INFLUENCE OF LOCAL $\text{C}_6\text{O}$ ORIENTATION ON ELECTRONIC PROPERTIES OF $\text{A}_3\text{C}_6\text{O}$ COMPOUNDS

Ph.D. Thesis

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Since what may be known God is plain to them, because God has made it plain to them. For since the creation of the world God’s invisible qualities — His eternal power and divine nature — have been clearly seen, being understood from what has been made.

Romans 1,19–20
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Abstract

We have investigated sodium containing Na\(_2\)AC\(_{60}\) fullerene superconductors (A = Cs, Rb, and K) by nuclear magnetic resonance (NMR) spectroscopy. The \(^{23}\)Na NMR spectrum, Knight shift, spin-lattice (\(T_1\)) and spin-spin (\(T_2\)) relaxation times have been measured in the temperature range of 10 to 400 K. Spin-echo double resonance (SEDOR) results are also presented at 80 K.

We show that the \(^{23}\)Na spectrum line splits into two lines at low temperature in all the three compounds investigated. The splitting occurs at 170 K for A = Cs. For A = Rb and K the splitting is between 80 K and room temperature. This is the first observation of line splitting in fullerene superconductors with simple cubic ground state. SEDOR experiments prove that the two spectral components originate from the same phase. We explain the spectral splitting as well as the temperature dependence of the spin-lattice and spin-spin relaxation times by a dynamic site exchange. The rate of the exchange process is found to be temperature activated in the range 125 to 299 K with an activation energy of 3300 K.

From a detailed analysis of several NMR properties, we show that the site exchange is caused by the reorientation of the C\(_{60}\) molecule between two different orientations. Assuming no correlation between the orientations of neighboring molecules, we determine the concentration of orientational defects. The defect concentration we infer is in good agreement with neutron scattering results [Prassides et al., Science 263, 950 (1994)].

In the light of our findings we revisit the problem of a similar spectral splitting in A\(_3\)C\(_{60}\) superconductors with face centered cubic structure, and provide a unified picture for the interpretation of the line splitting.

We also show that the sodium spin lattice relaxation rate \(1/(T_1 T)\) follows a different temperature dependence than the expected Korringa law. We explain the temperature dependence of the \(^{23}\)Na Knight shift and relaxation rate by the effect of librational phonons on the electron density at the \(^{23}\)Na nuclei.
Kivonat

Jelen értekezés keretében Na₂AC₆₀ összetételű (A = Cs, Rb vagy K) egyszerű köbös szerkezetű szupravezetőkön végzett mágneses magrezonancia (NMR) kísérleteinket ismertetjük. Mértük az NMR spektrumot, a Knight–eltolódást, a spin-rács ($T_1$), illetve spin-spin ($T_2$) relaxációs időt a 10–400 K hőmérséklet–tartományban, továbbá 80 K-en spin-echo kettős rezonancia (SEDOR) kísérleteket folytattunk.

Megmutattuk, hogy alacsony hőmérsékleten a tetraéderes C₆₀ koordinációjú ²³Na magok spektrumvonala mindhárom vegyületben felhasad, azaz két különböző fullerenkörnyezet alakul ki a nátriumok körül. A felhasadás Na₂CsC₆₀-ban 170 K-en, míg Na₂RbC₆₀-ban és Na₂KC₆₀-ban 80 és 290 K közötti, általunk pontosan meg nem határozott hőmérsékleten következik be. SEDOR kísérletekkel igazoltuk, hogy a két spektrális komponens a minta egyazon fázisából származik. A különböző NMR jellemzők hőmérséklet–függésének elemzésével megmutattuk, hogy a felhasadás nem fázisátalakulás, hanem a két ráchely közötti dinamikus kíscserélődés fokozatos lelassulásának következménye. A kíscserélődési rátát hőmérséklettel aktiválható, a minta egyazon fázisából származik.

Számos NMR paraméter vizsgálatából arra a következtetre jutottunk, hogy a két nátrium ráchely közötti különbség az elsősömzséd C₆₀ molekulák különböző orientációjából ered. Ha a szomszédos fullerénmolekulák orientációját egymástól függetlennek tekintünk, akkor az orientációs hibák koncentrációja az NMR spektrális vonalak relatív intenzitásából kiszámítható. Eredményünk jól egyezik a neutronszórás kísérletekkel meghatározott hibakonzentrációval [Prassides et al., Science 263, 950 (1994)].

Eredményeink fényében áttekintettük a lapcentrált köbös szerkezetű A₃C₆₀ szupravezetőkben megfigyelt hasonló vonalfelhasadásra vonatkozó szakirodalmi adatokat és a jelenség értelmezésére egy mindkét anyagcsaládra alkalmazható egységes leírást dolgoztunk ki.

A dolgozatban kitérünk arra is, hogy Na₂CsC₆₀-ban alacsony hőmérsékleten a ²³Na Knight–eltolódás és spin-rács relaxációs idő a fémekben várvtól eltérő viselkedést mutat. Az eltérést sikeresen értelmeztük a C₆₀ molekulák librációs mozgásával.
Introduction

For centuries, it was considered evident that carbon had two allotropic forms, diamond and graphite. Therefore the discovery of cage-like all-carbon molecules\(^1\) by Harold Kroto, James Heath, Sean O’Brien, Robert Curl, and Richard Smalley in 1985 was welcome by the scientific community as an astonishing breakthrough. The new allotropic forms of carbon, baptized fullerenes after the architect R. Buckminster Fuller who constructed geodesic domes with similar structure, were uncovered in carbon soot containing various carbon clusters. Clusters of 60 carbon atoms proved to be the most stable and most abundant. For the structure of this cluster, a truncated icosahedron had been suggested and later confirmed by various techniques.

The advent of large-scale fullerene science dates to 1990 when Krätschmer \textit{et al.}\(^2\) developed an arc-vaporization method for the mass production of fullerenes. In the next year, two significant discoveries lay down the main direction of fullerene research. Iijima\(^3\) opened the “nano era” of carbon structures with the observation of carbon nanotubes. Their interesting electronic and mechanical properties make the nanotubes ideal candidates not only for basic but also for applied science. In the last decade, numerous ordered carbon nanostructures were discovered including carbon onions,\(^4\) crossed nanotubes,\(^5\) peapod nanotubes,\(^6\) etc. The other discovery in 1991, closely related to the present work, was the observation of superconductivity in a potassium containing fulleride by Hebard \textit{et al.}\(^7\) with a surprisingly high critical temperature 18 K. Shortly after, Fleming \textit{et al.}\(^8\) showed that the proper stoichiometry of the superconducting compound is $K_3C_{60}$. Cooper pair formation in this and similar materials is thought to be mediated by high-frequency vibrational modes\(^9\) of the fullerene molecule.

Very quickly a large number of alkali fullerides $A_3C_{60}$ were synthesized with various alkali metals A. The alkali atoms are situated in spacious voids between the large-diameter $C_{60}$ molecules.\(^{10,11}\) The energy associated with the electronic interactions between the fullerene molecules as well as between the fullerene molecules and alkali ions is minimized in an orientationally ordered structure.\(^{12}\)
1. **INTRODUCTION**

At high enough temperature, however, the entropy associated with the rotational freedom of the molecules dominates over these electronic interactions leading to an almost free rotation of the molecule,\(^{13-15}\), \textit{i.e.,} to a plastic crystal. Even in the low-temperature orientationally ordered phase,\(^{16,17}\) molecular reorientations are frequent and orientational defects are abundant.

It turns out that the orientational order (or disorder) has a significant effect on the electronic and superconducting properties. In all \(A_3C_{60}\) superconductors the \(C_{60}\) molecules sit on the vertices of a face centered cubic (fcc) lattice. Depending on the size of the alkali atoms, however, two different kinds of orientational order may form at low temperature. In one class of \(A_3C_{60}\) compounds the Bravais lattice is fcc\(^{10}\) while in some other \(A_3C_{60}\) compounds the order is simple cubic\(^{11}\) (sc) similar to the pure \(C_{60}\) crystal. Although the only difference between the two structures is the orientational order, the superconducting properties are remarkably different. As an example the dependence of the critical temperature on the distance between \(C_{60}\) molecules is much steeper in the sc phase.\(^{8,18}\) Most studies of \(A_3C_{60}\) superconductors have been carried out on fcc systems; in the present work we turn our attention to the sc phase.

Orientational defects and short-scale orientational correlations are difficult if not impossible to investigate with diffraction techniques. Local probes such as NMR, on the other hand, are ideally suited to the problem. In this work we put a broad arsenal of NMR techniques into action to investigate molecular motion, orientational order, and orientational correlation in a class of \(A_3C_{60}\) superconductors with sc ground state.

This thesis is organized as follows: After a short introduction to the world of fullerenes in Chapter 2 and to the relevant NMR techniques in Chapter 3 we describe the experimental techniques used in our investigations in Chapter 4. The experimental findings are depicted in Chapter 5 and discussed in Chapter 6. The conclusions are drawn in Chapter 7.
2

The world of fullerenes

In this chapter we review some of the most interesting properties of fullerenes and C\textsubscript{60}-based systems with focus on alkali fulleride compounds. First, we give a general introduction on pure fullerenes. Then we turn our attention to alkali intercalated C\textsubscript{60} compounds with special emphasis on A\textsubscript{3}C\textsubscript{60}, where A denotes an alkali atom. These compounds are metallic and superconducting below a remarkably high critical temperature. In the superconductivity of A\textsubscript{3}C\textsubscript{60} salts, the crystal structure plays an important role, thus the structural properties of different compositions are discussed.

In the literature numerous excellent reviews exist which we recommend for further reading including the introductory text by Dresselhaus et al.\textsuperscript{19} and some more specialized review articles. We cite the reviews of Forró and Mihály\textsuperscript{20} on the electronic properties of doped fullerenes, Pennington and Stenger\textsuperscript{21} on NMR of fulleride superconductors, Moret\textsuperscript{22} on the structural and orientational properties of C\textsubscript{60} monomers and polymers, Kuzmany et al.\textsuperscript{23} on the optical properties of fullerides, Rosseinsky\textsuperscript{24} on the chemistry and physics of the metal fullerides together with Gunnarsson’s theoretical work\textsuperscript{25} on electron correlations and superconductivity.

2.1 The buckminsterfullerene C\textsubscript{60}

In this section the molecular and the electronic structure as well as the crystalline form of C\textsubscript{60} are presented. Local fullerene order at low temperature and the orientational ordering transition are also reviewed.

2.1.1 The molecular structure of C\textsubscript{60} fullerene

The buckminsterfullerene molecule C\textsubscript{60} shown in Fig. 2.1 is a very elegant formation in itself showing the very high degree of symmetry of a truncated icosahedron. C\textsubscript{60} has 60 vertices, 90 edges, 20 hexagonal and 12 pentagonal
2. THE WORLD OF FULLERENES

Figure 2.1: The structure of a $C_{60}$ molecule reprinted from Ref. 20. In the left panel atomic configuration is shown with bonds while in the right panel electronic wavefunctions are also illustrated.

faces. The 12 pentagons give rise to a curved surface and thus enable a closed quasi-spherical structure of the molecule. The buckminsterfullerene is well approximated by a surface of a sphere with diameter of 7.1 Å. The electronic wave functions extend inside and outside of the sphere by 1.5 Å as illustrated in the right panel of Fig. 2.1.

The symmetry of the molecule is the icosahedral point group $I_{h}$, the highest possible molecular symmetry. There are 6 five-fold axes (through the pentagons), 10 three-fold axes (through the hexagons) and 15 two-fold axes (through the bonds shared by two hexagons). As a consequence of symmetry, the 174 vibrational degrees of freedom reduce to 46 vibrational modes which can be obtained from a group theoretical analysis:

$$\Gamma_{\text{vib}}^{C_{60}} = 2A_g + 3F_{1g} + 4F_{2g} + 6G_g + 8H_g +$$
$$+ A_u + 4F_{1u} + 5F_{2u} + 6G_u + 7H_u. \quad (2.1)$$

10 modes are Raman active ($2A_g, 8H_g$) and 4 modes are infrared active ($4F_{1u}$).

Each carbon atom in the molecule is equivalent and is a member of one pentagon and two hexagons, being thus bonded to three carbon neighbors. There are two types of bonds:\textsuperscript{15} (i) a longer bond (1.45 Å) positioned between a hexagon and a pentagon and (ii) a shorter bond (1.40 Å) situated between two hexagons. They are often referred to respectively as single and double bonds in the literature. The different bonds can be recognized as the 60 single bonds forming the pentagonal edges as well as the 30 double bonds shared by two
hexagons. The difference in bondlengths indicates that the electron density is not distributed evenly over the molecule.

**Electronic structure**

The high degree of symmetry simplifies the calculation of molecular orbitals which could otherwise be very difficult to obtain for such a large number of electrons. The molecular orbitals originate from the overlap between neighboring atomic $p_z$ orbitals ($\pi$-bonding). Most of the electronic properties of interest can be derived from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These states can be calculated using the Hückel theory of molecular orbitals\(^{26}\) (see the left panel of Fig. 2.3) resulting in a five-fold degenerate (spin degeneracy not included) HOMO and a three-fold degenerate LUMO level with symmetries $h_u$ and $t_{1u}$, respectively. The HOMO–LUMO energy gap is on the order of 1 eV (Ref. 27).

### 2.1.2 Fullerite, the crystalline form of fullerene

The $C_{60}$ molecules form a closed-packed plastic crystal structure\(^{16,17}\) due to the weak van der Waals interaction between the neighboring molecules. The crystalline form of fullerene is called fullerite. The centers of the $C_{60}$ molecules are situated on the vertices of an fcc lattice\(^{17,28}\). At room temperature the fullerene molecules are orientationally disordered and undergo continuous reorientation, therefore all the 4 $C_{60}$ molecule of the cubic cell become equivalent in time average. The symmetry of the developed fcc structure is $Fm\bar{3}m$ and the lattice

![Schematic representation of the carbon–carbon chemical bondings](image)
constant is $a_0 = 14.17 \text{ Å}$ (Ref. 17). Such a crystal with rapidly reorienting molecules with effective symmetry higher than the molecular symmetry is called a plastic crystal.

In the ground state, however, the structure is simple cubic\textsuperscript{16} with space group $Pa\bar{3}$. The reason why the structure is sc rather than fcc is that the orientation of the 4 molecules in the cubic cell becomes different as the nature of the reorientational dynamics changes. The orientational order in the ground state is the consequence of the orientation dependent interaction of neighboring fullerene molecules.\textsuperscript{12} This order is best described with reference to the so-called standard orientations depicted in Fig. 2.4. In the standard orientation, the cubic axes coincide with two-fold axes of the molecule bisecting C–C double bonds. Actually there are two such orientations related by a 90 degree rotation around any of the cubic axes. In the $Pa\bar{3}$ structure, for each molecule there is exactly one body diagonal of the cubic cell which is a three-fold axis of the molecule. Each molecule is rotated away from the standard orientation by $98^\circ$ about this three-fold axis.\textsuperscript{16} This way electron-rich double bonds of the molecule face electron-poor pentagons therefore minimizing the intermolecular interaction.

**Figure 2.3:** Electronic structure of $C_{60}$ from Hückel theory and band structure and density of states of $K_3C_{60}$ from using local density approximation (right) reprinted from Ref. 21.
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Figure 2.4: The two standard orientations of C\textsubscript{60} as the manifestation of merohedral disorder from Ref. 28. The molecular orientation of the fullerene molecule on the right can be accessed by a 90°-rotation around [100] of one on the left.

At high enough temperature long-range orientational order is destroyed as the entropy associated with different molecular orientations dominates the intermolecular interaction, leading to a phase transition which can be regarded as an orientational melting. This phase transition is first of order and takes place at about 260 K in fullerite.\textsuperscript{13,14,29,30} Although the rotation of the C\textsubscript{60} molecules in the high temperature phase is nearly free and nearly isotropic, there are preferred orientations in the average molecular electron density resulting in anisotropic single-molecule orientational probability distribution and sizable neighboring orientational correlation\textsuperscript{12} as the precursor to the orientationally ordered phase.

Nevertheless, the precise refinement of the high accuracy powder neutron diffraction data\textsuperscript{16} on retaining the Pa\textsubscript{3} space group and introducing a second rotational angle of 38 degree shows evidence for orientational defects in the low temperature phase. In this case a hexagon faces a double bond of the neighboring fullerene. The nearest neighbor fullerenes are visualized in Fig. 2.5 for both the majority 98° and the minority 38° fullerene orientations. Neutron\textsuperscript{31} and x-ray\textsuperscript{32} diffraction measurements show that the two configurations have a completely random distribution. Upon cooling, the weight of majority phase increases from 55% at 240 K to 84% at 86 K. Below 90 K the fullerene reorientations are frozen and a glassy state develops\textsuperscript{16} since the thermal energy is not sufficient to overcome the potential barrier of about 250-300 meV that separates the two orientational configurations. In the lowest temperature region only librations (small angle rotational oscillations around the equilibrium position) are observed in the inelastic neutron scattering experiments.\textsuperscript{33,34}

NMR is a very efficient tool for the investigation of short-range (below 100 Å) orientational correlation not accessible with scattering methods. In
addition NMR is sensitive to timescales over which the molecular reorientations occur. The 300-K $^{13}$C NMR spectrum of fullerite powder shows a sharp line$^{13,35}$ indicating a fast rotation of fullerene molecules. Furthermore, NMR spin-lattice relaxation measurement revealed$^{15}$ at 283 K that the correlation time of C$_{60}$ molecular reorientations $\tau = 9.1$ ps, which is only three times longer than expected for free rotation. Therefore this phase is called the rotator phase.

