Raman Scattering Study of the Superconducting Pairing in CaKFe$_4$As$_4$

Master’s Thesis

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Acknowledgements
1 Introduction

The success of superconductors in modern science goes back to a discovery by Heike Kamerlingh-Onnes more than a century ago: in 1911, he observed the abrupt drop of the electrical resistivity of mercury (Hg) at a temperature of approximately 4.2 K [1]. This abrupt drop was counterintuitive and not easily explained, as the resistivity above $T = 4.2$ K allowed for an extrapolation to a finite value at absolute zero. For his discovery, Kamerlingh-Onnes was awarded the Nobel prize in 1913. The understanding of superconductivity grew throughout the 20th century, with two major milestones being the discovery of the Meißner-Ochsenfeld effect in 1933 [2] and the development of the microscopic BCS theory in 1957 [3, 4].

Concerning the application of superconductors, cooling is a major obstacle. Until 1985, no superconductor with a transition temperature above 30 K had been found. The discovery of high-$T_c$ superconductivity one year later promptly changed the entire research field: Bednorz and Müller found superconductivity in the copper oxide LaBaCuO [5]. Within a few years, materials with transition temperatures up to 135 K were found [6].

The search for high-$T_c$ superconductivity was again boosted by a discovery of Kamihara et al. in 2008. The group found superconductivity in the iron pnictide LaO$_{1-x}$F$_x$FeAs, the first high-$T_c$ superconductor which contains iron [7]. Until now, several iron-based superconductors (FeSCs) have been discovered. They show relatively high transition temperatures, some with a $T_c$ above 50 K.

Cuprates and FeSCs are unconventional superconductors and of special interest not only due to their high transition temperatures. The pairing mechanism is still unknown. As opposed to conventional superconductors, the coupling of two electrons to a Cooper pair can not or not exclusively be mediated by phonons [8]. It is crucial to find the origin of the coupling mechanism in unconventional SCs. Maybe then,
one can design high-$T_c$-superconductors and reach the ultimate goal: finding a superconductor, that can be operated at room temperature.

Inelastic light (Raman) scattering experiments provide access to the electronic properties of solids and therefore allocate a powerful tool for probing the pairing mechanism [9]. The superconducting gap can be derived from the spectra as well as in-gap states, which can be interpreted as signs of competing pairing mechanisms or at least anisotropies in the pairing potential.

For this work, Raman scattering measurements have been performed on the superconducting iron arsenide CaKFe$_4$As$_4$. The family of the iron arsenides includes several superconducting compounds. One cannot yet be sure about their application potential, but the scientific relevance of the iron arsenides cannot be overestimated as they provide a laboratory for the understanding of the pairing mechanism in high-$T_c$ superconductors.

The basic properties of the iron arsenides are presented in chapter 2. Chapter 3 deals with the most essential properties of Raman scattering. In chapter 4, the experimental setup is described. The results of the measurements on CaKFe$_4$As$_4$ are presented and discussed in chapter 5.

An additional part of this work was the contribution to assembling a setup for tip-enhanced Raman spectroscopy. This advanced measurement technique and the current state of the setup will be presented in appendix A.
2 Iron-Based Superconductors

The iron-based superconductors (FeSCs) are of special interest because the pairing mechanism cannot be exclusively phonon-mediated [8]. CaKFe$_4$As$_4$, the material which has been investigated for this thesis, belongs to the family of the iron arsenides. The purpose of this chapter is to list the basic properties of this material class. The presented characteristics are essential for understanding the measurement results, which will be presented in chapter 5.

2.1 BaFe$_2$As$_2$ and CaFe$_2$As$_2$

The iron arsenides are built up in a layered structure. The tetragonal unit cell of BaFe$_2$As$_2$ is shown in figure 2.1. Stacked between the Ba-atoms (purple) are layers of Fe (red) and As (green) atoms. The FeAs layers are characterised by covalent Fe-As bonds (shared valence electrons) and metallic Fe-Fe bonds (delocalised electrons). The Ba$^{2+}$ ions form atomic bonds of more ionic character with the FeAs$^{-}$ layers (due to the polarity of the bond) [10]. In the figure, red bonds signify metallic bonds, the red-green bonds represent the covalent bonds.

As arsenic is in the same column as nitrogen in the periodic table, the iron arsenides belong to the iron pnictides. BaFe$_2$As$_2$ is referred to as a member of the so called 122-compounds due to the constitution of one barium and two iron as well as arsenic atoms in the crystallographic unit cell.
Figure 2.1: Crystal structure of BaFe$_2$As$_2$. Barium atoms are represented in purple, iron atoms in red and arsenic atoms in green. The layered structure is clearly visible. The Fe-Fe bonds are metallic (displayed in red) and Fe-As bonds are covalent (shown in red-green). The Ba$^{2+}$ ions form atomic bonds of more ionic character with the FeAs$^-$ layers. From [11].

At room temperature, the crystal possesses $D_{4h}$ symmetry and belongs to the point group $I4/mmm$. With all axes crossing the center of the unit cell, the cell is 90° rotational symmetric about the c-axis, and 180° rotational symmetric along the a-, b-, (a+b)- and (a-b)-axes. In addition, mirror planes perpendicular to all of these axes exist.

The conduction in the Fe planes is nearly two-dimensional. The out-of-plane dispersion along $k_z$ is smaller than in the plane, and the shared electrons can be treated in a quasi-2D layer [12]. In figure 2.2 (a), the 1-Fe unit cell (solid lines) and the 2-Fe cell (by including the outer As atoms) are introduced. The 1-Fe unit cell can be defined along the axes $\tilde{a}$ and $\tilde{b}$, which are rotated by 45° with respect to the axes $a$ and $b$ of the crystal unit cell.
2.1 $\text{BaFe}_2\text{As}_2$ and $\text{CaFe}_2\text{As}_2$

Figure 2.2: The 1-Fe and 2-Fe cells. (a) The iron atoms (red) form a quasi-2D layer with the arsenic atoms (green). This layer dominates the electronic properties of the FeSCs. The 1-Fe unit cell is indicated by solid lines, the 2-Fe unit cell includes the outer As atoms. (b) 1-Fe 2D Brillouin zone (solid lines). Two hole pockets are centered at the $\Gamma$-point, electron pockets are found around the X- and Y-points. The green arrow indicates the folding vector $(\pi, \pi)$. (c) The 'folded' Brillouin zone for the 2-Fe unit cell (dashed line) with the 1-Fe BZ (solid lines). The electron bands at the X- and Y-points overlap, which can lead to hybridization. Taken from [11, 13].

Figure 2.2 (b) shows the 2D Brillouin zone (BZ) of the 1-Fe unit cell (solid lines). In addition, the Fermi surfaces (FS) of the hole and the electron bands are shown. Two hole pockets (black) are centered around the $\Gamma$-point. Electron pockets can be found around the X- and Y-points (red and grey, respectively). The real space 2-Fe unit cell has twice the size of the 1-Fe unit cell, so the so-called 'folded' BZ of the 2-Fe unit cell (shown with dashed lines in figure 2.2 (c)) has half the size of the 1-Fe BZ. The corresponding folding vector $(\pi, \pi)$ is depicted as the dashed green arrow in figure 2.2 (b). Due to the folding, the FS-cuts of the electron bands at the X- and Y-points overlap, as indicated in red and grey. This causes hybridisation of these pockets, resulting in a strong curvature of the FS. In the Raman response, these regions are strongly highlighted and therefore need to be taken into account in the interpretation of the spectra [14].

$\text{BaFe}_2\text{As}_2$ undergoes a phase transition into the so called spin-density-wave (SDW) phase at a transition temperature $T_{SDW} \approx 135$ K [15]. The material experiences a structural change from a tetragonal to an orthorhombic unit cell. In addition, a magnetic transition takes place, which involves a change from a paramagnetic spin state to an antiferromagnetic ordering along the $\tilde{a}$-direction of the 1-Fe unit cell and a ferromagnetic ordering perpendicular to it along $\tilde{b}$.

As the atoms occupy the Wyckoff positions 2a (Ba), 4d (Fe) and 4e (As) in the
point group $I4/mmm$ [16], the material shows four Raman-active phonon modes, one $A_{1g}$ phonon, one $B_{1g}$ phonon and two $E_g$ phonons (cf. Table 2.1) [17]. In $A_{1g}$ and $B_{1g}$ symmetry, the atoms oscillate along the $c$-axis, they are so-called out-of-plane phonons. At $E_g$ phonons, the Fe and As atoms oscillate in the respective plane.

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>$A_{1g}$</th>
<th>$A_{2g}$</th>
<th>$B_{1g}$</th>
<th>$B_{2g}$</th>
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</table>

Table 2.1: Raman-active phonons in BaFe$_2$As$_2$. The atoms occupy the Wyckoff positions 2a (Ba), 4d (Fe) and 4e (As) in the point group $I4/mmm$ [16]. In total, four phonon modes are Raman-active, one in $A_{1g}$ symmetry, one in $B_{1g}$ symmetry and two $E_g$ phonons [17].

In figure 2.3, the phonons are displayed. Here, Barium atoms are represented in green, iron atoms in red and arsenic atoms in grey. The small black arrows indicate the displacement directions of the atoms.

Calcium and barium both belong to the earth alkali metals. Not surprisingly, BaFe$_2$As$_2$ and CaFe$_2$As$_2$ share a lot of properties. For CaFe$_2$As$_2$, the structural and
magnetical transition occurs at $T_{SDW} \approx 173$ K, so approximately 40 K above the transition temperature of BaFe$_2$As$_2$ [19]. The Raman active phonons in CaFe$_2$As$_2$ are in analogy to figure 2.3 as well [20].

Though BaFe$_2$As$_2$ and CaFe$_2$As$_2$ are metallic, they do not show superconductivity. The transition to a superconducting state is achieved in the doped compounds, which will be introduced in the following section.

2.2 $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$

Substitution of barium with potassium atoms in the material $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ yields a superconducting phase for substitution concentrations $0.16 < x \leq 1$. The substitution is called hole doping, as the K atom with configuration [Ar]4s$^1$ delivers one electron less (and therefore one hole more) than the Ba atom (configuration [Xe]6s$^2$). Figure 2.4 shows the $x$-$T$ phase diagram of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. The dome shaped superconducting phase with a maximum critical temperature of $T_c \approx 39$ K at optimal doping level in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ is indicated in blue. The phase stretches up to fully doped KFe$_2$As$_2$ at $x = 1$, for which $T_c \approx 3$ K [21].
Figure 2.4: Phase diagram for Ba$_{1-x}$K$_x$Fe$_2$As$_2$. At zero doping (BaFe$_2$As$_2$), no superconducting phase is present. Yet, the material undergoes a structural and magnetical transition at $T_{\text{SDW}} \approx 135$ K. Above this transition, it has a tetragonal structure and is paramagnetic. Below $T_{\text{SDW}}$, the spin-density-wave (SDW) phase is present. The crystal structure becomes orthorhombic and the spins are ordered ferromagnetically along the $\tilde{b}$ direction, while following an antiferromagnetic pattern perpendicular to it along $\tilde{a}$. With increasing doping, $T_{\text{SDW}}$ decreases. Simultaneously, a superconducting phase emerges with a maximum transition temperature of $T_c \approx 39$ K for optimally doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. Superconductivity does not disappear for heavy doping and remains for KFe$_2$As$_2$ at $x = 1$. The green area indicates the existence of fluctuations near to $T_{\text{SDW}}$. Taken from [22].

As visualised in the phase diagram, the structural and magnetic transition to the SDW phase is present in the doped compound as well. With increasing doping, $T_{\text{SDW}}$ is decreasing until the phase disappears for higher doping levels [23]. Close to the SDW phase, fluctuations are present (indicated in green) [24].

