

Cooper pairing and fluctuations in Fe-based superconductors

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Abstract

Unconventional superconductivity generally occurs in proximity to magnetic phases. Raman spectroscopy affords a window into most of the related excitations including pairing interactions. Thus, the superconducting ground state and putative sub-leading pairing tendencies can be probed along with magnetic excitations and fluctuations. Here, Raman spectroscopy identifies the hierarchy of pairing channels in CaKFe₄As₄ and critical fluctuations in Ba(Fe_{1-x}Co_x)₂As₂. The fluctuations are analysed using a novel method tailored for the low energy Raman response.

Kurzzusammenfassung

Supraleitung in Hochtemperatursupraleitern könnte durch eine Vielzahl ineinadergreifender Mechansimen entstehen. Ramanspektroskopie stellt eine Möglichkeit dar diese Mechanismen zu untersuchen: einerseits durch die direkte Untersuchung des supraleitenden Grundzustands und andererseits durch die Messung von kritischen Fluktuationen. Diese Arbeit zeigt die Vielseitigkeit der Ramanspektroskopie auf, indem ein subdominanter Paarungskanal in CaKFe₄As₄ und quantenkritische Fluktuationen in Ba(Fe_{1-x}Co_x)₂As₂ identifiziert werden. Zusätzlich wird eine neue Methode zur Analyse des Niedrigfrequenz-Ramanspektrums der Fluktuationen präsentiert.

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Chapter 1

Introduction

If it turns out it's like an onion with millions of layers and we're just sick and tired of looking at the layers, then that's the way it is, but whatever way it comes out its nature is there and she's going to come out the way she is, and therefore when we go to investigate it we shouldn't predecide what it is we're trying to do except to try to find out more about it.

R. P. Feynman [1]

The discovery of LaOFeP in 2006 [2] marked the beginning of the "iron-age of superconductivity" [3]. The Fe-based superconductors (FeSC) exhibit high transition temperatures T_c [4–9] similar to the cuprates [10,11]. However, the mechanisms behind superconductivity in the FeSC are not entirely disentangled. To reveal these mechanisms one usually tries to pin down the symmetry of the superconducting order parameter and the momentum dependence of the gap function Δ_k first [12]. In the early stages of the FeSC, the order parameter was quickly proposed to have s^{\pm} symmetry [12–15] in which superconductivity is mediated by spin fluctuations. Yet, at the same time, it was suggested, that such an s^{\pm} ground state may be competing with *d*-wave pairing [16–18], thereby painting a more intricate picture.

The investigation into these pairing mechanisms is facilitated by the wealth of different phase transitions which one can generate by chemical substitution [4,19]. For instance BaFe₂As₂ [20] exhibits a magneto-structural transition at $T_s = 135$ K. Upon substituting Fe with Co [21], the two transitions split giving rise to a nematic

phase with a structural distortion and a magnetic spin-density-wave transition [22]. Further doping destabilises these transitions and superconductivity emerges.

This concomitant doping dependence is observed in K doped $Ba_{1-x}K_xFe_2As_2$ as well where the magneto-structural transition temperature decreases and superconductivity develops [4, 19]. Ba_{1-x} K_x Fe₂As₂ represents an interesting case study due to the anisotropy of its pairing potential [23,24] which highlights the aforementioned intricacies of the Cooper pairing in the FeSC. In $Ba_{1-x}K_xFe_2As_2$ the ground state is most likely dominated by an interaction having s^{\pm} -symmetry [25, 26]. Additionally, spectroscopic fingerprints of competing interactions with *d*-wave symmetry were detected [24, 27, 28] revealing a hierarchy of pairing channels. It is not clear, if these subdominant pairing channels are a generic feature of FeSC with a dominant s^{\pm} ground state as theoretically argued [16–18] or unique to $Ba_{1-x}K_xFe_2As_2$. To test this experimentally, the stoichiometric CaKFe₄As₄ [29] proves to be a good candidate due to its similarities with optimally doped $Ba_{1-x}K_xFe_2As_2$ [30] including possibly the s[±]-symmetry of the superconducting ground state [30–32]. CaKFe₄As₄ belongs to the recently discovered 1144- $AeAFe_4As_4$ compounds with Ae = Ca, Sr and A = K, Rb, Cs having superconducting transition temperatures around 35 K [29].

Superconductivity in CaKFe₄As₄ may not be influenced by an s^{\pm} interaction only. One can substitute Fe with Ni which yields CaK(Fe_{1-x}Ni_x)₄As₄ [33]. Here, a putative magnetic quantum critical point (QCP) was found [34] close to x = 0 which may affect the superconducting pairing [35]. The investigation of a QCP is challenging due to its nature as a second-order phase transition at T = 0 K [36]. Thus, investigating a QCP itself is possible only via the observation of the associated critical fluctuations which may play a role in mediating the pairing [35] or enhancing T_c [37]. Such fluctuations leading up to a QCP have been discussed to exist in Ba(Fe_{1-x}Co_x)₂As₂ as well [38,39] but these findings were subsequently called into question [40,41].

This leaves us with the two objectives of this thesis: (i) answering the question, if subleading pairing channels are observable in compounds other than $Ba_{1-x}K_xFe_2As_2$, and (ii) if it is possible to make a case for a QCP in $Ba(Fe_{1-x}Co_x)_2As_2$ after all. To this end, the inelastic scattering of light (Raman spectroscopy) is utilised. Raman spectroscopy provides access to the energy and

symmetry of the subleading interactions in the superconducting state [24,27,42] on the one hand. On the other, critical fluctuations and magnetic excitations can be probed [43,44].

This thesis is structured as follows: Chapter 2 presents the material class of the FeSC with an emphasis on the doped BaFe₂As₂ compounds and the stoichiometric CaKFe₄As₄. Chapter 3 introduces the method of inelastic light (Raman) scattering. Chapter 4 shows the experimental setup used for the Raman scattering experiments. The characterisation of the samples is described and an overview of the measured samples is given. Chapter 5 expands on the work in Ref. [45], arguing in favour of a subleading interaction in CaKFe₄As₄. Chapter 6 discusses the evolution from thermal to quantum fluctuations in Ba(Fe_{1-x}Co_x)₂As₂. A summary is given in chapter 7.

Chapter 2

The iron-based superconductors

The following chapter gives an overview over the FeSC, and in particular the doped BaFe₂As₂ [20] and stoichiometric CaKFe₄As₄ [29] compounds. It places the properties of CaKFe₄As₄ alongside those of K-doped Ba_{1-x}K_xFe₂As₂ [4] on the one hand and Co-doped Ba(Fe_{1-x}Co_x)₂As₂ [21] on the other, introducing the three main actors of this thesis.

2.1 Crystallography - unit cells and Brillouin zone

CaKFe₄As₄ and BaFe₂As₂ share the D_{4h} point group of the tetragonal lattice. Fig. 2.1 shows the crystallographic unit cells next to each other. The tetragonal unit cell of the BaFe₂As₂ is made up of Ba atoms at the corner and in the centre separating the Fe-As layers. Superconductivity emerges, if, for instance, the Fe atoms are replaced by Co in Ba(Fe_{1-x}Co_x)₂As₂ [21] which is akin to electron doping or Ba atoms are replaced by potassium giving rise to hole doped Ba_{1-x}K_xFe₂As₂ [4]. These replacements take up equivalent crystallographic sites preserving the *I*4/*mmm* space group [29] as the atomic radii between Ba and K or Fe and Co do not deviate substantially from each other¹.

¹The deviations between the radii are of the order of ~ 5 pm: $r_{Ba} = 215$ pm, $r_K = 220$ pm; $r_{Co} = 140$ pm, $r_{Fe} = 135$ pm. From Ref. [46].