In the orientationally ordered phase resonance methods indicate$^{14,15,36}$ that the nature and the correlation time of the reorientation C$_{60}$ dynamics are drastically changed. While in the fcc phase the molecules reorient rapidly, in the sc phase a pseudorandom sequence of small amplitude uniaxial rotation is observed$^{15}$ (ratcheting phase). Moreover, a two-dimensional NMR “separation of interaction” experiment$^{37}$ identifies two different dynamical processes in the sc phase, a relatively slow process corresponding to the flipping of the rotational axis and a fast one corresponding to the uniaxial rotation of the C$_{60}$ molecules around their rotation axis. Around 150 K the broadening of the homogeneous line width reflects the freezing of the flipping process of the rotation axes. Below 90 K the NMR spectra signal that the uniaxial rotation also freezes in agreement with the observed glassy state in the diffraction measurements.

Finally, we mention one of the most spectacular manifestations of the ordering phenomenon. This is the formation of polymers$^{38}$ where one, two, or several double bonds open on each C$_{60}$ molecule, allowing the formation of various types of intermolecular bonding. The appropriate orientation and reorientational rate of the neighboring C$_{60}$ molecules play an important role in polymer formation.
2.1.3 Fullerene compounds

The hollow structure of the C\(_{60}\) molecule makes the insertion of a foreign atom inside the fullerene cage possible. These structures are the endohedral fullerene complexes M@C\(_{60}\) (Refs. 39, 40) where M denotes the implanted atom or cluster and @ symbolizes the endohedral nature of the structure (left panel of Fig. 2.6). The encapsulated species can be a metallic atom or cluster, a noble gas atom, a nitrogen atom, or even muonium\(^{41}\) which plays an important role in muon spin rotation (\(\mu\)SR) investigations.\(^{14}\)

Another way to form a fullerene compound with a modified structure is to replace one of the 60 carbon atoms with a different atom (right panel of Fig. 2.6). For this compound the best known example is the azafullerene molecule C\(_{59}\)N (Ref. 42). In this case the nitrogen donates an additional electron to the surface of the molecule which makes this compound very reactive and thus forms dimers\(^{42}\) in the solid state.

In the close packed structure of fullerite, there are large empty spaces between the molecules where smaller atoms, ions, or molecules can be inserted. If the inserted object is an alkali atom, a large family of materials can be synthesized. These alkali fulleride compounds exhibit very interesting physical properties presented briefly in the next section.

2.2 Alkali fulleride salts

The high electron affinity of the fullerene molecule and the dimensions of the voids in the crystal structure motivated research on intercalating alkali atoms into the fullerene structure. In the fcc lattice of solid C\(_{60}\) there are two types of interstitial sites: one with octahedral C\(_{60}\) coordination and one with
tetrahedral coordination (see Fig. 2.7). There are twice as many tetrahedral sites as octahedral sites. Geometrical considerations reveal that while the size of the octahedral voids is large enough to accommodate any alkali ion, the tetrahedral hole is smaller than the ionic radii of $K^+$, $Rb^+$, and $Cs^+$, but slightly larger than that of $Na^+$. Therefore a series of alkali fulleride materials $A_nC_{60}$ can be synthesized where $A$ is an alkali metal and $n = 1, 2, 3, 4, \text{ or } 6$. These structures are illustrated in Fig. 2.8. Upon the alkali insertion, the fcc structure of the host lattice is preserved in most cases but it can be modified by inserting larger or more alkali atoms. For example body centered tetragonal and body centered cubic lattices form in $A_4C_{60}$ and $A_6C_{60}$, respectively. Also the large diameter of the cesium ion is responsible for the body centered cubic structure of $Cs_3C_{60}$ (Ref. 43).

The band structure of alkali-$C_{60}$ compounds is derived from the $C_{60}$ molecular orbitals which hybridize to form bands (right panel of Fig. 2.3). The electronic bands are narrow because of the small intermolecular overlap. Due to the high electron affinity of the fullerene molecule the charge transfer from alkali atoms to fullerenes is complete. The transferred charge fills the conduction band derived from the LUMO orbitals. In the rigid band model the partial filling of the conduction band should lead to metallic behavior. However, the $A_2C_{60}$ and $A_4C_{60}$ salts are insulating and only the $AC_{60}$ and $A_3C_{60}$ compounds exhibit metallic behavior. The failure of the rigid band picture indicates the existence of strong electronic correlation.

The fact that the electrons in the conduction band are mainly concentrated on the fullerene molecules results in ineffective electron screening and a strong on-site Coulomb repulsion. The interplay of molecular and band physics leads very diverse properties of these compounds ranging from “Mott–Jahn–Teller insulators” to superconducting metals.
2. THE WORLD OF FULLERENES

2.2.1 $A_3C_{60}$ superconductors

Since the discovery of superconductivity in the $A_3C_{60}$ family\textsuperscript{7,8} with unusually high transition temperatures, a large number of alkali fullerides $A_3C_{60}$ have been synthesized with various alkali metals $A$. In these materials the origin of superconductivity is a conventional phonon-mediated electron-electron interaction. The high-frequency molecular vibrations are thought to be responsible for the high critical temperatures.\textsuperscript{9} The fact that the transition temperatures scale with the lattice constant,\textsuperscript{8} that carbon isotope substitution\textsuperscript{48} has an observable effect on the critical temperature, and that a Hebel–Slichter peak\textsuperscript{49} appears just below the critical temperature in muon spin rotation\textsuperscript{50} and NMR\textsuperscript{51} spin-lattice relaxation rates confirm that the superconductivity can be described within the framework of the Bardeen-Cooper-Schrieffer theory. Nevertheless, the application of the strong coupling limit (Eliashberg theory\textsuperscript{52}) is needed due to the strong electron correlations.

In the $A_3C_{60}$ binary and $A_2A'C_{60}$ ternary compounds ($A$ and $A'$ indicate different alkali metals) all interstitial sites are fully occupied by alkali ions. Several aspects of the structure depend on the alkali ionic radii. In the $A_2A'C_{60}$ case, the larger alkali ions prefer the octahedral voids as these are more spacious than the tetrahedral voids. The alkali dopant often hampers the nearly free rotation of the $C_{60}$ molecules observed in fullerites at room temperature, and influences the low-temperature structure.

If large alkali atoms (K, Rb, Cs) are introduced in the tetrahedral site, a merohedrally disordered fcc structure forms (space group $Fm\bar{3}m$) in which the $C^{3-}_{60}$ ions are randomly distributed between the two standard orientations (see Fig. 2.4). The random distribution of the fulleride ions between standard orientations is called merohedral disorder.\textsuperscript{10} On decreasing the temperature, the structure does not undergo any phase transition as the alkali atoms do not
allow the neighboring fullerides to optimize their interaction. Therefore, the merohedral disorder is retained at low temperatures where the molecular reorientations are frozen.

However, if the tetrahedral void is filled by a small diameter sodium ion, the optimization of interfullerene interaction is allowed; and then the same fcc–sc phase transition is observed near room temperature in Na$_2$AC$_{60}$ family as in pure C$_{60}$. Moreover, in the low temperature Pa$_3$ phase the majority 98° and minority 38° C$_{60}$ orientations are also detected. In some Na$_2$AC$_{60}$ materials polymer formation is also observed as a consequence of the small interfullerene distance and frequent molecular reorientations. The small lattice constant is the result of the attractive interaction between the small size sodium ions and the C$_{60}$ ions. The most remarkable example of the influence of local C$_{60}$ order on the electronic properties is the different lattice constant dependence of the superconducting transition temperature in Fm$\bar{3}$m and Pa$_3$ superconductors as shown in Fig. 2.9. This relation is well described by McMillan’s formula with the assumption that only the parameters describing the intermolecular distance dependence of the electronic density of states differ in the two families of A$_3$C$_{60}$ materials. Recently, Yang et al. and Brouet et al. found by angle resolved photoemission spectroscopy (ARPES) that the alkali fulleride monolayers deposited on different Ag surfaces exhibiting different orientational order have remarkably different electronic structures. This suggests that the
different sensitivities of the density of states to the lattice constant has its origin in the difference of electronic structure in the two types of $A_3C_{60}$ compounds.

The $C_{60}$ reorientational dynamics has been investigated by NMR.\textsuperscript{61–63} In the temperature dependence of $^{13}C$ relaxation rate $1/T_1$ a so-called \textit{motional peak} is found\textsuperscript{61} around 200 K (the exact temperature depends on the material investigated). Furthermore, Yoshinari \textit{et al.}\textsuperscript{62} invoke two different processes in reorientational dynamics similarly to the findings of Blinc \textit{et al.}\textsuperscript{36} in undoped $C_{60}$. One is a rapid uniaxial reorientation around an easy axis and the other is a less frequent jump of this axis. Barett and Tycko\textsuperscript{63} investigated the latter process by 2D NMR.

However, the biggest surprise of NMR investigation of $A_3C_{60}$ fullerides came from alkali NMR. Walstedt \textit{et al.}\textsuperscript{64} investigated Rb$_3$C$_{60}$ by $^{87}$Rb NMR. One expects two $^{87}$Rb lines, one for the octahedral (O) and one for the tetrahedral (T) site symmetry with intensity ratio 1 : 2. This is exactly what is seen above 370 K. Below that temperature, however, the NMR line associated with the tetrahedral site is split into two lines (T and T') with relative weights T : T' = 5.5 : 1 (see Fig. 2.10). It has been shown by spin-echo double resonance that T' is a modified T site. Since this result challenges the basic understanding of the structure of $A_3C_{60}$ compounds, it has attracted much interest.\textsuperscript{65–70}

Later this phenomenon was demonstrated in the whole family of merohe- drally disordered $A_3C_{60}$ fullerides. Moreover, the splitting of the NMR line of the

\textbf{Figure 2.10:} The first observation of the T–T' splitting: $^{87}$Rb NMR spectrum of Rb$_3$C$_{60}$ salt by Walstedt \textit{et al.}\textsuperscript{64}
octahedral site (O–O’ splitting) has also been observed\textsuperscript{67} by magic angle spinning (MAS) technique. Walstedt \textit{et al.}\textsuperscript{64} put forward several possible explanations for the T–T’ splitting, including a deviation from the expected C\textsubscript{60} orientational configuration, displacement of the alkali ions, Jahn–Teller distortion of the C\textsubscript{360}\textsuperscript{2–} ion, etc. However, all attempts to distinguish between these possibilities failed. This makes the so-called T’–problem one of the oldest unresolved problems related to the structure of A\textsubscript{3}C\textsubscript{60} fulleride salts. These efforts will be further discussed in the context of our new results in Chapter 6.

Our aim was to contribute to the resolution of this longstanding problem by examining the T site NMR properties in A\textsubscript{2}A’C\textsubscript{60} compounds of sc symmetry.
Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) has proven to be a remarkably versatile tool for the elucidation of key properties of condensed matter. In this method, which we apply to study certain fulleride compounds, transitions of nuclear spin states are excited and detected afterwards. The degeneracy of nuclear spin states is split by the applied large magnetic field. There are two main features which make NMR spectroscopy widely applied:

(a) the large quality factor of the nuclear magnetic resonance results an excellent resolution, i.e., the very small variation of resonance frequency ($\sim 10^{-8}$) can be detected

(b) nuclei (contrary to electrons) are weakly coupled to their surroundings, thus the effect of their environment can be treated perturbatively in most cases.

Hence nuclei behave as local probes which sense their magnetic and electronic surroundings, and from their behavior much can be deduced about the system being studied including the underlying geometrical and/or chemical order as well as the electronic structure. Moreover, the nuclei are able to provide information about static and dynamic processes occurring in the investigated material.

In this chapter we shall review some aspects of NMR spectroscopy including the fundamental parameters, i.e., resonance frequency and shifts, the relaxation mechanisms, motional narrowing as well as the spin-echo double resonance (SEDOR). For further reading we recommend the excellent NMR textbooks of Slichter$^{71}$ and Abragam.$^{72}$
3.1 Physical background of NMR

3.1.1 Nuclear spin transition

The nuclear spin ($I$) is one of the fundamental characteristics of a nucleus, and magnetic dipole couples to spins:

$$\hat{\mu} = \gamma_n \hbar \hat{I}$$

(3.1)

where $\hat{\mu}$ represents the magnetic dipole operator, $\hat{I}$ corresponds to the nuclear spin operator, $\gamma_n$ is the gyromagnetic ratio of the nuclei, $\hbar$ is the Planck constant divided by $2\pi$. For that reason the Hamiltonian of a nuclear spin in magnetic field can be described as follows:

$$\mathcal{H}_{\text{Zeeman}} = -\hat{\mu} \cdot \mathbf{B} = -\gamma_n \hbar \hat{I} \cdot \mathbf{B}$$

(3.2)

where $\mathbf{B}$ is the magnetic induction vector which embodies both the applied external as well as local magnetic fields: $\mathbf{B} = \mu_0 (\mathbf{H}_0 + \mathbf{H}_{\text{local}})$ where $\mu_0$ stands for the permeability of vacuum. Let us direct a homogeneous external magnetic field along the $z$-direction, in this case the operator (3.2) simplifies to a constant times $I_z$, hence its eigenvalues are

$$E_m = -\hbar \gamma_n B m$$

(3.3)

where $m$ is the eigenvalue of the $I_z$ operator, and $E_m$ is the corresponding energy. Moreover, the energy difference between two consecutive states is $\Delta E = \hbar \gamma_n B$.

To induce a transition between nuclear spin states a perturbing magnetic field $\mathbf{B}_1$ is required. Because of the selection rules the perturbing field has to be perpendicular to the external field, its magnitude $B_1$ has to be small enough to be treated perturbatively ($B_1 \ll B_0$), and its frequency $\omega$ has to be set to fulfill energy conservation. Therefore, the perturbing Hamiltonian is

$$\mathcal{H}_{\text{pert}} = -\hbar \gamma_n B_1^2 \hat{I}_x \cos \omega t.$$  

(3.4)

The selection rules for dipole transitions allow only $\Delta m = \pm 1$, therefore from Eq. (3.3) the resonance condition becomes

$$\omega = \gamma_n B$$

(3.5)

where $\omega$ is called Larmor (angular) frequency and denoted in the following by $\omega_L$. 
3.1.2 Nuclear magnetization

In equilibrium the energy levels (3.3) are populated according to the Boltzmann distribution: \( N_m \propto \exp(-E_m/k_BT) \) where \( k_B \) and \( T \) are the Boltzmann constant and the temperature, respectively. The nuclear magnetization obeys the Curie law:

\[
M = \chi_0 \frac{1}{\mu_0} \mathcal{B}_0 = N \frac{\gamma_n^2 \hbar^2}{3k_B T} (I+1) \mathcal{B}_0 \tag{3.6}
\]

where \( N \) is the number of nuclear spins and \( \chi_0 \) is the nuclear spin susceptibility. The nuclear magnetization is very weak because of the small value of the nuclear gyromagnetic ratios.

3.1.3 Larmor precession

Though the time evolution of nuclear magnetization is fundamentally a quantum mechanical phenomenon, and shall thus be described by a density operator, one can show that in most cases it is suitable to treat the magnetization as a classical vector quantity. Below the nuclear spins are modeled as classical magnetic dipole vectors, and this treatment is exact for spins \( I = 1/2 \) with the substitution of \( \mu \) by the expectation value of the dipole operator \( \langle \hat{\mu} \rangle \). Using the classical equation of motion of a classical magnetic dipole in static magnetic field and taking into account Eq. (3.1), one can obtain the following equation for the time development of nuclear spins:

\[
\frac{d\mu}{dt} = \mu \times \left( \gamma_n B_0 \right) \tag{3.7}
\]

To solve Eq. (3.7) we change to a rotating system of reference. The transformation of the time-derivative of a vector \( \mathbf{F} \) from the laboratory frame to the rotating frame follows

\[
\frac{dF}{dt} = \frac{\partial F}{\partial t} + \Omega \times F \tag{3.8}
\]

where \( \Omega \) is the angular frequency vector of the rotating frame, \( d/dt \) and \( \partial/\partial t \) denote time derivatives in the laboratory and rotating frames, respectively. In the rotating frame, therefore, Eq. (3.7) transforms to

\[
\frac{\partial \mu}{\partial t} = \mu \times \left( \gamma_n B_0 + \Omega \right)_{\gamma_n B_{\text{eff}}} \tag{3.9}
\]
In the rotating frame the magnetic moment experiences an effective magnetic field \( B_{\text{eff}} = B_0 + \Omega / \gamma_n \). With the choice of \( \Omega = -\gamma_n B_0 \) the static magnetic field can be eliminated \( B_{\text{eff}} = 0 \), and \( \mu = \text{const} \) in the rotating frame. This means that the magnetic moment precesses with angular velocity \( \Omega \) on the surface of a cone.