Due to their proximity, the superconducting phase is supposed to be in close relation of the antiferromagnetic SDW phase. At zero doping, the FSs of hole and electron bands can well be mapped onto each other by the nesting vectors $(\pm \pi, 0)$ and $(0, \pm \pi)$. With increasing hole doping, the electron bands at the X- and Y-points shrink while
the hole bands at the $\Gamma$-point expand, so the nesting gets worse. Therefore, the antiferromagnetic SDW phase becomes less stable \[25\]. Simultaneously, superconductivity emerges. Consequently, pairing via the exchange of spin fluctuations was proposed in 2008 \[26\]. In $\text{KFe}_2\text{As}_2$, the pockets around the corners of the BZ totally vanish due to hole doping \[27\].

Besides doping, antiferromagnetic ordering can also be suppressed by applying pressure. As a result, $\text{BaFe}_2\text{As}_2$ as well as $\text{CaFe}_2\text{As}_2$ show a superconducting phase under pressure, which disappears again at high pressures \[28, 29\]. This observation supports a strong correlation between structural, magnetic and electronic degrees of freedom. This supports the assumption of spin fluctuations being the mediator for the formation of Cooper pairs.

For completeness it should be noted that the iron arsenides can be electron doped as well. In $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$, Fe atoms are substituted with Co atoms. Similarly as in the hole doped compound $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, a superconducting phase arises as the SDW phase vanishes. Superconductivity collapses for heavy doping though. In addition, a nematic phase lies on top of the SDW phase, as the structural and the magnetic transitions are decoupled. Cobalt has $[\text{Ar}]3d^74s^2$ configuration, the configuration of Fe is $[\text{Ar}]3d^64s^2$. However, it remains unsettled if the substitution really adds an electron to the FeAs plane or if superconductivity emerges due to impurity scattering \[30\]. In the next paragraph it will be shown that $\text{CaKFe}_4\text{As}_4$ is similar to optimally doped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. Therefore, this thesis focusses on the hole doped compounds.

### 2.3 $\text{CaKFe}_4\text{As}_4$

$\text{CaKFe}_4\text{As}_4$ is a FeSC and has been discovered just recently in 2016 \[31\]. In contrast to the materials presented above, $\text{CaKFe}_4\text{As}_4$ belongs to the 1144-FeSCs. The crystallographic unit cell is very similar to the one of the 122-compounds. By alternatively stacking potassium and calcium atoms, the point group changes from $I4/mmm$ in the 122 compounds to $P4/mmm$ in $\text{CaKFe}_4\text{As}_4$. The $D_{4d}$ symmetry remains untouched. This also gives rise to the most important difference to the doped compounds: in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, the hole doping leads to a random substi-
tution of Ba atoms [32], while CaKFe$_4$As$_4$ is a stoichiometric compound. The unit cell of CaKFe$_4$As$_4$ can be seen in figure 2.5 (a). The 1-Fe (dashed lines) as well as the 2-Fe unit cells are again depicted in figure 2.5 (b).

Above the transition to the superconducting phase, no other phase transitions have been reported on CaKFe$_4$As$_4$. In particular, no structural or magnetic transition could be observed as opposed to the undoped BaFe$_2$As$_2$ and CaFe$_2$As$_2$ and the underdoped Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [33].

Despite the difference in the crystal structure, CaKFe$_4$As$_4$ shows several similarities to other FeSCs, especially the optimally doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. Most importantly, essential similarities in the band structure can be seen, as ARPES data suggest [34]. The 2D-BZ of CaKFe$_4$As$_4$ is shown in figure 2.5 (c). Three hole pockets at the Γ-point and at least one electron pocket at the X-point can be observed. Those pockets lead to a full superconducting gap with a corresponding $T_c = (35.0 \pm 0.2)$ K. This transition temperature has been observed in thermodynamic and transport
measurements, which have been performed by W. R. Meier et al. [33]. These measurements also show a decrease of $T_c$ under pressure.

In CaKFe$_4$As$_4$, the atoms occupy the Wyckoff positions 1a (Ca), 1d (K), 2g & 2h (As) and 4i (Fe) in the point group $P4/mmm$ [34]. Consequently, the material has eight Raman-active phonon modes. Table 2.2 shows the respective phonon symmetries [17]:

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>$A_{1g}$</th>
<th>$A_{2g}$</th>
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</tr>
<tr>
<td>4i</td>
<td>1</td>
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<td>2</td>
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</tbody>
</table>

Table 2.2: Raman-active phonons in CaKFe$_4$As$_4$. The atoms occupy the Wyckoff positions 1a (Ca), 1d (K), 2g & 2h (As) and 4i (Fe) in the point group $P4/mmm$ [34]. In total, eight phonon modes are Raman-active, three in $A_{1g}$ symmetry, one in $B_{1g}$ symmetry and four $E_g$ phonons [17].

The displacement directions of the atoms for each phonon are shown in Figure 2.6. The primitive cell of CaKFe$_4$As$_4$ has twice the size of the unit cell of BaFe$_2$As$_2$. A base vector to project the BaFe$_2$As$_2$ unit cell onto itself is ($\frac{1}{2}a$, $\frac{1}{2}b$, $\frac{1}{2}c$). For CaKFe$_4$As$_4$, it is (a,b,c). Atoms that are projected onto each other by the base vectors need to oscillate in phase. Therefore, twice as many Raman-active phonon modes than in BaFe$_2$As$_2$ exist in CaKFe$_4$As$_4$. 

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As the electronic properties of the iron arsenides are dominated by the 1-Fe unit cell, which is rotated by 45° with respect to the crystallographic unit cell, the phonon symmetries will be denoted with \( A_{1g, \text{cryst}} \), \( A_{2g, \text{cryst}} \), \( B_{1g, \text{cryst}} \) and \( B_{2g, \text{cryst}} \) from here. This differentiation becomes essential at the introduction of the Raman selection rules in section 3.3.

### 2.4 The Pairing Mechanism

The conventional electron-phonon coupling does not provide enough condensation energy in order to reach the high transition temperatures in the cuprates and the FeSCs [8]. Therefore, additional mechanisms must be present. Starting with a short overview on conventional superconductivity, it is the purpose of this section to introduce electronic and magnetic pairing mechanisms. An insight into experimental
2.4 The Pairing Mechanism

results and possible pairing mechanisms in specific iron arsenides will be addressed.

According to the BCS-Theory, superconductivity occurs due to a condensation of bound electrons (Cooper pairs) into a boson-like ground state. Therefore, an attractive interaction between two electrons is needed, which is mediated by an exchange boson. For conventional superconductors, lattice vibrations (phonons) play this role.

The electronic energy that is gained due to the formation of a Cooper pair from two electrons with momentum \((k, -k)\) is denoted with \(\Delta_k(T)\). Consequently, the energy that is needed for the breaking of a Cooper pair is \(2\Delta(T)\). The condensation energy is given by the BCS-gap equation:

\[
\Delta_k(T) = -\sum_{k'} V_{k,k'} \Delta_{k'} \frac{\tanh(E_{k'}/k_B T)}{2E_{k'}} ,
\]

with the interaction potential \(V_{k,k'}\) [6].

The pair-condensate can be described by a macroscopic wave function, which has the same symmetry as the gap and which can be associated with the Ginzburg-Landau order parameter of the superconductor. As the Cooper pair is formed by two electrons, the wave function needs to be fermionic, meaning it needs to be antisymmetric overall. It can be divided into a spin- and a spatial part. An antisymmetric spin part \((S = 0\), spin singlet state\) thus requires a symmetric orbital part \((L = 0, 2, ...\)), while a symmetric spin part \((S = 1\), spin triplet state\) entails an antisymmetric spatial part \((L = 1, 3, ...\)). The overall pairing states then are called \((s-, d-, g-, ...\)) and \((p-, f-, h-, ...\)) wave states [13].

The BCS-gap equation (cf. equation 2.1) can be solved analytically only for an isotropic gap. Then, the interaction potential simplifies to

\[
V_{k,k'} = \begin{cases} 
-V_0, & \xi_k \leq \omega_0 \\
0, & \text{else} 
\end{cases},
\]

with the quasiparticle energy \(\xi_k\) and \(\omega_0\) being a cutoff of the order of the Debye frequency. Therefore, conventional superconductors necessarily need to have \(s\)-wave
In principle, other pairing channels are possible as the gap can be anisotropic. They also can be present subdominantly, when they do not provide as much condensation energy as the dominant pairing mechanism. Some possible pairing channels for the FeSCs shall be presented in the following.

Knight shift measurements in the FeSCs suggest that no triplet pairing is present in those materials [35]. Therefore, the pairing must have singlet character. Figure 2.7 shows the different order parameter symmetries for the most prominent pairing channels in the FeSCs. Different colours indicate the different signs of the gap.

One distinguishes between conventional $s^{++}$ and the so-called extended $s$-wave character ($s_{\pm}$). $s^{++}$ may be a result of pairing mediated by orbital fluctuations, e.g. by a fluctuating occupation of the $d_{xz}$ and $d_{yz}$ orbitals. $s_{\pm}$ on the other
2.4 The Pairing Mechanism

hand represents a pairing via magnetic interactions (spin fluctuations), which, owing to their repulsive nature, require a sign change in the order parameter. In addition, the gap can have nodes. For example, the nodal $s_\pm$ state in the picture has nodes on the electron pockets. Therefore, the gap vanishes at certain points of these pockets. Still, the average sign of the order parameter on the electron pockets is different from the sign of the hole pockets. The three mentioned pairing channels have the same symmetry ($s$-wave), but differ in structure. All of them are symmetric under $90^\circ$ rotation ($A_{1g}$), but the pairing mechanism is different. A $d$-wave channel with $180^\circ$ rotational symmetry ($B_{1g}$) is also conceivable, as illustrated in the figure.

The gap structure is not necessarily dictated by a single pairing mechanism. Though a dominating interaction must be present, subdominant channels can compete with the ground state. In most superconductors, subdominant channels are believed to be either not present at all or at least much weaker than the ground state. Some materials on the other hand are decisively influenced by a strong subdominant pairing mechanism.

One indicator for a subdominant pairing channel, that can be observed in Raman spectra, is the Bardasis-Schrieffer mode. It is a collective, bosonic mode in the superconducting state [36], and results from the formation of two electrons from a broken Cooper pair into a bound state inside the gap. This in-gap state exists due to the influence of the subdominant channel and results from the anisotropies in the pairing potential $V_{k,k'}$. The importance of Bardasis-Schrieffer modes is explicitly addressed in the PhD thesis by Thomas Böhm [22].

Due to the proximity to a magnetically ordered phase (SDW phase), superconductivity mediated by spin fluctuations seems to be a viable way for the iron arsenides. For multiband superconductors, the gap is probably nodeless but changes sign. This is expected also for CaKFe$_4$As$_4$, the material that will be further studied in this thesis. Muon spin relaxation studies [37] as well as IR spectroscopy experiments [38] suggest the $s_\pm$ symmetry of the order parameter. Yet, even small variations in the electronic structure can lead to qualitatively different structures of the gap. For example, besides the dominant $s$-wave pairing, subdominant $d$-wave channels were discovered in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [24]. Two Bardasis-Schrieffer modes appear in the Raman spectra. Raman spectroscopy experiments on Ba(Fe$_{1-y}$Co$_y$)$_2$As$_2$ show evidence of nodal gaps [18], while other studies suspect more or less isotropic gaps in that material [39]. Single band superconductors like KFe$_2$As$_2$ on the other hand definitely need a nodal
character of the gap under the assumption of pairing mediated by spin fluctuations. In addition, KFe$_2$As$_2$ is believed to be a $d$-wave superconductor [40, 41].

In order to understand the pairing mechanism of the FeSCs, Raman spectroscopy experiments can be performed. One of the most powerful assets of this experimental method in this context is the ability to gather evidence on dominant as well as subdominant pairing channels. The full gaps as well as bound states inside the gaps can be accessed. Particularly, Bardasis-Schrieffer modes are visible in the spectra, as the formation or destruction of a bound state inside the gap will result in a prominent peak. For this thesis, Raman measurements have been performed on CaKFe$_4$As$_4$. The spectroscopy method will be explained in the subsequent chapter 3 and the results are presented in chapter 5.
3 Raman Scattering

The purpose of this chapter is to give a short introduction to the basic principles of inelastic light (Raman) scattering, as they are essential for understanding the experimental results that are presented in this thesis. More details can be found in the article by T. P. Deveraux and R. Hackl [9].