Figure 2.1: Tetragonal unit cells of BaFe₂As₂ and CaKFe₄As₄ as indicated. (a) The Ba atoms (cyan) occupy the corners as well as the centre of the unit cell. The Fe (red) and As (green) atoms of the Fe-As layers in the a-b plane. Ba (Fe) atoms can be randomly replaced by K (Co) yielding Ba_{1-x}K_xFe₂As₂ (Ba(Fe_{1-x}Co_x)₂As₂) which preserves the I4/mmm space group. (b) The Fe-As layers are separated by alternating layers of Ca (blue) and K atoms (yellow) giving rise to the P4/mmm space group in which the upper As atoms As(1) are to be distinguished from the lower As(2) atoms.

In contrast, the mismatch of the atomic radii of Ca and K of the order ~ 40 pm facilitates the formation of the P4/mmm space group [29] in which the Fe-As layers are separated by alternating layers of Ca and K. Thus, the positions of the As atoms become distinguishable and the following notation is introduced: As(1) indicates the As atoms associated with the Ca layers and the As(2) the As atoms closer to K layer. Thus, the primitive unit cell of CaKFe₄As₄ is twice as large as that of BaFe₂As₂. This has a profound effect on the number of Raman-active phonons as described in Ref. [47] and appendix A.

As the electronic interactions contributing to superconductivity in the FeSC

lie in the focus of this thesis, we turn to the Fe-As layers which carry the electronic properties [48].

The pseudo-3D representation of these Fe-As layers is drawn in Fig. 2.2 (a) with the As atoms in green (out-of-plane) and the Fe atoms in red (in-plane). At this point, it is useful to define two unit cells: the crystallographic 2-Fe unit cell (red) and the electronic 1-Fe unit cell (dark blue). The electronic properties are dominated by the Fe 3*d* orbitals [26] depicted in panel (c). Therefore, the 1-Fe unit cell captures the essential electronic properties [49] discussed throughout this thesis. For completeness: the magnetic SDW phase present in the BaFe₂As₂ compounds, but not in CaKFe₄As₄, where hopping via the As atoms occurs [26] requires the use of the 2-Fe unit cell. Here, the As superstructure introduces an additional translational symmetry with the vector (π , π). As the SDW phase was not subject of scrutiny in this thesis, the results are given with respect to the 1-Fe unit cell, if not indicated otherwise.

The first Brillouin zone (BZ) of this 1-Fe unit cell is presented in Fig. 2.2 (b). For both, BaFe₂As₂ and CaKFe₄As₄, three hole pockets h^+ are located at the Γ point [30, 50–52] represented as idealised circular Fermi surfaces in blue.



Figure 2.2: (a) Quasi-2D unit cell from the Fe-As layers with the crystallographic 2-Fe unit cell (black) and the electronic 1-Fe unit cell (dark blue). (b) Brillouin zone of the 1-Fe unit cell with schematics of the idealised hole (blue) and electron (red) pockets at the Γ , *X* and *Y* points. (c) 3*d* orbitals contributing to the electronic structure of BaFe₂As₂ and CaKFe₄As₄ from Ref. [23].

At the *X* and *Y* points, in turn, one finds two electron pockets e^{-} [30, 50–52], where the shape of these pockets differ from each other in BaFe₂As₂ and

CaKFe₄As₄. In the BaFe₂As₂ compounds, they are more elliptic, while being rather isotropic in CaKFe₄As₄. For hole and electron pockets, the experimental evidence [30, 50–52] is well in agreement with theoretical band structure calculations [53, 54]. Additionally, the effect of atomic substitution in the BaFe₂As₂ compounds showed a drastic effect on the topology of the Fermi surfaces. In the hole-doped Ba_{1-x}K_xFe₂As₂ the K substitution expands the pockets at the Γ point and shrinks the electron pockets [50, 55]. In contrast, electron doping in Ba(Fe_{1-x}Co_x)₂As₂ yields the opposite effect [56, 57]. This drastic change of the Fermi surface topology due to doping is accompanied by a variety of phases described in the next section.

2.2 Phase diagram

The phase diagrams of $Ba_{1-x}K_xFe_2As_2$ and $Ba(Fe_{1-x}Co_x)_2As_2$ are depicted in Fig. 2.3, where the phase separation lines are drawn as a function of the normalised doping x/x_c . At the critical doping x_c the superconducting transition temperature T_c is maximal and reaches 38 K for $Ba_{1-x}K_xFe_2As_2$. CaKFe₄As₄ is similar to optimally or overdoped $Ba_{1-x}K_xFe_2As_2$, when it comes to the transport and thermodynamic properties [58]. These similarities include the electronic structure. In particular the Fermi surfaces and the superconducting energy gaps can be treated in a similar fashion [30]. Upon doping CaKFe₄As₄, T_c decreases [33] suggesting CaKFe₄As₄ to be intrinsically optimally doped. Concomitantly, CaKFe₄As₄ exhibits no other phase transition apart from superconductivity.

For electron-doped Ba(Fe_{1-x}Co_x)₂As₂, the superconducting dome has its maximum at $T_c = 24.6$ K for $x_c \approx 0.060$. This critical concentration coincides with the end point of the phase separation line of the nematic phase at T = 0. In contrast to Ba_{1-x}K_xFe₂As₂ [59], the nematic and SDW phase have two separate transition lines for x > 0 and the nematic transition is of second order [60,61].



Figure 2.3: Phase diagrams of hole doped $Ba_{1-x}K_xFe_2As_2$ and electron doped $Ba(Fe_{1-x}Co_x)_2As_2$ as a function of the normalised doping x/x_c . The maximum transition temperature T_c^{max} is 38 K and 24.6 K for $Ba_{1-x}K_xFe_2As_2$ and $Ba(Fe_{1-x}Co_x)_2As_2$, respectively. The orange circles indicate the position of the QCP beneath the superconducting dome [62]. The grey area indicates the spin-density-wave and the magenta stripe is the nematic phase. These transitions coincide in $Ba_{1-x}K_xFe_2As_2$. Data adopted from Ref. [19] and Ref. [22].

Fluctuations can be observed over a wide doping range, preceding the magneto-structural transition in $Ba_{1-x}K_xFe_2As_2$ and the nematic phase in $Ba(Fe_{1-x}Co_x)_2As_2$. These fluctuations are most likely magnetic in origin for underdoped $Ba(Fe_{1-x}Co_x)_2As_2$ [44] and may give relevant information about the superconducting ground state [63].

2.2.1 Spin-density-wave and nematicity

The interplay of the nematic and magnetic order in iron-based superconductors are well described by Fernades *et al.* in Ref. [63]. On the basis of this article, these transitions shall be outlined here. The SDW phase is a stripe-like magnetic order breaking the spin-rotational O(3) symmetry. This is illustrated in Fig. 2.4 (a). The corresponding ordering vectors are either $\mathbf{Q}_X = (\pi, 0)$ or $\mathbf{Q}_Y = (0, \pi)$ in momentum space. The SDW phase is characterised by the spins being oriented parallel along one direction and anti-parallel along the other. This breaks the Z_2 symmetry as below T_{SDW} the system decides between one of the two directions. One can express the breaking of these symmetries in terms of the order parameters in momentum space

$$\mathbf{M}_{\mathbf{X}} = \sum_{\mathbf{k}} c^{\dagger}_{\mathbf{k}+\mathbf{Q}_{\mathbf{X},\alpha}} \sigma_{\alpha,\beta} c_{\mathbf{k},\beta}$$
(2.1a)

