectrum is well fitted by $\nu_{Q1} = 198$ kHz and $\nu_{Q2} = 207$ kHz with $\eta = 0$. We cannot resolve the splitting of the other two satellites within the line-width, because the two V sites had the same shift for the central transition. And
the effect is clearer with the frequencies away from the central line (the outer satellites) for two slightly different quadrupole frequencies. In this orientation ($B_0 \parallel b$) I did not observe line 1 and line 2 as it was in $B_0 \parallel a$. The absence of sites 1 and 2 can be explained through the quadrupole tensors: $\nu_Q$ for $B_0 \parallel a$ is three times $\nu_Q$ $B_0 \parallel b$; we assume that the distance between line 2 and line 3 for $B_0 \parallel b$ reduces correspondingly to one third of the spacing for $B_0 \parallel a$ (90 kHz $\parallel a$), because I had concluded before in Sec. 4.1.1, that the origin of the three lines is overwhelmingly due to the difference in valence, which we linked to the change in EFG; the same argument holds for the spacing between line 1 and 3 (135 kHz $\parallel a$). For the observed line-widths for $B_0 \parallel b$, we would not expect to resolve line 1 and line 2 from line 3.

![Fig. 4.1.11: The $^{51}$V spectrum at 10, 20 and 30 K for $B_0 \parallel b$: From left to right the seven transitions for vanadium are shown, line positions are scaled with respect to the well defined Na line position; at 10 and 20 K, the (3/2;5/2) and (5/2;7/2) satellites are split because of the further crystallographic sites mentioned in the text.](image)

### 4.1.2 $^{51}$V-NMR in the doped sample

Here, I will present two different kinds of doping: Li-Doped sample of 0.34 % and Ca-doped sample of 0.15%, all samples are single crystals. The NMR data were collected with the same method as for the pure sample. The magnetic field has been applied parallel to a and c axes, respectively.
4.1.2.1 Li-doped sample

Like for the pure compound, on cooling through $T_0$ three V valences appear (Fig. 4.1.2.1 and Fig. 4.1.2.2) and their positions fit in the frequency range of valence 4+ and 5+. By the same procedure as in Sec. 4.1.1.4, I estimate the valences, and again find that model three is the only one which satisfactorily explains the data.

![Graph](image)

**Fig. 4.1.2.1:** The $^{51}V$ spectrum of $\alpha'\cdot Na_{0.9966}Li_{0.0034}V_2O_5$ for $B_0 || a$ at various temperatures.

The lines had different relative intensities. Line 2 is in the same position as the single line position of the high temperature phase, which indicates, that this line has the same valence 4.5+. The line-width in the Li-doped sample is the same as in the pure sample for $B_0 || a$ and for $B_0 || c$. As for the pure sample, line 3 has the biggest relative intensity in the two orientations $B_0 || a, c$. The same kind of line broadening occurs for $B_0 || c$ and in this direction lines number 1 and 2 also do not settle for the true intensity ratio 1 : 1 : 4.

The spacing between the lines for $B_0 || a$-axes is: line 1 : 2 is 60 kHz, line 2 : 3 is 80 kHz. The spacing between the V lines does not change with the temperature. For $B_0 || c$ the spacing between the lines is: line 1 : 2 is 80 kHz line 2 : 3 is 120 kHz.
4.1.2.2 Ca-doped sample

The Calcium doping of 0.15 % on the Na site reduces the transition temperature to ~ 32.5 K, as it has been shown in the specific heat measurement for our single crystals. As it was for the pure and for the Li-doped sample, there are three V valences in the low-temperature phase for \( B_0 \parallel c \). But for \( B_0 \parallel a \), I observed two lines only. The spacing between the lines for \( B_0 \parallel c \)-axes is: line 1 : 2 is 70 kHz and line 2 : 3 is 95 kHz. The line-width in the low-temperature for \( B_0 \parallel c \) is still the same as in the Li-doped, as well as the pure sample. Line number 3 has the biggest relative intensity. The position of the three lines fit in the valence range from 4+ to 5+ according to Fig. 4.1.2. For \( B_0 \parallel a \), the spacing between the two peaks is 20 kHz, their position is closer to the valence 5+. I found that the fitting model three for the experimental line spacing is the only one, which satisfactorily explains the data.
Results and Discussion

Fig. 4.1.2.3: The $^{51}V$ spectrum of $\alpha'$-Na$_{0.9985}$Ca$_{0.0015}$V$_2$O$_5$ for $B_0 || c$ at various temperatures.

Fig. 4.1.2.4: The spin echo intensity for $^{51}V$ spectrum of $\alpha'$-Na$_{0.9985}$Ca$_{0.0015}$V$_2$O$_5$ for $B_0 || a$ at various temperatures. The $(1/2;1/2)$ vanadium spectrum is strongly changed for $B_0 || a$ but not for $B_0 || c$ (Fig. 4.1.2.3) indicating that Ca in the Na chains affects the ladder plane.
4.1.2.3 Comparison between the doped samples and the pure sample

The three sodium vanadate compounds show that there is a charge ordering transition. This is evidenced by the appearance of three V valences in the (in) low-temperature phase. The rather small amount of doping changed the transition temperatures only marginally from 34 K to about 32 K for both dopings. As it is known from specific heat measurements, Ca substitution suppresses the charge order transition more abruptly (suppression of peak in specific heat) than Li. I find evidence for a microscopically different behaviour for Ca doping in that for $B_0 \parallel a$ only two V lines appear. This is interesting in so far as 0.15 % Ca substitution affect only every 667th unit cell directly. Since it is reasonable to assume a random build-in process for such low concentrations, this means that every 167th (or 83rd if one counts both adjacent V planes as equal, although in one case the oxygen coordination pyramid points towards the Ca and the opposite one away from it) vanadium has a Ca in its nearest Na-coordination sphere. Yet, in Fig. 4.1.2.4 we see a clear effect of this doping on the average vanadium’s spectrum.

Interestingly, the change occurs only for $B_0 \parallel a$ and not for $B_0 \parallel c$, meaning that the disturbance acts along the crystallographic $a$-axis (see Fig. 4.1.3.7, for V the EFG axes are collinear to the crystallographic axes, whereas they are not for Na), i.e. along the rung of the ladder. If one considers the effect that the doping of the extra electron of Ca has on $\alpha'$-NaV$_2$O$_5$, it is apparent that the presence of this extra charge interrupts the 1d-magnetic chain that the vanadiums build along the ladder direction. Hopping takes place along the rung of the ladder.

<table>
<thead>
<tr>
<th>Positions $\parallel c$</th>
<th>Line 1</th>
<th>Line 2</th>
<th>Line 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>–310</td>
<td>–380</td>
<td>–490</td>
</tr>
<tr>
<td>Li doped</td>
<td>–235</td>
<td>–315</td>
<td>–435</td>
</tr>
<tr>
<td>Ca doped</td>
<td>–275</td>
<td>–345</td>
<td>–440</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spacings/compound</th>
<th>Line 1–2 $\parallel a$</th>
<th>Line 2–3 $\parallel a$</th>
<th>Line 1–2 $\parallel c$</th>
<th>Line 2–3 $\parallel c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>45</td>
<td>90</td>
<td>70</td>
<td>110</td>
</tr>
<tr>
<td>Li doped</td>
<td>(+15) 60</td>
<td>(-10) 80</td>
<td>(+10) 80</td>
<td>(+10) 120</td>
</tr>
<tr>
<td>Ca doped</td>
<td>–</td>
<td>–</td>
<td>(0) 70</td>
<td>(-15) 95</td>
</tr>
</tbody>
</table>
Another instance, where differences between the doped and the pure sample can be found, regards the line spacings and line positions. The line positions differ already for the high temperature phase (compare Fig.s 4.1.2.3-4 for Ca, 4.1.2.1 for Li, 4.1.8, and for the pure 4.1.3 and 4.1.1).

Li doping shifts all lines towards 4+-like valences (Fig. 4.1.1) and so does Ca, but to a lesser extent. This result indicates that doping with isoelectronic and non-isoelectronic dopants influences the oxygen coordination of vanadium. That effect has to occur through the ion size of the dopant.

According to Shannon [88], the ionic radii for 8-fold coordinated Li+ is 0.92 Å, which is smaller than Na+ 1.18 Å as is Ca2+ with 1.12 Å. The sodium site is not 8-fold coordinated, in fact there is no simple coordination sphere, and the distances to all neighbours except to the apex oxygen of the vanadium pyramid are relatively large. Thus, the ionic radii for a big coordination number seem to reflect the situation most reliably. As a result, both dopants will give rise to the same effect in valence shift, if the driving force is indeed the different ionic radius. More space for the vanadium apex atom, should allow it to situate itself slightly further away from the V. With reference to Fig. 1.2.1, we expect that the original V coordination in α′-NaV2O5 has drifted from a slightly trigonal bipyramidal towards a more square pyramidal arrangement.

Fig. 4.1.2.3.1-3 shows the temperature dependence of the line positions of vanadium ($\pm \frac{1}{2} \leftrightarrow \mp \frac{1}{2}$) lines 1, 2 and 3 as defined in Fig. 4.1.1 and the figures in doped sample section. All line shift scales have been defined relative to the sharp $^{23}$Na ($\pm \frac{1}{2} \leftrightarrow \mp \frac{1}{2}$) resonance line. The NMR line shift in $B_0 || a$ for the three samples is smaller than the shift in the $B_0 || c$. While shifts for $B_0 || a$ occur in the vicinity of $T_0$ and become constant immediately below the transition temperature, for $B_0 || c$ the transition appears more continuous in nature. The major part of the shift of the line happens between $T_0$ and 20 K, but to the lowest temperatures observed a small shift continues to be present. The behaviour for $B_0 || b$ is in between that of the two other orientations: The shift appears in the vicinity of $T_0$, but the magnitude of the shift is comparable to the shift for the $c$ direction.

From these behaviours, I conclude that the shift for the $c$ direction probes the dimerization (compare to Sec. 4.1.3), while the shift in $a$-direction is sensitive to the charge ordering transition. This means, that the dimerization is felt strongly in the direction perpendicular to the ladder plane, whereas the charge ordering dominates the plane and in particular the direction
along the rung of the ladder. Along the legs of the ladder, a mixture of the two transitions is experienced.