3.1 Basics of Raman Scattering

Raman scattering is named after Chandrasekhara V. Raman, who experimentally detected the effect in the year 1928, after the theoretical prediction by Adolf Smekal in 1923 [42]. Together with K. S. Krishnan, Raman performed inelastic light scattering measurements on organic liquids [43]. Although G. Landsberg and L. I. Mandelstam discovered Raman scattering simultaneously in 1928 [44], Raman was exclusively awarded the nobel prize in the year 1930.

The Raman process can be described as follows: An electron in the target material is situated in an initial state \( |i\rangle \). An incoming photon, which is characterised by its momentum, energy and polarisation \( (k_i, \omega_i, e_i) \), generates an excitation to an intermediate (virtual) state \( |v\rangle \). The lifetime of this virtual state is shorter than the limit given by Heisenberg’s uncertainty relation. From this state, the electron relaxes into a final state \( |f\rangle \) and the scattered photon \( (k_s, \omega_s, e_s) \) is emitted.
As usual, energy and momentum are conserved quantities. Thus:

\[
\hbar \Omega = \hbar \omega_i - \hbar \omega_s \tag{3.1}
\]

\[
\hbar \mathbf{q} = \hbar \mathbf{k}_i - \hbar \mathbf{k}_s \tag{3.2}
\]

\(\Omega\) denotes the Raman shift, which describes the difference in energy between \(|i\rangle\) and \(|f\rangle\), while \(\mathbf{q}\) is the change in momentum.

\(|f\rangle\) can be higher or lower in energy than \(|i\rangle\). One distinguishes between the Stokes and Anti-Stokes process. In the Stokes process, an excitation is created, while it is destroyed in the Anti-Stokes process. Both effects are depicted in figure 3.1. In solid state systems, there are several Raman-active excitations. Besides the generation of electron-hole pairs, there are for example phonons or magnons.

\[\text{Figure 3.1: Stokes (a) and Anti-Stokes (b) process. A system transitions from an initial state } |i\rangle \text{ via a virtual state } |v\rangle \text{ into a higher (Stokes) or lower (Anti-Stokes) final state } |f\rangle. \text{ Energy and momentum are conserved. The incoming photon is characterised by } (\mathbf{k}_i, \omega_i), \text{ the scattered photon by } (\mathbf{k}_s, \omega_s). \text{ The transferred momentum is described by } \mathbf{q}, \text{ the change in energy by the Raman shift } \Omega. \text{ From [45].}\]

Figure 3.2 shows a typical Raman spectrum. The electronic continuum (the creation of electron-hole pairs) is shown in red. Phonons are visible as the sharp blue peaks on top of the electronic continuum. The large yellow peak in the middle visualises the elastically scattered photons (laser line, \(\Omega \approx 0\)). The number of photons scattered in the Anti-Stokes process decreases exponentially with lower temperatures.
3.2 Theory of Electronic Raman Scattering

with respect to the scattering rate in the Stokes process. Since most electrons in a system are scattered elastically, and only one out of $10^{13}$ photons does not relax back into the initial state $|i\rangle$ but into another state $|f\rangle$, the Raman intensity is low.

![Figure 3.2: Scheme of a typical Raman spectrum. The number of detected photons per unit time is plotted against the Raman shift $\Omega$. The contributions from electron-hole pairs are depicted in red, phonons are shown in blue. The yellow laser line at $\Omega \approx 0$ shows the elastically scattered photons. For a narrow laser, its width is limited by the resolution of the spectrometer. The intensity of Anti-Stokes processes ($\Omega < 0$) decays exponentially at lower temperatures with respect to the intensity of the Stokes processes ($\Omega > 0$). Taken from [46].](image)

3.2 Theory of Electronic Raman Scattering

In the experiment, the scattered photons are collected by a detector. A detailed description of the experimental setup can be found in chapter 4. As visualised in figure 3.2, a typical Raman spectrum shows the rate of scattered photons $\dot{N}$ plotted against the Raman shift $\Omega$.

In this section, it will be shown theoretically, that, in order to interpret and compare the measurement results, it is essential to find a correlation between $\dot{N}$ and the Raman response function $\chi(q, \Omega)$. As a consequence of the relations presented in this section, all Raman measurements displayed in this work will show the imaginary part $\chi''$ of the Raman response function ($\chi = \chi' + i\chi''$) as a function of the Raman shift. One needs to distinguish between Raman scattering from electronic excitations, phonons and magnons. The relations in this section describe the effect of electronic Raman scattering.
In Raman scattering experiments, the photons that are scattered into a certain solid angle $\tilde{\Omega}$ and which are in a certain frequency interval $[\omega_s, \omega_s + d\omega_s]$ are counted. Therefore, the scattering rate is proportional to the differential scattering cross section:

$$\tilde{N}(\omega, T) \propto \frac{\partial^2 \sigma}{\partial \Omega \partial \omega_s} = \hbar r_0^2 \frac{\omega_s}{\omega_i} \mathcal{R}$$  \hspace{1cm} (3.3)

$\mathcal{R}$ denotes the transition rate from an initial state $|i\rangle$ to a final state $|f\rangle$ and $r_0 = e^2/4\pi\epsilon_0 mc^2$ is the Thomson (classical electron) radius.

$\mathcal{R}$ is given by Fermi’s Golden Rule:

$$\mathcal{R} = \frac{1}{Z} \sum_{i,f} e^{-\beta E_i} |\mathcal{M}_{f,i}|^2 \delta(E_f - E_i - \hbar \Omega)$$  \hspace{1cm} (3.4)

Here, $Z$ is the partition function, $\beta = 1/k_B T$, and we use the matrix element $\mathcal{M}_{f,i} = \langle f | \hat{\mathcal{M}} | i \rangle$ with the perturbation operator $\hat{\mathcal{M}}$, which describes the scattering process. $E_i$ and $E_f$ represent the energy levels of $|i\rangle$ and $|f\rangle$.

$|i\rangle$ and $|f\rangle$ describe states of a many electron system. The transition from $|i\rangle$ to $|f\rangle$ due to the interaction with light is described by an interaction Hamiltonian $\hat{\mathcal{H}}_{\text{int}}$, which enables us to find an expression for the matrix elements $\mathcal{M}_{f,i}$.

The Hamiltonian for $N$ electrons coupled to electromagnetic fields reads [47, 48]:

$$\hat{\mathcal{H}}_e = \hat{\mathcal{H}}_{\text{Coulomb}} + \hat{\mathcal{H}}_{\text{fields}} + \sum_i \left[ \hat{p}_i + e \hat{\mathbf{A}}(\mathbf{r}_i) \right]^2 / 2m,$$  \hspace{1cm} (3.5)

with the momentum operator $\hat{p} = -i\hbar \nabla$ and the vector potential $\hat{\mathbf{A}}(\mathbf{r}_i)$. The Coulomb interaction is represented by $\hat{\mathcal{H}}_{\text{Coulomb}}$ and the free electromagnetic field is incorporated with $\hat{\mathcal{H}}_{\text{fields}}$.

$^1\tilde{\Omega}$ denotes the solid angle, and should not be confused with the Raman Shift $\Omega$. 

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By following several steps from here, which are described in detail in [9, p. 8-13], the matrix elements $M_{fi}$ can be found and equation 3.4 is simplified to a correlation function $\tilde{S}(q,i\Omega)$, that reads:

$$\tilde{S}(q,i\Omega) = \sum_i \frac{e^{-\beta E_i}}{Z} \int d\tau e^{i\Omega \tau} \langle i|T_\tau \tilde{\rho}(q,\tau)\tilde{\rho}(-q,0)|i\rangle \ ,$$

(3.6)

with the time ordering operator $T_\tau$ with respect to the complex time $\tau$. The effective density operator $\tilde{\rho}(q)$ can be expressed by:

$$\tilde{\rho}(q) = \sum_{k,\sigma} \gamma(k,q)c_{k+q,\sigma}^\dagger c_{k,\sigma} \ ,$$

(3.7)

using the creation operator $c_{k+q,\sigma}^\dagger$, which creates an electron with momentum $k+q$ and spin $\sigma$. The annihilation operator $c_{k,\sigma}$ destroys an electron with momentum $k$ and spin $\sigma$. Therefore, a scattering process is described. The scattering amplitude $\gamma$ will be discussed in detail in section 3.3.

Via the fluctuation-dissipation theorem, the correlation function can be written as:

$$\tilde{S}(q,i\Omega) = -\frac{1}{\pi}[1 + n(\Omega,T)] \cdot \chi''(q,\Omega) \ ,$$

(3.8)

in terms of the imaginary part of the Raman response function $\chi$, with $n(\Omega,T)$ being the Bose-Einstein distribution.

It was pointed out above, that $R \propto \tilde{S}(q,i\Omega)$, so equation 3.3 results in

$$R \cdot \chi''(q,\Omega) = \frac{\dot{N}(\Omega,T)}{[1 + n(\Omega,T)]} \ .$$

(3.9)

Here, a correlation between $\dot{N}$ and $\chi$ was found, as aimed for in this section. $R$ denotes a scale factor.

For completeness it should be noted, that in the case of Raman scattering from phonons, the Hamiltonian $\hat{H}_e$ for electronic Raman scattering from equation 3.5
needs to be extended by two terms: a phonon term $\hat{H}_p$ and an electron-phonon interaction term $\hat{H}_{ep}$. This yields:

$$\hat{H} = \hat{H}_e + \hat{H}_p + \hat{H}_{ep}.$$ (3.10)

The appearance of phonon modes in Raman spectra will not be conducted mathematically here, but will be grounded on a more vivid picture in the subsequent section. For a mathematical description, refer to the review by M. V. Klein [49]. Raman scattering from magnons will not be treated as it is not necessary for understanding the results that are presented in this thesis.

### 3.3 Symmetry and Selection Rules

As already mentioned in section 3.1, photons are not only characterised by their momentum and energy $(k, \omega)$, but also by their polarisation $e$. One of the most powerful assets of Raman scattering are the selection rules. The excitations that are projected out in the measurements can be selected by their symmetry.

The symmetry of the excitation $\Gamma_x$ is that of the operator, that projects the initial state $|i\rangle$ with symmetry $\Gamma_i$ onto the final state $|f\rangle$ with symmetry $\Gamma_s$. It follows [50]:

$$\Gamma_x = \Gamma_s \times \Gamma^* \Gamma_i$$ (3.11)

$\Gamma_i$ and $\Gamma_s$ are hereby represented by the polarisation vectors $e_i$ and $e_s$. All scattering processes that do not fulfill the condition in equation 3.11 are forbidden processes.

In the case of electronic Raman scattering, the scattering amplitude $\gamma$ is determined from the Raman matrix elements $\gamma_{\alpha,\beta}$ and the polarisation vectors of the incoming as well as the scattered light:

$$\gamma(k, q) = \sum_{\alpha,\beta} e_\alpha^i \gamma_{\alpha,\beta}(k, q) e_\beta^s$$ (3.12)

Equation 3.12 can be rewritten with $q \to 0$ and the effective mass approximation [47, 51]:

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3.3 Symmetry and Selection Rules

\[ \gamma_{\alpha\beta}(k, q \to 0) \approx \frac{1}{\hbar^2} \frac{\partial^2 \epsilon_k}{\partial k_\alpha \partial k_\beta} = \frac{1}{m_{\text{eff}}} \] , \hspace{1cm} (3.13)

with \( \epsilon_k \) being the energy dispersion.

The scattering amplitude, also called Raman vertex, yields:

\[ \gamma(k) \approx e_s^* m_{\text{eff}}^{-1} e_i \] \hspace{1cm} (3.14)

The matrix elements \( M_{fi} \) can be decomposed. The charge density fluctuations during the scattering process are modulated in dependence on the polarisation directions \( e_i \) and \( e_s \). Therefore, they are connected with the irreproducible point group representations \( \mu \) of the crystal:

\[ M_{fi}(q \to 0) = \sum_\mu M_\mu \Phi_\mu \] \hspace{1cm} (3.15)

\( \Phi_\mu \) are the basis functions of the irreproducible point groups.