$$\mathbf{M}_{\mathrm{Y}} = \sum_{\mathbf{k}} c^{\dagger}_{\mathbf{k}+\mathbf{Q}_{\mathrm{Y},\alpha}} \sigma_{\alpha,\beta} c_{\mathbf{k},\beta}$$
(2.1b)

associated with the directions \mathbf{Q}_X and \mathbf{Q}_Y , where $c_{\mathbf{k}+\mathbf{Q}_X,\alpha}^{\dagger}$ is the fermionic creation operator for a particle having momentum $\mathbf{k} + \mathbf{Q}_X$ and spin α , and $\sigma_{\alpha,\beta}$ are the Pauli spin operators. Below T_{SDW} , the magnetisation $\langle \mathbf{M}_X \rangle$ is different from zero along the ferromagnetically ordered axis and zero along the anti-ferromagnetically ordered axis $\langle \mathbf{M}_Y \rangle$ or vice versa. The breaking of the Z_2 symmetry corresponds to unequal magnetisations: $\langle \mathbf{M}_X^2 \rangle \neq \langle \mathbf{M}_Y^2 \rangle$. It is convenient to describe this in terms of the order parameters of two sublattices with $\mathbf{M}_1 = \mathbf{M}_X + \mathbf{M}_Y$ and $\mathbf{M}_2 = \mathbf{M}_X - \mathbf{M}_Y$ as indicated in green and yellow in Fig. 2.4 (a). Thus, within the magnetic phase, these are $\langle \mathbf{M}_i \rangle \neq 0$ and $\langle \mathbf{M}_1 \cdot \mathbf{M}_2 \rangle = \pm 1$. Nematic order can be placed in this framework as a state in which the Z_2 symmetry is broken and therefore $\langle \mathbf{M}_1 \cdot \mathbf{M}_2 \rangle = \pm 1$ holds. Yet at the same time, the spin-rotational symmetry is preserved as $\langle \mathbf{M}_i \rangle = 0$.



Figure 2.4: Real and momentum space nematic order representation. (a) The stripe-like order in real space consists of two interlocked Neél sublattices with magnetisations \mathbf{M}_1 and \mathbf{M}_2 which are given by the magnetic order parameters in momentum space \mathbf{M}_X and \mathbf{M}_Y with $\mathbf{M}_{1,2} = \mathbf{M}_X \pm \mathbf{M}_Y$. (b) Magnetic susceptibility $\chi(\mathbf{q})$ in the BZ. Above T_s $\langle M_X^2 - M_Y^2 \rangle \equiv \langle \mathbf{M}_1 \cdot \mathbf{M}_2 \rangle = 0$. For $T_{\text{SDW}} < T < T_s \langle M_X^2 - M_Y^2 \rangle \equiv \langle \mathbf{M}_1 \cdot \mathbf{M}_2 \rangle \neq 0$. From [63].

Fig. 2.4 (b) illustrates nematic order by means of the magnetic susceptibility $\chi(\mathbf{q})$ which is plotted within the first BZ. Above the nematic transition, the susceptibility is equal $\chi(\mathbf{Q}_X) = \chi(\mathbf{Q}_Y)$ at the ordering vectors and $\langle \mathbf{M}_i \rangle = \langle \mathbf{M}_1 \cdot \mathbf{M}_2 \rangle = 0$. This means, that both directions are equivalent, and no long-range order is established. Below the nematic transition temperature T_{nem} , $\chi(\mathbf{Q}_X)$ is not equivalent to $\chi(\mathbf{Q}_Y)$ and $\langle \mathbf{M}_1 \cdot \mathbf{M}_2 \rangle = \pm 1$ but $\langle \mathbf{M}_i \rangle = 0$. Within this spin-driven scenario, it is the spin-nematicity which gives rise to the orthorhombic distortion of the lattice corresponding to the structural transition at T_s .

Nematicity in FeSC could be explained in terms of orbital [64–66] or charge [67, 68] degrees of freedom rather than spin degrees of freedom as well. A previous study [44] favours a spin-driven scenario at least for Ba(Fe_{1-x}Co_x)₂As₂.

2.2.2 Superconductivity

Superconductivity, in turn, might be influenced by the same kind of interaction which affect the magneto-nematic transition and interrelated with nematicity as illustrated in Fig. 2.5.



Figure 2.5: Magnetic versus charge fluctuations dominating the phase transitions in the pnictides. On the left hand side, the SDW phase as well as the spin-nematic state come about due to spin-fluctuations. The corresponding superconducting ground state has s^{\pm} symmetry. On the right hand side, charge fluctuations lead to a charge-density-wave and a ferro-orbital nematic phase. This ferro-orbital ordering leads to the SDW. The superconducting ground state corresponding to charge fluctuations has s^{++} symmetry. From Ref. [63].

On the left side, the dominant interaction in form of spin fluctuations may lead to both, the SDW as well as the spin-nematic state connecting the Fermi sheets at the Γ and X, Y points with the ordering vector $\mathbf{Q}_{X,Y}$. Then a superconducting state having s^{\pm} symmetry forms due to the same repulsive interband interaction. On the other hand, the orbital or charge fluctuations with an attractive interaction could yield a charge-density-wave (CDW) and a ferro-orbital state. The nematic

order yields the SDW phase. Consequently, the superconducting ground state arising from this interaction would have s^{++} symmetry.



Figure 2.6: Superconducting order parameter for different pairing symmetries on Fermi surfaces in a quasi-2D BZ. The colours indicate the different signs of the order parameter. From [26].

Generally, the symmetry of the order parameter in the pnictides is not universally agreed on. This makes the situation here distinct from the situation in the cuprates where the *d*-wave nature of the order parameter is well established [69, 70]. In the case of the BaFe₂As₂ systems, the candidates describing the dominant interaction generally boil down to *s*-wave symmetry, i.e. transforming like A_{1g} [26,71]. This can either mean an s^{\pm} or an s^{++} ground state, depending on the sign of the interaction mediating the Cooper pairing. In Fig. 2.6 different order parameters are displayed within the first BZ. The s^{++} ground state is characterised by the same sign on the different FS sheets which is in contrast to the sign-changing character of the s^{\pm} ground state. For nodal s^{\pm} symmetry, the order parameter changes sign within individual bands. The *d*-wave symmetry, although not dominating the interaction in the BaFe₂As₂ compounds, may be present as a subleading interaction in at least some of the pnictides such as $Ba_{1-x}K_xFe_2As_2$ and CaKFe₄As₄ which will be discussed in chapter 5.



Figure 2.7: BZ of the 1-Fe unit cell with sketches of the band structure as derived from ARPES experiments for CaKFe₄As₄ and Ba_{0.65}K_{0.35}Fe₂As₂. (a) Three hole bands (α , β , γ) at the Γ point were resolved for CaKFe₄As₄ by Mou *et al.* [30]. One single electron band (δ) was found at the *X* point. (b) For Ba_{0.65}K_{0.35}Fe₂As₂, two hole bands (*h*1, *h*3) were resolved at the Γ point. Two electron bands *e*1 and *e*2 were found at the *X* and *Y* point, respectively. From Nakayama *et al.* [72].

To prelude these results, a qualitative comparison of the band structure in CaKFe₄As₄ and Ba_{0.65}K_{0.35}Fe₂As₂ is given in Fig. 2.7 as derived from angleresolved photo emission spectroscopy (ARPES). Greek letters correspond to the bands in CaKFe₄As₄. In Ba_{0.65}K_{0.35}Fe₂As₂, the hole and electron bands are indexed as (h1, h2, h3) and (e1, e2), respectively. The band h2 was not resolved by Nakayama *et al.* [72], and is most likely similar in size as h1 [23]. The comparison between the gap energies of CaKFe₄As₄ and Ba_{0.65}K_{0.35}Fe₂As₂ found by ARPES are summarised in Tab. 2.1. The ARPES gap energies are similar in magnitude. This is true particularly for the β band of CaKFe₄As₄ and the h1band of Ba_{0.65}K_{0.35}Fe₂As₂ and the electron bands.