Setting \( \Omega = \omega \hat{z} \) and taking into account the radiofrequency (rf) perturbation with angular frequency \( \omega \), the effective magnetic field in the rotating frame becomes

\[
B = (B_0 + \omega / \gamma_n)\hat{z}' + B_1 \hat{x}'
\]

(3.10)

where \((\hat{x}', \hat{y}', \hat{z}')\) are the unit vector of the rotating frame. If the resonance condition \( \omega = -\omega_L \) is satisfied, then in the rotating frame the static field \( B_0 \) is eliminated while the rf field becomes constant, \( B_1 = B_1 \hat{x}' \). As a consequence, the magnetic moment precesses in the rotating frame around \( B_1 \) with angular frequency \( \omega_1 = \gamma_n B_1 \). The tip of the magnetic moment vector executes circular motion in the \( y' - z' \) plane (see Fig. 3.1).

If the magnetic field \( B_1 \) is turned on for only a finite time \( \tau \), one obtains \( \varphi = \gamma_n B_1 \tau \) for the angle of rotation of the magnetic moment around the \( x' \) axis. Thus the length of an rf pulse which rotates the magnetic moment by an angle \( \varphi \) is \( \tau_{\varphi} = \varphi / (\gamma_n B_1) \). The special pulse which rotates the magnetic moment away from its initial position parallel to the \( z' \) axis to the direction parallel to the \( y' \) axis is called a \( \pi/2 \) pulse. After a \( \pi/2 \) pulse is turned off, the magnetic moment precesses in the \( x-y \) plane of the laboratory frame with the Larmor frequency (see Fig. 3.2). The precessing magnetic moment causes magnetic flux variation which
induces voltage in the NMR pick-up coil which contains the investigated sample with its longitudinal axis aligned perpendicular to the external magnetic field.

### 3.1.4 Relaxational processes

The nuclear magnetization \( M_0 \) in thermodynamical equilibrium is parallel to the external field as given by Eq. (3.6). If the nuclear magnetic moments are rotated into the \( x-y \) plane by a \( \pi/2 \) pulse, the state of the moments is very different from equilibrium, therefore the magnetization tends to revert back to the initial equilibrium via relaxational processes which are characterized by relaxation times. We note that energy exchange between the nuclear spins and their surroundings is occurring only if the angle between \( B_0 \) and the moment varies. As a consequence, the relaxation of the \( z \)-component \( M_z \) of nuclear magnetization \( M \) (longitudinal relaxation) is very different from the relaxation of magnetization \( M_{x,y} \) in the \( x-y \) plane (transverse relaxation) as in the latter case there is no energy exchange. For a phenomenological description of relaxation of the magnetizations, two additional terms are added to Eq. (3.7):

\[
\begin{align*}
\frac{dM_{x,y}}{dt} &= \gamma [\mu \times B_0]_{x,y} - \frac{M_{x,y}}{T_2} \\
\frac{dM_z}{dt} &= \gamma [\mu \times B_0]_z + \frac{M_0 - M_z}{T_1}.
\end{align*}
\]

The Eqs. (3.11)-(3.12) are the *Bloch equations*. These equations take into account the different relaxation times \( T_1 \) and \( T_2 \) for the longitudinal and transverse components of the magnetization, respectively. The equilibrium magnetization \( M_0 \) has only a \( z \) component. \( T_1 \) is called the *spin-lattice* relaxation time which characterizes energy exchange between nuclear spins and their environment. \( T_2 \) is the *spin-spin* relaxation time which results from the interaction between nuclear spins. In solids \( T_2 \sim 100 \) \( \mu s \), and \( T_2 \ll T_1 \) (in certain insulators, \( T_1 \) can be as long as 100 s). Relaxational mechanisms cause decay of the observed NMR signal as well as a finite width of the spectral lines. Moreover, the relaxation times are much longer than the period \( 2\pi/\omega_L \) of the resonance because of the weak coupling between the nuclear spin system and its environment. This weak coupling makes the NMR method very useful and accurate in condensed matter spectroscopy.

To elucidate the relaxational processes, an illustration is shown in Fig. 3.3. The main stages of the relaxation are represented for both components of the nuclear
magnetization on the left panel. The right panel illustrates the transitions of the underlying spin system.

(i) In equilibrium (upper left subfigure) the nuclear magnetization is parallel to the $z$-axis (i.e., to the external magnetic field $B_0$), and the occupation of the spin levels follows the Boltzmann distribution. (ii) After an rf excitation (upper right subfigure) the magnetization turns into the $x$–$y$ plane, $M_z = 0$ and the levels have the same occupancies indicating a spin transition from the initial state to a higher energy state. (iii) Different relaxational mechanisms occur indicating by arrows in the left panel. In the case of spin-spin relaxation (lower right subfigure) the magnetization spreads in the $x$–$y$ plane involving no energy exchange between spins and the environment which is a consequence of mutual spin-flips in the spin system. (iv) However, in spin-lattice relaxation (lower left subfigure) the nuclear magnetization recovers to $z$-direction indicating energy exchange with its surroundings: a spin-transition is observed from a higher energy state to a lower energy state, and the corresponding energy is transferred to its environment called “lattice”.

Microscopic background of nuclear relaxation

The spin-lattice relaxation rate $1/T_1$ can be calculated microscopically via transition probabilities. Using Fermi’s Golden Rule the transition probabilities $W_{m \rightarrow m'}$ are
\[ W_{m \rightarrow m'} = \frac{2\pi}{\hbar} \sum_{\beta \beta'} |\langle m\beta | \hat{V} | m'\beta' \rangle|^2 p_\beta (1 - p_{\beta'}) \delta(E_m + E_\beta - E_{m'} - E_{\beta'}) \] (3.13)

where \( m \) and \( m' \) are initial and final nuclear spin states, \( \beta \) and \( \beta' \) are initial and final "lattice" states, \( p_\beta \) and \( p_{\beta'} \) are the occupational probabilities for the corresponding states, \( \hat{V} \) is the operator of the interaction causing the relaxation and Dirac \( \delta \) function expresses energy conservation. For a spin 1/2, \( 1/T_1 = 2W_{1/2 \rightarrow -1/2} \). For larger spins relaxation rates can be obtained by appropriate summation over the transition probabilities. The effect of the interaction is often expressed in terms of a fluctuating local magnetic field which causes the same transition rates as those in Eq. (3.13). The correlation function of this fluctuating fields is characteristic of the interaction producing relaxation. Let us assume a simple correlation function

\[ G(\tau) = \sum_\alpha |h_\alpha|^2 \exp(-|\tau|/\tau_c) \] (3.14)

where \( h_\alpha \) is the amplitude, \( \alpha = \{x, y, z\} \) is a spatial component of the fluctuating field and \( \tau_c \) is the correlation time of the magnetic field fluctuations. Using Eq. (3.13) the transition probabilities can be expressed\(^71\) in Fourier space as

\[ W_{mm'} = 2\gamma_n^2 \tau_c \frac{|h_x|^2 + |h_y|^2}{1 + \omega_{mm'}^2 \tau_c^2} \] (3.15)

where \( \hbar \omega_{mm'} \) is the energy difference of the levels. Note that only the component of the fluctuations perpendicular to the external field produce spin-lattice relaxation. In practice, by calculating the correlation function of the interaction in question, its contribution to the \( T_1 \) relaxation rate can be obtained. This is the basis of the pioneering work of Bloembergen, Purcell, and Pound\(^73\) on the \( T_1 \) relaxation caused by molecular reorientations.

In addition, the spin-spin relaxation can also be specified\(^71\) in terms of fluctuating magnetic fields:

\[ \frac{1}{T_2} = \frac{1}{2T_1} + \gamma_n^2 |h_z|^2 \tau_c. \] (3.16)
A short note about timescales

The timescale of the measurement provides essential information for evaluating the data and drawing the correct conclusions and it is often referred to as “the timescale of the method” in the literature. Nevertheless, in NMR spectroscopy there is no unique timescale because each type of NMR measurements has its own timescale. For example, the timescale of a spectral measurement is the inverse of the line width while spin-lattice and spin-spin relaxation times are naturally attributed to the timescale of the corresponding relaxational processes. The $T_1$ relaxation senses the magnetic field fluctuations at the Larmor frequency in the $x$–$y$ plane, while the $T_2$ relaxation is susceptible to low frequency fluctuations. In summary, the typical NMR timescales range from $10^{-2}$ s to $10^{-12}$ s.

3.2 Pulse sequences

In NMR spectroscopy an enormous variation of pulse sequences exists depending on what kind of information is searched for, although only a few of them are used routinely in condensed matter physics. Here we give a short summary of the most common sequences. The simplest “sequence” which consists of a $\pi/2$ pulse and causes the free induction decay has already been mentioned, therefore, is not in the list.

3.2.1 Spin-echo

Nuclei are sensitive to the spatial inhomogeneity of the magnetic field which leads to a distribution of Larmor frequencies. The distribution leads to dephasing of the precessing magnetic moments and faster decay of the induced signal. However, some of the dephasing can be eliminated by the spin-echo sequence. First, a $\pi/2$ pulse is used to excite the nuclear spin system, then an additional $\pi$ pulse is applied after a time $\tau$. One can observe the formation of an echo signal at time $\tau$ after the second pulse, i.e., $2\tau$ time after the first one (see Fig. 3.4). At $t = \tau$ the previously collected phase advance (or delay) of each magnetic moment is reversed since the moments are rotated by $180^\circ$ around the $x'$ axis by the $\pi$ pulse which acts as a time-reversal operator in the $x$–$y$ plane. Therefore at $t = 2\tau$ the accumulated individual phase gains and losses of magnetic moments
are compensated resulting in the recovery of the phase coherence and hence the formation of the spin-echo.

It should be remarked that the intensity of the echo signal is smaller than the intensity of the free induction decay, indicating that the phase recovery is only partial. This is because certain interactions are not inverted by the $\pi$ pulse. These interactions are the sources of the spin-spin relaxation. Finally, by varying the interpulse delay time $\tau$, the spin-spin relaxation time can be extracted from the $M_{xy}(2\tau)$ magnetization values. A more detailed description is given in Chapter 4.

### 3.2.2 Measurement of the spin-lattice relaxation time

For the determination of spin-lattice relaxation time the spin system is initially excited in order to be taken out of equilibrium and later the nuclear magnetization parallel to the external field (in our notation: $M_z$) is monitored. For the excitation we can use a $\pi/2$ pulse causing $M_z = 0$ at $t = 0$ (saturation recovery). Alternatively we can employ a $\pi$ pulse resulting $M_z = -M_0$ at $t = 0$ (inversion recovery). A comb of $\pi/2$ pulses with short delay between them is also often
applied (saturation comb). The fact that the pick-up coil detects the magnetization in the $x$–$y$ plane implies that $M_z$ has to be rotated into this plane for determining its magnitude. Hence, after time $\tau$ from the initial pulse the $M_z$ magnetization is inspected by applying a $\pi/2$ pulse to rotate the magnetization into the $x$–$y$ plane. Repeating the pulse sequence with various time separations $t$ of the excitation and the inspection allows the determination of the magnetization recovery curves $M_z(t)$. An experimental fit to $M_z(t)$ yields the relaxation time $T_1$.

### 3.3 Interactions in NMR spectroscopy

The reason that NMR spectroscopy is widely used is partly based on the fact that a very large set of physical parameters related to different interactions can be investigated. In the solid state the interactions may be anisotropic described by tensors. The energy levels of spin states may be shifted resulting in a direct manifestation of these interactions in the NMR spectra. Moreover, they affect relaxation mechanisms as well as line shape. Generally, the external magnetic fields related to Zeeman coupling are much larger than the local fields produced by internal mechanisms, hence the high-field approximation is justified, i.e., the internal interactions can be treated as perturbations on the Zeeman Hamiltonian.
3. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

3.3.1 Interactions between nuclear spins

The dipolar interaction results from the coupling between one nuclear spin and the local magnetic field generated by another nuclear spin at the place of the former nucleus, and vice versa. This is referred to as direct dipolar interaction which is described by the following Hamiltonian

$$\mathcal{H}_{DD} = \frac{\mu_0}{4\pi} \gamma_k \gamma_l \hbar^2 \frac{1}{2} \sum_{k<l} \frac{(1 - 3 \cos^2 \Theta_{kl})}{r_{kl}^6} (3I_kz I_lz - \hat{I}_k \cdot \hat{I}_l)$$

(3.17)

where $\mu_0/(4\pi)$ is the magnetic constant, $\gamma_{(k,l)}$ is the gyromagnetic ratio of the corresponding nuclei, $\hat{I}_{(k,l)}$ and $I_{(k,l)z}$ are spin operators and their eigenvalues, $r_{kl}$ is the distance between nuclei $k$ and $l$, and $\Theta_{kl}$ is the angle between the external magnetic field $B_0$ and the internuclear vector $r_{kl}$. Using the method of moments one can calculate the second moment of the spectra, i.e., the direct dipolar contribution to the NMR line width:

$$\Delta^2_{II} = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^4 \gamma^2 \hbar^2 I(I+1) \frac{3}{4} \sum_i \frac{(1 - 3 \cos^2 \theta_{kl})^2}{r_{kl}^6}$$

(3.18)

$$\Delta^2_{IS} = \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^2 \gamma^2 \hbar^2 S(S+1) \frac{1}{3} \sum_i \frac{(1 - 3 \cos^2 \theta_{kl})^2}{r_{kl}^6}$$

(3.19)

where $\Delta^2_{II}$ and $\Delta^2_{IS}$ are the second moments coming from homonuclear and heteronuclear couplings, respectively. In powder samples the crystallites have random orientations, therefore the averaging of the spatial part over all orientations is necessary: $(1 - 3 \cos^2 \theta_{kl})^2 = 4/5$, where the bar denotes the average over all orientations. Although in the case of a rigid lattice the direct dipolar coupling severely broadens the NMR spectra, in the presence of any spin motion (e.g., spin-diffusion, molecular reorientation) the nuclear spins experience a time average of the spatial part of the interaction which leads to a narrower NMR line. This phenomenon is the *motional narrowing* of the NMR line.

Another possible manifestation of motion in solids is *site exchange*. In this case, the nuclei feel different local environments with different resonance frequencies in the absence of motion. If the environment of the studied nuclei varies fast enough, i.e., the jumping rate $1/\tau_c$ is fast compared to the frequency difference of the sites, then a single resonance line is observed at an averaged frequency. Sometimes this is also called motional narrowing.
Indirect spin-spin coupling mediated by electrons also exists. Different types of indirect interaction are $J$-coupling, \textit{RKKY} coupling and transferred hyperfine coupling.

### 3.3.2 Quadrupolar interaction

If the spin of a nucleus is larger than 1/2, it possesses a nonzero quadrupolar moment which interacts with the electric field gradient tensor (EFG) in the crystal structure. Therefore, the quadrupolar interaction is very useful for obtaining information about crystal structure, symmetry and sample homogeneity. Moreover, it may lift the degeneracy of the nuclear spin states without an external magnetic field allowing nuclear quadrupole resonance (NQR) spectroscopy. The quadrupolar Hamiltonian is

$$
\mathcal{H}_{\text{quadrupolar}} = \frac{e^2 q Q}{4I(2I-1)} \left\{ (3I_z^2 - I^2) + \eta (I_x^2 - I_y^2) \right\}
$$

(3.20)

where $e$ is the electric charge, $Q$ is the quadrupolar moment, $e \bar{q} = V_{zz}$ is the largest element of the EFG tensor, and $\eta$ is the asymmetry parameter of the EFG tensor. As a consequence of Eq. (3.20) several satellite resonance lines appear at equal $\omega_Q$ spacing on both sides of the original resonance line in first order. If the quadrupolar coupling is even stronger, second-order effects become important, the resonance lines are heavily broadened, and the satellites are often difficult to detect. In addition the central line originated from $\frac{1}{2} \rightarrow -\frac{1}{2}$ nuclear spin transition is shifted and its shape is a double-horn spectrum characteristic of second-order quadrupolar lines.