The decomposition of 3.15 for the \( D_{4h} \) point group (which is common for iron based superconductors) reads:

\[ M_{fi} = \frac{1}{2} \hat{O}_{A_{1g}}^{(1)} (e_x^i e_x^s + e_y^i e_y^s) + \frac{1}{2} \hat{O}_{A_{2g}}^{(2)} (e_x^i e_x^s) \]
\[ + \frac{1}{2} \hat{O}_{B_{1g}} (e_x^i e_y^s - e_y^i e_x^s) + \frac{1}{2} \hat{O}_{B_{2g}} (e_y^i e_y^s - e_x^i e_x^s) \]
\[ + \frac{1}{2} \hat{O}_{A_{2g}} (e_x^i e_y^s - e_y^i e_x^s) + \frac{1}{2} \hat{O}_{E_g}^{(1)} (e_x^i e_x^s + e_y^i e_y^s) \]
\[ + \frac{1}{2} \hat{O}_{E_g}^{(2)} (e_y^i e_y^s + e_x^i e_x^s) \] \hspace{1cm} (3.16)

\( \hat{O}_\mu \) are the projection operators.

Figure 3.3 shows the Raman vertices (top row) and their squares (bottom row) depending on the symmetry operation for \( D_{4h} \) crystals, like the iron based superconductors (cf. chapter 2). The dashed lines represent the nodes of \( \gamma_\mu \). As can be seen, only certain parts of the Brillouin-zone (BZ) are projected. \( B_{1g} \) projects the X- and Y-points. \( B_{2g} \) resolves the centers of each quadrant in the 2D-BZ.
$A_{1g}$ symmetry needs to be addressed carefully. Principally, the center ($\Gamma$-point) and the corners ($M$-Point) of the BZ are highlighted. Due to Coulomb screening, negative and positive regions of $\gamma(k)$ do not necessarily add up equally [52]. $A_{1g}$ is the only symmetry that is influenced by this screening, as the Coulomb interaction can only couple to the totally symmetric Raman vertex. $A_{2g}$ symmetry is not shown, as it can often be neglected due to a lack of accessible excitations [53].

![Diagram showing Raman vertices and their squares for different symmetries](image)

Figure 3.3: Raman vertices (top row) and their squares (bottom row) in $A_{1g}$, $B_{1g}$ and $B_{2g}$ symmetry for $D_{4h}$ crystals. The dashed lines represent a vanishing scattering amplitude $\gamma_{\mu}$. Different parts of the Brillouin zone are projected for each symmetry. In $B_{1g}$, the X- and Y-points are projected. $B_{2g}$ symmetry resolves the centers of each quadrant in the 2D-BZ. $A_{1g}$ symmetry highlights the $\Gamma$-point and the corners of the Brillouin-zone, but needs to be addressed carefully due to Coulomb screening. The $A_{2g}$ vertex is not shown, as contributions in this symmetry can often be neglected due to a depletion of excitations. From [18].

Scattering from other excitations, like phonons, also needs to obey the condition in equation 3.11. For each phonon, a symmetry-dependent Raman Tensor $\overrightarrow{R}$ can be assigned. The scattering intensity then follows [54]:

$$I \propto |\mathbf{e}_i \cdot \overrightarrow{R} \cdot \mathbf{e}_s|^2$$  \hspace{1cm} (3.17)

The common polarisation vectors $\mathbf{e}_i$ and $\mathbf{e}_s$ are shown in table 3.1. In the following,
the selected polarisations will be denoted as $xx$, $xy$, $RL$ etc., with the first letter representing $e_i$ and the second letter representing $e_s$. $R$ and $L$ thereby represent circularly polarised light, whereas the others denote linearly polarised light, with $x$ and $y$ orientated along the axes $\hat{a}$ and $\hat{b}$ of the 1-Fe unit cell, which dominates the electronic properties in the iron arsenides (cf. section 2.1), while $x'$ and $y'$ are rotated by 45 degrees.

$$
\begin{pmatrix}
1 \\
0 \\
0 \\
1
\end{pmatrix}
\quad
\begin{pmatrix}
0 \\
1 \\
\frac{1}{\sqrt{2}} \\
\frac{1}{\sqrt{2}}
\end{pmatrix}
\quad
\begin{pmatrix}
x' \\
y'
\end{pmatrix}
\quad
\begin{pmatrix}
1 \\
-1 \\
1 \\
i
\end{pmatrix}
\quad
\begin{pmatrix}
R \\
L
\end{pmatrix}
$$

Table 3.1: Normalised polarisation vectors. The configuration in the experiment is denoted by $xx$, $xy$ etc., with the first letter referring to $e_i$ and the second to $e_s$.

The polarisation configurations as well as the projected symmetries (which can be found directly from equation 3.16) are shown in figure 3.4. The red circles represent the Fe-atoms in the iron based superconductors, with the solid and dashed lines visualizing the 1-Fe and 2-Fe unit cell (cf. chapter 2), respectively. It should be noted, that the symmetries do not correspond to the symmetries with respect to the crystallographic unit cell, as the 1-Fe unit cell is rotated by 45°. Therefore, $B_{1g, \text{cryst}}$ corresponds to $B_{2g}$ and $B_{2g, \text{cryst}}$ corresponds to $B_{1g}$ in the Raman spectra.

Figure 3.4: Polarisation configurations for the experiment and the correlated symmetry contributions. The red circles represent the Fe-atoms in the iron based superconductors. The solid and dashed lines visualise the 1-Fe and 2-Fe unit cell, respectively. Each measurement extracts contributions from two symmetries. Due to a lack of accessible excitations in $A_{2g}$-symmetry, the independent contributions from the other symmetries often can be found directly by performing only one experiment in the respective polarisation configuration. Taken from [18].
As can be seen, each polarisation configuration leads to a combination of contributions from two symmetries. The independent contributions from each symmetry can be extracted by performing experiments in multiple polarisation configurations:

\[
\begin{align*}
I_{A_{1g}} &= (1/3)[(xx + x'x' + RR) - (1/2)(xy + x'y' + RL)] \\
I_{A_{2g}} &= (1/3)[(xy + x'y' + RR) - (1/2)(xx + x'x' + RL)] \\
I_{B_{1g}} &= (1/3)[(xy + x'x' + RL) - (1/2)(xx + x'y' + RR)] \\
I_{B_{2g}} &= (1/3)[(xx + x'y' + RL) - (1/2)(xy + x'x' + RR)]
\end{align*}
\]

(3.18)

As mentioned above, in \(A_{2g}\)-symmetry, there often is a lack of excitations. Therefore, the calculations shown in formula 3.18 do not necessarily have to be performed, as the sole contributions for \(A_{1g}, B_{1g}\) and \(B_{2g}\) symmetry can be extracted by measuring in \(RR, x'y'\) and \(xy\) configuration, respectively.
4 Experimental Setup

In this chapter, all experimental setups as well as the used parameters will be presented. The setup of the 'Raman Lab 130' will be described in section 4.1. In section 4.2, the procedure for the $T_c$-measurement is explained.

4.1 Raman Spectroscopy

The Raman spectroscopy setup in the 'Raman Lab 130' is schematically depicted in figure 4.1. A yellow laser beam (577 nm) is generated by a solid state laser (Coherent, Genesis MXSLM).

In the scheme, lenses are numbered and abbreviated with the letter $L$, $M$ stands for mirror, $O$ for objective and $S$ for slit.

Two pin-hole systems (PH1 and PH2) are installed, which serve as beam expanders and improve the beam quality. A slit is positioned between two lenses in their shared focal point. As a result, the pin-hole system can only be passed by beams, that have been parallel before the first lens and will be parallel behind the second lens. The desired wavelength is filtered using a prism monochromator (PMC).

$L_8$ focusses the laser beam on the sample. Deflected by $M_4$, the laser beam hits the sample under an incident angle of $\alpha \approx 66^\circ$, with respect to the sample’s surface normal.

In section 3.3, the selection rules have been introduced. In order to pick $e_i$, a polariser (P) and a Soleil-Babinet compensator (SBC) are needed. The linear parts are chosen by P, the circular parts can be selected using the SBC. The compensator basically is a variable retarder - by moving a wedge, a continuous relative phase shift between the ordinary and the extraordinary beam can be introduced. A $\lambda/2$-plate in
front of the polariser is used to set the desired laser power, which can be measured with the help of a movable Powermeter (PM).

As the beam does not hit the sample surface perpendicularly, the laser power, which is absorbed by the sample, depends on the incident polarisations $e_i$. Most polarisations then have a perpendicular as well as a parallel component with respect to the sample surface. In order to match the parallel components, the index of refraction, the polarisation and the angle of incidence need to be taken into account when setting the power of the laser beam. Only then, a quantitative comparison between different polarisation configurations is possible.

Figure 4.1: Setup for Raman spectroscopy in the 'Raman Lab 130'. The sample is mounted inside the vacuum chamber of a cryostat. The beam generated by the solid state laser passes an optical system before hitting the sample surface. Two pin-hole systems (PH1 and PH2) are used to filter divergent fractions and therefore improve the beam quality before the scattering process. The incoming polarisation $e_i$ is set using a polariser (P) and a Soleil-Babinet compensator (SBC). Parts of the scattered light enter the spectrometer and are detected in the charge-coupled device (CCD). With the help of a $\lambda/4$-waveplate and an analyser (A), $e_s$ is selected. Taken from [22].

The scattered light is focussed onto the entrance slit of the spectrometer with objec-
4.2 $T_c$ - Measurement

Before performing Raman scattering measurements on a sample, it is crucial to measure its superconducting transition temperature $T_c$ due to two reasons. On the one hand, knowing $T_c$ is helpful for developing a measurement schedule. Some interesting measurement temperatures can often be determined in advance, as they lie around $T_c$. On the other hand, a $T_c$-measurement can be used to characterise the sample, e.g. concerning its homogeneity.

For the $T_c$-measurement of the samples, a contactless method is used. This is beneficial, as damaging the surface should be avoided, since light scattering measurements shall be performed later. A detailed description of the setup can be found in the doctoral thesis of Francesca Venturini [55], who installed this experimental setup.
The method is based on the measurement of the third harmonic $\chi_3$ of the \textit{ac}-susceptibility when applying a sinusoidal magnetic field $H_{ac}\sin\omega t$ to the sample. The induced magnetisation can be described as a sum of sinusoidal components which oscillate at harmonics of the driving frequency [56]:

$$M(t) = H_{ac} \sum_{n=1}^{\infty} [\chi'_n \sin(n \omega t) - \chi''_n \cos(n \omega t)], \quad (4.1)$$

with the Fourier coefficients $\chi_n = \chi'_n - i\chi''_n \ (n = 1, 2, 3, \ldots)$.

In the normal phase, above $T_c$, the response is linear, the third harmonic $\chi_3$ vanishes. In the superconducting phase, $|\chi_3|$ of a type-II superconductor is proportional to:

$$|\chi_3| \propto \delta(H^*) \theta(1 - \delta(H^*)) + \frac{\theta(\delta(H^*) - 1)}{\delta(H^*)} \sqrt{\frac{20}{\delta^2(H^*)} - \frac{44}{\delta(H^*)} + 25}, \quad (4.2)$$

with the Heavyside function $\theta(x)$ and $\delta(H^*)$, which measures the penetration depth of an external field into the material slab. At $H^*$, the slab is completely penetrated.