Thus, the similarities between $CaKFe_4As_4$ and $Ba_{0.65}K_{0.35}Fe_2As_2$ inferred earlier extend to their electronic band and gap structure. Chapter 5 explores the

spectroscopic similarities found in the inelastic light scattering data.

Table 2.1: Comparison of twice the gap energies from ARPES data on $CaKFe_4As_4$ [3]	30]
and $Ba_{0.65}K_{0.35}Fe_2As_2$ [72].	

	CaKFe ₄ As ₄		$Ba_{0.65}K_{0.35}Fe_2As_2$	
band index <i>i</i>	$2\Delta_i^{\text{ARPES}}$ (meV)	band index <i>i</i>	$2\Delta_i^{\text{ARPES}}$ (meV)	
α	21	h1	24.6	
β	24			
γ	16	h3	12	
δ	24	e1	24.4	
		e2	23	

The second part of this thesis is the investigation of fluctuations above the superconducting dome in the electron doped $Ba(Fe_{1-x}Co_x)_2As_2$ which may originate from a quantum critical point (QCP) located at optimal doping [73,74].

QCPs in metals have been discussed for many years [75–79] and are thought to enhance superconductivity. Recently, it has been suggested, that this enhancement might be present close to a nematic QCP as well [37] which may reside underneath the superconducting dome. This will be described in the next section.

2.2.3 Quantum phase transitions

A quantum critical point (QCP) [80] is a second order phase transition at T = 0. While the QCP itself is inaccessible by its very nature, the QCP leads to quantum fluctuations which can extend over a wide temperature range and may be probed by different methods [73,74,81–83].

QCPs might be relevant to the formation of superconducting domes [84]. Their fluctuations may play the role of exchange bosons mediating the Cooper pairing [78,85]. In fact, there are theoretical calculations [35,84] which suggest, that a QCP always leads to superconductivity. To illustrate this in a qualitative manner², consider Fig. 2.8.

 $^{^2 {\}rm The}$ description is based on a talk by A. Chubukov [86] where the general ideas behind Ref. [35] are outlined.



Figure 2.8: (a) Phase diagram. The blue area represents a long-range order (LRO). The orange area is the superconducting dome. The purple circle indicates the location of the QCP. (b) Feynman diagrams of the competing mechanisms: the pair bonding of fermions (arrows) via a bosonic mode (wavy line) with interaction constant g_p leading to superconductivity and fermionic self energy effects with interaction constant g_{Σ} . (c) The $T - (g_{\Sigma}/g_p)^2$ phase diagram. Below a critical threshold indicated by the purple circle the system develops superconductivity at T = 0. Above this threshold, superconductivity is present for T > 0 and vanishes at T = 0. The qualitative behaviour of the anomalous vertex ϕ_{Ω} along the path A and path B is depicted in (d1) and (d2). Path A develops superconductivity down to T = 0. Path B develops superconductivity for $0 < T < T_c$ which vanishes at T = 0. Adapted from Ref. [86].

In panel (a) we find a T-x phase diagram with a tuning parameter x being, e.g. pressure or doping. Within the blue phase, the system exhibits a

magnetic long-range order (LRO). Following the phase separation line of this second order phase transition down to zero temperature, one finds a quantum critical point (QCP) above which a superconducting dome may exist. The competing interactions at T = 0 are depicted in panel (b). The first diagram represents the pair bonding interaction of two fermions (straight lines) via a bosonic mode (wavy line) with interaction constant g_p . This pairing mechanism competes with self-energy effects depicted in the second diagram (Schwinger-Dyson, *cf.* [87,88]) in which the interaction constant is g_{Σ} . The self-energy effects are destroying fermionic coherence, thereby preventing a superconducting ground state from forming. Using an Eliashberg-like approach for this problem, one can calculate the anomalous vertex ϕ which is not explicitly shown here. The reader is referred to Ref. [35] for details instead.

The conclusion of this calculation is represented in Fig. 2.8 (c). Here, $(g_{\Sigma}/g_p)^2$ is drawn as a function of temperature T. At T = 0 one finds two distinct regimes: superconductivity below and Fermi liquid behaviour above a certain threshold marked by the purple circle. The calculations of the anomalous vertex ϕ however gives a finite T_c for T > 0 regardless of the ratio $(g_{\Sigma}/g_p)^2$. This becomes clear by considering the two paths A and B through the phase diagram which yield a different temperature dependence of ϕ as depicted in panels (d1) and (d2). Along path A, ϕ_{Ω} is finite for $T < T_c$ and especially at T = 0. Path B [panel (d2)] exhibits superconductivity only for the temperature window $0 < T < T_c$. At T = 0, the self-energy



Figure 2.9: Nematic quantum critical point. The blue shaded area shows the nematic phase as a function of the tuning parameter x. A nematic QCP is found at x_c . The red dashed line shows the pairing eigenvalue λ . From [37]. The black-dashed line indicates the disordered regime.

effects destroy the fermionic coherence and $\phi_{\Omega} = 0$. One is left with a non-

superconducting ground state at T = 0. Thus: a QCP may induce superconductivity at temperature T > 0, even if the destruction of fermionic coherence at T = 0 yields a non-superconducting state.

Not only is a QCP considered to induce superconductivity at finite T_c , it may also play a role by just enhancing T_c . Lederer *et al.* [37] investigated the enhancement of superconductivity due to a nematic quantum critical point (NQCP). A sketch of the weak-coupling scenario is depicted in Fig. 2.9 where we follow the nematic phase down to zero transition temperature. Again, we find a quantum critical point, this time associated with the nematic long-range order. From this NQCP, a critical interaction $V^{(ind)}$ contributes to the effective interaction

$$V_{k,k'}^{(\text{eff})} = V_{k,k'}^{(0)} + V_{k,k'}^{(\text{ind})}$$
(2.2)

in which $V^{(0)}$ is the direct interaction between the electrons of a Cooper pair. $V^{(\text{ind})}$ results from fluctuations of the NQCP which play the role of the interaction bosons. This interaction is attractive in all channels, therefore contributing to the pairing regardless of the exact form of $V^{(0)}$. With this, one finds the gap equation

$$\int d\hat{k}' \, \tilde{V}_{\hat{k},\hat{k}'}^{(\text{eff})} \phi_{\hat{k},\hat{k}'}^{(a)} = -\lambda_a \phi_{\hat{k}}^{(a)} \tag{2.3}$$

where $\phi_{\hat{k},\hat{k}'}^{(a)}$ is the pair wave function, and λ_a are the eigenvalues. $\tilde{V}_{\hat{k},\hat{k}'}^{(\text{eff})}$ is the effective renormalised interaction, now consisting of an renormalised interaction term

$$V^* = \frac{V^{(0)}}{1 + V^{(0)} \log(W/\Omega)}$$
(2.4)

which introduces a high energy cutoff *W* and in which Ω results from Landau damping. From Eqn. 2.3, *T*_c is determined by the largest $\lambda_a \equiv \lambda$ via

$$T_{\rm c} \sim \exp\left[-1/\lambda\right]. \tag{2.5}$$

Treating the indirect interaction by means of first order perturbation theory, one

can write λ_a as

$$\lambda_a = \lambda_a^{(*)} + \delta \lambda_a^{(\text{ind})} \tag{2.6}$$

with $\lambda_a^{(*)}$ being the eigenvalue of the renormalised direct interaction and $\delta \lambda_a^{(ind)}$ of the indirect direction being treated as perturbative term. T_c is then renormalised

$$T_{\rm c} \sim T_{\rm c}^{(0)} \exp\left[\delta \lambda^{(\rm ind)} / (\lambda^{(0)})^2\right].$$
 (2.7)

with $\lambda^{(0)}$ being the eigenvalue of $V^{(0)}$. This means, that T_c can grow considerably for $\delta \lambda^{(\text{ind})} >> (\lambda^{(0)})^2$ if one approaches the nematic quantum critical point [37].