### 3.3.3 Interactions between electrons and nuclear spins

The magnetic moments of electrons have both orbital and spin contributions. The interaction between electrons and nuclei creates two different frequency shifts. The local magnetic fields produced by electronic orbitals as well as diamagnetic currents induced by the external field interact with nuclear spins which leads to the \textit{chemical shift}

$$
B_{\text{local}} = (\mathbf{1} - \tilde{\sigma}) B_0
$$

(3.21)

where $B_{\text{local}}$ is the local magnetic field experienced by the nuclei and $\tilde{\sigma}$ is the chemical shift tensor which is usually temperature independent. The coupling
causing the chemical shift to be sensitive to the structure of the electronic orbitals is often referred as orbital shift. Different chemical and bond configurations lead to different NMR line positions, therefore the chemical shift has a very important role in structural chemistry. The spins of electrons and nuclei interact with each other resulting in the hyperfine coupling. In metals the Fermi contact term created by s-electrons and the nuclear-electron dipole-dipole term for other types of electrons can be separated in the Hamiltonian:

$$\mathcal{H}_{\text{HF}} = \left( \frac{\mu_0}{4\pi} \right) \gamma_n \gamma_e \hbar^2 \left[ \frac{8\pi}{3} \hat{I} \cdot \hat{S} \delta(r) + \frac{3(\hat{S} r)(\hat{r} I) - (\hat{S} I)r^2}{r^5} \right]$$ (3.22)

where \( r \) is the position vector of electron, the nucleus being taken at the origin, \( \hat{I} \) is the nuclear spin operator, \( \hat{S} \) is the electron spin operator, while \( \gamma_n \) and \( \gamma_e \) denote nuclear and electron gyromagnetic ratios, respectively. While the Fermi contact term, i.e., the first term of Eq. (3.22), leads to an isotropic shift, the second term produces an anisotropic shift. The contact term results a frequency shift which depends on the electron spin susceptibility \( \chi^s \)

$$K^s = \frac{\Delta B}{B_0} = \left( \frac{\mu_0}{4\pi} \right) \frac{8\pi}{3} \left( \langle |\psi(0)|^2 \rangle_{E_F} \chi^s \right)$$ (3.23)

where \( \langle |\psi(0)|^2 \rangle_{E_F} \) is the average over the Fermi surface of the squared magnitude of the Bloch wave functions at the nucleus. \( K^s \) is known as the Knight shift. It is clear that non-s electrons have no contact interaction since their wave functions have no contributions at the site of the nucleus. The spin-lattice relaxation rate can be calculated for noninteracting conduction electrons using Eq. (3.13):

$$\frac{1}{T_1} = \int_0^\infty \langle i | V_{e-n} | f \rangle |^2 \rho^s(\epsilon) f(\epsilon)(1 - f(\epsilon)) d\epsilon$$ (3.24)

where \( \langle i | V_{e-n} | f \rangle \) is an effective hyperfine scattering matrix element, \( \rho(\epsilon) \) is the electronic density of states and \( f(\epsilon) \) is the Fermi distribution function. If the Fermi contact interaction is dominant, then the relaxation rate is given by

$$\frac{1}{T_1} = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{64}{9} \pi^3 \gamma_n^2 \gamma_e^2 \left( \langle |\psi(0)|^2 \rangle_{E_F} \right)^2 \rho^s(E_F) k_B T$$ (3.25)

where \( T \) is the temperature. \( 1/T_1 \propto T \) is the Korringa law. Combining Eqs. (3.23) and (3.25) one can obtain the Korringa relation which connects the \( 1/T_1 \) relaxation rate and Knight shift:
3. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Figure 3.7: SEDOR pulse sequence. At the resonance frequency of $\alpha$ nuclei a spin-echo sequence is applied, and at the resonance frequency of $\beta$ nuclei an additional pulse is utilized simultaneously with the $\pi$ pulse for $\alpha$ nuclei.

Finally, we cite the famous Moriya’s law which treats the electron-electron interaction through the electronic susceptibility assuming $\delta$ function-type interaction in a random phase approximation to connect the dynamic spin susceptibility with spin-lattice relaxation through the fluctuation–dissipation theorem:

$$(K^\alpha)^2 T_1 = \left( \frac{\hbar}{4\pi k_B} \right) \left( \frac{\gamma_e}{\gamma_n} \right)^2 \quad (3.26)$$

Spin-echo double resonance is a very powerful tool to determine whether two species of nuclei ($\alpha$ and $\beta$) are physically close to each other by testing the dipolar coupling between them. The strength of the method is due to the very strong distance dependence of dipolar interaction. The SEDOR experiment is regarded as a modified $T_2$ measurement (see Fig. 3.7). In an ordinary $T_2$ experiment only $\alpha$ spins are flipped and the influence of their environment during the dephasing and rephasing period (before and after the applied $\pi$ pulse) is observed. However, in a SEDOR measurement $\pi$ pulses are applied simultaneously at the resonance frequency of both the $\alpha$ and $\beta$ nuclei. If these species of spins are physically close to each other, then the $\beta$ spins produce an extra dephasing during the echo formation of the $\alpha$ nuclei since the $\pi$ pulse of the

$$\frac{1}{T_1} = \frac{4k_B T}{\hbar^3 \gamma_e^2} \sum_{\alpha\alpha=\perp} |A(q)|^2 \chi''_{\alpha\alpha}(q, \omega) \quad (3.27)$$

where $\chi''_{\alpha\alpha}(q, \omega)$ is the imaginary part of the dynamic spin susceptibility tensor at wave vector $q$ spin vectors and Larmor angular frequency $\omega$; $A(q)$ is the hyperfine coupling tensor. The summation over $\alpha$ is performed for the plane perpendicular to the magnetic field.

3.4 Spin-echo double resonance

Spin-echo double resonance is a very powerful tool to determine whether two species of nuclei ($\alpha$ and $\beta$) are physically close to each other by testing the dipolar coupling between them. The strength of the method is due to the very strong distance dependence of dipolar interaction. The SEDOR experiment is regarded as a modified $T_2$ measurement (see Fig. 3.7). In an ordinary $T_2$ experiment only $\alpha$ spins are flipped and the influence of their environment during the dephasing and rephasing period (before and after the applied $\pi$ pulse) is observed. However, in a SEDOR measurement $\pi$ pulses are applied simultaneously at the resonance frequency of both the $\alpha$ and $\beta$ nuclei. If these species of spins are physically close to each other, then the $\beta$ spins produce an extra dephasing during the echo formation of the $\alpha$ nuclei since the $\pi$ pulse of the
α nuclei will not refocus the dephasing contribution because of the $\pi$ pulse of the β nuclei. To quantify the effect the so-called SEDOR fraction\textsuperscript{76} \( SF \) is introduced with the following definition

\[
SF = 1 - \frac{I(\beta \text{ on})}{I(\beta \text{ off})}
\]  

(3.28)

where \( I(\beta \text{ on}) \) and \( I(\beta \text{ off}) \) are the spin-echo intensities with the excitation to the β nuclei on and off, respectively. Additionally, for small \( t \) values it can be shown\textsuperscript{76} that the time dependence of \( SF \) is given by

\[
SF(t = 2\tau) = \frac{1}{2} \Delta^2 t^2 + O(t^4)
\]  

(3.29)

where \( \Delta^2 = \frac{4}{15} \gamma_\alpha^2 \gamma_\beta^2 h^2 S_\beta (S_\beta + 1) \sum_\beta \frac{1}{r_{\alpha\beta}} \) is the second moment of the spectrum line as in Eq. (3.19).
This chapter contains the technical information necessary to reproduce the experiments and data processing we have done. It includes an outline of sample preparation and characterization protocols, a schematic review of the NMR spectrometer as well as of the measurement setup. We also describe the data processing and fitting methods used as ordinary daily routines, the more particular cases being presented together with the experimental results in Chapter 5.

### 4.1 Sample preparation and characterization

This thesis describes an investigation of sodium containing ternary alkali fullerides $\text{Na}_2\text{CsC}_{60}$, $\text{Na}_2\text{KC}_{60}$ and $\text{Na}_2\text{RbC}_{60}$ that were synthesized by Slaven Garaj in the research group led by László Forró at the Ecole Polytechnique Fédérale de Lausanne, according to the alkali intercalation protocol conventionally applied to prepare fullerides. Because most fullerene derivatives are air sensitive and alkali metals are very reactive, the sample is prepared in an inert atmosphere, usually in a glove box. For the direct solid state diffusion controlled reaction, high purity commercially available $\text{C}_{60}$ and alkali metals were mixed in stoichiometric quantities and sealed in a quartz tube filled with He gas to about 80 kPa. The tube was heat treated at 470 K for 12 hours and then at 700 K for 3 weeks with intermittent regrinding of the contents about 2 or 3 times. The final sample quality depends mainly on the accuracy of the weighing of the alkali metals, especially for small batches.

The samples were characterized by x-ray diffraction, SQUID magnetometry and ESR spectroscopy, as well as by NMR measurements. For NMR measurements about 50-100 mg powder was sealed in a quartz tube under He atmosphere. The typical diameter of the NMR tube was 5 mm and the length 25 mm to fit in our NMR coils. It should be noted that even if single crystals
of certain compounds can be grown, they are unfortunately too small for NMR measurements.

The superconducting transition temperature of Na$_2$CsC$_{60}$ was $T_c = 12$ K determined by SQUID magnetization measurement shown in Fig. 4.1. NMR has proven very helpful for the characterization of sample quality: $^{23}$Na NMR spectra on 3 different batches taken in the high temperature phase at 400 K are shown in Fig. 4.2. It is to be noted that sample No. I has much larger line width than the other two samples, and sample No. III has the narrowest line width. A larger NMR line width can be attributed to a higher degree of residual disorder, thus a narrower line width indicates better sample quality. Since the NMR lines investigated in the present work are situated very close to each other, the narrow line width is crucial. Although we carefully tested our key findings on all samples, namely each one was cooled down to 80 K and the sodium line splitting was verified, throughout this thesis we only report experimental results on samples of best quality.

To test the residual C$_{60}$ content of fulleride salts $^{13}$C NMR spectroscopy was applied. This procedure is based on the fact that undoped fullerene and Na$_2$AC$_{60}$ salts have different carbon chemical shifts and they have, therefore, distinct spectral contributions. Due to the extremely long spin-lattice relaxation time of pure fullerene,$^{13}$ this experiment requires sufficiently slow (order of minutes)
4. EXPERIMENTAL

4.2 NMR apparatus

In our NMR experiments, a 7.5-T static magnetic field generated by a superconducting coil from Magnex Corporation was used. The homogeneity and the accurate value of the magnetic field were probed by the sodium NMR spectrum of a NaI reference solution. The reference sample was measured under the same experimental setup as the fullerides, i.e., the same coil at the same position was used in both cases. The field homogeneity was 1.2 ppm and the $^{23}\text{Na}$ resonance frequency was 84.3947 MHz. The NMR probehead was inserted into a continuous-flow cryostat manufactured by Oxford Instruments.

In the measurements we used a homodyne NMR spectrometer (see Fig. 4.3) which was designed and assembled in the laboratory in Orsay supervised by Olivier Duarte. The experiment was controlled by a personal computer (PC).

\footnotesize
\textsuperscript{8}Recently, we have used this technique\textsuperscript{77} and found it to be very useful for Na$_2$CsC$_{60}$ not only to characterize the samples but to confirm the structural nanosegregation suggested previously by infrared absorption and electron paramagnetic resonance measurements.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4_2.png}
\caption{Sample characterization: $^{23}\text{Na}$ NMR spectra of various Na$_2$CsC$_{60}$ samples at 400 K. The frequency scale represents the deviation from the carrier frequency 84.409 MHz.}
\end{figure}
4. EXPERIMENTAL

Figure 4.3: Block diagram of the home-built homodyne NMR spectrometer. In the transmission side there is a pulse formation unit which generates the rf pulses with phases of 0 and 180 degree controlled by a computer. Then the signal is amplified by a power amplifier and fed into the probehead via a circulator which separates the high and low power parts of the electronics. At the reception unit the induction signal is amplified and demodulated into quadrature components which are captured by an analog-to-digital converter located in the computer.

equipped with Microsoft MS–DOS operating system and QBasic interpreter along with previously written modules to control the spectrometer and to acquire data. On the hardware side, the PC consisted of a clock card to trigger an IEEE488 (General Purpose Interface Bus) card to set up pulse widths and delay times for the external transmission unit as well as a fast analog-to-digital converter card from GaGe (a subsidiary of Tektronix Inc.) for data acquisition. Furthermore, an rf generator from Marconi Inc. was applied to provide the carrier frequency for both the transmission and reception units. The final rf pulse trains were amplified by various pulse power amplifiers from Kalmus, ranging from 300 W to 1000 W.

The circulator of the high and low level signal path consisted of a $\lambda/4$ cable along with cross-linked PIN diodes connected on the input of an industry-standard wide band, very low noise preamplifier (LNA) manufactured by Doty Scientific Inc. The output of the preamplifier was further amplified by 40-60 dB and demodulated by a quadrature demodulator to DC frequency and filtered by a low-pass filter. The filter output was captured by a fast transient recorder card in the computer. The NMR probehead (shown in Fig 4.4) which is a capacitively
tuned parallel resonant circuit, is also a home-made design and fabrication. The probehead has to be tuned so that the resonance frequency of the circuit matches the nuclear Larmor frequency of the investigated nuclei, and the impedance of the circuit should be set to 50 Ω, the impedance of transmission line. Since the physical parameters of the NMR coil (mainly its inductance and rf resistance) determine the frequency interval in which the probehead is tunable, the NMR pick-up coil has to be made with these constructions in mind. During the tuning process, a swept rf frequency is split by a “magic tee” hybrid power splitter/combiner device and guided toward the probehead as well as to the oscilloscope. The reflected signal of the probehead can also be directed to the oscilloscope by the magic tee. The oscilloscope was used in XY-mode in order to be able to monitor the result of the tuning of the capacitors of the probehead.

The quality factor (Q) of the circuit is also important: A higher quality factor means stronger \( B_1 \) field during irradiation and better signal-to-noise ratio during acquisition. A maximization of the filling factor which is the ratio of sample and coil volume is crucial in enhancing the signal-to-noise ratio. In plain language, the sample should fill the coil as much as possible which means another restriction for the dimensions of the coil. However, there is a disadvantage in an overly high quality factor as the higher Q causes a longer decay of the transmitted rf signal which results a longer dead time of the receiver system.
4. EXPERIMENTAL

We also employed spin-echo double resonance experiments to probe the relative spatial distance of the investigated nuclei. The frequency difference of two species was only about 6 kHz (see Fig. 4.5). Since a single resonant probehead was able to excite both lines its application was straightforward. The typical quality factor of the probehead is about 50-100 which corresponds to a bandwidth of 500-1000 kHz, well beyond the required value. However, different pulse generators were needed for different lines. This required the pulse formation unit to be duplicated and the different rf pulses were combined by a mixer, and they were finally fed to the power amplifier. The SEDOR spectrometer described above was constructed and assembled from subunits available in the laboratory and the computer software code was extended by the author of this thesis.

4.3 Measurement setup, data processing

In order to obtain the NMR spectra, the free induction decay (FID) signal was collected and Fourier transformed. During the acquisition, we applied the a phase alternation method named “DC correct” to eliminate baseline errors and some other systematic errors. We did not employ any apodization for improving the signal-to-noise ratio to avoid artificial line broadening. In addition, we used phase correction mostly in zeroth order; first order was also applied but only in a few cases. Unfortunately, the quadrature demodulation was not perfect due to the not completely balanced mixer, hence, in some cases a small intensity mirror spectrum could be observed by the same frequency shift but in the opposite direction from the carrier frequency. In the NMR spectra presented in this thesis, the origin of the frequency scale is the resonance frequency of the NMR reference solution unless a different frequency scale is given in the figure captions. Notably in certain cases the frequency scale is relative to the carrier frequency. A ppm scale represents fractional frequency shifts ($\Delta f / f_0$) from the standard reference solution ($f_0$).

During the measurements, the typical $\pi/2$ pulse length was about 2 $\mu$s, the corresponding rf $B_1$ field was about 10 mT. At each temperature, the length of the $\pi/2$ pulse was determined in such a way that we recorded spectra as a function of the pulse length and calculated their integrated intensities. The pulse length belonging to the smallest spectral intensity corresponds to the $\pi$ pulse which we halved to obtain the $\pi/2$ pulse length.
In the spin-lattice relaxation measurements, we employed the saturation-recovery pulse sequence with the choice of delay times between very small values (usually about $0.001 \times T_1$) and values beyond achieving the saturation magnetization (usually at least $5 \times T_1$). The number of different delay times was typically 18-20, and they were evenly distributed on a logarithmic time scale. The magnetization values were obtained by integrating the corresponding part of the spectra. The reduced magnetization $m(t)$ was determined from the magnetization $M(t)$ at a time $t$ and the saturated magnetization $M_0$ so that

$$m(t) = 1 - \frac{M(t)}{M_0}.$$  

The time dependence of the reduced magnetization was fitted by a double-exponential function:

$$m(t) = m_a \exp \left\{ - \frac{t}{T_{1a}} \right\} + m_b \exp \left\{ - \frac{t}{T_{1b}} \right\},$$  

then the $T_1$ relaxation times were obtained as the weighted average of the components $T_{1a}$ and $T_{1b}$ as

$$\frac{1}{T_1} = \frac{m_a}{T_{1a}} + \frac{m_b}{T_{1b}}.$$  

note that: $m_a + m_b = 1$. 

Figure 4.5: Quadrature detected free induction decay signal (left panel) and Fourier transformed spectrum (right panel) taken at 100 K. The red lines represent the real part and green lines symbolize the imaginary part of complex signal and spectrum. The frequency scale is measured from the carrier frequency 84.405 MHz.
Figure 4.6: Decay of reduced magnetization in $T_1$ measurement recorded at 100 K. The squares and circles represent data for $T$ and $T'$ lines, and lines symbolize the applied fits. The black lines denote single exponential fits, red lines denote double exponential fits and green lines correspond to stretched exponential fits.