In the Bean model, the penetration depth is given as $\delta(H^*) = H_{ac}/H^*$ [57]. Equation 4.2 reduces to:

$$|\chi_3| \propto \begin{cases} 
\delta(H^*), & \text{if } H_{ac} < H^* \\
\frac{1}{\delta^2(H^*)} \sqrt{25\delta^2(H^*) - 44\delta(H^*) + 20}, & \text{if } H_{ac} > H^* 
\end{cases}, \quad (4.3)$$

In our measurements, we keep $H_{ac}$ below $H^*$. The Bean model also assumes a critical current $J_c$ in the superconducting phase, which is proportional to $H^*$. $J_c$ is given as [58]:

$$J_c = \left[1 - \left(\frac{T}{T_c}\right)^2\right] \left[1 - \left(\frac{T}{T_c}\right)^4\right]^{1/2} \quad (4.4)$$

Therefore, $|\chi_3|$ is only nonzero close to the phase transition. The value of $T_c$ can be found by investigating the peak when plotting $|\chi_3|^2$ against $T$. In the normal conducting phase, the third harmonic will be zero immediately, so the peak starts building up at $T_c$ when cooling respectively vanishes at $T_c$ when warming up the sample.
5 Superconductivity and Lattice Vibrations in Stoichiometric CaKFe$_4$As$_4$

This chapter comprises the results from Raman spectroscopy experiments on stoichiometric CaKFe$_4$As$_4$, which were measured and analysed during this thesis.

Section 5.1 shows the result from the $T_c$ determination. The recorded Raman data are depicted in section 5.2. Subsequently, a detailed analysis of the superconducting phase as well as of characteristic phonon modes will be performed in section 5.3. The consequences of the results will be discussed in section 5.4 and an outlook to possible future experiments, which are related to the measurements on CaKFe$_4$As$_4$, will be given.

5.1 Determination of $T_c$

The superconducting transition temperature $T_c$ was determined before performing Raman scattering experiments. Figure 5.1 shows $|\chi_3|^2$ in dependence on the temperature, with $\chi_3$ being the third harmonic of the magnetic susceptibility. The results during warmup and cooldown are displayed in red and blue, respectively.
\[ \chi_3 \] is only different from zero near \( T_c \). During cooldown, the increase of the third harmonic becomes visible just when reaching the transition temperature. When warming up, \( \chi_3 \) vanishes at \( T_c \). Therefore, \( T_c \) can be found by plotting a straight line to the right flank of both peaks. The warmup-peak shows a 'foot' on the right flank. It appears due to inhomogeneities in the sample. Due to regions with slightly different \( T_c \), the signal vanishes in a larger temperature range. Averaging the two values \( T_{c, \text{cooldown}} = 35.08 \) K and \( T_{c, \text{warmup}} = 35.24 \) K leads to the result \( T_c = 35.16 \) K, which is in good agreement with the result \( T_c = (35.0 \pm 0.2) \) K that was found by W. R. Meier in the group of P. Canfield [33].
5.2 Experimental Raman Scattering Results

Figure 5.2 (a) shows the A$_{1g}$ Raman spectra for the temperature range between $T = 6$ K and $T = 310$ K. For recording these spectra, the $RR$ polarisation configuration was selected. One assumes that this directly projects A$_{1g}$ symmetry due to a lack of excitations A$_{2g}$ symmetry (cf. section 3.3). This conjecture will be confirmed below. The polarisation vectors with respect to the 1-Fe unit cell are shown in figure 5.2 (b). Hereby, the polarisation vector of the incoming light is depicted in blue, the polarisation of the red-shifted scattered light is represented by the red arrow. As described in section 3.3, electronic Raman scattering in A$_{1g}$ symmetry principally projects the $\Gamma$-point and the corners of the Brillouin zone (M-point), but needs to be addressed carefully due to Coulomb screening. The $k_x$- and $k_y$-dependent scattering intensity $\gamma^2_{A_{1g}}$ is displayed in figure 5.2 (c). In addition, $E_g$ modes can be accessed, as the incident polarisation has a component which is perpendicular to the sample surface and A$_{1g}$ phonon modes are visible in the spectra.
5 Superconductivity and Lattice Vibrations in Stoichiometric CaKFe$_4$As$_4$

Figure 5.2: Raman spectra in $A_{1g}$-symmetry at temperatures as indicated. (a) Six phonon modes can be observed for almost all temperatures. At low temperatures, the edge of the laser line is superimposed on the spectra for small $\Omega$ due to the adsorption of residual gas molecules on the sample surface. (b) The $RR$ polarisation configuration was chosen. Due to a lack of other accessible excitations, $A_{1g}$ spectra are projected out directly. (c) The $k_x$- and $k_y$-dependent scattering intensity $\gamma^2_{A_{1g}}$. Concerning electronic Raman scattering, the $\Gamma$- and the M-points of the Brillouin zone can be projected out by selecting $A_{1g}$ symmetry, but due to Coulomb screening, negative and positive regions of $\gamma(k)$ do not necessarily add up equally. In addition, $A_{1g}$ and $E_g$ phonon modes can be accessed.

All spectra have been recorded in an interval $\Omega \in [10, 310] \text{ cm}^{-1}$, with an absorbed laser power of 2 mW (4 mW for temperatures above $T = 230 \text{ K}$ in order to decrease the measurement time). They show six phonon modes at almost all temperatures. Only at $T = 310 \text{ K}$ and at $T = 80 \text{ K}$, the peak at $\Omega = 232 \text{ cm}^{-1}$ is not clearly visible. The energies of the phonon modes at $T = 6 \text{ K}$ will be denoted as $\Omega^{(1)}_{Ph} = 42 \text{ cm}^{-1}$, $\Omega^{(2)}_{Ph} = 66 \text{ cm}^{-1}$, $\Omega^{(3)}_{Ph} = 120 \text{ cm}^{-1}$, $\Omega^{(4)}_{Ph} = 188 \text{ cm}^{-1}$, $\Omega^{(5)}_{Ph} = 232 \text{ cm}^{-1}$ and $\Omega^{(6)}_{Ph} = 288 \text{ cm}^{-1}$ throughout this chapter. For temperatures below $T = 30 \text{ K}$, the edge of the laser line is superimposed on the spectrum for small Raman shifts $\Omega$. This happens as residual gas molecules inside the cryostat condense on the sample surface at very low temperatures. These molecules enhance the amount of elastically scattered light.
5.2 Experimental Raman Scattering Results

Figure 5.3 (a) shows spectra in B_{1g} symmetry in the temperature range between \( T = 6 \) K and \( T = 38 \) K, which is well above the superconducting transition temperature \( T_c = 35 \) K. The spectra have been recorded by selecting \( x'y' \) polarisation with respect to the 1-Fe unit cell (cf. section 3.3). The polarisation vectors are shown in figure 5.3 (b).

The symmetries correspond to the electronic unit cell, which is rotated by 45° with respect to the crystallographic unit cell. Therefore, the B_{1g} Raman measurements correspond to B_{2g,\text{cryst}}. As discussed in section 2.3, CaKFe_{4}As_{4} does not show any Raman-active phonon mode in B_{2g,\text{cryst}}. The E_{g}-phonons cannot be accessed because the incident polarisation is parallel to the sample surface. Only an electronic response is expected in the B_{1g} spectra. The X- and Y-points of the Brillouin zone are projected out, as displayed with the scattering intensity \( \gamma_{B_{1g}}^2 \) in figure 5.3 (c).

For temperatures above \( T_c \), the spectra show no features beyond the normal electronic response. Only for temperatures below \( T_c \), a broad peak can be seen. With decreasing temperature, its width decreases and its height increases. It is identified as the pair-breaking peak, which represents the breaking of Cooper pairs during the Raman process. The temperature dependence of the pair-breaking peak will be further investigated in section 5.3.
Figure 5.3: Raman spectra in $B_{1g}$-symmetry at temperatures as indicated. (a) At $T = 38$ K, above $T_c$, only the electronic continuum contributes to the cross section. Below $T_c$, the broad pair-breaking peak becomes visible. Its width decreases and its height increases with decreasing temperature. (b) Interactions in $B_{1g}$ symmetry can be measured by selecting $x'y'$ polarisations with respect to the 1-Fe unit cell. The blue and red arrows represent the polarisations of the incoming and scattered photons, respectively. (c) For electronic scattering processes the $B_{1g}$ symmetry only projects the X- and Y-points of the Brillouin zone, as visualised with the scattering intensity $\gamma^2_{B_{1g}}$.

The results of the $B_{2g}$-measurements are displayed in figure 5.4 (a). $B_{2g}$ measurements can be performed by setting the $xy$ polarisation configuration with respect to the 1-Fe unit cell. The respective polarisation vectors are shown in figure 5.4 (b). Concerning electronic Raman scattering, $B_{2g}$ symmetry projects the centers of each quadrant of the Brillouin zone, as displayed in figure 5.4 (c). In addition, a mode corresponding to the $B_{1g}$, cryst should be visible. The $E_g$-modes can be accessed as the incident polarisation has a component perpendicular to the sample surface. Spectra in the temperature range between $T = 6$ K and $T = 310$ K have been recorded. A dominating phonon mode at $\Omega_{Ph}^{(3a)} = 216$ cm$^{-1}$ can be identified. The inset enlarges the spectra. It shows three additional peaks at $\Omega_{Ph}^{(1a)} = 40$ cm$^{-1}$, $\Omega_{Ph}^{(2a)} = 120$ cm$^{-1}$ and, hardly visible, $\Omega_{Ph}^{(4a)} = 288$ cm$^{-1}$. They are visible at all temperatures, not only those which are shown in the inset. Strikingly, $\Omega_{Ph}^{(1a)}$, $\Omega_{Ph}^{(2a)}$ and $\Omega_{Ph}^{(4a)}$ coincide with $\Omega_{Ph}^{(1)}$, $\Omega_{Ph}^{(3)}$ and $\Omega_{Ph}^{(4)}$, three phonons which appear in the $A_{1g}$ spectra. The consequences of this relation will be further discussed in section 5.3.
5.2 Experimental Raman Scattering Results

![Graph of Raman spectra in B2g-symmetry at various temperatures.](image)

Figure 5.4: Raman spectra in B2g-symmetry at temperatures as indicated. (a) A dominant phonon mode at $\Omega_{\text{Ph}}^{(3a)} = 216 \text{ cm}^{-1}$ can be identified. The inset enlarges the spectra. Here, three additional peaks at $\Omega_{\text{Ph}}^{(1a)} = 42 \text{ cm}^{-1}$, $\Omega_{\text{Ph}}^{(2a)} = 120 \text{ cm}^{-1}$ and $\Omega_{\text{Ph}}^{(4a)} = 288 \text{ cm}^{-1}$ can be seen. Strikingly, they coincide with $\Omega_{\text{Ph}}^{(1)}$, $\Omega_{\text{Ph}}^{(3)}$ and $\Omega_{\text{Ph}}^{(4)}$, three phonons which appear in the A1g spectra. (b) For the measurements in B2g-symmetry, the xy polarisations with respect to the 1-Fe unit cell have been selected. (c) Concerning electronic Raman scattering, the centers of each quadrant in the Brillouin zone are projected out. In addition, the phonon mode corresponding to B1g, crys and the E modes can be accessed.

It was assumed above, that A2g contributions can be neglected. Indeed, the measurements in A1g, B1g and B2g symmetry show exclusive features. The B1g measurements show no phonon modes, but exclusively show the prominent pair-breaking peak. As they would be visible in all of the above spectra, no prominent A2g features interfere with the measurements. The pair breaking peak as well as the phonon modes can be assigned to the respective symmetries. The spectra from figures 5.2, 5.3 and 5.4 will be further analysed in the following section 5.3, especially with respect to their significance regarding superconductivity and lattice vibrations.
5.3 Analysis

In this section, the experimental data from all three symmetries $B_{1g}$, $A_{1g}$ and $B_{2g}$ will be analysed in detail. The first part of the analysis concerns the superconducting phase, subsequently, the temperature dependence of the phonon modes will be in the focus.

5.3.1 The Superconducting Phase

Figure 5.5 shows the $B_{1g}$ spectra in the superconducting phase (blue). In each plot, the normal spectrum at $T = 38 \, \text{K} > T_c$ is shown for comparison (red). In the right column, the respective difference spectra (superconducting - normal conducting) are displayed in black. The shape and position of the pair-breaking peak are of importance here.