Fig. 4.1.2.3.1: Temperature dependence of line shift of all three vanadium lines for $B_0 || a$ and $B_0 || c$. and for the central transition of the $B_0 || b$ spectrum for the pure sample.

Fig. 4.1.2.3.2: Temperature dependence of line shift of all three vanadium lines for $B_0 || a$ and $B_0 || c$. and for the central transition of the $B_0 || b$ spectrum for the 0.15% calcium-doped sample.
It is remarkable, that all three vanadium show qualitatively and quantitatively very similar behaviours in these respects. According to the models of the low-temperature structure, the dimerization between the magnetic vanadium creates physically non-equivalent vanadium sites. But this does not reflect in the shift data although one of the vanadium lines refers to dimerized vanadium, another to non-magnetic vanadium, and the last one to an in-between vanadium, possibly of the 4.5+ type which is described by Bernert as V1.

For Li doping, my data are incomplete especially in the vicinity of $T_0$ (Fig. 4.1.2.3.3). But the trends that can be seen agree for the most part with the case of the pure compound. For $B_0 \parallel b$, it looks like the shift would occur above $T_0$ and that would certainly be an important finding, but the means of interpretation are limited for incomplete data.

For the Ca-doped sample (Fig. 4.1.2.3.2), the situation differs somewhat from the un-doped case. Again, for $B_0 \parallel b$ the shift seems to have finished by the time one cools through $T_0$. Secondly, for $B_0 \parallel c$ the temperature dependence of the shift seems to have two different slopes, a flatter one for temperatures near $T_0$ and then a steep increase below $\sim 30$ K. It may be argued that the two slopes resolve the two different transitions, first, at $T_0$, the charge ordering, which

![Fig. 4.1.2.3.3: Temperature dependence of line shift of all three vanadium lines for $B_0 \parallel a$ and $B_0 \parallel c$. and for the central transition of the $B_0 \parallel b$ spectrum for the 0.34% lithium-doped sample.](image-url)
happens instantly, and then near 30 K the dimerization which is smeared out over a wide temperature range well into the low-temperature phase. The latter should reflect a continuous very slight reorganization of ion positions. According to calculations by Bernert [67], both, vanadium and oxygen, change positions minimally through the dimerization process. It is possible that the associated energies ‘lock in’ to a low temperature arrangement at different temperatures. I conclude that calcium doping suppresses the onset of dimerization stronger than that of the charge-ordering transition.

4.1.3 $^{23}\text{Na-NMR}$

In the next section, I will present the $^{23}\text{Na-NMR}$ in the pure and in the Li and Ca-doped samples. The Na atoms are located between the V—O planes and build chains along the $b$-axis in the compound, which are offset from the plane of the ladder. $^{23}\text{Na}$ is quadrupolar ion with spin $3/2$, this will result in set of three lines in the NMR spectrum representing one Na site (main line and two satellites situated symmetrically on the left and right hand site of the main line) above $T_0$. In the low-temperature phase, the V central line splits into three lines, which provide that there are three V valences, and because of tumbling of the V spins that belong to $V^{4+}$, like it was not possible to calculate the abundances directly for the V sites. In the case of Na, there exist no different valences or magnetic ions in $\alpha'$-NaV$_2$O$_5$, so for Na it is possible to determine the site abundances directly.

4.1.3.1 The pure compound

4.1.3.1.1 $^{23}\text{Na-NMR for } B_0 \parallel a$

The $^{23}\text{Na-NMR}$ spectrum for the pure sample is shown in Fig. 4.1.3.1. For $B_0 \parallel a$ above $T_0$, there are three Na lines, the main line and the two quadrupolar satellites, which are attributed to one Na site. The spin Hamiltonian and quadrupolar tensor are used with principle value $\nu_{\alpha\alpha} = eQV_{\alpha\alpha}/2\hbar$ to analyze the Na spectrum; $\alpha = Z, Y, X, V_{\alpha\alpha}$ are the principal values of the EFG, where the $X, Y, Z$ axes are taken as the principal axes ($|V_{ZZ}| \geq |V_{XX}| \geq |V_{YY}|$), $\hbar$ is the Planck constant and $Q$ is the electric quadrupole momentum [77]. The quadrupole frequency can be extracted from the experimental data by finding the separation between the satellite lines and the main line. For the local symmetry of the Na site in Pmmn, the $a, b, c$ are identified as the principal axes. I found $\nu_{ZZ} = 679$ kHz, $\nu_{YY} = 112$ kHz, and $\nu_{XX} = 581$ kHz at 40 K. Hence, the $b$-axis is the
maximum principal axis. This means, that the EFG tensor for Na is tilted against that one for V (Fig. 4.1.3.8). Furthermore, I fitted $\eta = V_{XX} - V_{YY} / V_{ZZ} = 0.69$, a case of severe non-axial symmetry.

![Image of 23Na spectrum of α'-NaV2O5 at various temperatures for B0 || a.](image)

**Fig. 4.1.3.1:** The $^{23}$Na spectrum of α'-NaV2O5 at various temperatures for $B_0 || a$. The appearance of at least 8–10 Na sites is observed in the low-temperature phase. The development of the spectrum continues to well below $T_0$.

Just below $T_0$, each satellite line starts to split into several satellite lines. The number of the lines continues to increase with decreasing the temperature (Fig. 4.1.3.1), the lines are narrow (FWHM ~ 4.8 kHz). In a first attempt to assign sites one counts eight to ten pairs of satellites, which point towards eight to ten Na sites in the low-temperature phase. In literature, eight sites have been reported [46,65]. There are several circumstances which make the assignment non-trivial. They will be discussed in the following and the chosen method of assignment will be described in detail.

1. The phasing of the whole spectrum (around twenty lines of Na) in principle is difficult in such a big frequency range. When Fourier Transform is applied on the recorded FID’s, the result will be a spectrum, which is not in pure absorption mode. To obtain an absorption spectrum, i.e. the real part of the spectrum which contains all the present intensity and can be used to quantify the result, a phase correction must be applied to frequency domain
spectra. The problem in phasing a big frequency range is that the baseline gets wavy with frequency difference [83]. The region that we look at is about 400 kHz wide. Only the main line can easily be phase corrected, but the others start to be distorted upon large linear correction.

2. The sodium spectrum overlaps with the vanadium one (Fig. 4.1.3). Where both $^{23}\text{Na}$ and $^{51}\text{V}$ are quadrupolar nuclei: V has $I = 7/2$ which gives rise to three pairs of quadrupolar satellites. In addition, each of the V satellites splits in the low-temperature phase into three. The overlapping of all these lines makes the phasing even more complicated. The comparison between the intensities on the left hand side and the right hand side of the Na central line becomes more difficult. The V (3/2 - 5/2) satellite coincides with the left hand part of the Na spectrum.

To resolve the problem of the phasing and the overlapping, I did the following:

a) First I started with standard analysis: In 1-D spectroscopy, the data are collected using quadrature detection. Quadrature detection uses two detector channels (real and imaginary) separated by 90° to determine the true intensity. The Fourier transform is applied to the quadrature signal to produce the real and imaginary spectra (A and B). In order to avoid the tedious phase corrections, magnitude spectra were calculated, which use the two detection channels as $\sqrt{A^2 + B^2}$, where A and B are the intensities. The advantage of magnitude spectra: no phasing necessary; disadvantages: noise artificially higher, some line shape distortion and sinusoidal-like artefacts for

![Fig. 4.1.3.2: Phase dependence of the magnitude spectrum of two overlapping peaks, Fig. a and Fig. b differ in the phasing angle. The regains and between the peaks and beside the peaks are different in the two Fig. a, b. [83]](image)
overlapping lines is possible. Lee et al. [83] have shown, how the magnitude spectrum of two overlapping lines, can give rise to a dependence of the line shape (and position) on the relative phasing of the two channels \( A, B \) (Fig. 4.1.3.2). When the peaks are close together and functions of the relative phase angle, this effect makes an appreciable contribution to the spectrum, the positive or negative intensity from the absorption or dispersion spectrum of one peak may add or subtract to the positive or negative absorption or dispersion intensity from the other peak. When the absorption and dispersion intensities are squared, the magnitude spectrum between the peaks is a function of this relative phase angle. And those peaks that arise from the relative phasing of two overlapping peaks, should be considered whenever precise information is to be extracted from the magnitude spectrum [83].

b) Fig. 4.1.3.3 shows an example of a manually phased spectrum at 10 K. The left hand side of the central peak has been phased independently of the right hand side, and later, the two sub-spectra were merged into one figure. Advantage: Problem 1 reduced (the phasing of the spectrum), but not completely resolved. Disadvantage: Some smaller lines may completely disappear for the benefit of getting mostly true intensities in the leading lines. That way we were able to match pairs of lines,

![Graph](image-url)

**Frequency (kHz)**

*Fig. 4.1.3.3: \(^{23}\text{Na satellites (1 – 10) and Na central line transition (0) at 10K for } B_0 \parallel a, \, \text{"?" indicate unclear or missing satellite position.})*
which belong to one crystallographic site (Fig. 4.1.3.3). The lines number 1 and 9 on the left hand side do not have a clear match on the right hand side. The possible positions for these two satellites are indicated by "?". Line number 6 on the left hand side is a combination of a Na and a V line. We distinguish between the Na and V by the line-width, where the Na lines (FWHM ~ 4.8 kHz) are narrower than the V lines (FWHM ~ 22 kHz || a).

c) To find the missing lines, I tried to phase the spectrum pair by pair and put the final spectrum together like a puzzle (Fig. 4.1.3.4). That way we were able to find the match for each line, including line 1 and 9. The error in phasing due to V overlap adds a systematic error to some Na site’s abundance (sites 6, 5). Table 4.1.3.1 summarizes the intensity of lines on the left hand side, and on the right hand side of the main Na line extracted from Fig. 4.1.3.4. The calculated average intensity of each line is also given in the table, as well as the final estimated abundances of Na sites, taking into account the relaxation effect on relative intensities, where lines have different relaxation times. The abundances were normalized by setting the lowest intensity to 1. The effect of the overlap with V lines was subtracted for line 6 on the left side. For this experiment I used RF pulses of 2μs, which corresponds

![Fig. 4.1.3.4: $^{23}$Na spectrum at 10K phased part by part and then matched together like a puzzle.](image-url)
to an excitation width of 500 kHz. This means that, we have to expect a distortion in the intensity for frequencies larger than 400 kHz from the centre frequency. In consequence, line 9 and 10 are underestimated in their abundances in my data.