Generally, the rules of the superconducting pairing in systems having a QCP are not entirely understood [89]. This motivates the experimental work on this phenomenon. As shall be seen in chapter 6, Raman spectroscopy proves to be a tool to investigate quantum critical fluctuations.

2.2. Phase diagram

Chapter 3

Raman spectroscopy

The following chapter gives an overview of Raman spectroscopy [90–93] with an emphasis on inelastic light scattering from electrons, and how experimental quantities are derived from general arguments about the crystal symmetry. For an in-depth analysis, the reader is referred to Ref. [94].

3.1 Principles of Raman scattering

Raman scattering represents an inelastic photon-in photon-out process. To illustrate the underlying effect (see Fig. 3.1), we assume an isolated, non-interacting electron to be in a state $|i\rangle$ with corresponding energy E_i . At $t_1 = 0$, a photon with momentum \mathbf{k}_i , energy ω_i and polarisation \mathbf{e}_i induces a first transition of the electron into a virtual state $|\nu\rangle$ with energy E_{ν} . This transition leaves a hole in the state $|i\rangle$. As the virtual state is short lived by nature, the second transition occurs within a time $\Delta t < \hbar/\Delta E$. Upon emitting a photon with momentum \mathbf{k}_s , energy ω_s and polarisation \mathbf{e}_s , the electron relaxes from $|\nu\rangle$ into its final state $|f\rangle$ having energy E_f . Electron and hole form a quasiparticle, an exciton, with frequency Ω and momentum \mathbf{q} which are given by the conservation laws for energy and momentum:

$$\Omega = \omega_i - \omega_s \tag{3.1}$$

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s \tag{3.2}$$



Figure 3.1: Sketch of the Raman effect with energy E vertically and time *t* horizontally. The incident photon of momentum \mathbf{k}_i , energy ω_i and polarisation vector \mathbf{e}_i excites an electron (orange) from the initial state $|i\rangle$ into a virtual state $|v\rangle$ leaving a hole (orange circle) in state $|i\rangle$. Upon relaxation into a final state $|f\rangle$ with $E_f \neq E_i$, a photon is emitted with momentum \mathbf{k}_s , energy ω_s and polarisation vector \mathbf{e}_s creating an electron-hole pair (exciton) having momentum \mathbf{q} and energy Ω .

Ω represents the shift in frequency which is called the Raman shift. It is a quantity measured relative to the initial energy $ω_i$ and thus may be negative for $ω_s > ω_i$. This is called anti-Stokes process in contrast to the Stokes process for $ω_s < ω_i$. The probability for the former is decreased by a factor exp[-βΩ]. The anti-Stokes process will not be used in this thesis.

3.2 Theory

The observation of real many-body states by Raman spectroscopy demands a more sophisticated mathematical approach. Experimentally, one measures the rate of the photons $\dot{N}(\Omega, T)$ scattered from the many-body electronic system into a solid angle $[\tilde{\Omega}, \tilde{\Omega} + d\tilde{\Omega}]$ and a frequency window of $[\omega_s, \omega_s + d\omega_s]$. A schematic of a Raman spectrum is shown in 3.2 in which \dot{N} is measured as a function of the Raman shift. The yellow shaded area results from elastic scattering (Rayleigh). The red shaded area corresponds to particle-hole excitations (excitons) and the blue peaks indicate vibrational excitations (phonons) which sit on top of the particle-hole continuum. The anti-Stokes regime ($\omega_s > \omega_i$) is accessible but is



Figure 3.2: Schematic of a Raman spectrum. The yellow line shows the response from elastic scattering at $\Omega = 0$ due to Rayleigh scattering. Phonon modes (blue) at Ω_1 and Ω_2 may sit superimposed on top of a particle-hole continuum (red). If these phonons are already thermally activated, they can be destroyed, yielding the response at $-\Omega_1$ and $-\Omega_2$. As these processes are exponentially damped down, they are challenging to detect in an experiment. From Ref. [97].

used only for temperature determination or special applications such as coherent anti-Stokes Raman scattering (CARS) [95,96].

Now it will be outlined how the scattering rate \dot{N} is related to the effective density-density correlation function. It is started with the fact, that \dot{N} is proportional to the differential cross section

$$\dot{N}(\Omega,T) \propto \frac{\partial^2 \sigma}{\partial \tilde{\Omega} \partial \omega_s}.$$
 (3.3)

The differential cross section is connected to the transition rate ${\cal R}$

$$\frac{\partial^2 \sigma}{\partial \tilde{\Omega} \partial \omega_s} = \hbar r_0^2 \frac{\omega_s}{\omega_i} \mathcal{R}$$
(3.4)

with the Planck constant \hbar and the Thomson radius r_0 . \mathcal{R} is given by Fermi's

golden rule

$$\mathcal{R} = \frac{1}{\mathcal{Z}} \sum_{I,F} \exp\left[-\beta E_I\right] |\langle F|M|I\rangle|^2 \delta(E_F - E_I - \hbar\Omega)$$
(3.5)

with the partition function Z and the inverse temperature $\beta = 1/k_BT$. The energies E_I and E_F correspond to the initial and final state $|I\rangle$ and $|F\rangle$, respectively. The δ function ensures energy conservation. The differential cross section is depending on the square of the Raman matrix element $M_{F,I} = \langle F | M | I \rangle$ in which M is the transition operator. In an electronic many-body state, this transition operator is determined by the interaction terms which are part of the Hamiltonian [94, 98, 99]

$$\mathcal{H} = \mathcal{H}' + \underbrace{\frac{e}{2mc}\sum_{i} \{\hat{\mathbf{p}}_{i}, \hat{\mathbf{A}}(\mathbf{r}_{i})\}}_{i} + \underbrace{\frac{e^{2}}{2mc^{2}}\sum_{i} \hat{\mathbf{A}}(\mathbf{r}_{i}) \cdot \hat{\mathbf{A}}(\mathbf{r}_{i})}_{i}$$
(3.6)

current-photon interaction charge-photon interaction

where *e* is the electric charge, *m* the electron mass, *c* the speed of light, $\hat{\mathbf{p}}$ the momentum operator and $\hat{\mathbf{A}}$ the vector potential operator. $\mathcal{H}' = \mathcal{H}_0 + \mathcal{H}_{\text{fields}}$ is the Hamiltonian of the electronic many-body state with $\mathcal{H}_0 = 1/2m \sum_i \hat{\mathbf{p}}_i^2 + \mathcal{H}_{\text{Coulomb}}$ and the free electromagnetic part $\mathcal{H}_{\text{fields}}$. The two underbraces in Eqn. 3.6 indicate the current interaction and the charge interaction. The explicit form of the vector potential operator $\hat{\mathbf{A}}(\mathbf{r}_i)$ is

$$\hat{\mathbf{A}}(\mathbf{r}_i) = \sum_{\mathbf{q}} \sqrt{\frac{hc^2}{\omega_{\mathbf{q}}V}} \exp\left[i\mathbf{q}\cdot\mathbf{r}_i\right] \left[\hat{\mathbf{e}}_{\mathbf{q}}a_{-\mathbf{q}} + \hat{\mathbf{e}}_{\mathbf{q}}^*a_{\mathbf{q}}^{\dagger}\right]$$
(3.7)