Theoretically, for temperatures close to absolute zero, one would expect zero excitations below the energy of the superconducting gap $2\Delta$, as all electrons form Cooper pairs. At $2\Delta$, a sharp edge should be seen, and a decrease down to the level of the electronic continuum with increasing $\Omega$. For higher temperatures, the position of the pair-breaking peak should move to lower $\Omega$, as the $\Delta(T)$ decreases with increasing temperature, as predicted by BCS theory [6]. Then, electronic excitations below $\Omega = 2\Delta(T)$ should be visible, while the spectral weight of the pair-breaking peak decreases. In other words, with increasing temperature, the superconducting spectrum should approach the normal conducting spectrum more and more.

This behaviour can be recognised in the spectra in figure 5.5. At $T = 6 \, \text{K}$, the pair-breaking peak is most prominent and is located at $\Omega \approx 134 \, \text{cm}^{-1}$, which corresponds to an energy $2\cdot\Delta(6 \, \text{K}) \approx 16.61 \, \text{meV}$. BCS theory predicts that for low temperatures, the gap energy does not differ significantly from the value at absolute zero. Consequently, $\Delta_0 \approx \Delta(6 \, \text{K}) = 8.3 \, \text{meV}$. This is slightly lower than the results by K. Cho (measurements of the magnetic penetration depth) and R. Yang (IR studies), who found gap energies in the region of $\Delta_0 \approx 9 \, \text{meV}$ [38, 59]. Further on, the $B_{1g}$ gap will be referred to as $\Delta(B_{1g})$. With increasing temperature, the pair-breaking peak becomes less prominent, moves to lower energies and the spectra do more and more align with the normal spectrum.
5.3 Analysis

Figure 5.5: Spectra in the superconducting phase (blue) with the normal conducting spectrum at $T = 38$ K (red) and respective difference spectra (black) in B$_{1g}$ symmetry. The pair-breaking peak is most prominent at $T = 6$ K. For higher temperatures, the peak position moves to lower $\Omega$ and the superconducting spectra adjust more and more with the normal conducting spectrum. This is expected, as fewer electrons form Cooper pairs at higher temperatures. The position of the pair-breaking peak at $T = 6$ K leads to $\Delta \approx 8.3$ meV. For $\Omega < 2\Delta$, the superconducting spectra lie well below the normal conducting spectrum, as less excitations are available due to electrons being bound to Cooper pairs. It should be noted that the spectrum at $T = 20$ K has been multiplied with a scale factor of 0.9, in order to make it fit with the normal conducting spectrum at high $\Omega$. Differences in intensity between spectra can appear as the coupling of the straylight into the spectrometer cannot be performed equally for all measurements.
The reduced number of excitations below the gap energy $2\Delta$ in the superconducting spectra with respect to the normal conducting spectrum can be seen for all temperatures. Below a cross-over point, the superconducting spectra lie well below the normal conducting spectrum at all temperatures, with the difference being smaller at high temperatures than at low temperatures.

The position of the pair-breaking peak at the different temperatures in $B_{1g}$ symmetry is further investigated in figure 5.6. The zero crossing of the difference spectra as well as the peak positions are plotted as a function of temperature. All values are normalised to the value at $T = 6$ K. The theoretical BCS-prediction is plotted as well, with numerical values from [60]. Therefore, the approximation $\Delta_0 = \Delta(6$ K) was used, as argued above.

We assume a laser heating of 2.5 K per 1 mW absorbed laser power, as this value fits well with the temperature correction for other iron arsenides. For example, in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, the laser heating is approximately 3 K per 1 mW absorbed laser power [22]. Therefore, the real temperature of the sample during the measurement is approximately 5 K higher than the value that was set on the temperature controller, as almost all measurements have been performed with an absorbed laser power of 2 mW. Then, both plots follow the theoretical prediction.
Figure 5.6: Comparison of the experimental $B_{1g}$ peak energies at different temperatures with the theoretical BCS-prediction (black). Two parameters have been plotted, the zero crossing in the difference spectra (green) and the maximum position of the pair-breaking peak (magenta). Both follow the theoretical prediction well. In order to find the theoretical prediction, the approximation $\Delta_0 = \Delta(6 \text{ K})$ was used. Due to the local heating of the sample by the laser, a laser heating of 2.5 K per 1 mW absorbed laser power is assumed.

In analogy to figure 5.5, the superconducting spectra in $A_{1g}$ symmetry are shown in figure 5.7. Again, the spectra, which have been recorded below $T_c$, are displayed in blue and are compared with the normal conducting spectrum at $T = 38 \text{ K}$ in red. The difference spectra (black) are found in the right column.
Figure 5.7: Spectra in the superconducting phase (blue) with the normal conducting spectrum at $T = 38 \, \text{K}$ (red) and respective difference spectra (black) in $A_{1g}$ symmetry. The pair-breaking cannot be observed as prominently as with the large pair-breaking peak in $B_{1g}$ symmetry. Still, the lack of excitations for $\Omega < 2\Delta$ can clearly be observed, being more pronounced for low temperatures than for temperatures near $T_c$.

In $A_{1g}$ symmetry, the pair-breaking peak is not as prominent as in $B_{1g}$ symmetry. Still, the reduced number of excitations for $\Omega < 2\Delta$ is observable. As expected, the difference between the superconducting and the normal conducting spectra is higher for temperatures well below $T_c$ than for temperatures near the phase transition. For $\Omega > 2\Delta$, the superconducting spectrum lies above the normal conducting spectrum until the two spectra merge at high $\Omega$. From the difference spectra, $\Delta(A_{1g}) = 8.7 \, \text{meV}$ can be derived, which is slightly higher than $\Delta(B_{1g}) = 8.3 \, \text{meV}$.
and close to the results by other groups [38, 59].

Similar as in figure 5.6, the zero crossing (brown) as well as the first maximum (blue) in the difference spectra have been plotted as a function of temperature in figure 5.8. All values are again normalised with respect to the value at \( T = 6 \text{ K} \). Both parameters follow the theoretical BCS-prediction well. Again, the laser heating of 5 K has to be taken into account, as all measurements were performed with an absorbed laser power of 2 mW.

![Figure 5.8](image)

**Figure 5.8:** Comparison of the experimental \( A_{1g} \) gap energies at different temperatures with the theoretical BCS-prediction (black). Two parameters have been plotted, the zero crossing (brown) as well as the maximum position (blue) in the difference spectra. Both follow the theoretical prediction (black) well. The laser heating of 2.5 K per 1 mW absorbed laser power needs to be taken into account.

The superconducting spectra (blue) in \( B_{2g} \) symmetry are compared with the normal conducting spectrum (red) at \( T = 38 \text{ K} \) in figure 5.9. In addition, the difference spectra are shown in black, in analogy to figures 5.5 and 5.7. The superconducting energy gap below \( \Omega = 2\Delta \) can hardly be seen in this symmetry. Both below and above the gap energy, the deviations from 0 are much smaller here than in the other symmetries. As the dominant phonon mode at \( \Omega_{\text{ph}}(3a) \) is not of special interest for the superconducting phase, it is not completely shown in the figure, in order to resolve the features with a smaller Raman cross section.
5.3.2 Phonon Modes

Besides the analysis of the superconducting phase, the six phonon modes in $A_{1g}$ are of importance. In section 5.2, they have been identified with the energies $\Omega_{Ph}^{(1)}$, $\Omega_{Ph}^{(2)}$, $\Omega_{Ph}^{(3)}$, $\Omega_{Ph}^{(4)}$, $\Omega_{Ph}^{(5)}$ and $\Omega_{Ph}^{(6)}$.

All these phonon modes have been fitted using a Voigt fit, which describes a convolution of a Lorentz oscillator and a Gaussian shape. The Lorentzian profile hereby represents the phonon shape, while the Gaussian takes the resolution of the spectrometer into account.

The Voigt profile obeys

$$y(\Omega) = y_0 + m \cdot \Omega + A \frac{2 \ln 2 \Gamma_L}{\pi^{3/2} \Gamma_G} \int_{-\infty}^{\infty} e^{-t^2} \left( \frac{\Gamma_L}{\Gamma_G} \right)^2 + \left( \frac{\Gamma_L \Omega - \Omega_c}{\Gamma_G} \right)^2 dt , \quad (5.1)$$

with the Gaussian width $\Gamma_G$, the Lorentz width $\Gamma_L$ and the peak position $\Omega_c$. The area is scaled with $A$. The terms $m \cdot \Omega + y_0$ take the linear background of the electronic continuum as well as the $y$-intercept of the phonon mode into account.
5.3 Analysis

Γ_G was fixed at 4.65 cm\(^{-1}\) as the resolution of the spectrometer was determined experimentally and does not change.

The \(x_c\) positions of these Voigt fits are depicted in figure 5.10 in dependence on temperature. The \(x_c\)-value at \(T = 260\) K is substracted from the values at other temperatures in order to facilitate a comparison. The values at \(T = 310\) K cannot be used as the phonon corresponding to \(\Omega_{Ph}^{(5)}\) is not visible at this temperature. In addition, it is missing at \(T = 80\) K. For all phonons, a shift to higher energies can be observed with decreasing temperature, which is expected due to the lattice contraction at low temperatures. In the superconducting phase, below \(T_c = 35\) K, the phonons do not seem to shift any further. Still, the shift is not equal for each mode. \(\Omega_{Ph}^{(3)}\) and \(\Omega_{Ph}^{(6)}\) shift the most, while \(\Omega_{Ph}^{(1)}\) and \(\Omega_{Ph}^{(2)}\) almost stay constant.

![Figure 5.10: Temperature dependence of the phonon positions Ω_c in A_{1g} symmetry. The Ω_c-value at T = 260 K is substracted from the values at other temperatures to simplify the comparison. All modes show an increase in energy with decreasing temperature. This effect is a consequence of lattice contraction at low T. Still, the energy shift is not equal for all phonons. The phonons corresponding to \(\Omega_{Ph}^{(1)}\) and \(\Omega_{Ph}^{(2)}\) hardly show any shift, while those at \(\Omega_{Ph}^{(3)}\) and \(\Omega_{Ph}^{(6)}\) shift by more than 7 cm\(^{-1}\). Below \(T_c\), the phonons do not seem to shift any further.](image-url)
As pointed out in section 2.3, three Raman-active phonon modes are expected in \( A_{1g} \) symmetry. In addition, four \( E_g \) modes should be present. As the modes at \( \Omega_{ph}^{(2)} \), \( \Omega_{ph}^{(4)} \) and \( \Omega_{ph}^{(5)} \) are visible exclusively in the \( A_{1g} \)-spectra, they can unambiguously be identified with the three \( A_{1g} \) phonons. The three phonon modes at \( \Omega_{ph}^{(1)} = 42 \text{ cm}^{-1} \), \( \Omega_{ph}^{(3)} = 120 \text{ cm}^{-1} \) and \( \Omega_{ph}^{(6)} = 288 \text{ cm}^{-1} \) coincide with the modes at \( \Omega_{ph}^{(1a)} \), \( \Omega_{ph}^{(2a)} \) and \( \Omega_{ph}^{(4a)} \) in the \( B_{2g} \) response. A direct comparison is shown in figure 5.11. Figure 5.11 (a) shows the spectra for selected temperatures in \( A_{1g} \) symmetry, while figure 5.11 (b) shows \( B_{2g} \) spectra. As they appear in both symmetries and the incident polarisations have a component along perpendicular to the sample surface, the coinciding phonon modes are identified as three \( E_g \) phonons. However, four \( E_g \) phonons should be Raman-active in \( \text{CaKFe}_4\text{As}_4 \) (cf. table 2.2). The fourth \( E_g \)-mode could not be identified in any symmetry. Possibly, it is situated above 310 \text{ cm}^{-1}.