We also tried to fit the reduced magnetization curves with the conventional single exponential function

$$m(t) = \exp\left\{-\frac{t}{T_1}\right\}$$  \hspace{1cm} (4.4)

but it clearly deviated from the measured data at longer delay times. Furthermore, we attempted a stretched-exponential fit

$$m(t) = \exp\left\{-\left\{\frac{t}{T_1}\right\}^\beta\right\}$$  \hspace{1cm} (4.5)

which resulted in a good agreement between measured and fitted data. The reason why we did not make use of the latter fit was that it provided very different $\beta$ stretching parameters for different spectral components ($\beta = 0.82$ and 0.64 for the $T$ and $T'$ lines, respectively) which would have made the further analyses very complicated.

For the spin-spin relaxation experiments, we employed a $\pi/2 - \tau - \pi$ spin-echo pulse sequence with varying $\tau$ delay time between the pulses. The shortest delay time was slightly longer than the dead time of the receiver, typically 12 to

\[\text{...}\]
15 $\mu$s. The longest delay time was chosen to be about five times longer than the spin-spin relaxation time. For attaining a better signal-to-noise ratio, the number of acquisitions was increased for longer interpulse delay because longer delays result in smaller signals. To correct for the different number of acquisitions at different delay times, the corresponding spectra were renormalized after the end of the experiment. The zero of the time axis of the recorded signal was displaced to the maximum of the echo signal. The data at negative times were discarded and the $t > 0$ part of the echo signal Fourier transformed. The magnetization values obtained by integrating the real part of the Fourier spectrum over the frequency range of interest were fitted to a single exponential function:

$$M(2\tau) = M_0 \exp \left\{ -\frac{2\tau}{T_2} \right\} , \quad (4.6)$$

where $\tau$ denotes the interpulse delay.

### 4.3.1 SEDOR

We use spin-echo double resonance to investigate the interaction between the nuclei giving rise to the T and T’ line of the $^{23}$Na spectrum. The difficulty of these experiments arises from the fact that both the $\alpha$ and the $\beta$ nuclei are sodium, and the frequency difference of the T and T’ lines is small, $\Delta f \approx 6$ kHz. In order to achieve a selective excitation of one of these lines, the length of the $\pi/2$ pulse...
needs to be long enough, $\tau_{\pi/2} > \pi/2 \times \Delta f \approx 110 \, \mu s$. We used $\tau_{\pi/2} \approx 150 \, \mu s$ with a correspondingly decreased rf power. The frequency of the $\beta$ channel was swept with small frequency increments through the T (T') line while the $\alpha$ frequency was kept constant at the T' (T) line. The SEDOR fractions (3.28) were calculated from the integrated spectral intensities of the T and T' lines.
In this Chapter we summarize the results of our extensive $^{23}$Na NMR investigations of Na$_2$AC$_{60}$ compounds with A = K, Rb, and Cs. First the $^{23}$Na NMR spectra of Na$_2$AC$_{60}$ salts are presented. In the remaining part of the Chapter, the $^{23}$Na NMR properties of Na$_2$CsC$_{60}$ are described in detail. The temperature dependence of the spectrum is presented along with the line shifts, line widths, and spin-echo double resonance characteristics. The temperature evolution of the spectral weight of the T’ line is given and compared to the width of the $^{13}$C NMR line. Spin-spin and spin-lattice relaxation rates as a function of temperature are described subsequently. One of the strengths of the present Thesis is the excellent spectral resolution allowing a separate characterization of the T and T’ lines. The analysis and discussion of the experimental results will be provided in Chapter 6.

5.1 Line splitting in the NMR spectra

5.1.1 $^{23}$Na NMR spectra of Na$_2$CsC$_{60}$

The $^{23}$Na NMR spectra of Na$_2$CsC$_{60}$ taken at various temperatures are displayed in Fig. 5.1. The sodium spectra exhibits two main characteristics: At around 300 K, one can observe an abrupt change in the NMR frequency that we associate with a first order fcc–sc phase transition observed by differential scanning calorimetry$^{53}$ (DSC). Another remarkable feature is the splitting of the NMR line, i.e., the appearance of a new line below about 170 K. A similar phenomenon was observed in A$_3$C$_{60}$ superconductors of fcc lattice. Therefore we adopt the same notation as in this latter case: We denote the line with larger spectral weight by T and the other line by T’. (T refers to a site with tetrahedral C$_{60}$ coordination.) The intensity of the T’ line increases with decreasing temperature, attaining a spectral weight of 29 ± 5% in the low-temperature limit.
Figure 5.1: $^{23}$Na NMR spectra of Na$_2$CsC$_{60}$ in 7.5 T magnetic field. The temperatures are indicated on the left of the spectra.
We have to remark that the sodium nucleus has $3/2$ spin, therefore, it possesses a nonzero quadrupolar moment which interacts with the electric field gradient (EFG) tensor. We recall that the EFG is nonzero at the tetrahedral site due to the site symmetry. Under these conditions 3 spectral lines are expected corresponding to the $\frac{1}{2} \rightarrow -\frac{1}{2}$ central transition as well as to $\frac{3}{2} \rightarrow \frac{1}{2}$ and $-\frac{1}{2} \rightarrow -\frac{3}{2}$ satellite transitions. One can decide whether all 3 lines are irradiated by examining the calibration of the $\pi/2$ pulse. If, under the same conditions, the optimal $\pi/2$ pulse length only is half of the $\pi/2$ pulse of the reference solution, then the central transition is only excited. If, on the other hand, there is no difference between the optimal $\pi/2$ pulses of the sample and the reference solution, then all transitions are irradiated. In our investigations, we excited not only the central transition but also the satellites. Nevertheless, in the $^{23}$Na NMR spectra in Fig. 5.1, only the central transition can be observed. The satellites are very sensitive to crystal imperfections, consequently their width could be extremely large with small overall intensity which smears out in the baseline making them unobservable.

5.1.2 $^{23}$Na NMR spectra of Na$_2$RbC$_{60}$ and Na$_2$KC$_{60}$ compounds

We have wondered whether the T–T$'$ splitting is restricted to Na$_2$CsC$_{60}$ or occurs in other $Pa\bar{3}$ fullerene structures as well, i.e., where the alkali dopant at the octahedral site differs from cesium. The main difficulty of such tests is that both Na$_2$RbC$_{60}$ and Na$_2$KC$_{60}$ polymerize spontaneously when cooled slowly in the vicinity of 250 K down to about 220 K. Rapid cooling, however, largely suppresses the polymer formation. In order to avoid the polymerization and preserve the cubic phase as much as possible, we have adopted the following cooling procedure: The samples were heated up to 400 K in the NMR probehead, well into the fcc phase, then immersed into liquid nitrogen. The sodium NMR spectra of Na$_2$RbC$_{60}$ and Na$_2$KC$_{60}$ taken at 400 K in the fcc phase and at 80 K in the quenched sc phase are compared in Fig. 5.2. The spectra of Na$_2$CsC$_{60}$ acquired at the same temperatures are also included in the figure for comparison. The main conclusion of these experiments is that at 80 K the T–T$'$ splitting is obvious in all the three compounds, therefore we have successfully detected the T–T$'$ phenomenon in all the A$_3$C$_{60}$ fulleride salts with $Pa\bar{3}$ structure. Moreover, a third line at about 240 ppm is also observed in Na$_2$KC$_{60}$ at 80 K. Based on the $^{23}$Na NMR spectrum of the polymer phase, we identify this line as arising from a residual polymer phase in our quenched sample.
Figure 5.2: $^{23}$Na NMR spectra of Na$_2$CsC$_{60}$ compounds in 7.5 T magnetic field: (a, b) Na$_2$CsC$_{60}$, (c, d) Na$_2$KC$_{60}$ and (e, f) Na$_2$RbC$_{60}$. The spectra on the left (a, c, e) were collected at 400 K and the ones on the right (b, d, f) at 80 K. The dashed line on the (b) panel shows the spectra with a 3 kHz-width Gaussian convolution. The (d, f) spectra were prepared by quenching the samples into liquid nitrogen.
5. **RESULTS**

![Figure 5.3: Comparison of $^{23}\text{Na}$ NMR spectra of $\text{Na}_2\text{CsC}_{60}$ at 80 K taken after quenching the sample into liquid nitrogen (black line) and after applying a very slow cooling $10^{-3}$ K/s (red line). Note that vertical offsets are different for the two spectra.](image)

Although the line widths of all the three $\text{Na}_2\text{AC}_{60}$ compounds are similar at high temperature and $\text{Na}_2\text{CsC}_{60}$ has only about 10-15% narrower line width than the other two compounds, at 80 K $\text{Na}_2\text{RbC}_{60}$ and $\text{Na}_2\text{KC}_{60}$ have remarkably larger line widths than $\text{Na}_2\text{CsC}_{60}$. The larger line widths may arise from a larger defect concentration in these compounds. The quenching process may increase the defect concentration, although in $\text{Na}_2\text{CsC}_{60}$ we do not observe any cooling rate dependence of the line width in the cooling rate range of $10^{-3}$ to $10^2$ K/s (see Fig. 5.3). If we apply an additional 3-kHz Gaussian broadening to the 80-K spectrum of $\text{Na}_2\text{CsC}_{60}$ in order to mimic the larger line widths of the other two fulleride salts, the three spectra become virtually identical (see the dashed line in Fig. 5.2(b)). Albeit that all $\text{Na}_2\text{AC}_{60}$ materials display the T–T’ splitting, in the following we restrict our detailed NMR investigations to $\text{Na}_2\text{CsC}_{60}$ because of the absence of the complicating polymer phase and because the narrower lines allow a better resolution.

**Satellite peak in the fcc phase spectrum of $\text{Na}_2\text{CsC}_{60}$**

Finally, we comment on the weak satellite line in the fcc phase of $\text{Na}_2\text{CsC}_{60}$ at 215 ppm (see Fig. 5.2(a)) which has also been observed by Saito *et al.*\textsuperscript{78} This
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Figure 5.4: Temperature dependence of full width at half maximum (FWHM) line width of $^{23}$Na NMR spectra in Na$_2$CsC$_{60}$. The squares denote data for T line, as well as the circles stand for T’ line.

line appears below 580 K and disappears at the fcc–sc phase transition. The fcc satellite line seems to be unrelated to the T–T’ splitting in the orientationally ordered phase as it is absent in the other two Na$_2$AC$_{60}$ compounds.

5.1.3 $^{23}$Na NMR line width in Na$_2$CsC$_{60}$

Because of its simplicity, the line width is often characterized by the full width at the half maximum (FWHM) value in the NMR spectroscopy. The FWHM line width can be obtained from the acquired spectra (Fig. 5.1) and its temperature dependence is displayed in Fig. 5.4. Decreasing the temperature, the FWHM line width of the T line slightly broadens and it has a small peak in the vicinity of 175 K, caused by the onset of the T–T’ line splitting. The FWHM line width of the T’ line decreases from the temperature of the T’ line formation down to 90 K and below this temperature it is constant within error.

We point out, however, that the T line obviously has a structure: Besides the peak at the maximum value, there is also a shoulder in the direction of negative shifts. We will discuss the shape of the T line in details in Section 6.2.
Figure 5.5: Temperature dependence of $^{23}$Na NMR line shifts in Na$_2$CsC$_{60}$. Squares and circles denote the T and T’ lines, respectively. The continuous line represents the first moments of the spectra and the triangles indicate the line positions in the fcc phase.

5.2 Is the detected T’ peak intrinsic?

Before we turn our attention to further investigations, it is indispensable to know whether the detected T’ line emerges from a separate phase with different structures, e.g. unreacted constituents, various impurities or any structural defect, or whether the appearance of this line is intrinsic to the investigated material. Below we present the results on the temperature dependence of the line shift as well as SEDOR experiments which clearly indicate that T’ line indeed originates from the same phases as the T line.

5.2.1 NMR line shifts in Na$_2$CsC$_{60}$

A very simple way to resolve the above problem is to examine the NMR line shifts which are very sensitive to local environment. The temperature dependence of the first moment of the spectrum is shown in Fig. 5.5. In this figure, the positions of both the T and T’ lines are indicated. The first moment is simply the position of the single tetrahedral NMR peak at high temperatures, in contrast to the situation below 200 K where the first moment is the weighted average of the positions of the tetrahedral NMR lines with the corresponding spectral weights. The fact that no singularity can be observed in the first moment
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Figure 5.6: SEDOR experiment and NMR spectrum taken at 80 K. The delay time between the pulses is 5 ms. The continuous line represents the NMR spectrum, and the geometrical symbols show the SEDOR fractions. During the experiment the $\alpha$ frequency is kept constant at $T$ (squares) or $T'$ (circles) while the $\beta$ frequency is swept in small increments in the region of spectrum.

at the temperature of the line splitting is of major importance. Based on this finding, the possibility that the $T'$ line originates from a segregated phase with different structure is very improbable.

5.2.2 Spin-echo double resonance experiments

In order to exclude the possibility that the $T'$ line originates from a phase separation, a more direct test, the SEDOR measurement, has also been carried out. We have seen in Section 3.4 that a spin-echo double resonance experiment probes the dipolar coupling between different nuclei by the application of an additional pulse at the resonance frequency of the interacting species in coincidence with the echo pulse. The decrease of echo intensity depends on the strength of the dipolar interaction between the involved nuclei and is quantified by the SEDOR fraction Eq. (3.28). As the dipolar interaction has a strong distance dependence, by this method one can distinguish different species spatially located close to each other. Fig. 5.6 demonstrates the SEDOR effect on the $T$ and $T'$ lines and the 80-K NMR spectrum is also shown for comparison.

First, a spin-echo measurement is performed at the $T$ site with reduced frequency window, i.e., the $\alpha$ frequency is fixed at $T$ the line. In addition another
pulse is applied at a $\beta$ frequency according to the SEDOR experiment. The $\beta$ frequency is swept in small increments in the frequency region of the NMR spectrum (squares in Fig. 5.6) in order to explore its effect on the echo intensity. The maximal echo suppression occurs at a SEDOR fraction of 1 while $SF = 0$ means that there is no dipolar coupling between the two species in question. It is obvious that the case $\beta$ frequency = $\alpha$ frequency is meaningless as it monitors the same kind of nuclei. The most important information of this experiment is obtained if $\alpha = T$ and $\beta = T'$ where a nonzero SF is observed. In our next experiment the $\alpha$ frequency is fixed if the $T'$ site and one can also detect the nonzero SEDOR fraction at $\beta$ located at the T line. Due to the different spectral weights, it is apparent that the SEDOR fraction is larger, i.e., the effect of the T line on the $T'$ line is stronger than the effect of the $T'$ line on the T line. In conclusion, a marked SEDOR effect is seen in both T–$T'$ combinations which is a strong argument for the mixing of the T and $T'$ nuclei on a microscopic scale. In other words, the T–$T'$ splitting is an intrinsic effect of the $A_2A'C_{60}$ phase.
5.3 Comparison of $T'$ spectral weight and $^{13}$C line width

Now that we have established the intrinsic nature of the observed line splitting, we now present a result which plays an important role in the subsequent argumentation. In Fig. 5.7 we have plotted the spectral weight of the $T'$ line which increases strongly with decreasing temperature and saturates below about 120 K at $29 \pm 5\%$. The width of the $^{13}$C NMR line is also displayed in Fig. 5.7 in order to demonstrate the similar temperature dependence of the two quantities. Since the broadening of the $^{13}$C line signals the slowing down of molecular reorientations, this finding suggests that the splitting of the T line is related to fullerene molecular dynamics and orientational order. This result is one of the bases of our interpretation of the T–$T'$ splitting presented in Chapter 6.

5.4 Relaxation rates

Up to this point, we have presented results gained from static NMR measurements like spectra, line shifts and SEDOR. In this section we present results on the investigated relaxation rates which enable us to probe the material on different timescales. In this way additional information about the dynamics of the studied system can be obtained.
5.4.1 Spin-spin relaxation

The temperature dependence of the spin-spin relaxation rate $1/T_2$ of the T line exhibits a peak at 170 K simultaneously with the appearance of the $T'$ line as shown in Fig. 5.8. Otherwise $1/T_2$ displays a weak temperature dependence without special features. The spin-spin relaxation rate of the $T'$ line increases sharply when the line splitting temperature is approached from below. We will interpret the characteristics of the spin-spin relaxation rate within the framework of local field fluctuations in Subsection 6.4.2.

5.4.2 Spin-lattice relaxation

To our knowledge spin-lattice relaxation time $T_1$ measurements on both tetrahedral lines (T and $T'$) were not performed earlier. The fact that the T–$T'$ splitting is well resolved in our Na$_2$CsC$_{60}$ sample makes this compound an ideal candidate for these investigations. The temperature-normalized spin-lattice relaxation rate $1/(T_1 T)$ is plotted in Fig. 5.9.

The remarkable feature is the bifurcation of the relaxation rates of the T and $T'$ lines at 125 K. This temperature is much lower than the temperature where the line splitting takes place. The difference of the two temperatures is due to the different timescales associated with these two NMR quantities and indicates
the absence of a sharp phase transition. Rather, a dynamic crossover is likely as will be discussed in Subsection 6.4.4. The sodium $1/(T_1 T)$ for both the $T$ and $T'$ lines continue to decrease with decreasing temperature down to the lowest temperature measured, 10 K. This finding is quite striking as it contradicts the Korringa law expected for a metal (see Subsection 3.3.3). Moreover, the relaxation rates of the two lines are very different.