with $\omega_{\mathbf{q}}$ being the photon frequency and $\hat{\mathbf{e}}_{\mathbf{q}}$ the polarisation direction. $a_{\mathbf{q}}^{\dagger}$ and $a_{\mathbf{q}}$ are the creation and annihilation operators of the photons, respectively. The polarisation dependence of the electromagnetic field operator appears in the derivation of the Raman cross section and is encapsulated in the Raman scattering amplitude $\gamma(\mathbf{k}, \mathbf{q})$ [100]. In the case of weakly interacting fermions, the current-photon and charge-photon interaction in Eqn. 3.6 can be treated by means of second and first order perturbation theory, respectively. Simplifying by using

commutator algebra, one finds an expression for $M_{F,I}$ of the form

$$M_{F,I} = \sum_{\alpha,\beta} \gamma_{\alpha,\beta} \langle F | c_{\alpha}^{\dagger} c_{\beta} | I \rangle$$
(3.8)

in which c_{α}^{\dagger} , c_{β} are fermionic creation and annihilation operators. The factor $\gamma_{\alpha,\beta}$ is

$$\gamma_{\alpha,\beta} = \rho_{\alpha\beta}(\mathbf{q}) \,\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_s + \frac{1}{m} \sum_{\beta'} \left(\frac{p^s_{\alpha,\beta'} p^i_{\beta',\beta}}{E_\beta - E_{\beta'} + \hbar\omega_i} + \frac{p^i_{\alpha,\beta'} p^s_{\beta',\beta}}{E_\beta - E_{\beta'} - \hbar\omega_s} \right). \tag{3.9}$$

The matrix element is thus connected to the matrix element of the single particle density fluctuation $\rho_{\alpha,\beta}(\mathbf{q}) = \langle \alpha | \exp[i\mathbf{q} \cdot \mathbf{r}] | \beta \rangle$ and the momentum density matrix $p_{\alpha,\beta}^{i,s}(\mathbf{q}) = \langle \alpha | \mathbf{p}\mathbf{e}_{i,s} \exp[i\mathbf{q}_{i,s}\mathbf{r}] | \beta \rangle$. Indexing the states with momentum quantum numbers, the matrix element $M_{F,I}$ may be transformed into the effective density

$$\tilde{\rho}(\mathbf{q}) = \sum_{\mathbf{k},\sigma} \gamma(\mathbf{k}, \mathbf{q}) c^{\dagger}_{\mathbf{k}+\mathbf{q},\sigma} c_{\mathbf{k},\sigma}$$
(3.10)

with momentum index **k** and spin σ . Here, $c_{\mathbf{k}+\mathbf{q},\sigma}^{\dagger}$ and $c_{\mathbf{k},\sigma}$ describe the scattering of a fermion from a state (**k**, σ) into a state (**k** + **q**, σ) which is weighted by the Raman scattering amplitude $\gamma(\mathbf{k}, \mathbf{q})$. Plugging the effective density into Eqn. 3.5 and expressing the δ function as a time integral, the scattering rate is rewritten as

$$\mathcal{R} = \sum_{I} \frac{\exp\left[-\beta E_{I}\right]}{\mathcal{Z}} \int dt \, \exp\left[i\Omega t\right] \langle I|\,\tilde{\rho}(\mathbf{q},t)\tilde{\rho}(-\mathbf{q},0)\,|I\rangle\,.$$
(3.11)

This expression can be connected to the correlation function given by the effective density which reads

$$\tilde{S}(\mathbf{q}, i\Omega) = \sum_{I} \frac{\exp[-\beta E_{I}]}{\mathcal{Z}} \int d\tau \exp[i\Omega\tau] \langle I | T_{\tau} \tilde{\rho}(\mathbf{q}, \tau) \tilde{\rho}(-\mathbf{q}, 0) | I \rangle$$
(3.12)

where τ is the complex time. To get a real-frequency expression, one deploys the analytic continuation from the imaginary to the real axis which is $i\Omega \rightarrow \Omega + i0$. The cross section is then given in terms of the effective density-density correlation

function:

$$\frac{\partial^2 \sigma}{\partial \tilde{\Omega} \partial \omega_s} = \hbar r_0 \frac{\omega_s}{\omega_i} \tilde{S}(\mathbf{q}, i\Omega \to \Omega + i0)$$
(3.13)

Furthermore, the differential cross section can be connected to the effective charge density susceptibility

$$\tilde{\chi}(\mathbf{q},\Omega) = \langle \langle [\tilde{\rho}(\mathbf{q}), \tilde{\rho}(-\mathbf{q})] \rangle \rangle_{\Omega}$$
(3.14)

via the fluctuation-dissipation theorem [101], as

$$\tilde{S}(\mathbf{q}, \Omega) = -\frac{1}{\pi} (1 + n(\Omega, T)) \operatorname{Im}[\tilde{\chi}(\mathbf{q}, \Omega)]$$
(3.15)

with the Bose-Einstein distribution $n(\Omega, T)$. Therefore, the response function χ can be linked to the experimentally measured scattering rate \dot{N} , as aimed for in the beginning of this section. The next section shall explore how one can utilise the modulation of the charge fluctuations from light scattering by using group arguments.

3.3 Selection rules

In the limit $\mathbf{q} \rightarrow 0$, the matrix element $M_{F,I}$ can be written as [102–106]

$$M_{F,I}(\mathbf{q}\to 0) = \sum_{\mu} M_{\mu} \Phi_{\mu}$$
(3.16)

where μ is the irreducible representation of the point group and Φ_{μ} the basis functions. For the D_{4h} point group which is appropriate for the materials discussed in chapter 2, this reads:
$$M_{F,I} = \frac{1}{2} \hat{O}_{A_{1g}^{(1)}}(e_i^x e_s^x + e_i^y e_s^y) + \frac{1}{2} \hat{O}_{A_{1g}^{(2)}}(e_i^z e_s^z) + \frac{1}{2} \hat{O}_{B_{1g}}(e_i^x e_s^x - e_i^y e_s^y) + \frac{1}{2} \hat{O}_{B_{2g}}(e_i^x e_s^y - e_i^y e_s^x) + \frac{1}{2} \hat{O}_{A_{2g}}(e_i^x e_s^y - e_i^y e_s^x) + \frac{1}{2} \hat{O}_{E_{g}^{(1)}}(e_i^x e_s^z + e_i^z e_s^x) + \frac{1}{2} \hat{O}_{E_{g}^{(2)}}(e_i^y e_s^z + e_i^z e_s^y)$$
(3.17)

with the projected operators \hat{O}_{μ} and the light polarisations $e_{i,s}^{\alpha}$. The choice of these light polarisations selects the corresponding operators. If the light polarisations are parallel to the *a-b* planes, one projects out a mixture of symmetries. For instance, the polarisation configuration $e_i^x e_i^y$ collects B_{2g} and A_{2g} terms. Considering, that $\langle \hat{O}_{\mu}^{\dagger} \hat{O}_{\mu'} \rangle = R_{\mu} \delta_{\mu,\mu'}$, the mixed terms in Eqn. 3.5 vanish and therefore $\mathcal{R} \sim R_{B_{2g}} + R_{A_{2g}}$.

The matrix element is proportional to the Raman vertex $\gamma(\mathbf{k}, \mathbf{q} \rightarrow 0)$. Therefore the crystal harmonics by and large determine the Raman cross section.

Fig. 3.3 depicts the three polarisation configurations which were mainly utilised during this thesis. The upper row shows the 1-Fe unit cell with the iron atoms as red spheres. The arrows correspond to the polarisation vectors which project out sums of symmetries. The A_{2g} response has been shown to be weak, flat and temperature independent for the pnictide systems [23,97,107].