From points (b) and (c) it follows, that there are clearly ten lines of Na on each side of the main Na. They are spread over the frequency range ~20 – ~210 kHz. They can be divided into two regions, one having four (number 1 – 4) lines close to the main line, in the frequency range (20 – 70 kHz), and a second region, which has six lines in the frequency range (130 – 210) kHz separated from the first region by 60 kHz. This division of the Na spectrum into two regions may indicate the presence of two main EFG values. Minor modification due to dimerization and charge ordering would then lead to the large number of observed sites. Which means different environments of Na, as is, for instance, the case in the double-layer structure detail in Bernert et al.[69] theoretical model. Ten pairs of satellites require ten crystallographically different Na sites.

<table>
<thead>
<tr>
<th>Table 4.1.3.1: Line position, left satellite intensity, right satellite intensity, averaged intensity and deduced site abundance.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line #</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
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<td>7</td>
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<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>

Table 4.1.3.1 shows four groups of abundances for the Na sites. Four sites had abundance of 4 and another four sites had abundance of 3, and one site with 2 abundances, and one site with abundance 1. I note, that throughout the spectrum ‘pairs’ of two lines are closely together in the
frequency position, and they have the same abundances, e.g. line #1 and line #2 (abundance of 4), and line #4 and line #3 and so on. The average separation between each such pair of lines is about 10 kHz. Within the layer like structure model with small difference between the two layers, we expect to get in the NMR signal such pairs with equal abundance and close together, because their EFGs hardly differ. In this interpretation, within each layer there are five Na sites. This result is in good agreement with my conclusion in the vanadium Sec. 4.1.1, that there is evidence for a layer like structure.

The model by Bernert et al. [69] allows for six to twelve inequivalent Na sites: six Na sites in first layer and due to the atomic positions in the second layer in Bernert’s model, which are slightly different from the first layer; a further six Na sites may be observed, provided that this difference is big enough, so that the change can be resolved in the 7 T field. The abundances of the Na sites in this model are equal. For the interpretation of my $^{23}$Na-NMR, Bernert’s model is a good starting point. In order to explain the V results too, a different stacking order of ladders is necessary. Instead of Dimerized (D) - NonDimerized (ND) sequence D - ND D - ND, I propose D - ND - ND D - ND - ND in order to explain the vanadium site occupancies.

The monoclinic crystal structure with the space group A 112, $(a-b) \times 2b \times 4c$, allows for eight Na sites with equal abundance [70]. This is still not enough to explain the ten sodium sites that I have found in the pure compound, the existence of frequency ‘pairs’, or the difference in Na abundances. As for this structural model, the results require some additional symmetry breaking as is possibly given in the triclinic variant.

In the work by Fagot-Revurat et. al. [65], the authors reported eight Na sites for $B_0 \parallel a$ (Fig. 4.1.3.5c a-axis). Comparing my results for the same orientation (Fig. 4.1.3.5b), with their result, one can clearly note that there are two lines missing in Fig. 4.1.3.5c for a-axis. With the best possible matching of the line positions in the two figures, i.e. 4.1.3.5b and 4.1.3.5c, it seems that line 7 and line 10 are the missed ones in the Fagot-Revurat et. al. result.

4.1.3.1.2 $^{23}$Na-NMR for $B_0 \parallel c$

For $B_0 \parallel c$ and above the transition temperature, only one Na site was observed as in $B_0 \parallel a$. Cooling through the transition temperature and below $T_0$ only three sites are visible. The relative intensity of the lines 1 : 2 : 3 for $B_0 \parallel c$ is like 1 : 2 : 1, and there is no change in the relative intensity of these lines with temperature. This result for $B_0 \parallel c$ agrees well with old NMR by
Fagot-Revurat [65] for $B_0 \parallel c$ (see Fig. 4.1.3.5). The smaller number of lines in $B_0 \parallel c$ than in $B_0 \parallel a$ can be explained by that, the lines (8 in Fagot-Revurat [65] and Ohama et. al.[46] work, 10 according to my result) in this orientation are overlapped. The relative intensity ratio of the lines indicates that there is such overlap of the lines and agrees quite well with Fagot-Revurat eight lines, but is a minor problem for my result because it is not as easy to add line intensities up to a ratio of 1:2:1, which we therefore attribute to experimental error.

Fig. 4.1.3.5a, b: The temperature dependence of $^{23}\nu_{\alpha\alpha}$ measured for $B_0 \parallel a,c$, of the sample that was used in my measurement, the transition occurs at $T_0 \sim 34$ K. c) Fagot-Revurat result [65].

4.1.3.1.3 $^{23}$Na versus $^{51}$V

The V shows a splitting of the main line at $T_0$, the splitting of the main line is the evidence for the different valences of V in the low-temperature phase. For Na there was no splitting for the main line, which shows that the Na does not have different valences below the transition. The
splitting happened to the satellites of the Na, which is due to the different quadrupolar frequency. The splitting of Na satellite starts to happen at temperature around 33 K, and in $B_0 \parallel a$ its continue to developed until 15 K (Fig. 4.1.3.5b), unlike the V, where the main line splits to 3 at $T_0 \sim 34$K and no development with temperature (Fig. 4.1.3.6).

From this, we know now the first phase transition in sodium vanadate happens due to the splitting of the vanadium to 3 valences at $T_0$, which is the charge ordering. I conclude that the second transition is a continuous transition and happened after the charge ordering transition, where the number of the line position and the intensity of the Na satellite continue to change well below the transition temperature down to about 15 K. All the previous work that had been done before my work did not show clearly that the second transition is a continuous transition.

The V EFG tensor with the principle value $\nu_{aa} = XX = 292$ kHz, $\nu_{bb} = YY = 103$ kHz and $\nu_{cc} = ZZ = 402$ kHz, thus the leading order $V_{ZZ}$ point in the crystallographic $c$-axis. Na main EFG tensor with $\nu_{ZZ} = bb = 650$ kHz and $\nu_{YY} = aa = 120$ kHz and $\nu_{XX} = cc = 530$ kHz, the leading order $V_{zz}$ in Na point in the crystallographic $b$-axis, this result shows that the Na EFG principle axes is different tilt in the structure than the V EFG principle axes (Fig. 4.1.3.7).
Results and Discussion

4.1.3.2 $^{23}\text{Na}$-NMR in the doped compound

Fig. 4.1.3.8 shows the spin echo intensity for $\alpha'$-$\text{Na}_{0.9966}\text{Li}_{0.0034}\text{V}_2\text{O}_5$ for $B_0 \parallel a$. Above $T_0$, three

![Crystal structure diagram](image)

Fig. 4.1.3.7: Crystal structure of $\alpha'$-$\text{NaV}_2\text{O}_5$ indicates in the principal axis of the Na and V EFG.

The spin echo intensity for $^{23}\text{Na}$ spectrum of $\alpha'$-$\text{Na}_{0.9966}\text{Li}_{0.0034}\text{V}_2\text{O}_5$ at various temperatures. The appearance of at least 7 – 8 Na sites, as indicated by arrows, is observed in the low temperature phase. The development of the spectrum continues to well below $T_0$. ‘*’ indicate probable positions of V satellites.

![Spectrum graph](image)
Na lines were observed, the main line and the two quadrupolar satellites, as it was in the pure sample for $B_0 \parallel a$. For this small doping concentration, $\nu_0$ and $\eta$ are unchanged as well as the line-width. Below $T_0$, each Na satellite splits into several lines. This splitting of the satellite is a continuous development with temperature as in the pure sample. At the lowest temperature that we can reach with our experimental setup (5 K), each Na satellite splits into about eight lines. Their intensities differ as it is the case in the pure sample. For $B_0 \parallel c$ and below (Fig. 4.1.3.9) the same result as in the pure sample was found.

![Graph showing temperature dependence of line position for Na in Na-based compounds](image)

**Fig. 4.1.3.9**: The development of the number of satellites lines with the temperature of $\alpha^\prime-\text{Na}_{0.9966}\text{Li}_{0.0034}\text{V}_2\text{O}_5$ for $B_0 \parallel c$.

Fig. 4.1.3.10 shows the temperature dependence of line position in $\alpha^\prime-\text{NaCa}_{0.0015}\text{V}_2\text{O}_5$ for $B_0 \parallel a$, as the case in the pure and in the Li-dope sample, above $T_0$ the same result. The $\nu_Q$ and $\eta$ are unchanged for this small doping concentration of Ca and the line-width of the line did not change. Below $T_0$, as before, I found eight Na sites in the low-temperature phase. For $B_0 \parallel c$ below $T_0$, only three lines are visible (Fig. 4.1.3.11) in Ca-doped sample, as in the previous samples.

In the slightly Li-doped sample and in the Ca sample, I found less number of Na satellites; eight satellites for Li-doped sample and nine satellites for Ca-doped sample. Lines 10 and 6 in Fig. 4.1.3.1 (pure sample) are missing in the Li-doped sample (Fig. 4.1.3.8). In the case of Ca, line 10 is missing. The smaller number of Na satellites in the doped compounds could occur due
to one of two possible causes. Firstly, it might imply an increase of symmetry for the doped compounds. Such a situation would be quite unusual and counter-intuitive. It is known, however, that α′-NaV₂O₅ is close to a structural instability. The structural disturbance, introduced by the small amount of doping with an ion smaller (Li ionic radius ranges) or bigger (Ca ranges) than Na (ionic size), may provide an opportunity to relax the structure locally into a substructure, which is energetically favourable and of higher symmetry, so that indeed less Na sites appear. On the other hand, there is no evidence for such a scenario from X-ray studies.