Above 200 K, a rapid increase of the $^{23}$Na $1/(T_1 T)$ rate is observed in the sc phase, suggesting that the relaxation is dominated by thermal activation, similarly to most fullerene compounds. The relaxation rate jumps at the sc-fcc phase transition and decreases weakly in the fcc phase.

The explanation of spin-lattice relaxation rates and the discussion of the underlying physics will be presented in the Subsection 6.4.3.
Discussion

The analysis of the experimental data, the description of several NMR properties by the site exchange model, the influence of libration modes on the Knight shift and spin-lattice relaxation rate and a unified explanation for the T–T' splitting in trivalent fulleride superconductors are proposed.

6.1 Orientational ordering transition

In each Na$_2$AC$_{60}$ compound an fcc-sc phase transition is observed by differential scanning calorimetry (DSC) and x-ray diffraction measurements. The temperature of the phase transition is 299 K for Na$_2$CsC$_{60}$, 305 K for Na$_2$KC$_{60}$ and 313 K for Na$_2$RbC$_{60}$ (Ref. 53). This transition has been also detected with sodium NMR by Saito et al., their results for Na$_2$CsC$_{60}$ are shown in Fig. 6.1 for further comparison. The discontinuous change in the NMR frequency observed in our measurements and the coexistence of the lines characteristic of the two phases in the 295-K spectrum are in agreement with a first order transition.

In the high-temperature phase exhibiting $Fm\bar{3}m$ structure, the sodium ions are situated at the center of the tetrahedron formed by their first-neighbor C$_{60}$ molecules. The Na site symmetry is cubic, hence the EFG tensor is zero, and no quadrupolar broadening of the NMR occurs (Fig. 5.1). However, in the low-temperature phase with $Pa\bar{3}$ structure, the sodium site symmetry lowers from $T_d$ to $C_3$, the Na$^+$ being displaced from the center of the tetrahedron along the three-fold axis (see Fig. 6.2). A uniaxial EFG tensor and quadrupolar broadening of the NMR lines will result. The small displacement of the sodium ions has been detected with neutron diffraction at low temperature. The broadening of the NMR line is obvious below the orientational ordering transition temperature (Fig. 5.1). The line shape is characteristic of the powder pattern of a $\frac{1}{2} \rightarrow -\frac{1}{2}$ central transition of a nucleus of spin 3/2 under the influence of a uniaxial
EFG. A more complete analysis of the line shape of the tetrahedral lines will be presented in Section 6.3.

On comparing the two sets of spectra in Fig 6.1 it is seen that NMR lines from the fcc and sc phases coexist to 20 K lower temperature in the data of Refs. 78 and 80 then for our data. This lower transition temperature may be attributable to a higher vacancy concentration and so a shift of the transition temperature towards that of pure C$_{60}$
6.2 Tetrahedral line splitting

Although the orientational ordering transition in Na$_2$CsC$_{60}$ was reported in the earlier NMR investigations,$^{78,80}$ the T–T$'$ splitting remained unobserved. The reason is that the width of the T line in these studies was larger than the frequency difference of the T and T$'$ lines and thus masked the splitting phenomenon. The lower magnetic field they used has a twofold effect. First, the width of the individual lines is larger, and second, the frequency splitting of the two lines is smaller. On one hand, the width of a central quadrupolar transition is inversely proportional to the applied magnetic field. On the other hand, if the T–T$'$ frequency splitting is due to the different Knight shifts of the two sides as we propose below, then the splitting frequency is proportional the magnetic field.

Previous NMR measurements have also been performed in Na$_2$KC$_{60}$ (Refs. 57, 80) and Na$_2$RbC$_{60}$ (Ref. 80). Again, the T–T$'$ splitting that we observe in these materials was not seen in these early experiments. Both the lower magnetic field, and the formation of a polymer phase in these studies made the observation of line splitting more difficult.

Our investigations are the first to show that the T–T$'$ splitting is not only a characteristic of the merohedrally disordered fcc alkali fullerides but appears also in alkali fullerides with sc structure. Although phenomenologically the splitting is very similar in the two cases, there is an important difference. In the fcc materials the low-temperature spectral weight of the T$'$ line is 10–15%, whereas is about 30% in the compounds we investigate.
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Figure 6.3: $^{23}$Na spectrum together with line fits at 100 K. The circles represent the NMR spectrum, the red and green lines symbolizes the line fits for T and T' lines, respectively, described in the text. The frequency scale is measured from the 84.405 MHz carrier frequency.

6.3 Influence of quadrupolar interaction on the line shape

The NMR powder spectrum of a central transition can be identified from its peculiar double-horn feature. Even though the double horn structure is not fully developed in our T spectrum, the peak and shoulder structure is suggestive of quadrupolar broadening (Fig. 5.1). The fact that the quadrupolar splitting is small compared to the overall line width explains why a complete double-horn structure does not develop. In the low temperature limit the width of the T line is about 2.5 kHz (Fig. 5.4), whereas the frequency difference between the peak and the shoulder, $\nu_{\text{splitting}}$, is only about 1 kHz. The strength of the quadrupolar interaction is characterized by the quadrupolar frequency $\nu_Q$ which can be calculated from a double horn structure as

$$\nu_Q = \sqrt{\Delta \nu_{\text{splitting}} \cdot \nu_{\text{Larmor}}}$$  \hspace{1cm} (6.1)

where $\Delta \nu_{\text{splitting}}$ is the frequency difference between the “horns” and $\nu_{\text{Larmor}}$ is the Larmor frequency.
Using Eq. 6.1 we infer a quadrupolar frequency \( \nu_Q = 290 \pm 20 \) kHz in the low temperature limit. This simple method to infer \( \nu_Q \), however, is not accurate because the substantial line broadening narrows the horn spacings and leads to an underestimation of the line splitting. For a more accurate analysis we use the dmfit software package\(^{81}\) which is well suited to fit \( \frac{1}{2} \rightarrow -\frac{1}{2} \) central transitions in powder samples. The fit parameters are the Larmor frequency, peak amplitude, line shift, quadrupolar frequency, asymmetry parameter \( \eta \) and the width of Gaussian convolution to describe other sources of line broadening.

We display the 100-K spectrum together with fits to the T and T’ lines in Fig. 6.3. The solid red line represents the fit to the T line with \( \nu_Q = 540 \) kHz, and \( \nu_{\text{shift}} = -13.9 \) kHz convolved with a Gaussian of width about 700 Hz. Although the axial symmetry of the sodium sites\(^{11}\) would imply that the asymmetry parameter \( \eta \) is zero, we get a better fit if we use a small nonzero value \( \eta = 0.15 \). The quadrupolar frequency is higher than what we get from the simple calculation based on Eq. (6.1), but it is still smaller than \( \nu_Q = 680 \pm 20 \) kHz measured in \( \text{Na}_2\text{C}_60 \) under the same conditions.\(^82\) The smaller quadrupolar frequency indicates that the displacement of the sodium nuclei from the center of the tetrahedra is smaller in \( \text{Na}_2\text{CsC}_60 \) than in \( \text{Na}_2\text{C}_60 \).

The characteristics of the T’ line are very different from those of the T line; T’ is well described by a single Lorentzian. It exhibits neither horns nor shoulders, therefore no quadrupolar splitting is observable. The width of the line, 2 kHz, however, is larger than the Gaussian broadening used to describe the T line. This is suggestive of higher disorder near the T’ sites. The high disorder may well mask the features of quadrupolar broadening. To demonstrate this possibility we fit the T’ line with the strategy of maximizing \( \nu_Q \) and using an additional broadening. In Fig. 6.3 the solid green line shows the fit to the T’ line with \( \nu_Q = 470 \) kHz, \( \nu_{\text{shift}} = -8.2 \) kHz, \( \eta = 0 \) convolved with a Lorentzian of width 1.6 kHz. The main deviation between the fit and the spectrum is the high frequency tail of the T’ line. Such a tail may appear if certain T’ nuclei near lattice defects experience a higher shift. The smaller quadrupolar frequency found for T’ indicates a different local environment causing a smaller EFG at the Na site. The displacement of sodium ions from the centers of the tetrahedron may be smaller for T’ nuclei.

We also calculated the contribution of the nuclear dipole–dipole interaction to the line width. Therefore, second moments are computed between all pairs of isotopes, \( ^{23}\text{Na–}^{23}\text{Na}, ^{23}\text{Na–}^{133}\text{Cs}, \text{and} ^{23}\text{Na–}^{13}\text{C} \), via the method of moments.\(^{74,83}\) Assuming that the line has a Gaussian shape and the probability of finding a...
$^{13}\text{C}$ nucleus is evenly distributed on the surface of a sphere with the radius of a C$_{60}$ molecule because of the fast rotation, the FWHM line width is 336 Hz (about 4 ppm) which is much smaller than the measured FWHM values. We conclude that other mechanisms such as quadrupolar broadening are responsible for the line width.

6.4 Sodium site exchange due to C$_{60}$ reorientations

We have reported in Section 5.3 that the spectral weight of the $^{23}\text{Na}$ T' line and the line width of $^{13}\text{C}$ line in Na$_2$CsC$_{60}$ have similar temperature dependences which suggests that C$_{60}$ rotational dynamics is playing a role in the T–T' splitting. One possible scenario$^{64,67}$ is that T and T' sites differ in the orientation of surrounding C$_{60}$ molecules relative to the Na$^+$ ion. In this section we will demonstrate that all our NMR results are compatible with this suggested picture.

6.4.1 $^{23}\text{Na}$ NMR spectrum

We have performed a line shape simulation in the vicinity of the onset of the T–T' splitting as the first step to show and quantify the influence of fullerene rotational dynamics on the $^{23}\text{Na}$ NMR spectra. The basic idea is that a T site becomes a T' site and vice versa due to the reorientation of fullerene molecules. In NMR spectroscopy this phenomenon is called site exchange. If the exchange is fast enough, i.e., faster than the inverse frequency separation of the two lines, the two lines merge into a single line, a phenomenon called motional narrowing. We describe the process by the following model. First, we extract the parameters of the simulation from the low-temperature spectral weights of the T and T' lines giving the probabilities $p_1 = 0.71$ and $p_2 = 1 - p_1 = 0.29$ which represent a given sodium nucleus contributing to the T or the T' line, respectively. Here and in the following subscripts 1 and 2 refer to the T and T' sites, respectively. We label the exchange rate from T to T' site by $k_{12}$, and by $k_{21}$ for the inverse process. Detailed balance requires that

$$p_1 k_{12} = p_2 k_{21}. \quad (6.2)$$

We suppose a thermally activated process

$$k_{12} = k_0 \exp(-E_a/k_B T) \quad (6.3)$$
where $E_a$ is the activation energy, $k_0$ the attempt rate, $T$ the temperature and $k_B$ the Boltzmann constant.

Following the treatment of the site exchange process described in general NMR texts,\textsuperscript{71,72} one can deduce an expression for the combined line shape of the two sites as:

$$I(\omega) = \Re \frac{p_1 \left[ I^{-1}_1(\omega) + k_{21} \right] + p_2 \left[ I^{-1}_1(\omega) + k_{12} \right]}{I^{-1}_1(\omega)I^{-1}_2(\omega) - k_{12}k_{21}}$$ \hspace{1cm} (6.4)

$$I_1(\omega) = \frac{1}{(\tau_1^{-1} + k_{12}) + i(\omega - \delta)}$$ \hspace{1cm} (6.5a)

$$I_2(\omega) = \frac{1}{(\tau_2^{-1} + k_{21}) + i(\omega - \delta)}$$ \hspace{1cm} (6.5b)
6. DISCUSSION

where $\delta_1$ and $\delta_2$ correspond to the angular Larmor frequencies, $\tau_1^{-1}$ and $\tau_2^{-1}$ represent the Lorentzian line broadening parameters while $\Re$ refers to the real part.

To include fully the second-order quadrupolar properties of the T line in this model would overly complicate the calculation, therefore, it is represented by an extra 1.32-kHz Gaussian line broadening. In Fig. 6.4 we show side by side the original NMR spectra and the result of the simulation between 150 and 200 K, i.e., in the vicinity of the line splitting. A good simultaneous fit is obtained to several spectra taken at different temperatures with the model parameters assumed to be temperature independent. The temperature dependence of the spectrum appears only via the temperature activated exchange rates in Eq. (6.3). The best fit parameters are $E_a = 3000 \pm 400$ K (260 meV) for the activation energy and $k_0 = 5 \times 10^{10}$ s$^{-1}$ for the attempt rate, while the Lorentzian line broadenings are $\tau_1^{-1} = 2\pi \times 1.3$ kHz and $\tau_2^{-1} = 2\pi \times 1.45$ kHz.

6.4.2 Spin-spin relaxation

The spin-spin relaxation rate $1/T_2$ can also be described in the framework of site exchange. As a consequence of the quadrupolar moment of the $^{23}$Na isotope, both the magnetic and quadrupolar contributions must be considered calculating the spin-spin relaxation rate:

$$\frac{1}{T_2} = \frac{1}{T_{2M}} + \frac{1}{T_{2Q}} + \frac{1}{T_{2cst}}$$

(6.6)

where $1/T_{2M}$ and $1/T_{2Q}$ terms describe the magnetic and quadrupolar contributions while $T_{2cst}$ represents dipole-dipole and other terms which make a temperature-independent contribution to the $1/T_2$ relaxation rate.

The magnetic part of the $T_2$ relaxation originates predominantly from local magnetic field fluctuations which can be described$^{67,84}$ by the following terms:

$$\frac{1}{T_{2M}} = \frac{1}{40} \Delta \omega_M^2 [4f(\Delta \omega_M) + 3f(\omega_0)]$$

(6.7)

where $\Delta \omega_M$ is the amplitude of local magnetic field fluctuations, $\omega_0$ is the Larmor frequency and $f(\omega)$ is the spectral density of fluctuations.

Generally, the quadrupolar relaxation induces a non-exponential magnetization decay which can be approximated as a quasi-isotropic motion for short delay times. Thus the quadrupolar part of the spin-spin relaxation rate is expressed for spin 3/2 as
6. DISCUSSION

Figure 6.5: Spin-spin relaxation rate of T line together with the fit described in the text. The squares represent $1/T_2$ data, the solid line symbolizes the fit.

\[
\frac{1}{T_{2Q}} = \frac{3}{40} \omega_Q^2 \left[ \frac{9}{5} J(\Delta \omega_M) + 3J(\omega_0) + \frac{6}{5} J(2\omega_0) \right], \tag{6.8}
\]

where $\Delta \omega_M$ is the amplitude of quadrupolar fluctuations. The spectral densities of both magnetic and quadrupolar fluctuations can be modeled by

\[
J(x) = \frac{2\tau}{1 + (x\tau)^2}, \tag{6.9}
\]

where $x$ stands for $\Delta \omega_M$ or $\Delta \omega_Q$, and $\tau$ is the correlation time of the fluctuations. We assume $\tau$ to be thermally activated as in Eq. (6.3):

\[
\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \tag{6.10}
\]

with activation energy $E_a$ and prefactor $\tau_0$. It is easily seen in Eqs. (6.7) and (6.8) that the terms that depend on the Larmor frequency are many orders of magnitude smaller than the local field fluctuation terms therefore we neglect them. By substituting the simplified (6.7) magnetic and (6.8) quadrupolar terms into the expression (6.6) the following form is obtained for the spin-spin relaxation rate:

\[
\frac{1}{T_2} = \frac{1}{10} \omega_M^2 J(\Delta \omega_M) + \frac{27}{200} \omega_Q^2 J(\Delta \omega_Q) + \frac{1}{T_{2\text{cst}}}. \tag{6.11}
\]
6. DISCUSSION

The measured $^{23}$Na spin-spin relaxation rates have been fitted with $E_a = 2900 \pm 200$ K (255 meV) and $\tau_0 = 5.1 \times 10^{-12}$ s. The fit agrees well with the measurement as shown in Fig. 6.5. Furthermore the values deduced for the local field fluctuation amplitudes $\Delta \omega_M = 2\pi \times 2500$ s$^{-1}$ and $\Delta \omega_Q = 2\pi \times 500$ s$^{-1}$ are in the order of magnitude of T–T' line shift difference indicating the consistency of the site exchange approach.

### 6.4.3 Spin-lattice relaxation

The spin-lattice relaxation rate $R = 1/T_1$ is strongly temperature dependent in the whole range investigated. A common rate for the two tetrahedral sites is observed above 125 K. In the high-temperature range above about 210 K but below the sc-fcc phase transition the relaxation is well described by thermal activation

$$R_{HT} = R_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

(6.12)

as expected for site exchange (see Fig. 6.6). From a fit to the relaxation rate measured between 210 K and 270 K, we infer an activation energy $E_a = 3200 \pm 100$ K (275 meV) and attempt frequency $R_0 = 3 \pm 1 \times 10^7$ s$^{-1}$. In this temperature range the dominant mechanism of $T_1$ relaxation is the rotation of fullerene molecules. The fast $^{23}$Na relaxation arises from quadrupolar coupling to the fluctuating electric field gradient produced by the rotating fullerene molecules.
On increasing the temperature the relaxation rate drops by a factor of 9 at the sc–fcc phase transition after which it decreases continuously (see Fig. 5.9). This behavior is seen at the orientational ordering transition in a variety of C_{60} systems because in the high-temperature nearly free-rotation state the molecular reorientations are too fast to be efficient in causing spin-lattice relaxation and become less efficient with increasing temperature, i.e., faster rotation.