The dominant contributions to the scattering amplitude stem from the A_{1g}, B_{1g} and B_{2g} symmetries, respectively. The second row shows the BZ of the 1-Fe unit cell with idealised hole and electron pockets as black circles (see chapter 2). The colours indicate the sign of the scattering amplitude γ_{μ} . This illustrates the utility of Raman spectroscopy: controlling the polarisation of the incident and scattered photons, one can target different parts of the Brillouin zone. For the A_{1g} symmetry, the second order A_{1g} vertex $\gamma_{A_{1g}}^{(2)}$ captures the situation in the pnictides more accurately [28, 108].



Figure 3.3: Polarisation configurations and Raman vertices in the 1-Fe unit cell and corresponding BZ, respectively. First row: the blue arrow indicates the incident polarisation, the red arrow the scattered polarisation state with respect to the Fe-Fe bonds (black lines connecting red Fe atoms). (a) *RR* projects out symmetries $A_{1g} + A_{2g}$, (b) x'y' projects out $B_{1g} + A_{2g}$ and (c) xy correspondingly $B_{2g} + A_{2g}$. The second row shows the momentum dependence of the Raman vertex γ .

3.4 Response for interacting particles

Raman spectroscopy provides access to interacting fermion systems. In particular, the superconducting response [106, 109, 110] and the response from fluctuations are outlined next.

3.4.1 Interband superconductivity

The superconducting interactions in the pnictides are dominated by interband interactions which can be probed by Raman scattering. Fig. 3.4 (a) shows a schematic representation of the first BZ as discussed in chapter 2. One idealised hole pocket at the Γ point is connected via an *s*-wave interband interaction with electron pockets β_1 and β_2 at the *X* and *Y* points. The superconducting Raman response in lowest order can be described by the Feynman diagrams in panel (b) where *G* is the single particle Green's function [23]

$$G(\mathbf{k}, \mathrm{i}\omega_n) = -\frac{\mathrm{i}\omega_n + E_{\mathbf{k}}}{(\mathrm{i}\omega_n)^2 + E_{\mathbf{k}} + \Delta_{\mathbf{k}}^2}$$
(3.18)

with the Matsubara frequencies ω_n . *F* is the Gorkov Green's function

$$F(\mathbf{k}, i\omega_n) = \frac{\Delta_{\mathbf{k}}}{(i\omega_n)^2 + E_{\mathbf{k}} + \Delta_{\mathbf{k}}^2}.$$
(3.19)

One can derive an expression for the Raman response from

$$\operatorname{Im}\left[\chi(\Omega)\right] = \operatorname{Im}\left[\sum_{n,\mathbf{k}} \gamma_n^2(\mathbf{k}) \cdot \lambda_n(\mathbf{k},\Omega)\right]$$
(3.20)

with the Raman vertex $\gamma_n(\mathbf{k})$ and the Tsuneto function [100, 111, 112]

$$\lambda_n(\mathbf{k}, \mathrm{i}\Omega) = \frac{\Delta^2(\mathbf{k})}{E^2(\mathbf{k})} \cdot \tanh\left[\frac{E(\mathbf{k})}{2k_{\mathrm{B}}T}\right] \cdot \left[\frac{1}{2E(\mathbf{k}) + \mathrm{i}\Omega} + \frac{1}{2E(\mathbf{k}) - \mathrm{i}\Omega}\right]$$
(3.21)

Then, the Raman response from a single band *n* in lowest order [100,113] reads

$$\chi''(\Omega) = \frac{4\pi}{\Omega} \left\langle \frac{\gamma_n^2(\mathbf{k}) \cdot |\Delta_n(\mathbf{k})|^2}{\sqrt{\Omega^2 - |2\Delta_n(\mathbf{k})|^2}} \right\rangle$$
(3.22)

for frequencies $\Omega > 2\Delta_n$ and zero below which is depicted in Fig. 3.4 (b) for an isotropic gap $\Delta_n(\mathbf{k}) = \Delta_0$ at T = 0. For T > 0, instead of a divergence, a peak is present at approximately $2\Delta(T) < 2\Delta(T = 0)$.



Figure 3.4: (a) An *s*-wave interband interaction V_s is present between the hole pocket α at the Γ point and the electron pockets β_1 and β_2 at the *X* and *Y* points. (b) The superconducting response at *T* = 0 is zero below 2 Δ . The singularity at 2 Δ indicates the pair-breaking energy. The two Feynman diagrams build up the response. Adapted from [42].

This applies to B_{1g} and B_{2g} symmetries. In A_{1g} , the particle number conservation demands a renormalisation of the response via [23,113]

$$\chi(\Omega) = \sum_{n,\mathbf{k}} \gamma_n^2(\mathbf{k}) \cdot \lambda_n(\mathbf{k},\Omega) - \frac{\sum_{n,\mathbf{k}} \gamma_n(\mathbf{k})\lambda_n(\mathbf{k},\Omega)}{\sum_{n,\mathbf{k}} \lambda_n(\mathbf{k},\Omega)}.$$
(3.23)

The processes contributing to the superconducting Raman process are depicted in Fig. 3.5 (a) and (b). In a fully gapped system, a fermion is either lifted above twice the band-gap 2Δ or a Cooper pair is split.



Figure 3.5: (a) A fermion is lifted above the energy gap of 2Δ . (b) A Cooper pair in the *s*-wave channel is broken up. (c) This Cooper pair recombines in the subdominant *d*-wave channel. From [23,27,28].

We now turn to the case, where a subdominant interaction is present. Fig. 3.5 (c) shows the underlying mechanism: additionally to the dominant *s*-wave channel, a *d*-wave channel is present. The Cooper pair is initially broken up, but recombines now in the *d*-wave channel. The additional diagram which builds up the response is presented in Fig. 3.6 with the subdominant interaction V_d as the green dashed line.



Figure 3.6: The first two Feynman diagrams are building up the response in the absence of a subdominant interaction. The last diagram gives an interacting term to the spectral function draining spectral weight from the pair breaking peak. From [23].

In the first BZ in Fig. 3.7, this subdominant interaction connects the electron pockets at the *X* and *Y* point. Fig. 3.7 (b) shows a sharp in-gap mode below 2Δ in B_{1g} symmetry. This mode occurs only in B_{1g} symmetry. The argument for that follows the description in Ref. [42]: the response from the β Fermi surfaces can

be written as [42]

$$\frac{\Delta\chi(\Omega)}{N_{\beta}(0)} = -(N_{\beta}(0)\mathbf{V}_{d}) \cdot \left(\frac{\Delta_{0}}{\Omega}\right)^{2} \cdot \left\langle\gamma_{\beta}(\theta)g_{\beta}^{d}(\theta)g_{\beta}^{s}(\theta)\bar{P}(\Omega,\theta)\right\rangle^{2}$$
(3.24)

where $N_{\beta}(0)$ is the density of states on the β Fermi surface and V_d the subdominant interaction potential. The **k** dependency is parametrised with the angle θ and $\langle \cdot \rangle$ means the angular average. Additionally, one has

$$\bar{P}(\tilde{\Omega}_{\theta}) = \begin{cases} \frac{\tilde{\Omega}_{\theta}}{\sqrt{1-\tilde{\Omega}_{\theta}}} \arcsin\left[\tilde{\Omega}_{\theta}\right], & \left|\tilde{\Omega}_{\theta}\right| < 1\\ \frac{\tilde{\Omega}_{\theta}}{\sqrt{\Omega_{\theta}^{2}-1}} \left[\ln\left(\left|\tilde{\Omega}_{\theta}\right| - \sqrt{\tilde{\Omega}_{\theta}-1}\right) + i\pi/2\right] & \left|\tilde{\Omega}_{\theta}\right| > 1 \end{cases}$$
(3.25)

with $\tilde{\Omega}_{\theta} = \Omega/2\Delta_{\beta}(\theta)$. The factor $\gamma_{\beta}(\theta)g_{\beta}^{d}(\theta)g_{\beta}^{s}(\theta)$ has to transform as A_{1g} in order to avoid cancellation. This is ensured, if $\gamma_{\beta}(\theta)$ and $g_{\beta}^{d}(\theta)g_{\beta}^{s}(\theta)$ transform as B_{1g} . Therefore, the response is finite in the B_{1g} symmetry channel as the angular average does not vanish. Such an in-gap collective excitation is called a Bardasis-Schrieffer (BS) mode [27, 42, 104, 114, 115].