I therefore suggest the second possibility as more likely: Li and Ca are built into the structure in rather specific ways, which enhance for certain sites disorder, which leads to a broadening of the correspondent Na line beyond observation, despite the continued existence of the site. The two main structural models considered in this work Bernert, Sawa (the monoclinic) do not investigate the doping effect on the structure. They do, therefore, not provide hints to support my claim.

Fig. 4.1.3.10. The development of the number of satellites lines with the temperature of α′-Na$_{0.9985}$Ca$_{0.0015}$V$_2$O$_5$ for $B_0||a$. 

Results and Discussion
4.1.3.3 **Summary**

In the low-temperature phase below $T_0$ 10 Na sites were found for $\alpha'\text{Na}_{0.9985}\text{Ca}_{0.0015}\text{V}_2\text{O}_5$ with different site abundances. The number of the Na sites is developed continuously with decreasing of the temperature below $T_0$. I found the leading order $V_{ZZ}$ point in other crystallographic direction for Na than for V. The conclusion in the V chapter is that the monoclinic structure describes the low-temperature phase better than Bernert’s model. But for Na the monoclinic model is not enough to explain all 10 Na sites. With a layer-like structure similar as in Bernert’s model, the monoclinic structure could allow for more than eight Na sites in the low-temperature phase. On the other hand, Bernert’s model would explain more than eight Na sites in low-temperature phase (up to twelve Na sites).

We know that the first phase transition in sodium vanadate happens due to the charge ordering of the vanadium to three valences at $T_0$. I conclude that the second transition is a continuous transition, where the number of the lines, position, and the intensity of the Na satellite continue to change well below the transition temperature, down to about 15 K in pure compound. All the previous work that had been done before my work did not show that the second transition is a continuous transition.

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**Fig. 4.1.3.11:** The development of the number of satellites lines with the temperature of $\alpha'\text{Na}_{0.9985}\text{Ca}_{0.0015}\text{V}_2\text{O}_5$ for $B_0 \parallel c$. 

![Graph showing the development of satellites lines with temperature](image)
4.2 Spin lattice relaxation

For the first time, orientational dependent spin lattice relaxation measurements for $^{23}$Na and $^{51}$V in of $\alpha$-$\text{NaV}_2\text{O}_5$ are presented for the un-doped, Li and Ca-doped sample. The same samples as in Sec. 4.1 have been used. The magnetic field has been applied parallel to three crystallographic axis $a$, $c$, $b$ in the temperature range 6 – 25 K for V and 5 – 100 K for Na. For V, I did not measure above 25 K because the V signal becomes too weak to determine its decay with an acceptable statistic.

We have studied the Na main line in un-doped and doped single crystals of the vanadate. Note, that in the low-temperature phase, each pair of Na satellites has its own main line. Within the limit of our resolution, we do not resolve these main lines. A relaxation experiment on “the” main line really is performed on all Na sites at the same time. The magnetic field has subsequently been applied parallel to the three crystallographic axes $a$, $b$ and $c$, respectively, in the temperature range 5 – 293 K. When we measure $T_1 \parallel a$, we probe the relaxation in the $b$-$c$ plane, which is perpendicular to the ladders plane. $T_1 \parallel c$ probes the relaxation in the $a$-$b$ plane, out of the plane of the ladders, but parallel to it. $T_1 \parallel b$ probes the relaxation in the $c$-$a$ plane. Note that this is done with respect to the EFG axes orientation in the structure (Fig. 4.1.3.7), which is different for sodium and vanadium.

The data have been collected by using the saturation recovery method (see the experimental chapter 3), and the fitting of the data to the recovery formula

$$M = M_0 + 0.9\left(1 - e^{-6t/T_1}\right) + 0.1\left(1 - e^{-t/T_1}\right)$$

(4.2.1)

where $M$ is the intensity of the signal, $M_0$ the remaining intensity of the signal at the smallest $t$, and $t$ is the delay time which is varied in the saturation recovery experiment.

The general formula that govern the spin lattice relaxation behaviour (see Sec. 2.1.3 equation 2.1.7): 

$$\frac{1}{T_1} = \frac{(2I + 3)}{5I(2I - 1)}(W_1 + 4W_2)$$

(4.2.2)
In my measurement, only the central transition $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ has been excited and the formula can be reduced to

$$\frac{1}{T_1} = Ce^{-\Delta T}$$  \hspace{1cm} (4.2.3)

where $C = 2I + 3/5I(2I - 1)$. The Equation will be used for the gap fitting for $^{23}$Na and $^{51}$V.

Troyer et al. did theoretical predictions, how the spin-gap should form in spin $\frac{1}{2}$ for 2-leg ladders [89]. The temperature dependence of $T_1$ has been predicted to be

$$\frac{1}{T_1} \approx \frac{3\gamma^2 A^2}{16\pi^2} e^{(-\Delta/T)}[0.80908 - \ln(\frac{\omega_0}{T})]$$  \hspace{1cm} (4.2.4)

the formula holds only for the temperature range $\omega_0 \approx 3 \text{ mK} \ll T \ll \Delta$.

$T_1 \cdot T^{-1}$ for $^{23}$Na shows some remarkable directional dependencies in $\alpha'\text{NaV}_2\text{O}_5$. At low temperatures, a gap like feature appears. For temperatures about the macroscopic transition temperature $T_0 \sim 34$ K, a sharp and structured peak is observed for $B_0 \parallel b, c$, but not for $B_0 \parallel a$. At temperatures well above $T_0$, all directions show little temperature dependence, if any. All regions show some directional dependence and the influence of Li doping (0.34 % and 0.11 %) and Ca doping (0.15 %) will be presented, first for $^{51}$V, then for $^{23}$Na-NMR.

Here I will prove that: The gap is anisotropic, and the phase transition is complex and has a number of sub-features, probably reflecting the onset of charge ordering and dimerization independently.

### 4.2.1 Result

#### 4.2.1.1 Pure sample

Fig. 4.2.1.1 shows the spin lattice relaxation as a function of temperature for the three crystallographic axes orientations ($a, b, c$) of the pure sample. $T_1 \parallel c$ is the longest relaxation time at 5 K and it obtains a minimum around $T_0$ at 34.2K. While $T_1 \parallel a$ is the shortest relaxation time at 5 K, it has a sharp peak around $T_0$ at 34.2 K. $T_1 \parallel b$ is a minimum value at 34.2 K. In contrast, at room temperature the relaxation time for $T_1 \parallel c$ is the longest, while $T_1 \parallel b$ is the shortest. Over the whole temperature range the anisotropy in $T_1$ is quite noticeable. Above 50 K, $T_1 \parallel a, c$ have almost the same behaviour, while $T_1 \parallel b$ is independent of temperature. Since no change in structure or in the physics of $\alpha'\text{NaV}_2\text{O}_5$ is reported above 50 K, it is reasonable to assume that $T_1$ develops smoothly between the room temperature data point and the next lowest temperature.
Results and Discussion

Data have not been acquired between 100 K and 300 K, because the experiment becomes more time consuming due to the Boltzmann factor, and temperatures in that range cannot be kept constant for long enough time in our gas flow cryostat. A further complication in this temperature range is the smaller and smaller density of the cooling gas at higher and higher temperatures, which leads to breakthrough problems in the tuneable capacitor of the NMR probe head, and associated difficulties for maintaining 90° pulse conditions for directly comparable results.

Fig. 4.2.1.2 shows \((T_i \cdot T)^{-1}\) as a function of \(T\) for the three orientations. A plot that is often found in literature is \((T_i \cdot T)^{-1}\) vs. temperature. Historically, it has been used for the evaluation of \(T_1(T)\) for metals where the Korringa relation holds:

\[
T_1 \cdot T \cdot K_S^2 = \text{constant}
\]

where \(K_S\) is the conduction electron spin-susceptibility related part of the Knight shift. This is not the situation for insulators; however, the plot is commonly used in the literature, presumably to outline the presence of phase transitions. At any rate, it works well for \(\alpha'\)-NaV\(_2\)O\(_5\). For \(B_0 \parallel a\), \((T_i \cdot T)^{-1}\) there are three different behaviour regions: The low temperature region, where \((T_i \cdot T)^{-1}\)

Fig. 4.2.1.1: The spin lattice relaxation time \((^{23}T_1)\) as a function of temperature for the \(^{23}\)Na main line of \(\alpha'\)-NaV\(_2\)O\(_5\).
“oscillates”, and then it starts to decrease sharply by almost one order of magnitude towards the transition temperature. The oscillation could be caused by the ongoing dimerization process, which continues to change over the entire temperature range, as was evidenced by the continued appearance, and change of intensities of Na satellites (see Sec. 4.1.3). In the region, where the charge ordering transition takes place there is a shallow minimum in $(T_1 \cdot T)^{-1}$ at 34.2 K. This minimum indicates the onset of the charge ordering in this compound.

For $(T_1 \cdot T)^{-1}$ || b, c, there are also three different regions of behaviour for $(T_1 \cdot T)^{-1}$ vs. temperature. In the high temperature region above 50 K, $(T_1 \cdot T)^{-1}$ has a small temperature dependence on temperature, as in the case of $(T_1 \cdot T)^{-1}$ || a. Above 25 K, $(T_1 \cdot T)^{-1}$ starts to increase towards the transition temperature and the increase is evidence for a gap. In the transition region there is a clear peak around $T_0$. This peak has a slightly different temperature value for the two orientations. For $(T_1 \cdot T)^{-1}$ || b the peak is at 34.2 K. This peak does not have a symmetric shape, it has a shoulder on the left hand side around 33 K. $(T_1 \cdot T)^{-1}$ || c has the peak at 33.8 K. This difference in the peak position in temperature could indicate different transition temperatures.
seen by different crystallographic sample orientation. In the low temperature region, below the transition region, \((T_s \cdot T)^{-1}\) starts to increase down to 5 K. In \((T_s \cdot T)^{-1} \parallel b\) we see another very sharp maximum (just one data point) at 35 K (Fig. 4.2.1.2 inserted figure). The measurements for this point at 35 K were repeated 3 times and re-analyzed with a number of methods (see remarks on data treatment throughout the experimental chapter), and still show this offset. This point (35 K) is not seen in any of the other orientations. I believe this point is real. Experiments show a similar but more pronounced peak for the sample with Ca 0.15 %.