Below about 210 K the temperature dependence of $R$ is weaker than exponential. In our interpretation at this temperature the Korringa relaxation becomes dominant over the site exchange mechanism as discussed in more detail below.

It is a striking feature of the relaxation rate with far-reaching consequences that even below the temperature of line splitting (170 K) the spin-lattice relaxation rates of the T and T' sites continue to be identical down to 125 K where the two relaxation rate curves for the two sites bifurcate. This phenomenon too can be understood in the framework of the site exchange model. We propose that the line splitting temperature and the bifurcation temperature of $R$ are different because of the different timescales involved. The C_{60} molecular reorientations become slow on the time scale of the inverse of the line splitting frequency but stay fast on the longer time scale of $T_1$ down to the bifurcation temperature. To model the effect of site exchange on the spin-lattice relaxation rate we use the following rate equations:

$$\frac{dM_1}{dt} = -(R_1 + k_{12})M_1 + k_{21}M_2 \quad (6.13)$$
$$\frac{dM_2}{dt} = -(R_2 + k_{21})M_2 + k_{12}M_1 \quad (6.14)$$

where $M_i$'s are the longitudinal magnetizations of the respective sites and the $R_i$'s are the relaxation rates in the absence of site exchange.

The site exchange rates are again described by Eqs. (6.2) and (6.3). In the slow-exchange limit $k_{12} \ll R_1, R_2$ Eqs. (6.13) and (6.14) reproduce the individual spin-lattice relaxation rates of the two sites without exchange, $R_1$ and $R_2$, whereas in the fast exchange limit $k_{12} \gg R_1, R_2$ both sodium sites have a common relaxation rate $R = p_1 R_1 + (1-p_1) R_2$ where $p_1$ is the spectral weight of the component 1. To solve Eqs. (6.13)-(6.14), we use the following form for the relaxation rates:
Figure 6.7: Spin-lattice relaxation rates with fits described in the text. The squares and circles represent the measured relaxation rate for the T and T′ lines, respectively, and the solid lines symbolizes the fits.

\[ R_1 = A_1 T + BT^3 + R_{HT} \]
\[ R_2 = A_2 T + BT^3 + R_{HT} \]  

(6.15)

The first term describes the Korringa relaxation and the last term corresponds to molecular reorientations as discussed above. The origin of the \( T^3 \) term is discussed in Section 6.5. As indicated in Fig. 6.7, a good fit to the measured relaxation rates is obtained with the following parameters: \( A_1 = 2 \times 10^{-5} \, s^{-1}K^{-1}, A_2 = 1.3 \times 10^{-3} \, s^{-1}K^{-1}, B = 1.85 \times 10^{-5} \, s^{-1}K^{-3}, R_0 = 3 \times 10^7 \, s^{-1}, k_0 = 1.5 \times 10^{12} \, s^{-1}, \) and \( E_a = 3450 \pm 100 \, K. \) The difference between \( A_1 \) and \( A_2 \) values, which correspond to the “Korringa term” in \( R_i, \) comes from the different hyperfine couplings of the T and T’ line.

### 6.4.4 Dynamical crossover

Several authors have proposed that the T–T’ splitting may result from a phase transition\(^6^2\) or the separation of two phases. Based on our NMR results, we argue...
Table 6.1: Exchange parameters: Activation energies and attempt rates inferred from various experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature range (K)</th>
<th>Activation energy $E_a$ (K)</th>
<th>Attempt rate $k_0$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motional narrowing</td>
<td>150–200</td>
<td>3000 ± 400</td>
<td>$5 \times 10^{10}$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>125–225</td>
<td>2900 ± 200</td>
<td>$2 \times 10^{11}$</td>
</tr>
<tr>
<td>$T_1$</td>
<td>125–299</td>
<td>3450 ± 100</td>
<td>$1.5 \times 10^{12}$</td>
</tr>
<tr>
<td>Inelastic neutron scattering$^{85}$</td>
<td>100–350</td>
<td>3500</td>
<td></td>
</tr>
</tbody>
</table>

in this section against these scenarios and propose that the origin of line splitting is a dynamic crossover.

The most reliable test for phase separation is SEDOR. Just like in $A_3C_{60}$ systems of fcc structure,$^{64,68}$ a phase separation at the temperature of the line splitting in Na$_2$CsC$_{60}$ is excluded on the basis of our $^{23}$Na SEDOR results.

An argument in favor of a phase transition at the splitting temperature is the peak in the spin-spin relaxation rate at the splitting. A weak anomaly in the order of experimental error in the differential thermal analysis of K$_3C_{60}$ has also been reported.$^{62}$ As we demonstrate below, our NMR data in Na$_2$CsC$_{60}$ are inconsistent with a phase transition and highly suggestive of a gradual dynamic crossover in the frequency of site exchange. The essential signature of a dynamic crossover is that characteristic features of the measured material properties occur at different temperatures depending on the characteristic time scale of the measurement.

In our experiments the peak in $1/T_2$ and the line splitting coincide whereas the splitting in $1/T_1$ occurs at a different temperature. However, the coincidence of the first two features is evident in the dynamic crossover picture since the characteristic time is the inverse of the frequency splitting of the lines in both cases (see Subsections 6.4.1 and 6.4.2). Conversely, the splitting of the $1/T_1$ curves occur at a markedly different temperature which is inconsistent with the phase transition scenario but consistent with a dynamic crossover as the characteristic time is $T_1$ in this latter case. Another argument against a phase transition is the fact that temperature dependence of the average line shift (Fig. 5.5) shows no anomaly at the line splitting temperature.

In the previous subsections we have shown that the temperature variation of $T_1$ and $T_2$ as well as the splitting of the $^{23}$Na line are well described assuming
6. DISCUSSION

A temperature-activated site exchange between the T and T' sites. In Table 6.1 we summarize the activation energies inferred from these various experiments together with the temperature range of data from which the activation energy has been obtained. The site exchange can be characterized with the same activation energy $E_a = 3300 \pm 240$ K in the whole temperature range 125 to 300 K. The activation energy can also be estimated from the energy of the C$_{60}$ librational modes measured with inelastic neutron scattering. Assuming that the potential as a function of the angular deflection of the molecule is sinusoidal, an activation energy of 300 meV (3500 K) is obtained from the measured libron energy 2.7 meV. This rough estimate agrees well with the NMR results. The attempt rate of the site exchange, $k_0$ in Eq. (6.3) is also indicated in Table 6.1. Given the exponential temperature dependence, the values obtained for the prefactor from the different experiments agree very well. The temperature-independent parameters of the site exchange are in agreement with the inelastic neutron scattering result of temperature-independent libron energy in the range of 100 to 300 K. A single activation energy suggests that there is no phase transition down to 125 K.

6.5 The influence of librations on $T_1$ relaxation rates

In this section we address the origin of the unusual $T^3$ term in the $1/T_1$ relaxation rate (see Eq. (6.15) and Fig. 6.7). In the discussion of the spin-lattice relaxation we conclude that below about 200 K, the relaxation rate is governed by the local electronic susceptibility, rather than by molecular motion. In this situation the Korringa relation is expected to hold:

$$K^2 = S \frac{1}{T_1 T'}$$  \hspace{1cm} (6.16)

where $S$ is the temperature independent Korringa constant. Indeed, the behavior of the Knight shift is also anomalous. As seen in Fig. 5.5, the Knight shift is temperature dependent down to 10 K, the lowest temperature investigated. This is in contrast to the expectations for a nearly-free-electron metal where the electronic spin susceptibility is temperature independent as, consequently, should be $K$ and $1/(T_1 T)$. In our case, however, both quantities are temperature dependent. Clearly the Knight shift has a contribution linear in temperature, although signs of saturation are observable in the low-temperature limit. A
Figure 6.8: $1/(T_1 T)^{1/2}$ displayed as a function of line shift together with the best linear fits. The black and red colors correspond to $T$ and $T'$ lines, respectively. The solid lines are the best linear fits and the dotted lines are 95% confidence bands.

A linear contribution in the Knight shift implies the existence of a cubic term in the relaxation rate as seen in our experiments.

To test the validity of the Korringa relation, in Fig. 6.8 we plot $1/(T_1 T)^{1/2}$ against $K$ for both the $T$ and $T'$ lines together with the best linear fits. A linear dependence is well obeyed by the $T$ line. Since the intensity of the $T'$ line is smaller, the experimental errors are larger for this line both in the $T_1$ and $K$ data. By extrapolating the linear relation to $1/(T_1 T)^{1/2} = 0$, the zero point of the Knight shift, i.e., the chemical shift is obtained. The chemical shift for the $T$ line is $-76 \pm 5$ ppm. Because of the substantial experimental error in the $T'$ data, the 95% statistical confidence bands of the linear fit are also included in the figure. The chemical shift for the $T'$ line is $-37$ ppm with a 95% confidence interval of $-87$ to $-20$ ppm. From the slope of the linear fit we obtain the Korringa constant $S = (4.2 \pm 0.5) \times 10^{-7}$ sK and $(9.3 \pm 1.5) \times 10^{-7}$ sK for the $T$ and $T'$ lines, respectively. These values are extremely small compared to the theoretical value for the isotropic contact interaction between the nuclear and electronic spins, $S = 3.8 \times 10^{-6}$ sK. This finding indicates that the anisotropic magnetic dipole-dipole interaction dominates the coupling of the nuclear and electronic spins.
spins. Such a coupling can only arise from the interaction of the nuclei with the oriented carbon $p_z$ orbitals.

Next we ask what may cause the temperature dependence of the susceptibility. One straightforward possibility is the existence of strong electronic correlations. Electronic correlations lead to a temperature-dependent enhancement of the electronic susceptibility. This would, however, result in a Knight shift decreasing rather than increasing with increasing temperature. Another possible effect of electronic correlations is the depletion of the electronic density of states (DOS) at the Fermi energy. This situation is exemplified by the famous case of pseudogap in certain high-temperature superconductors. A pseudogap would lead to a Knight shift decreasing with decreasing temperature, in agreement with our observations. However, the Korringa relation is based on an energy-independent low-energy DOS, thus in a pseudogap state the Korringa relation is violated. Moreover, if the electronic correlations are of finite wave number, the Korringa relation is again violated. We thus reject the possibility that the origin of the temperature dependence of $K$ and $1/T_1$ is strong electronic correlations.

Another well-known cause of a temperature dependent Knight shift is the temperature variation of the DOS due to thermal expansion. This effect is seen above the Debye temperature, i.e., usually above at least 100 K. However, in C$_{60}$ compounds and in Na$_2$CsC$_{60}$ in particular there exists a low-lying optical mode involving the rigid librational motion of C$_{60}$ molecules. The energy of librons in Na$_2$CsC$_{60}$ is found to be $\hbar \omega_0/k_B = 31$ K (2.7 meV) by inelastic neutron scattering. Although thermal expansion may well contribute to the observed temperature dependence, the variation of the DOS should lead to a similarly strong temperature dependence of the $^{13}$C and $^{133}$Cs relaxation rates contrary to the observations. We propose, however, another mechanism by which the librons may influence the Knight shift as outlined below.

The result on the Korringa constant suggest that the exact orientation of the carbon $p_z$ orbitals have a strong influence on the $^{23}$Na Knight shift. Therefore the librons should strongly influence the Knight shift. Up to second order in the angular excursion of the C$_{60}$ molecules, the Knight shift is written as

$$K = K_0 + K_1 A \langle \cos \omega_0 t \rangle + 2K_2' \langle A^2 \cos^2 \omega_0 t \rangle = K_0 + K_2' A^2,$$

(6.17)

where $K_0$ is the Knight shift in the absence of librons, $\omega_0$ is the libron frequency, $A$ is the libron amplitude, $K_1$ and $K_2$ are coefficients that depend on the shape of the carbon orbitals as well as on the relative orientation of the C$_{60}$ molecules.
with respect to the sodium nucleus. A time average—indicated by angular brackets—has to be taken since $\omega_0 \gg \omega_L$.

For $k_B T \gg \hbar \omega_0$, $\langle A^2 \rangle \propto T$ yielding a contribution to the Knight shift linear in $T$. For a stricter condition on the lower bound of $T$-linear behavior, we take the Einstein model of lattice vibrations in which the temperature-dependent part of the amplitude square is given by

$$A^2 \propto \hbar \omega_0 / [(\exp(\hbar \omega_0 / k_B T) - 1)]. \quad (6.18)$$

$A^2$ of this model is linear in $T$ with good approximation down to $\omega_0 / 2$ (15 K), i.e., to the lowest temperature we have investigated. This is demonstrated in Fig. 6.9 where a fit of the form

$$K = K_0 + K_2 \hbar \omega_0 / k_B / (\exp(\hbar \omega_0 / k_B T) - 1) \quad (6.19)$$

to the measured Knight shift is given. The fit parameter is $K_2 = 0.17 \times 10^{-6} \text{ K}^{-1}$ and $0.27 \times 10^{-6} \text{ K}^{-1}$ for the T and T' lines, respectively. Since the local $C_{60}$ environments are different at the T and T' sites, the different fit parameters for the two lines are natural.

This interpretation is in agreement both with the anomalous value of the $^{23}\text{Na}$ Korringa constant and with the different temperature dependence of the $^{23}\text{Na}$
and $^{13}\text{C}$ spin-lattice relaxation rates since the latter nucleus is expected to be much less sensitive to the angular orientation of the $\text{C}_{60}$ molecules. Remarkably, there is a big jump in $^{23}\text{Na} \, 1/T_1$ at the orientational ordering transition (see Fig. 5.9) while the jump is unresolved within experimental error in $^{13}\text{C} \, 1/T_1$ (Ref. 88). The jump in the $^{23}\text{Na}$ case is well understood with the assumption that the excess Knight shift is proportional to the libron amplitude. The difference between the Knight shift in the fcc phase and in the low temperature limit is 190 ppm, whereas the excess Knight shift acquired in the sc phase until the phase transition is reached is 60 ppm. If one considers a “Lindemann criterion of orientational melting,” the cited data correspond to a Lindemann constant $c_L = \sqrt{60/190} = 0.56$, a realistic number. The jump in the lattice constant at the phase transition, on the other hand, is only 25% of the increase acquired in the sc phase. Assuming that the excess Knight shift is the result of the increase in the DOS due to thermal expansion, the big jump seen in the experiment is difficult to interpret.

Finally we note that a similarly strong temperature dependence of $^{39}\text{K} \, 1/(T_1 T)$ has been observed in $\text{K}_3\text{C}_{60}$ of fcc structure. It remains to be seen if the phenomenon can be interpreted in terms of $\text{C}_{60}$ librations in this material of different orientational structure.

### 6.6 T–T′ splitting due to $\text{C}_{60}$ orientational environments

The conclusion of the previous section is that all NMR properties of $\text{Na}_2\text{CsC}_{60}$ reported in this article are well described by a temperature-activated site exchange process; in this section we ask what exactly this site exchange might be. We will argue that the sites giving rise to the T and T′ lines differ in the local fullerene environments. This conjecture has been repeatedly put forward to explain the line splitting in $\text{A}_3\text{C}_{60}$ compounds but some experimental findings cast doubt on this explanation. Finally, we revisit the T′–problem and make suggestions on how the apparently conflicting results can be reconciled with this mechanism.

#### 6.6.1 The origin of splitting in $\text{Na}_2\text{AC}_{60}$

There is little doubt that just below the fullerene orientational ordering transition the narrow $^{13}\text{C}$ line and both the $^{13}\text{C}$ and $^{23}\text{Na}$ spin-lattice relaxation result from the rapid reorientation of the fullerene molecules. This phenomenon has been
thoroughly analyzed in a broad range of C\textsubscript{60} compounds based of a wealth of experimental techniques. Since we observe a single activation energy for the \( ^{23}\text{Na} \) site exchange down to 125 K, it follows that the site exchange process is due to fullerene reorientation.

Another argument is the concomitant \( ^{23}\text{Na} \) line splitting and \( ^{13}\text{C} \) line broadening at 170 K: Since the width of the low-temperature \( ^{13}\text{C} \) NMR line, 7 kHz (Fig. 5.7), is very close to the splitting of the \( ^{23}\text{Na} \) line, 6 kHz (Fig. 6.3), this behavior also strongly suggests that the \( ^{23}\text{Na} \) site exchange is the consequence of different fullerene orientational environments of the T and T' sites. In the following we analyze quantitatively how the NMR results can be explained by different fullerene orientational environments.

The orientation of fullerene molecules in \( \text{Na}_2\text{CsC}_{60} \) has been studied with x-ray\textsuperscript{90} and neutron diffraction\textsuperscript{11} and found to be very similar to pure C\textsubscript{60}.\textsuperscript{16} From Subsection 2.1.2 we recall that in the orientationally ordered \( \text{Pa}\overline{3} \) structure the molecules are rotated away from the standard orientation by 98° around the threefold symmetry axis through the center of the molecule. The typical orientational defect corresponds to an angle of rotation of 38° around the same axis. The energy difference between these two orientations is very small, in the order of 10 meV.