Figure 5.11: Comparison of \( A_{1g} \) and \( B_{2g} \) spectra. (a) \( A_{1g} \) spectra are shown for selected temperatures. (b) Two spectra in \( B_{2g} \) symmetry are shown as a comparison. The phonons corresponding to the energies \( \Omega_{ph}^{(1)} \), \( \Omega_{ph}^{(3)} \) and \( \Omega_{ph}^{(6)} \) in \( A_{1g} \) correspond to the phonons at \( \Omega_{ph}^{(1a)} \), \( \Omega_{ph}^{(2a)} \) and \( \Omega_{ph}^{(4a)} \) in \( B_{2g} \) symmetry. They can be identified as \( E_g \) phonons, which are visible in both symmetries as the incident polarisations have a component perpendicular to the sample surface.
In addition to the $A_{1g}$ and $E_g$ phonons, one $B_{1g,\text{cryst}}$ mode is expected to be Raman active in CaKFe$_4$As$_4$. As the polarisations are selected with respect to the 1-Fe unit cell in the iron arsenides (rotated by 45°), but the phonon corresponds to the tetragonal crystal, it appears in the $B_{2g}$ spectra as the dominant phonon mode at $\Omega_{\text{ph}}^{(3a)}$.

### 5.4 Discussion

In the previous section 5.3, the superconducting phase as well as the phonon modes in the symmetries $B_{1g}$, $A_{1g}$ and $B_{2g}$ have been analysed. It is the purpose of this section to discuss the results and to present a comparison to other iron arsenides, especially the optimally doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$.

The analysis of the phonon modes in $A_{1g}$ and in $B_{2g}$ symmetry shows some interesting features. The six phonon modes in $A_{1g}$ symmetry all follow the expected shift to higher energies for lower temperatures due to lattice contraction. Below $T_c$, they do not shift any further. Still, the energy shift is not equal for all modes, some are affected stronger than others by a change in temperature. In total, eight Raman-active phonons are expected for CaKFe$_4$As$_4$ (see table 2.2). Three of the modes appear exclusively in the $A_{1g}$ spectra, they are identified as the $A_{1g}$ phonons. The $B_{1g}$ mode appears in the $B_{2g}$ spectra as the polarisations are set with respect to the 1-Fe unit cell.

Three of the $A_{1g}$ modes coincide with peaks in the $B_{2g}$ spectra. They are suspected to correspond to three $E_g$-phonons. The fourth $E_g$ phonon though could not be identified in any spectrum. Future experiments should aim at finding this mode, possibly, it is situated above 310 cm$^{-1}$. To be absolutely sure about the identification of the $E_g$ phonons, the sample could be rotated by 45° in future measurements. Then, the polarisation configurations for $B_{1g}$ and $B_{2g}$ symmetries are exchanged. As one has a incident polarisation component perpendicular to the sample surface along $z$ and the other has not, the $E_g$ phonons would then appear in the $B_{1g}$ spectra and disappear in the $B_{2g}$ spectra.

As pointed out in section 2.3, CaKFe$_4$As$_4$ shows many similarities to other iron arsenides, especially optimally doped $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$. Not only does it have a similar crystal structure, but also the electronic structure is similar. $T_c$ is similar
to overdoped \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 and also shows a comparable pressure dependent behaviour [33]. Further insight can be expected from a comparison of the results on the 1144 compound \text{CaKFe}_4\text{As}_4 with those of Böhm \textit{et al.} [24] on the 122-compound \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2.

Essentially, the \textit{s}-wave superconductor \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 shows strong evidence for subdominant \textit{d}-wave pairing channels. Two Bardasis-Schrieffer modes in $B_{ig}$ symmetry (cf. section 2.4) inside the gap of \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 were observed around optimal doping, which is a novelty for the FeSCs and possibly also for superconductors in general. A detailed analysis and comparison to theoretical predictions supports spin fluctuations to be the leading interaction for the formation of Cooper pairs in \text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2 [24].

For \text{CaKFe}_4\text{As}_4, the superconducting gap in the $B_{ig}$ spectrum at $T = 6$ K was identified with $\Delta(B_{ig}) = 8.3$ meV, appearing as a broad pair-breaking peak in the Raman spectrum. In contrast to the results for \text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2, no other modes are visible, the result suggests a superconducting \textit{s}-wave pairing without a subdominant channel present. The value of $\Delta(B_{ig})$ is smaller than the expected value of $\Delta_0 = 9$ meV though. It is conceivable, that the broad pair-breaking peak is rather formed by a superposition of two peaks. This scenario is visualised in figure 5.12 with calculations that were performed in analogy to [61]. The difference spectrum in $B_{ig}$ symmetry at $T = 6$ K is shown in blue, two calculated modes in red. The first mode could then be identified as a Bardasis-Schrieffer mode, and the second mode as the pair-breaking peak. This would give strong evidence for a subdominant \textit{d}-wave pairing channel in \text{CaKFe}_4\text{As}_4. If the peak can be resolved more clearly in future experiments, e.g. by the use of a different laser, this hypothesis can either be supported or falsified.
5.4 Discussion

Figure 5.12: Possible superposition of two modes in the B_{1g} spectra. The difference spectrum in B_{1g} symmetry at T = 6 K is shown in blue, two calculated modes in red. An experimental affirmation of this hypothesis would give strong evidence for a subdominant d-wave pairing channel in CaKFe_{4}As_{4}, similar to optimally doped Ba_{0.6}K_{0.4}Fe_{2}As_{2}. To avoid negative values, 0.1 was added to the difference spectrum. From [11].

In the context of the iron arsenides and the iron-based superconductors in general, the crucial matter of the pairing mechanism remains unsettled. Although the application potential of iron based superconductors is not fully explored yet, the scientific relevance of those materials cannot be overestimated. The discovery of the high-\(T_c\) FeSCs in 2008 was unexpected. Not only does this discovery give hope for the finding of other crystallographic families with superconducting properties, the iron-based superconductors also provide a laboratory for the understanding of the pairing mechanism in high-\(T_c\) superconductors. With the newly discovered \(E_A\)AF_{4}As_{4} (1144) compounds (\(E_A = Ca, Sr, Eu\) and \(A = K, Rb, Cs\)), a whole new family of high-\(T_c\) superconductors has been added to the pool. Intensive research in this field will contribute immensely to reaching the ultimate goal - the discovery of a superconductor, that can be operated at room temperature.
6 Summary

The thesis comprises two parts, the contribution to completing a setup for tip-enhanced Raman scattering (TERS) and experimental studies on CaKFe$_4$As$_4$. The TERS technique and the progress in the buildup is described in appendix A. For the major part of this thesis, Raman spectroscopy measurements on the superconducting iron arsenide CaKFe$_4$As$_4$ were performed.

The experiments on CaKFe$_4$As$_4$ show the response from phonons and superconducting gap excitations. CaKFe$_4$As$_4$ is expected to show eight Raman-active phonon modes. Seven of them could be identified, the $B_{1g}$ phonon, three phonons that appear exclusively in $A_{1g}$ spectra and three modes that appear in the $A_{1g}$ and $B_{2g}$ spectra. They could be identified as $E_g$ phonons. Only one $E_g$ phonon could not be observed in any symmetry.

A symmetry-dependent superconducting gap of $\Delta(A_{1g}) = 8.7$ meV and $\Delta(B_{1g}) = 8.3$ meV could be identified, which is in good agreement with measurements of the magnetic penetration depth as well as IR measurements [38, 59]. The temperature dependence of the gap follows the prediction of the BCS-theory.

The results of CaKFe$_4$As$_4$ are compared with those of optimally doped Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$. In spite of similarities in the crystal structure, superconducting transition temperature and in particular the electronic structure, the Raman spectra show distinct differences between the compounds. While two doping dependent Bardasis-Schrieffer modes in $B_{1g}$ symmetry could be observed for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [24], no clearly separated BS mode is visible in the CaKFe$_4$As$_4$-spectra. While the results for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ strongly support a subdominant $d$-wave pairing channel and therefore the interaction mediation via spin fluctuations in Ba$_{1-x}$K$_x$Fe$_2$As$_2$, such a subdominant mechanism could not unambiguously be identified for CaKFe$_4$As$_4$. However, a Bardasis-Schrieffer mode may be hidden below the pair-breaking peak in the $B_{1g}$ spectra due to a superposition of the peaks.
Appendix A

Tip-Enhanced Raman Spectroscopy

Conventional Raman spectroscopy provides a powerful tool for the study of superconductors, but the spatial resolution is limited by the wavelength of the laser light to approximately $\lambda/2$. This criterion was formulated by Abbe in 1873 and is closely related to Heisenberg’s uncertainty relation. Consequently, small features with the scale of one or a few atoms, like interfaces, crystal defects or grain boundaries, cannot be studied with conventional Raman scattering experiments. As superconductivity is induced at such features in some materials [62, 63], studies close to inhomogeneities are of special interest. In addition, conventional Raman spectroscopy is not surface sensitive. The penetration depth of the light amounts to several 10 nm in a metal. Therefore, a response from the bulk material will always be part of the Raman signal.

The limitation of the spatial resolution can be overcome with the implementation of near-field techniques [64, 65], for example in tip-enhanced Raman spectroscopy (TERS). Consequently, small features in a crystal can be studied with regard to their impact on the properties of the material. Therefore, the buildup of an experimental realisation of TERS started by former co-workers [66, 67]. One important part of the work for this thesis were the implementation of a new spectrometer to the setup and the realisation of the Raman selection rules. In the following, the experimental concept of TERS, the progress of the setup and some test-measurements will be addressed. Most importantly, chances as well as difficulties of the setup will be pointed out.

Tip-Enhancement

Imagine a common Raman spectroscopy setup and add a movable metallic tip, that can approach the sample surface. The approach has several effects:
Tip-Enhanced Raman Spectroscopy

- The incoming laser beam excites surface plasmons in the tip, which lead to a locally enhanced field. Therefore, excitations in the sample around the tip apex, in a spatial domain in the order of the tip diameter, will lead to a stronger Raman signal than in the rest of the spot region. One differentiates between the far-field, which produces the conventional Raman response, and the near-field, which is induced by the tip.

- Propagating as well as evanescent waves are emitted from the sample. While the propagating waves are measurable in the far-field, the evanescent waves decay exponentially with the distance from the sample. When approaching the tip, they excite surface plasmons in the tip as well. Then, the tip serves as an antenna and makes the near-field information measurable.

- The so-called depolarisation effect occurs: The metallic tip depolarises parts of the polarised scattered light. Therefore, the near-field response is partially depolarised even if the far-field signal is purely polarised.

It is crucial to distinguish the near-field from the far-field response. Therefore, the contrast between the two signals needs to be notable. The contrast can be improved by studying systems with strongly anisotropic Raman tensors. Then, the far-field response will be high for some polarisation configurations, but negligible for others, in accordance with the Raman selection rules (cf. section 3.3). By suppressing the far-field, the contrast is increased and near-field effects can be resolved clearly, as the depolarisation effect brings to bear.

In order to reach a high enhancement factor, the dielectric response of the tip material needs to match the excitation frequency of the laser. For TERS experiments, gold and silver tips are most commonly used. The laser in our TERS lab operates at 532 nm (see below), therefore silver tips with a resonance at approximately 500 nm are used for this setup. They are more difficult to produce than gold tips, but the production procedure has been optimised by G. Eckleder and P. Cova Fariña [68].
The TERS-Setup

The TERS setup in our lab is depicted in figure A.1. The abbreviations are consistent with those in section 4.1. The solid state laser (Coherent, Sapphire SF 532) emits a green beam ($\lambda = 532$ nm). Similar to conventional Raman spectroscopy, the beam passes two spatial filters, and the incident polarisation can be selected. For the moment, an SBC for the selection of circular polarisations is not in use. The first difference to the setup depicted in figure 4.1 is, that the beam is split into three parts at an optical flat (OF). While the middle beam is used for the measurements, the two other beams are needed for the alignment, as will be described below. The light enters the cryostat through a window and hits a parabolic mirror, which focusses the beams onto the sample.

The straylight path is shown in red. Only light that is scattered onto the parabolic mirror can leave the cryostat parallel to the optical axis of the parabola, as the sample is aligned exactly onto the focal point of the parabolic mirror. The beam splitter (BS 1) directs the straylight into the collection optics, where a system of an objective lens (O1) and a lens (L5) reduces the beam diameter. An edge filter (F) cuts off the laser. The final polarisation is selected with an analyser (A). The $\lambda/2$ waveplate rotates the transmitted polarisation into the direction of maximal efficiency of the spectrometer. $L6$ focusses the beams on the entrance slit of the spectrometer (Princeton Instruments, Isoplane SCT 320).