### 4.2.1.2 Li-doped sample

Fig. 4.2.1.3 shows the spin lattice relaxation for Na as a function of temperature for the three crystallographic axes \(a\), \(b\), \(c\) in the Li-doped sample. \(^{23}T_1 \parallel c\) is the longest relaxation time at 5 K and it obtains a minimum around \(T_0\) at 32.2 K. While \(^{23}T_1 \parallel a\) had the shortest relaxation time at 5 K, \(T_1 \parallel b\) had the longest one. \(^{23}T_1 \parallel b\) had a minimum value at 34.2 K. Over the whole temperature range the anisotropy in \(T_1\) is quite noticeable. Above 50 K, \(T_1 \parallel a\), \(c\) have almost the same behaviour. On the other hand \(T_1 \parallel b\) is almost independent of \(T\).

![Graph showing spin-lattice relaxation time for Na as a function of temperature for the three orientations (a, b, c) in the Li-doped sample.](image)

**Fig. 4.2.1.3:** The spin-lattice relaxation time for Na as a function of temperature of \(\alpha'Na_{0.9966}Li_{0.0034}V_2O_5\), the black points are for \(T_1 \parallel a\), the red points are for \(T_1 \parallel b\) and the green ones are for \(T_1 \parallel c\). The lines are drawn as guides to the eye.

Fig. 4.2.1.4 shows \((T_s \cdot T)^{-1}\) as a function of temperature for the three orientations \(B_0 \parallel a\), \(b\), \(c\). For \(B_0 \parallel a\) \((T_s \cdot T)^{-1}\) there are three different behaviour regions: The low temperature region,
where $(T_1 \cdot T)^{-1}$ “oscillates” and then, it starts to decrease sharply by almost one order of magnitude towards the transition temperature until 29 K. Above 29 K it increases slightly until 30 K. In the transition region from 30 K to 34 K $(T_1 \cdot T)^{-1}$, there is almost no temperature dependence and above 34 K it starts to decrease. The third region is above about 50 K, $(T_1 \cdot T)^{-1}$ has small temperature dependence and decreases slowly with increasing temperature.

For $(T_1 \cdot T)^{-1}$ $\parallel b$, $c$, there are three different regions of behaviour for $(T_1 \cdot T)^{-1}$ vs temperature. The high temperature region above 50 K, $(T_1 \cdot T)^{-1}$ has small temperature dependence as well as in the case of $(T_1 \cdot T)^{-1}$ $\parallel a$. Above 25 K, $(T_1 \cdot T)^{-1}$ starts to increase towards the transition temperature. In the transition region is a clear peak around $T_0$. This peak has a slightly different temperature value for the two orientations $(B_0 \parallel b, B_0 \parallel c)$. For $(T_1 \cdot T)^{-1}$ $\parallel b$ the peak is at 32.2 K. This peak does not have a symmetric Gaussian shape; it has more structural details. There are two shoulders, one on the left hand side and another on the right hand side. $(T_1 \cdot T)^{-1}$ $\parallel c$ has a peak at 32 K, again the shape of the peak is not Gaussian and there are shoulders, on the left hand side around 31 K and on the right hand side in temperature range 32.6 – 34.5 K. In the low
temperature region below the transition region, \((T_1 \cdot T)^{-1}\) starts to increase down to 5 K for the two orientations.

4.2.1.3 Ca-doped sample

Fig. 4.2.1.5 shows the spin lattice relaxation time as a function of temperature for \(B_0 \parallel b\), \(c\) of the Ca-doped sample. \(T_1 \parallel c\) has the longest relaxation time at 5 K and it obtains a minimum around \(T_0\) at 33.4 K. \(T_1 \parallel b\) has two minimum value at 34 K and 33 K. For \((T_1 \cdot T)^{-1} \parallel b, c\) (Fig. 4.2.1.6), above 25 K, \((T_1 \cdot T)^{-1}\) starts to increase towards the transition temperature. In the transition region, there is a clear peak around \(T_0\). This peak has a slightly different temperature value for the two orientations. For \((T_1 \cdot T)^{-1} \parallel b\) there are two peaks, one at 33 K and another one at 34 K. The first peak on the left does not have a symmetric shape and also there is a shoulder to the left hand side around 32.2 K. \((T_1 \cdot T)^{-1} \parallel c\) has the peak at 33.4 K. In \((T_1 \cdot T)^{-1} \parallel c\) we see another maximum at 35 K (Fig. 4.2.1.6).

Fig. 4.2.1.7 shows \(23^T_1 \parallel a\), in this orientation we see that \(23^T_1\) oscillate in the transition region. It does not show any regular shape. In \(1/23^T_1T\) vs. temperature plot, there is small temperature dependence in the transition temperature. It can be described as a saturated region from 32 –
35 K, and the average is 32.5 K, which is around the transition temperature in the Ca-doped compound.

![Graph](image)

**Fig. 4.2.1.6:** $1/^{23}T_1T$ for Na as a function of temperature in the transition temperature region, the red points are for $T_1 \parallel b$ and the green ones are for $T_1 \parallel c$. The lines are drawn as guides to the eye.

![Graph](image)

**Fig. 4.2.1.7:** The spin-lattice relaxation time as a function of temperature for $T_1 \parallel a$. Insert: $1/T_1T$ for Na as a function of temperature.
4.2.2 Determination of the spin-gap from $^{51}T_1$

In the next section, the NMR result for V spin-lattice relaxation rate in the pure and in doped sample will be presented. Also the result for the gap in these samples will be presented. I will discuss the influence of the orientation on the gap value in the samples.

4.2.2.1 The Pure sample

Fig.s 4.2.2.1-3 show the relaxation rates for $^{51}$V as a function of the inverse temperature. In this plot, $T_0$ occurs at 0.03 on the left hand side of the plots. For the fitting of the gap, I used the standard gap equation [90, 93]

$$\frac{1}{T_1} = C \cdot e^{-\Delta/T}$$

to extract the magnitude of the gap from the data. The fitting has been done for the 5+ like V in the low temperature region, because it has the strongest intensity. The other two lines, which belong to the other two valences, are too weak for measuring the relaxation. In the case of $B_0 \parallel b$, I measured $T_1$ for the strongest line of V (see section 4.1.1.1). I found an anisotropic gap with $\Delta = 65$ K for $B_0 \parallel a$, $\Delta = 80$ K for $B_0 \parallel b$ and $B_0 \parallel c \Delta = 108$ K (Table 4.2.2.1).

The fitting of the gap is quite good for $B_0 \parallel c$, the data scatter more for $B_0 \parallel a, b$, resulting in a rather substantial error of ± 15 K. Still, the difference between the three gap values within error is clearly established. From the V point of view, we see that the gap is anisotropic. Ohama et al.[45] reported a spin-gap fitting for V in oriented powder sample for $B_0 \parallel c$ of 108 K. This agrees well
with my result for the gap for $B_0 || c$ for the single crystal. On the other hand, they [45, 62] did not report any anisotropy for spin-gap in $\alpha'$-NaV$_2$O$_5$.

When applying $B_0 || a$, we test the fluctuations in the b-a plane, which is the plane of the ladders, where the V—O exists. When applying $B_0 || c$, we test the c-b plane, out of the plane of the ladders. $B_0 || b$ tests the a-b plane, which is along the legs of the ladders.

In order to clarify the anisotropy of the gap, a study of the influence of isoelectronic and non-isoelectronic dopants should shed light on these processes, and may answer the question “Is the gap really anisotropic”.

![Graph](image1)

**Fig. 4.2.2.2**: The spin–lattice relaxation rate $1/\tau_1$ as a function of inversed temperature for $B_0 || a$ for V. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.

![Graph](image2)

**Fig. 4.2.2.3**: The spin–lattice relaxation rate $1/\tau_1$ as a function of inversed temperature for $B_0 || b$ for V. The red line is the fitting curve and the black points are the experimental result for $1/T_1$. 

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4.2.2.2 Spin-gap and doping

4.2.2.2.1 Li-doped samples

For Li-doped sample, two different Li-doping levels, single crystals, are studied, 0.34 % and 0.11 % Li, using the same method for the measurements to collect the data and the same fitting equation as in the previous samples.

Fig. 4.2.2.4a, 4.2.2.5, and 4.2.2.6a shows the relaxation rate of $V$ as a function of the inverse temperature in the 0.34 % Li-doped sample. Again we obtained an anisotropic value for the spin-gap for $B_0 \parallel c \Delta = 108 \text{ K}$, $B_0 \parallel b \Delta = 120 \text{ K}$ and $B_0 \parallel a \Delta = 56 \text{ K}$. The gap in Li 0.34 % dopent for $B_0 \parallel a$ and $B_0 \parallel c$ had the same value as in the pure sample. For $B_0 \parallel b$ it increased by factor of 1.5 compared to the pure. The Li doping increases the $V$ gap value compared to the pure for $B_0 \parallel b$ (a-b plane), while the gap is still the same in the other two orientations as in the pure sample.

Fig. 4.2.2.4b and Fig. 4.2.2.6b show the spin–lattice relaxation rate of $V$ for 0.11 % Li-doped sample as a function of the inverse temperature. For this sample I measured two orientations $B_0 \parallel a, c$. I found almost the same gap value in these two orientations, as it was in 0.34 % Li dopent. In the 0.11 % Li dopent the gap for $B_0 \parallel c \Delta = 111 \text{ K}$ and $B_0 \parallel a \Delta = 63 \text{ K}$.

![Graphs showing spin–lattice relaxation rate](image)

**Fig. 4.2.2.4:** The spin–lattice relaxation rate $1/5^1T_1$ as a function of inversed temperature for $B_0 \parallel a$. a) For $V$ in 0.34 % Li-doped sample. b) For $V$ in 0.11 % Li-doped sample. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.

The overall relaxation behaviour of $T_1$ below $T_0$ resembles the opening of an exponential gap, shown for the un-doped compound in Fig.4.2.2.1–3. For $B_0 \parallel c$; the gap value $\Delta = 108 \text{ K}$ describes
the data well between $1/T_0 = 0.3$ and $1/T = 0.125$ (8 K). The gap obeys the simple exponential equation $\frac{1}{T_1} = Ce^{-\Delta/T}$.