The fraction of fullerene molecules in the majority orientation, \( p_{98} \), is found in neutron scattering experiments to increase with decreasing temperature in agreement with thermodynamic expectations. In the \( T \to 0 \) limit, however, \( p_{98} \) tends to about 0.88, i.e., a value different from 1. A similar situation is encountered in pure C\textsubscript{60} where a marked glass transition is observed at \( T \approx 90 \) K by neutron scattering\textsuperscript{16} and thermodynamic measurements.\textsuperscript{91} In \( \text{Na}_2\text{CsC}_{60} \) \( p_{98} \) varies little below about 140 K without any sharp feature.\textsuperscript{92} The successful description of our \( T_1 \) data with the same activation energy as at higher temperatures suggests that the glass transition is below 125 K.

Next we consider what local environments of the sodium atoms are formed by its 4 nearest neighbor fullerene molecules taking into account the two frequent orientations (see Fig. 6.10). The sodium atom sits on the threefold symmetry axis of exactly one of its C\textsubscript{60} neighbors. This axis goes through the center of a C\textsubscript{60} hexagon in both orientations. The other three neighbors turn a C–C double bond towards the sodium atom in the majority (98°) orientation and an off-centered pentagon in the minority (38°) orientation. The possible fullerene environments are listed in Table 6.2. If we assume that the two orientations are spatially uncorrelated and use \( p_{98} = 0.88 \), the neutron diffraction result\textsuperscript{11}}
6. DISCUSSION

Figure 6.10: Local $C_{60}$ order around the tetrahedral interstices seen from Na$^+$ ions. If all neighboring fullerenes are in major orientation sodium ion faces (a) one hexagon and (b) three double bonds. In case of all neighboring $C_{60}$s are in minor orientation Na$^+$ faces (c) one hexagon and (d) three off-centered pentagons.

in the low-temperature limit, the frequency of these configurations are readily calculated; the results are listed in Table 6.2.

The different local environments should result in different $^{23}$Na NMR frequencies with spectral weights equal to the frequencies of the corresponding configurations. The frequencies of the two most frequent configurations, labeled A and B in the Table 6.2, are $p_A = 0.69$ and $p_B = 0.27$. These values are very close to the measured NMR spectral weights of the T and $T'$ lines in the low-temperature limit, 0.71 and 0.29, respectively. We have obtained these latter values by averaging the measured spectral weights of the two lines, displayed in Fig. 5.7, in the temperature range 10 to 120 K, and the errors represent the scattering in the data. The remaining two configurations, C and D in Table 6.2, carry a combined spectral weight of 5% and are easily missed in the NMR
Table 6.2: Calculated probabilities and second moments as well as building blocks of local fullerene configurations surrounding the tetrahedral site.

<table>
<thead>
<tr>
<th>Config</th>
<th>$p$</th>
<th>$\Delta^2$ (ms$^{-2}$)</th>
<th>hexagons</th>
<th>double bonds</th>
<th>pentagons</th>
<th>major</th>
<th>minor</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.689</td>
<td>0.1518</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>{4</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0.274</td>
<td>0.1525</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>{3</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>0.036</td>
<td>0.1532</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>{2</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>0.001</td>
<td>0.1538</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td>{1</td>
<td>3</td>
</tr>
</tbody>
</table>

measurements with the resolution we have, especially if these lines are broad or overlap with the two observed lines.

The good agreement between the model calculation and the experimental spectral weights persuasively suggests that the two $^{23}\text{Na}$ NMR lines at low temperatures lie in different fullerene orientational environments. Although a theoretical calculation of the Knight shifts in the two different environments does not seem to be feasible, the interpretation of the line splitting and of the temperature dependence of the Knight shift in terms of librational phonons are consistent: The variation of the Knight shift from low temperature to the ordering transition, 77 ppm, is comparable to the Knight shift difference of the T and T' lines about 70 ppm (see Fig. 5.5).

If T–T' splitting in sodium containing alkali fullerides has such a structural origin as described above, it could be tested by $^{13}\text{C}$–$^{23}\text{Na}$ multinuclear SEDOR experiments distinguishing the different fullerene neighborhoods. Using Eq. (3.29) the expected SEDOR fractions for these configurations can be calculated ($\text{SF} \propto \Delta^2$). Unfortunately, the difference of second moments of related configurations showed in Table 6.2 is smaller than 1% which is well below the usual accuracy of a SEDOR measurement. To resolve this problem one might think that a $^{13}\text{C}$ enriched sample would help. In this case we would have larger second moments because of the increased abundance of $^{13}\text{C}$ isotopes, but the scaling factor, i.e., the abundance of $^{13}\text{C}$ isotope is the same for all configurations, therefore the relative differences of second moments remain unchanged, hence the differences in corresponding SEDOR fractions cannot be detected. For that
reason $^{13}\text{C}-^{23}\text{Na}$ multinuclear SEDOR has not the necessary power to classify the fullerene neighbors of sodium ions.

### 6.6.2 T–T’ problem in $\text{A}_3\text{C}_{60}$ with merohedral disorder revisited

The T–T’ splitting has been thoroughly studied in $\text{A}_3\text{C}_{60}$ compounds of fcc structure such as $\text{Rb}_3\text{C}_{60}$ and $\text{K}_3\text{C}_{60}$. Most NMR properties of the fcc compound are consistent with the picture that the difference between the T and T’ sites is different orientational environments. The most convincing support of this suggestion is the observed $^{87}\text{Rb}$ T–T’ thermally activated site exchange in several NMR properties including direct 2D exchange NMR spectroscopy in $\text{Rb}_3\text{C}_{60}$. The activation energy inferred agrees well with the characteristic energy of fullerene reorientations similarly to our finding in $\text{Na}_2\text{CsC}_{60}$. Moreover, the larger the diameter of the alkali ion inserted into the tetrahedral void, the higher the temperature observed for the appearance of the T–T’ splitting according to the fact that the larger ions hamper the fullerene dynamics more strongly.

Finally, we mention that Yoshinari et al. found a $^{13}\text{C}$ NMR line broadening and the appearance of the T’ line in $\text{K}_3\text{C}_{60}$ similar to our results in $\text{Na}_2\text{CsC}_{60}$. Despite the strong support for the influence of C$_{60}$ structure on the T–T’ splitting, this scenario has been repudiated on the basis of SEDOR experiments. Our purpose in the present subsection is to show that SEDOR results are in fact compatible with the orientational-environment scenario.

The SEDOR measurements in question were performed by Pennington et al. on $\text{Rb}_2\text{CsC}_{60}$, a superconductor with fcc structure. They used the $^{87}\text{Rb}$ T or T’ sites as $\alpha$ nucleus and $^{13}\text{C}$ as $\beta$ nucleus. They found that the SEDOR fraction vs. $\tau$ delay time curves for the T and T’ sites are identical with high accuracy. It means that the fullerene surroundings of the T and T’ sites are virtually identical, as the time dependence of the corresponding SEDOR fraction curves differ by 1% only.

We recall the existence of merohedral disorder in $\text{A}_3\text{C}_{60}$ compounds with fcc ground state: The C$_{60}$ molecules take one of the two standard orientations (see Fig. 2.4) randomly. No matter which of these two orientations is taken by a certain C$_{60}$ molecule, it will show a six-member carbon ring towards the alkali ion at the tetrahedral site. To investigate the effect of orientational defects, Walstedt et al. propose another kind of disorder where certain molecules take an orientation different from the standard orientation. Specifically, they take an orientational defect where the molecule turns a 5-member ring, rather than a 6-member ring towards the alkali ion. Pennington et al. calculate the SEDOR
6. DISCUSSION

fraction for the case where there is one such defect around the alkali ion. They find that the SEDOR fraction differs by 5% from the case where all neighbors are in one of the standard orientations. This is well above the experimental error of their SEDOR experiment. On this basis orientational defects as the origin of the T–T′ splitting has been ruled out by these authors.

There are some alternative explanations for this effect but they are far less convincing than ones involving the local fullerene configurations. Among the researchers a general consensus is found that the existing alkali vacancies in $A_3C_{60}$ fullerides are not related to the T–T′ splitting as the characteristic energy and time scale of vacancy diffusion is remarkably different from the values observed in T–T′ site exchange.$^{69}$

Another suggested possibility is the displacement of the octahedrally co-ordinated cations. This proposition is based on the anomalous Debye–Waller factor observed at the octahedral site. However, SEDOR experiments between the octahedral and tetrahedral sites found a unique O–T distance which is inconsistent with the displacement of the O nucleus.$^{68}$

Although static Jahn–Teller distortion is not observed$^{68}$ in $C_{60}^{3−}$, a dynamical Jahn–Teller effect along with charge disproportionation has been proposed by Brouet et al.$^{94}$ in analogy with the observed NS, S, and 2S lines$^{95}$ in the quenched cubic phase of CsC$_{60}$ revealed by $^{133}$Cs NMR. In this compound the Cs nuclei are located at the octahedral site, therefore, the consequences of charge disproportionation should be seen also at the octahedral site, which is not the case.

Pennington et al.$^{68}$ also observed that the T′ site has the same number of T site neighbors as the T site which excludes any clustering. Therefore T′ cannot be a neighbor of a defect, because this situation evidently leads to clustering. This is the strongest constraint for the origin of the T–T′ line splitting.

We find that the arguments in favor of local $C_{60}$ order in the explanation of the T–T′ splitting are too strong to be discarded on the basis of the results of Pennington et al.$^{68}$ They investigated only the case when a pentagon of a misoriented $C_{60}$ molecule faces a tetrahedrally coordinated alkali ion instead of a hexagon, and draw their conclusion from that calculation. We have extended the calculation of the second moments arising from the interaction of the tetrahedral nucleus and the surrounding fullerene molecules to several different $C_{60}$ configurations. The results of these calculations are summarized in Table 6.3. Out of the special orientations listed in the Table, the five-member ring considered by Pennington et. al. gives the smallest deviation from the


Table 6.3: Relative deviation of the second moment in some special $C_{60}$ orientations referenced to the standard orientations

<table>
<thead>
<tr>
<th>Orientation</th>
<th>$\Delta^2 / \Delta_0^2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard orientation</td>
<td>0</td>
</tr>
<tr>
<td>Pentagon</td>
<td>13.5</td>
</tr>
<tr>
<td>Double bond</td>
<td>15.0</td>
</tr>
<tr>
<td>Single bond</td>
<td>17.0</td>
</tr>
<tr>
<td>C1 atom</td>
<td>18.7</td>
</tr>
<tr>
<td>C2 atom</td>
<td>18.9</td>
</tr>
<tr>
<td>C3 atom</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Figure 6.11: Relative deviation of the second moment from the standard orientation. The black color represents the zero value, and the white color corresponds to 19.1%, and the applied scale is linear.

standard orientation. If one of the 4 first neighbors, only one molecule takes this “pennington orientation”, then the fractional change of the second moment is 3%. This is somewhat different from 5% obtained in Ref. 68, but still much higher than the experimental limit of 1%.

Next we extended the calculations to a dense grid on the surface of the $C_{60}$ molecule. A contour plot constructed from the results of these calculations is displayed in Fig. 6.11. To summarize the results of these calculations, we have shown that any orientational defect of the merohedral phase should give a larger difference in the SEDOR fraction than observed in the experiments.

The merohedral disorder indicates that the $C_{60}$ orientational environment of the tetrahedral alkali sites is not unique, but this fact is often forgotten because
Figure 6.12: Fullerene configurations around a T site in the $Fm\overline{3}m$ structure. The upper panel the standard orientations while the lower panel shows a hexagon facing the tetrahedral site. The red and green circles symbolize $C_2$ and $C_3$ atoms, respectively.

**Table 6.4:** $C_{60}$ configurations around a tetrahedral site in $Fm\overline{3}m$ structure.

<table>
<thead>
<tr>
<th>Local order</th>
<th>Configuration</th>
<th>Site symmetry</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4(a) or 4(b)</td>
<td>$T$</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>3(a)1(b) or 3(b)1(a)</td>
<td>$C_3$</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>2(a)2(b)</td>
<td>$S_4$</td>
<td>3</td>
</tr>
</tbody>
</table>

the carbon atoms are thought to be equivalent. However, in $A_3C_{60}$ compounds with $Fm\overline{3}m$ cell symmetry there are 3 inequivalent carbon atoms in the lattice. The nearest surface features of $C_{60}$ molecule to tetrahedral ions are hexagons which form $C_2$ and $C_3$ carbon atoms, where $C_2$ has only $C_3$ neighbors and vice versa, forming configuration (a) and (b) demonstrated in Fig. 6.12. Due to the merohedral disorder the $C_2$ and $C_3$ atoms are interchangeable depending on the variant of the host fullerene. Therefore the local symmetry is different at the tetrahedral sites according to the neighboring fullerides (see Table 6.4).

Earlier Lüders *et al.*\textsuperscript{70} proposed almost the same scenario, but the site symmetry was different. Similarly to the $Na_2AC_{60}$ case, assuming $p = 0.5$ from x-ray experiments for merohedral configuration “a” and binomial distribution of different configurations, one can obtain the spectral weight of T and T’ lines.
Assuming that local order A contributes to the T' line while local order B and C give rise to the T line, one can obtain the ratio of the two lines: $T : T' = (3+4) : 1 = 7 : 1$, while the measured ratio is about $T : T' = 5.5 : 1$ (Ref. 64).

The discrepancy of the calculated and the measured values could originate from the wrong initial assumption, maybe the distribution of the fullerene balls is not completely random in the lattice as the binomial distribution treats them. In Ref. 96 demonstrated by measuring the neutron pair distribution function of Rb$_3$C$_{60}$ that nearest neighbor C$_{60}$ molecules prefer an “orientational antiferromagnetic state” where neighboring fullerides are in different variant of the merohedral configuration. Furthermore Goldoni et al. found by high-resolution synchrotron radiation photoemission and absorption experiments on K$_3$C$_{60}$ films that the charge distribution is not homogeneous on the C$_{60}$ surface, but around C2 carbon atoms an increased electron-density is observed which can be the cause the NMR line shift difference between T and T' site. However, Pennington et al. also discarded the possibility of different spin densities at the different alkali NMR sites. Nevertheless, it seems to be contradictory because the effect is too small to observe directly but causes a shift difference.

Consequently, we argue that the T–T’ splitting also originates from the local C$_{60}$ structure in Fm$ar{3}$m A$_3$C$_{60}$ compounds similarly to Pa$ar{3}$ structured ones. In the former case the different site symmetries are caused by variants of the host fullerene molecule configuration.
Conclusion

1. I have observed in an alkali-fulleride superconductor of simple cubic structure that the NMR line associated with the alkali nucleus of tetrahedral C$_{60}$ coordination splits into two at low temperature.$^{MP1,MP2}$ I have demonstrated this phenomenon in three different materials:$^{MP3}$ Na$_2$CsC$_{60}$, Na$_2$RbC$_{60}$, and Na$_2$KCs$_{60}$. Using a two-dimensional NMR technique, spin-echo double resonance (SEDOR), I have proven that the two lines originate from the same phase$^{MP4}$ (i.e., the second line does not result from phase segregation).

2. By measuring the temperature dependence of the $^{23}$Na NMR spectrum, spin-lattice and spin-spin relaxation times in Na$_2$CsC$_{60}$, I have found that the origin of the splitting of the NMR line is a dynamic two-site exchange.$^{MP4}$ The exchange rate is temperature activated in the temperature range 125 to 299 K with a single activation energy 3300 ± 240 K. This finding rules out the existence of a phase transition in the above temperature range. I have proposed that the two sites differ in the fullerene orientational environment$^{MP1,MP2}$ reflecting the large concentration of orientational defects observed by neutron diffraction [Prassides et al., 1994] in the same material. The mechanism of the site exchange is the reorientation of the C$_{60}$ molecule. Assuming no correlation between the defects, I have obtained the same defect concentration$^{MP3}$ as found in neutron diffraction experiments.

3. I have shown that the temperature dependence of both the $^{23}$Na Knight shift and the spin-lattice relaxation differ from rigid-lattice expectations for a metal: At low temperature the Knight shift is temperature dependent and the spin-lattice relaxation time violates the Korringa law. I have successfully interpreted this phenomenon as arising from modes involving the librational motion of the C$_{60}$ molecules.$^{MP3}$
4. In alkali-fulleride superconductors of face centered cubic ground state (such as $K_3C_{60}$ and $Rb_3C_{60}$) I have revisited the problem of the line splitting of the alkali nuclei with tetrahedral $C_{60}$ coordination. I have re-analyzed the result of SEDOR experiments in the literature and I confirmed that, just as in the simple cubic structure, the line splitting in the face centered cubic structure can be interpreted as due to site exchange between different fullerene orientational environments. The result of this analysis is a unified description of the alkali line splitting in trivalent fulleride superconductors.
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*Fullerene local order in Na$_2$CsC$_{60}$ by $^{23}$Na NMR*

*Fullerénmolekulák lokális orientációjának vizsgálata mágneses magrezonancia (NMR) spektroszkópiával Na$_2$CsC$_{60}$-on*

*Influence of local fullerene orientation on the electronic properties of A$_3$C$_{60}$*
cond-mat/0608715 and submitted to Physical Review B.

*Configurational fluctuations around tetrahedrally coordinated sodium sites in Na$_2$CsC$_{60}$ by NMR*