The inset picture shows the parabolic mirror as well as the sample stage, which is movable as it is mounted on piezoelectric actuators. The tuning fork is soldered onto a second piezoelectric stage. At its end, the tip can be attached. The parabolic mirror is regarded as the essential innovation in the setup. Not only does it deliver ideally parallel straylight, but it also maintains its optical properties at all temperatures as opposed to commercial glass objectives. In addition, it allows optimal focussing and minimal spot size [69, 70, 71]. It was cut off-axis, so that the sample stage can be accessed more easily [72].

The Köhler optics were installed for the illumination of the sample stage. Two observation cameras (OO1 and OO2) allow the experimenter to see the sample stage, which is essential for alignment purposes. $BS2$ directs the image to camera OO1. The movable black rectangle at the position of $BS2$ represents a powermeter.
Figure A.1: TERS Setup. Many elements are those of a conventional Raman spectroscopy setup as depicted in figure 4.1. The optical flat (OF) splits the beam into three parts. The middle beam is used for the measurements, the outer beams are needed for the alignment procedure. A parabolic mirror focusses the laser beams onto the sample. The Köhler optics illuminates the sample. Two observation optics (OO1 and OO2) are used for alignment purposes. The inset picture shows the sample stage and the parabolic mirror. The sample stage is mounted on piezoelectric actuators and therefore can be moved. Taken from [11].

The incident laser beam has a diameter of approximately 6 mm and a divergence of $2 \cdot 10^{-4}$ mrad. The beam needs to be aligned parallel to the optical axis of the parabolic mirror and the spot on the sample is supposed to lie exactly in the focal point of the parabola. The direction of the laser beam can be changed with two screws on the optical flat. In order to move the sample surface into the focal point, one needs the two outer beams, which are reflected from the OF. Using the observation optics, both beams can be seen on the sample. When the sample surface is located in the focal point of the parabola, the beams coincide. This alignment enables two achievements: (i) parallel straylight beams are leaving the cryostat and (ii) the spot size is minimal. Assuming perfect alignment, the focus size on the sample is less than 2 $\mu$m.

At the beginning of the work for this thesis, the new spectrometer and the new charge-coupled device (CCD) were not yet part of the setup. The scattered light
had to be coupled into a glass fiber, which transported the signal into another lab, where it could be coupled into a spectrometer. The implementation of the new spectrometer brought major change to the setup, and the efficiency could be increased by a factor of approximately 20.

Another improvement to the setup was brought by the installation of an additional observation optics (OO2), which offers a view on the sample table from a different angle than OO1. Therefore, finding the exact spot position becomes easier and more reliable than before.

**AFM and STM**

By attaching the tip onto a piezoelectric stage, it can be moved in every spatial direction. This does not only enable the approach to the sample surface, but also makes the scanning of the sample surface possible. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) measurements can be performed.

For scanning tunneling microscopy, a bias voltage is applied between the tip and the conducting sample surface. The resulting tunneling current is measured. STM can be driven in two different operation modes: in constant height mode, the tip or the sample are only moved in $xy$-directions and the topography of the sample surface is mapped as a function of the tunneling current. When keeping the tunneling current constant on the other hand, the piezo movement in $z$-direction represents the topography.

Atomic force microscopy can be operated in the TERS-setup, as the tip is glued to a tuning fork that is vibrating at its resonance frequency. When approaching the tip, interactions between sample and tip (e.g. van-der-Waals interactions, Coulomb repulsion etc.) influence the resonance frequency. In analogy to the STM measurements, the topography of the sample surface can be mapped either by investigating the changes in phase and amplitude of the tuning fork oscillation or by monitoring the piezo movement in $z$-direction when keeping the vibration constant during the scanning.
As STM is based on a bias voltage and the tunneling current, a metallic tip is needed. Only the end of the tip is of importance, where a single atom is needed. When cutting a metallic tip at an angle, this condition usually already is achieved. For AFM tips, the shape of the entire tip is relevant, not only the apex. A sharp and symmetric tip needs to be prepared, as the resolution is given by the diameter of the tip end.

**Measurements in the TERS Lab**

In addition to the advances of the setup, polarised Raman scattering measurements were performed on silicon during this thesis as in order to validate the selection rules. Figure A.2 (a) shows exemplary measurements on silicon. The mode at $\Omega \approx 520 \text{ cm}^{-1}$ was measured before (left) and after (right) the installation of the new spectrometer. Two aspects are of importance: on the one hand a strong contrast between different polarisation configuration is recognised. This enables the observation of near-field effects in future TERS measurements. On the other hand, the strength of the signal could be enhanced by a factor of 20 by the installation of the IsoPlane SCT 320 spectrometer.

Before the beginning of this thesis, AFM and STM measurements were performed on the setup [66]. The STM measurements are displayed in figure A.2 (b). A thin layer of Au was deposited on insulating Si. With the grey scale on the left hand-side, the sample topography is visualised. On the right, line scans in forward and backward direction are shown, corresponding to the uppermost line of the topography images. In the STM measurements, a horizontal resolution of 3 nm could be achieved. The vertical resolution was better than 1 nm. At low temperatures and in vacuum, further improvements can be expected. AFM measurements on silicon (displayed in figure A.2 (c) reached a resolution in the 50 nm range.
Figure A.2: Test measurements on the TERS setup. (a) Raman scattering measurements on silicon of the mode at $\Omega \approx 520 \text{ cm}^{-1}$ before (left) and after (right) the installation of the new spectrometer. A clear contrast between different polarisation configurations is observed. In addition, the new spectrometer delivers an increase in intensity by a factor of 20. (b) STM measurements on a thin layer of Au, that was sputtered onto the Si sample. They grey scale images on the left show the topography, the images on a right show line scans in forward an backward direction. These scans correspond to the uppermost line in the topography images. (c) AFM measurements on silicon. From [11, 66].

Discussion and Outlook for TERS

With the installation of the spectrometer and the ability to operate scanning probe measurements as well as Raman scattering experiments independently, the buildup of the TERS setup is now complete. Nevertheless, it brings along several challenges.

The Raman setup for TERS can be regarded in analogy to a conventional Raman spectroscopy setup as described in section 4.1. The most essential difference lies in
the use of a parabolic mirror instead of a common lens in order to focus the light on the sample surface. A second difference is the collection of the straylight. In the conventional setup, only straylight that is emitted almost perpendicularly to the sample surface is collected. In the TERS lab on the other hand, the collected straylight is emitted from the sample at an angle and has to pass the parabolic mirror again. As the conventional setup works extremely well for symmetry resolved Raman spectroscopy, it should be the goal to find out how these differences affect the physics of the TERS experiment and to eliminate all negative impacts.

The most important difficulty with the TERS setup is that the parabolic mirror does not leave the polarisations untouched. Three effects play a role: firstly, polarisation directions are rotated by the reflection at the mirror, as the electric field always oscillates perpendicularly to the propagation direction of a transverse (light) wave. Secondly, the metallic coating of the parabolic mirror creates a nonzero phase shift between those polarisation parts that oscillate in the plane of incidence and those that oscillate perpendicular to it. Thirdly, the reflectivities of the parallel and the perpendicular parts depend on the angle of incidence. For a metallic mirror, the differences lie within a few percent though.

All three effects play a role for the incoming laser light as well as for the straylight. For simplicity, only linear $x$ and $y$ polarisations will be taken into account in this paragraph. $P$ sets $x$ polarisation parallelly to the optical table, $y$ polarisation perpendicular to it.

At first, the relevance for the incident light will be discussed (all directions are with respect to the coordinate system in the inset of figure A.1): the laser beam should be coupled into the parabolic mirror at $x = 0$ and at maximum $y$-position. Then, the $x$-polarisation will not get rotated as it is perpendicular to the propagation direction of the beam before and after the reflection. The $y$-polarisation will be rotated by the same angle as the propagation direction of the beam, but, importantly, the projection on the crystal axes remains equal. Then, the polarisations are conserved with respect to the plane of incidence and only an intensity correction needs to be performed as will be seen below. For linear polarisations, the phase shift at the mirror does not play any role as well. $x$-polarisation purely lies in the plane of incidence, $y$-polarisation purely lies perpendicular to it, there are no parts to be retarded against one another. The reflectivities for $x$- and $y$-polarisations are different, but the final polarisation direction is not affected. An intensity correction is sufficient again.
The straylight is scattered into all directions. When collecting light from the entire parabola, an interpretation of the received signal is not possible. Each beam followed a different path, so the polarisations have been affected differently. This problem can only be resolved when covering the whole parabola except for the part, where the incident beam is coupled into the mirror. Then, the scattered light follows the same path as the incident light, only in opposite direction. The same intensity correction as for the incoming light needs to be performed again, as will be explained in the following. Then, the true Raman response is measured.

As mentioned above, two intensity corrections need to be taken into account for the incoming light. One comes from the angle of incidence of the beam onto the sample surface. As the beam does not hit the sample surface perpendicularly, only the projections of the polarisations onto the sample surface contribute to the symmetry dependent Raman response. In the configuration that is described above, the $x$-polarisation lies in the surface plane. Therefore, only the projection for the $y$-polarisation is relevant. The intensity correction only depends on the angle of incidence. This angle can be either calculated or a trick can be used: the sample table also contains a piece of silicon that is tilted by approximately $30^\circ$, so a direct reflex hits the parabola again. When aligning the setup so that this direct reflex leaves the cryostat at the same position as the incident beam enters it, one can be sure that the laser beam will hit the untilted (flat) samples at an angle of $30^\circ$ with respect to the surface normal.

The second intensity correction originates in the unequal reflectivities of $x$- and $y$-polarisations. As $x$-polarisation is orientated perpendicularly to the plane of incidence in the above configuration and $y$-polarisation is parallel to the plane of incidence, the reflectivity for $y$-polarisation will be smaller than for $x$-polarisation. Both lacks of intensity at the sample in $y$-polarisation can be overcome by setting a higher intensity in $y$- than in $x$-polarisation before the light enters the cryostat. In fact, this factor needs to be squared as the same effects come to bear for the straylight.

The arguments above only take $x$- and $y$-polarised light into account. As circular polarisations as well as $x'$- and $y'$-polarisations are superpositions of $x$- and $y$-polarised portions, all configurations can be used with the help of a polariser and a SBC.
The polarisation control with the parabolic mirror is the major difficulty in the TERS setup. There are other problems that can occur but shall only be mentioned. The laser beam needs to be oriented parallel to the optical axis of the parabola and the sample surface needs to be moved into the focus of the parabolic mirror. This alignment procedure is difficult as the inside of the crystal can only be seen with the help of the cameras OO1 and OO2. In addition, the approach of the tip to the sample surface can drastically increase the amount of elastically scattered straylight that is superimposed on the Raman response. The buildup of the TERS setup is now finished and tip-enhanced Raman spectroscopy measurements should be possible to be performed now.

TERS setups are not unique in the world. At ambient temperature, they are well established [73]. Low temperature TERS experiments on the other hand, like they will be performed in our lab, are not common yet.

The exploration of physics ‘beyond the diffraction limit’ offers several scientific chances. Superconductivity sometimes is induced at interfaces or by twin and grain boundaries [62, 63]. TERS offers the possibility to explore materials around these features and to search for differences in the Raman spectra. Magnetic textures in the nm range, like skyrmions, will also be of interest.

Besides achieving a spatial resolution close to the size of an atom and being surface sensitive, a TERS setup provides the ability to combine different measurement techniques in situ. Conventional symmetry-resolved Raman scattering experiments can be performed together with atomic force or scanning tunneling microscopy (AFM, STM). This gives access to single-particle properties (scanning tunnelling spectroscopy) as well as two-particle information (Raman spectroscopy). Still, the setups for the respective spectroscopy methods are built up independently and can be used exclusively as well.
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