![Graph](image)

**Fig. 4.2.2.5:** The spin–lattice relaxation rate $1/\beta T_1$ as a function of inverted temperature for $B_0 \parallel b$ for $V$ in 0.34 % Li-doped sample. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.

![Graph](image)

**Fig. 4.2.2.6:** The spin–lattice relaxation rate $1/\beta T_1$ as a function of inverted temperature for $B_0 \parallel c$. a) For $V$ in 0.34 % Li-doped sample. b) For $V$ in 0.11 % Li-doped sample. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.

The gap displays a strong anisotropy (Table 4.2.2.1) with a value as low as 60 % of the maximum size along $a$, the direction along the rung of the ladder, where electron hopping is
expected to take place. This finding is new and quite unexpected and has not been suggested in
the literature. The data in the literature [45] have been given for $B_0 \parallel c$, for the un-doped
compound only, and reports $\Delta = 108$ K in excellent agreement with the leading term of my
orientation dependent data. The idea of the spin-gap does not require a preferred axis, but the
mechanism that is thought to cause the gap, the electron hopping between two neighbouring
vanadium with differing valences, either directly from vanadium to vanadium or via the close-by
oxygen atoms, is highly preferential with respect to the rung chain direction [69,94]. We can,
therefore, accept the presence of an anisotropic gap which is bound to the ladder plane. It is
helpful to remember that the measurement of $T_1$ along a particular crystallographic axis, say $a$,
actually probes the magnetic fluctuations in the plane perpendicular to $a$, i.e. the $b$–$c$ plane. With
this in mind, we see that the spin-gap appears strongest for $T_1 \parallel c$; hence in the $a$–$b$ plane, the
ladder plane. My data show that small amounts of lithium doping have a complex effect on the
development of the gap. For the smallest amount of 0.11 % lithium doping for $T_1 \parallel a$, $c$ the gap
values are hardly affected. 0.11 % doping refers to about every thousandth sodium atom in a
chain being replaced by lithium, assuming random lithium build-in, and, indeed, $T_0$ is only
marginally reduced. The slightly stronger doping of 0.34 % lithium, which has the macroscopic
effect to reduce $T_0$ by about 2 K, shows a slight diminishing of about 15 % of the gap size along
the $a$-axis, but a strong enhancement of 50 % along $b$.

Both quantities measure the electron hopping impact on $T_1$ in planes perpendicular to the
ladder plane $a$–$b$. The increase of $T_1$ measured along $b$, i.e. in the $a$–$c$ plane, indicates that the
electron hopping is changed upon lithium doping perpendicularly to the ladder, and suggests a
bulging out of the ladder plane influencing the electron transfer pathway, probably associated
with a small displacement of either the oxygen or the vanadium out of the ladder plane.

4.2.2.2.2 Ca-doped sample

Using the same method of measurement and the same fitting equation for the spin-lattice
relaxation of vanadium in the Ca-doped sample, again an anisotropic gap values were obtained,
for $B_0 \parallel a \Delta = 71$ K (Fig. 4.2.2.7), $B_0 \parallel b \Delta = 122$ K (Fig. 4.2.2.8) and $B_0 \parallel c \Delta = 127$ K (Fig.
4.2.2.9). The fitting was good for the three orientations. The difference in the gap value, between
$B_0 \parallel b$ and $B_0 \parallel c$, is within the error. On the other hand, the value of the gap for $B_0 \parallel a$ shows
difference outside the error. The magnitude of the gap, in the Ca-doped sample, is slightly higher
than in the pure sample for $B_0 \parallel a, c$. For $B_0 \parallel b$ the gap increased by a factor of 1.5 from the value
for the pure sample in the same orientation. Over all, I consider it as established, that the gap shows anisotropy for the Ca-doped sample, as it was in the pure sample and Li-doped samples.

![Diagram showing spin–lattice relaxation rate $1/\tau_1$ as a function of inverse temperature for $B_0 \parallel a$ for V. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.]

**Fig. 4.2.2.7:** The spin–lattice relaxation rate $1/\tau_1$ as a function of inverse temperature for $B_0 \parallel a$ for V. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.

![Diagram showing spin–lattice relaxation rate $1/\tau_1$ as a function of inverse temperature for $B_0 \parallel c$ for V. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.]

**Fig. 4.2.2.8:** The spin–lattice relaxation rate $1/\tau_1$ as a function of inverse temperature for $B_0 \parallel c$ for V. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.

The Ca doping increases the value of $\tau_1$ by five to seven times, compared to the pure compound for $B_0 \parallel c$, in measured temperature region. And in the $T_1 \parallel b$, the value was increased by almost thirty times at 10 K and two times around 20 K. The effect on $T_1 \parallel a$ is opposite to the other two orientations, where $T_1 \parallel a$ value in Ca-doped sample, is smaller than the one in the pure.
Results and Discussion

![Graph showing 1/51T1 vs 1/Temperature](image)

**Fig. 4.2.2.9:** The spin–lattice relaxation rate $1/51T_1$ as a function of inversed temperature for $B_0 || b$ for V. The red line is the fitting curve and the black points are the experimental result for $1/T_1$.

<table>
<thead>
<tr>
<th>Crystal axes</th>
<th>EFG axes V</th>
<th>Gap ($\Delta$) K Un-doped</th>
<th>Gap ($\Delta$) K Li 0.11%</th>
<th>Gap ($\Delta$) K Li 0.34%</th>
<th>Gap ($\Delta$) K Ca 0.15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
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<td>65</td>
<td>63</td>
<td>56</td>
<td>71</td>
</tr>
<tr>
<td>y</td>
<td>b</td>
<td>81</td>
<td>No data</td>
<td>120</td>
<td>122</td>
</tr>
<tr>
<td>z</td>
<td>c</td>
<td>108</td>
<td>111</td>
<td>108</td>
<td>127</td>
</tr>
</tbody>
</table>

Table 4.2.2.1: Spin-gap size determined from $51T_1$ temperature dependence for doped and un-doped $\alpha'\text{-Na}_0.9985\text{Ca}_{0.0015}\text{V}_2\text{O}_5$ in three crystallographic directions.

Over all, the four $\alpha'\text{-NaV}_2\text{O}_5$ samples which are presented here as pure, Li and Ca-doped show anisotropy in the spin-gap as probed by $51T_1$. The gap size and its anisotropy are both affected by the doping. The relevant relaxation mechanisms are the hopping of electrons along the rung of the ladder between V ions and, to a lesser degree, the connection between V along the legs. When probing perpendicular to that, we feel the gap anisotropy, i.e. that the gap is confined to the ladder plane.

### 4.2.3 Determination of the spin-gap from $23T_1$

In the low temperature region below $T_0$, the spin relaxation rate decreases for all three orientations. In $b$ and $a$ direction $1/T_1$ is a complicated function in the low temperature region. In
order to be able to quantify values for the spin-gap, we restricted the preliminary analysis to the temperature region, to where a gap-like decay starts to dominate the dependence.

For the two different orientations (1/\(T_1\) || a, 1/\(T_1\) || b), I obtained an anisotropic value for the spin-gap (\(\Delta\)) in the two orientations. For 1/\(T_1\) || a the spin-gap is \(\Delta \approx 60\) K (Fig. 4.2.3.1a) and for 1/\(T_1\) || b \(\Delta \approx 20\) K (Fig. 4.2.3.1b). For 1/\(T_1\) || c there is no spin-gap (Fig. 4.2.3.1c).

While the fit of the gap is quite good for \(B_0\) || b, the data scatter more for \(B_0\) || a resulting in a rather substantial error of \(\pm 25\) K. Still, the difference between the two gap values within error is clearly established. What are the possible causes for the larger error?

Fig. 4.2.3.1: 1/\(T_1\) as a function of inversed temperature for \(B_0\) || a,b,c. The red line is the fitting curve and the black points are the experimental result for 1/\(T_1\).
However, in the case of $\alpha'\text{-NaV}_2\text{O}_5$, the gap feature is overlapped by the peak of the $T_0$ phase transition. In literature, I found (Fig. 4.2.3.2) a situation similar to my case [95]: Up to about 50 K a gap is assigned and fitted, but at temperatures above 50 K a peak in $1/T_1$ appears. The peak can be subtracted from the data if necessary, but in my case there is no severe overlap, so that a correction was not performed.

![Figure 4.2.3.2: Temperature dependent of H-NMR spin lattice relaxation rate. $1^\text{-H}$-$T_1^{-1}$ of $(BDTFP)_2\text{AsF}_6(\text{PhCl})_{0.5}$ for a single crystal.](image)

There is a great amount of literature, which qualifies $\alpha'\text{-NaV}_2\text{O}_5$ as a spin-gap material [38, 42, 65, 96]. How is a spin-gap distinguished from regular gaps? It is a gap which is only observed by magnetic methods like neutron scattering, ESR, and NMR.

In the case of ladder materials, gaps are common due to the low dimensional nature of magnetism in these compounds. Spin-1 ladders display the so called Haldane gap [97]. The case is not so clear cut for spin $\frac{1}{2}$ ladders. Here it seems to be important how many legs a ladder possesses, in whether it develops a gap or not. Ohama had reported a spin-gap of 98 K determined from the susceptibility for $\alpha'\text{-NaV}_2\text{O}_5$ [62], and later they had reported, using the $^{51}\text{V}$-NMR, a spin-gap of 108 K [45]. Also Fujii et al. did an X-ray and neutron scattering and they reported a spin-gap about 116 K [41].

The absence of the gap in $1/T_1^{23}$ can be understood: When we measure $23T_1^{23}$, we probe the relaxation in the a-b plane, such that it contains Na ions, but no V or O ions. As it is seen from the crystal structure, Na ions are shifted away from the V and O ladder plane. Thus, the absence of the gap for $23T_1^{23}$ prove that the spin-gap is associated to a mechanism, which, I conclude, is confined strictly to the ladder plane. I suspect that the hopping electrons between the
V ions may be responsible for the spin-gap, since the hopping provides a potentially dominant relaxation mechanism, which would be detected by the $T_1$ measurements.

### 4.2.3.1 Li-doped sample

In the low temperature region below $T_0$ for 0.34 % Li-doped sample, the spin relaxation rate decreases for all three orientations, as in the pure sample. Using the same fitting equation as before to fit the data of $1/T_1$ below 25 K, for the three different orientations ($1/^{23}T_1 \parallel a, b, c$), obtained an anisotropic value for the spin-gap in the three orientations. For $1/^{23}T_1 \parallel a$ the spin-gap is $\Delta \sim 3$ K, for $1/^{23}T_1 \parallel b \Delta \sim 15$ K and for $1/^{23}T_1 \parallel c \Delta \sim 82$ K (Fig. 4.2.3.3a, b, c).

![Graphs showing the spin–lattice relaxation rate $1/^{23}T_1$ as a function of inversed temperature for $B_0 \parallel a, b, c$ in 0.34 % Li doped sample. The red line is the fitting curve and the points are the experimental result for $1/^{23}T_1$.](image-url)

*Fig. 4.2.3.3: The spin–lattice relaxation rate $1/^{23}T_1$ as a function of inversed temperature for $B_0 \parallel a, b, c$ in 0.34 % Li doped sample. The red line is the fitting curve and the points are the experimental result for $1/^{23}T_1$.***
First, this result confirms, that there is anisotropy in the gap. The gap value for the $B_0 \parallel a$ in the Li sample is a lot smaller, almost non-existent, not like in the pure sample, where it was 60 K. For $B_0 \parallel b$ the gap value is almost the same as in the pure. In the third orientation, $B_0 \parallel c$ in Li-doped sample is a gap while in the pure compound was no gap. As we see, the effect of the Li dopent is more in the $b$-$a$ plane (the ladders plane) and $b$-$c$ plane than in $a$-$c$ plane ($B_0 \parallel b$ which is along the Na chain); this is similar to the gap from vanadium $T_1$ in the same Li-doped sample.

The anisotropy in the spin-gap, as probed by $^{23}T_1$, agrees well with what was found before for the spin-gap, as probed by $^{51}T_1$, where I studied the spin relaxation time temperature dependence for V in pure, Li and Ca-doped samples. The anisotropic value of the spin-gap between V and Na shows that the spin-gap in this compound is not a simple one.

### 4.2.4 Charge ordering and dimerization

For temperatures about the macroscopic transition temperature $T_0 \sim 34$ K, a sharp and structured peak is observed for $B_0 \parallel b, c$, but not for $B_0 \parallel a$. At temperatures well above $T_0$, all directions show only little temperature dependence (partially shown in Fig. 4.2.4.1).

![Graph](image-url)

**Fig. 4.2.4.1**: $1/^{23}T_1 T$ as a function of temperature of $\alpha'$-NaV$_2$O$_5$ in the transition region.

At temperatures near the bulk transition temperature $T_{tr}, T_0 \sim 34$ K, $1/^{23}T_1$ turns from a gap-like feature into a peak. Such behaviour is indicative of a phase transition. Remarkably, the peak does
not appear for the same directions \( (B_0 \parallel b, c) \) as the spin-gap \( (B_0 \parallel a, b) \). An accuracy of the assignment of the gap and of the phase transition depends on the precision of the distinction between the two phenomena. As it is seen in Fig. 4.2.1.2, the areas are adjacent, but there is no severe overlap. Hence, the evaluation of the gap and of the transition temperature depends slightly on each others assignment.

![Fig. 4.2.4.2: \( 1/T_1 \) for \( ^{23}Na \) as a function of temperature of \( \alpha' \)-Na\(_{0.9966}\)Li\(_{0.0034}\)V\(_2\)O\(_5\) in the transition temperature region, the black points are for \( T_1 \parallel a \), the red points are for \( T_1 \parallel b \) and the green ones are for \( T_1 \parallel c \).](image)

At any rate, it is clear, that the peak is not of Gaussian shape, but has a more detailed structure (Fig. 4.2.4.1). This is true for \( B_0 \parallel b \) and \( B_0 \parallel c \). In a first order analysis, I take the largest value of \( 1/23 T_1 \) as the bulk transition temperature. It turns out, that this \( T_tr \) is not the same for the two directions, but differs by 0.4 K: For \( B_0 \parallel b \) \( T_tr = 34.2 \) K and for \( B_0 \parallel c \) \( T_tr = 33.8 \) K. This difference is small and near the limit of temperature resolution \( (\Delta T = 0.2 \) K). The difference between the peak’s temperature positions, in the two orientations, is within the predicted difference, between the two transitions, as found from thermal expansion and from specific heat \( \Delta T_tr \simeq 0.3 \) K.

The main peak at 34.2 K is beyond doubt. This corresponds to a significant lowering of the spin-lattice relaxation time in the ordered phase as it is typically observed for transitions in low-dimensional ladder compounds [95, 98, 99]. \( 1/23 T_1 \) is also increased by a factor of about four,
when compared to the temperature region, well above the transition in $1/^{23}T_1$ (here taken at 40 K), and of about 3, when compared to the value at room temperature.

The shoulder near 33 K is reflected in three data points and the values of $1/^{23}T_1$ remain at 1.5 to 5 times the low temperature value. The determination is less accurate here, because the shoulder interferes with the region, which is assigned for the gap.

At this point, it is legitimate to ask: Could the peak structure be due to a not phase-pure sample, where the different constituents of the phase mixture possess different transition temperatures? The answer is no:

The specific heat shows one peak; but there have been other samples with more peaks indicating phase impurity, they are easily resolved; the Na satellites remain narrow, that strongly indicates a reasonably high degree of phase purity or absence of disorder.

For the Li-doped sample, the over all temperature dependent behaviour of the spin lattice relaxation rate, is the same as in the pure sample (Fig. 4.2.4.2). The spin lattice relaxation rate in the doped sample shows a peak around the transition temperature for $B_0 \parallel b, c$, as it was the case in the pure. The difference in the temperature position of the peaks in the doped and in the pure was in $^{23}T_1 \parallel c$ 1.8 K and $^{23}T_1 \parallel b$ 2 K. The specific heat measurement shows, that the transition temperature for 0.34 % Li-doped sample is about 32 K, and in the pure sample its about 33.8 K. The difference in transition temperature between the pure and the 0.34 % Li-doped sample measured by the specific heat is about 2 K. The difference in the peaks temperature position in the pure and in the Li-doped in ($^{23}T_1 \cdot T$)$^{-1}$, agrees well with the difference in the transition temperatures for the two samples, as it was found by the specific heat measurement. Thus, the $1/^{23}T_1$ peak agrees with the bulk transition temperature, found with the specific heat. This demonstrates also the dependability of my temperature measurements.

In consequence, the appearing of the peaks in $B_0 \parallel c$ and in $B_0 \parallel b$ at different temperatures in the two samples, the pure and the 0.34 % Li-doped, cannot be just coincident. It should have physical relevance. This result for the Li-doped sample proves my point for the pure sample, that the difference in the peak’s temperature position for $B_0 \parallel b, B_0 \parallel c$ indicates two different transitions. These two transitions are closer together for Li doping.

The peaks in the Li-doped sample are not symmetric. The main peak possesses shoulders on the left hand side 31- 31.4 K, and on the right hand side 32.6 – 33 K for $B_0 \parallel c$. In the pure sample, was a shoulder on the right hand side at 35 – 35.4 K, but no shoulder on the left hand
side. For $B_0 \parallel b$ in Li-doped sample are also shoulders on the left hand side 31.8 – 32 K, and on the right hand side 32.6 — 33 K. While in the pure sample was a shoulder to the left 33 – 33.5 K and a single point peak at 35 K. This finding confirms the significance of the single data point peak for the pure sample.

Those shoulders which appear in $(^{23}T_1 \cdot T)^{-1}$ Li-doped sample did appear in the pure sample at higher temperature, the shift is approximately about 2 K, which means those shoulders had been shifted toward lower temperature, approximately in the same amount as the main peak had been shifted from the temperature position in the pure compound.

The spin lattice relaxation time in the Ca-doped sample is faster than in the pure sample. For $B_0 \parallel c$, the $^{23}T_1$ in the pure sample is longer by a factor of three at the lowest measured temperature. In the transition region, the relaxation time in the pure compound is slightly higher for the pure sample than in the Ca-doped sample.

The effect of the Ca doping on the Na relaxation is stronger in the low temperature than in the transition region. And in the low temperature region it is even stronger than the Li doping. This difference in the effect on the $^{23}T_1$ can be understood by: when we dope Ca, we introduce new charge to the system; also the size of the Ca ions is different than that of the Na ions and Li ions. Changing the size of the ions and adding extra charge will both alter the spin lattice interaction.

![Fig. 4.2.4.3: $1/^{23}T_1 \cdot T$ as a function of temperature in the transition temperature region, the red points are for $T_1 \parallel b$ and the green ones are for $^{23}T_1 \parallel c$.](image)

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In the Ca-doped sample (Fig. 4.2.4.3); the main peak in \( B_0 \parallel c, b \) is shifted down about 1 K from the temperature position of the peak in the pure sample. This shift is in agreement to the shift of the peak in the specific heat for the Ca-doped sample. In the Ca-doped sample, the peak is more pronounced at 34 K for \( B_0 \parallel b \) than in the pure sample at 35 K. The existence of two distinct peaks indicates the onset temperatures of two transitions in the Ca-doped compound.

For \( B_0 \parallel b \) a shoulder appears on the left hand side of the peak, which exists also in the pure and Li-doped samples. In Ca-doped sample, the shoulder looks more like a small peak rather than just a shoulder. The small peak is shifted by 1 K from the temperature position of the shoulder in the pure sample. The shoulder in the pure sample, on the right hand side of the peak, for \( B_0 \parallel c \) is in the temperature range 35 – 35.4 K; and here in the Ca-doped sample we find a peak resolved at temperature position 35 K (Fig. 4.2.4.3).

The good agreement of the appearance of the peaks, in the pure and the doped samples, with the bulk transition temperature, shows how well the spin lattice relaxation measurements were. The details of the peak structure demonstrate that the charge ordering transition in this compound in itself is complex and that it is very close in temperature to the dimerization onset, but that doping changes the difference in onset temperatures.

Could the strongest peak is attributed to charge ordering, the shoulder on the low temperature side to the onset of dimerization, which as we know from the study of the Na satellite appearance, then continues to very low temperatures. The feature above the bulk \( T_0 \) occurs in various widths for all dopings, it may indicate yet another transition. However, no such transition has been claimed in literature. I therefore propose that this ‘transition temperature’ is either related to the charge ordering or the dimerization. To understand this relation better, further studies are necessary.

### 4.2.5 Comparison with other compounds for spin lattice relaxation

For comparison three compounds have been chosen: The spin-Peierls compound CuGeO\(_3\) [100], the insulator LiVGe\(_2\)O\(_6\) [101] and a quasi-one dimensional spin \( \frac{1}{2} \) systems Va\(_2\)V\(_3\)O\(_7\). The transition temperature for CuGeO\(_3\) is \( T_0 = 14 \) K, \( T_1 \) measurements were done for \(^{63}\)Cu (Fig. 4.2.4.4a). The \(^{23}T_1\) in \( \alpha'\)-NaV\(_2\)O\(_5\) has a higher value than the \(^{63}T_1\) in CuGeO\(_3\) almost for all
temperatures, except for the very low temperature range, where they are almost equal. The overall behaviour of the spin relaxation rate in the $\alpha'$-NaV$_2$O$_5$ and CuGeO$_3$ is different: In CuGeO$_3$, the spin relaxation rate does not have any prominent peak like in $\alpha'$-NaV$_2$O$_5$ around the transition temperature. $1/T_1$ decreases with decreasing the temperature below $T_0$. This difference in the $1/T_1$ behaviour gives evidence that the transition in $\alpha'$-NaV$_2$O$_5$ is not a simple spin-Peierls transition.

Fig. 4.2.4.4: a) The temperature dependence of the $^{63}$Cu $1/T_1$ of Cu$_{1-x}$Zn$_x$GeO$_3$. [100], b) The temperature dependence of the $^{23}$Na $1/T_1$ of $\alpha'$-NaV$_2$O$_5$ (my result).

LiVGe$_2$O$_6$ has been chosen for comparison even though it has $s=1$, because it is the only low dimensional compound that I found in literature which qualitatively has a similar $1/T_1$ behaviour to the $\alpha'$-NaV$_2$O$_5$. $1/T_1$ for $^7$Li in LiVGe$_2$O$_6$ has a prominent peak at the transition temperature as the case for $\alpha'$-NaV$_2$O$_5$ (Fig. 4.2.4.5). $1/T_1$ in LiVGe$_2$O$_6$ has small temperature dependence above $T_0$ like $1/T_1$ in $\alpha'$-NaV$_2$O$_5$. The absolute values for $^{23}T_1$ in $\alpha'$-NaV$_2$O$_5$ are higher than for $^7T_1$ in LiVGe$_2$O$_6$. At present we do not understand why $T_1$ in the $s = 1/2$ insulator shows the same overall behaviour as in $s = 1$ insulator, since the physics of $s = 1$ ladder are quite different than those of $s = 1/2$ ladders.
I found another interesting example, which had a peak at the transition temperature in spin lattice relaxation rate vs. temperature for $^{23}\text{Na}$ in Na$_2$V$_3$O$_7$, which is similar to ours (see Fig. 4.2.4.6) [102]. This compound is a quasi-one dimensional spin $\frac{1}{2}$ systems. And they had interrupted the sharp peak as indication for onset of the transition. But there is no orientation dependent reported.

Fig. 4.2.4.6: Spin-lattice relaxation rate as a function of temperature of Na$_2$V$_3$O$_7$: A sharp peak near 2.5 K signals the onset of a cooperative phase transition of unknown origin. [102]
4.2.6 Summary

The results in the low temperature dependence of $^{51}T_1$ and $^{23}T_1$ in pure, Li and Ca-doped indicate an anisotropic spin-gap. The temperature dependence of the spin lattice relaxation for $^{23}$Na in $\alpha'$-NaV$_2$O$_5$ as pure, Li and Ca-doped samples, gave an evidence for double or even more complex transition.
5 Conclusion

At the beginning of this thesis, we had set out to contribute to the clarification of the contradictory literature regarding the low-temperature phase of $\alpha'$-$\text{NaV}_2\text{O}_5$. On the one hand, there was the early microscopic NMR evidence:

Charge ordering occurs as proven by two vanadium valences below $T_0$ [45], magnetic $V^{4+}$ and non-magnetic $V^{5+}$. Eight sodium sites of equal abundance appear below $T_0$ which do not change in the low-temperature phase, they are ‘somehow’ related to a spin-Peierls transition [65]. A spin-gap of size 108 K opens [45, 65].

On the other hand, sophisticated theoretical models and their combination with carefully carried out newer X-ray studies were neither able to explain just two vanadium valences in the low-temperature phase nor eight sodium sites [69,71,70]. The size of the spin-gap, measured by a variety of other methods [41, 45, 62,61, 63, 64], reported values somewhat lower than 108 K. The models also established that the dimerization was not of the spin-Peierls type and it is now generally agreed that sodium vanadate is not the second inorganic spin-Peierls system. Still, there is a rather mysterious double transition of first and second order which exact nature and inter-dependence is unknown [66, 67].

At the end of this thesis, I am unable to confirm a single claim of the old NMR work about $\alpha'$-$\text{NaV}_2\text{O}_5$ in the low-temperature phase:

I find consistently for a number of un-doped and very slightly doped samples three vanadium valences, confirming a charge ordering transition at $T_0$, and in good qualitative agreement with Bernert’s model [69], and in quantitative and qualitative agreement with Sawa’s monoclinic structure [70]. Quantitative agreement with Bernert’s model can be achieved when we modify the
stacking sequence of ladders within the layers of the model from D-ND, D-ND (where D refers to
dimerized and ND to non-dimerized) to D-ND-ND, D-ND-ND.

The monoclinic model fails to explain the NMR data. It is possible that a further symmetry
reduction to a triclinic structure, which had been discussed in literature [71], but had been
discarded based on the old two-valence NMR data, would be in better agreement with my Na-
NMR. It is unclear whether a triclinic model would still be in quantitative agreement with the V-
NMR.

Neither the monoclinic nor Bernert’s model are capable of explaining all my NMR results
without modification of the model.

My detailed $T_1$ study on single crystals of the $T_0$ transition region provided evidence for a non-
symmetric, complex transition peak structure which we relate to the onset of more than one
transition, which occurs at slightly different temperatures. These scale with the $T_0$ reduction
provided by lithium and calcium doping. The two transitions, dimerization and charge ordering,
are intimately related. However, doping shifts the transition temperatures in a slightly different
way. A third feature which appears above $T_0$, may indicate a so far unknown transition or may be
related to either of the well-known transitions.

Finally, I investigated the spin-gap by means of $^{51}$V and $^{23}$Na $T_1$ temperature dependence well
below $T_0$. My analysis of the single crystal data reveals an anisotropy of the gap in the sense that
it is constrained to the ladder planes. Sodium $T_1$ has been presented for the first time and the
evidence for gap anisotropy is a new feature too, which has not been reported in former NMR
studies on powder samples or other studies on single crystals. The anisotropy occurs for
vanadium and sodium NMR.

The range of the gap size, when obtained for different crystallographic directions and different
positions in the structure, explains the different values found in literature.

To date, not all questions that arise for the low-temperature phase of $\alpha'$-NaV$_2$O$_5$ can be fully
answered. But one of the greatest obstacles, the disagreement between NMR data and models has
been clarified to a large degree by this work.
Appendix

Rotation patterns

Theory

The rotation patterns are produced by plotting the resonance frequency as a function of the angle of rotation, for the single crystal, inside the magnet about an axis normal to $B_0$. The interpretation of rotation patterns permits location of the principle axis of the electric field gradient relative to the crystallographic axis and the evaluation of the parameters $\nu_Q$ and $\eta$. The rotation pattern yields the most accurate values for the parameters $\nu_Q$ and $\eta$ [103].

Experiment and Result

I did the NMR study on a single crystal of $\alpha'$-$\text{Na}_0.9966\text{Li}_0.0034\text{V}_2\text{O}_5$. The sample has been placed on the rotator, so that we can control the rotating of the sample in the magnetic field. This rotator can rotate the sample in 10° steps. The sample has been rotated in the $a$-$c$ plane, where $B_0$ in the beginning was parallel to the $a$-axis. We used the spin echo program to collect the data. After applying the FT on the FID signal (as shown in Fig. (a)) we see clearly the changing of the satellite position with the angle. The line position of one of the satellites (the left satellite) is extracted as the distance to the main line for each angle. These line positions are plotted vs. the angle as shown in Fig. b. The resulting experimental curve is well fitted by the following function

$$y = A\sin(\pi (\theta - \theta_c)/w)$$  \hspace{1cm} (A.1)

where $A$ is the amplitude of the sin wave.
This fitting of the data shows that the EFG axes \((xyz)\) are not collinear with the crystallographic axes \(a, b, c\), and they are shifted by nearly 6°. This result does not agree with the Fagot-Revurat et al. result [65], where it was claimed that the EFG axes are collinear with the \(a-, b-, c\)-axes. This result had a minor correction to EFG principal in the NMR result. Since I could not measure the second angle I did not use it in the calculation.

**Fig. a:** Spin echo intensity for \(^{23}\text{Na}\) in \(\text{Na}_{0.9966}\text{Li}_{0.0034}\text{V}_2\text{O}_5\) at various degrees 0° (bottom) 180° (top).

**Fig. b:** Rotation patterns for \(^{23}\text{Na}\) in \(\text{Na}_{0.9966}\text{Li}_{0.0034}\text{V}_2\text{O}_5\). The points are the experimental data and the line the fitting curve.
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2. NMR study of doped $\alpha$-NaV$_2$O$_5$ single crystals
   R. Michalak, H. Mohammad, M. Dischner and C. Geibel

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