Figure 3.7: Phenomenological model for the Raman response of a BS excitonic mode. Additionally to the dominant *s*-wave interaction with interaction potential V_s , a subdominant *d*-wave interaction connects the electron pockets at the *X* and *Y* point with interaction potential V_d . (b) The Raman response in B_{1g} shows a sharp collective mode below 2 Δ which drains spectral weight from the pair breaking peak. From [42].

The total response in B_{1g} is then given as

$$\chi_{B_{1g}}^{\prime\prime}(\Omega) = \frac{4\pi}{\Omega} \operatorname{Re}\left(\frac{\left|\Delta_{\beta}(\theta)\right|^{2}}{\sqrt{\Omega^{2} - (2\Delta_{\beta}(\theta))^{2}}}\right) + a \operatorname{Im}\left[\frac{\left(\frac{\left|2\Delta_{\beta}(\theta)\right|}{\Omega}\bar{P}(\Omega,\theta)\right)^{2}}{\lambda_{d}^{-1} - \lambda_{s}^{-1} - \langle\bar{P}(\Omega,\theta)\rangle}\right]$$
(3.26)

with the subdominant and dominant coupling constant λ_d and λ_s , respectively. Raman spectroscopy thereby provides a tool to probe different pairing channels in systems with D_{4h} symmetry and dominant *s*-wave interacting, regardless of s^{++} or s^{\pm} ground state. Nonetheless, the existence of such subdominant modes has been linked to Cooper pairing mediated by spin-fluctuations in Ba_{1-x}K_xFe₂As₂ [24], thereby pointing towards an s^{\pm} scenario.

3.4.2 Fluctuations

Fluctuations can be probed by Raman scattering in a more direct way as well [44]. Charge, orbital or spin fluctuations can manifest themselves as a broad peak at low frequencies in some temperature interval $[T_f, T^*]$ above a phase transition at T^* [43]. In the pnictide systems, these spectral signatures have been observed in underdoped Ba(Fe_{1-x}Co_x)₂As₂ as well as underdoped Ba_{1-x}K_xFe₂As₂ compounds [44,62].



Figure 3.8: AL diagrams contributing to the Raman response. G_i are fermionic propagators, γ is the Raman vertex and the wavy lines are photonic propagators. The dashed lines are fluctuation propagators carrying momenta \mathbf{q}_c and $-\mathbf{q}_c$. The triangles correspond to the electronic loop of Eqn. 3.28. From [23].

Generally, this broad signature from fluctuations is superimposed on the Raman response. The Feynman diagrams describing this response are called Aslamazov-Larkin (AL) diagrams and were first discussed in the context of paraconductivity in superconductors [116].

The AL diagrams [43, 117–122] are depicted in Fig. 3.8. The dashed lines represent propagators carrying momenta \mathbf{q}_c and $-\mathbf{q}_c$. This propagator reads [43]

$$D(\mathbf{q}, \omega_m) = \frac{1}{|\omega_m| + \nu |\mathbf{q} - \mathbf{q}_c|^2 + m(T)}$$
(3.27)

with a constant energy scale ν , Matsubara frequencies ω_m and mass m(T). The mass, in general, scales with the transition temperature T^* at which the fluctuations vanish as a simple power law. These transition temperatures T^* may correspond to the charge order in the cuprates [43] or the nematic transition in the pnictides [62]. The mass is related to the correlation length with $m(T) \propto \xi^{-2}$ [43]. The propagator becomes maximal for the critical wave vector $\mathbf{q} = \mathbf{q}_c$ of the fluctuations. The diagrams in Fig. 3.8 yield selection rules via their fermionic loops represented as solid triangles. The loop can be written as [43,123]

$$\Lambda_{\alpha,\beta}(\Omega_l;\mathbf{q},\omega_m) = CT \sum_n \sum_{\mathbf{k}} \gamma_{\alpha,\beta}(\mathbf{k}) G(\mathbf{k},\epsilon_n,\Omega_l) G(\mathbf{k}-\mathbf{q},\epsilon_n-\omega_m) G(\mathbf{k},\epsilon_n)$$
(3.28)

in which $\gamma_{\alpha,\beta}(\mathbf{k})$ is the Raman vertex and *C* is a constant. The sum over \mathbf{k} space has contributions cancel out, if they originate from regions with opposite signs of the Raman vertex. To illustrate this further, the Raman vertex in first [(a1) to (c1)] and second order [(a2) to (c2)] derived solely from the crystal symmetry is depicted in Fig. 3.9 alongside the hole and electron pockets in the BZ of the 1-Fe unit cell.

The critical wave vector $\mathbf{q}_c = (\pi, 0)$ connects points on the hole pockets with points on the electron pockets indicated by the yellow ellipses. For these, the largest contribution to the fluctuation response is to be expected in the summation over all \mathbf{k} vectors, but only if the sign of $\gamma_{\alpha,\beta}(\mathbf{k})$ does not change. Otherwise, the contributions cancel out. This is true for the first and second order B_{1g} vertex. Additionally, the first order A_{1g} vertex would, in principle, yield a contribution just from the point of crystal symmetry.



Figure 3.9: Selection rules for AL-fluctuations. (a1) to (c1) show the first order Raman vertices in the first BZ with the idealised hole pocket at the Γ point and two elliptical electron pockets at the *X* and *Y* point. (a2) to (c2) depict the second order vertices. The colour scheme indicates the sign of the vertex. The red arrows connect the Fermi surfaces by the critical vector \mathbf{q}_c . (a3) to (c3) show the projection of the Raman vertex onto the band structure using a five-band tight binding model. Adapted from [28] and [97].

However, Böhm *et al.* [28] showed, that the Raman vertex derived from the electronic band structure via an effective mass approximation changes sign between electron and hole pockets in A_{1g} symmetry as can be seen in Fig. 3.9. Therefore, the only contribution to the Raman response is expected in B_{1g} symmetry.

The spectral shape of this fluctuation contribution to the Raman response reads [43]

$$\chi_{\rm fluct}''(\Omega, T) = \Lambda_{\rm B_{1g}}^2 \int_0^\infty dz \left[b(z - \Omega/2) - b(z + \Omega/2) \right] \frac{z_+ z_-}{z_+^2 - z_-^2} \left[F(z_-) - F(z_+) \right]$$
(3.29)

with the Bose function b(z) and

$$F(z) = \frac{1}{z} \arctan\left[\Omega_0/z\right] - \arctan\left[m/z\right]$$
(3.30)

and

$$z_{\pm} = (z \pm \Omega/2) \left[1 + (z \pm \Omega/2)^2 / \Omega_0^2 \right].$$
(3.31)

 Ω_0 is a cutoff, $\Lambda_{B_{1g}}$ is the vertex strength in B_{1g} symmetry and m(T) is the mass introduced with the fluctuation propagator in Eqn. 3.27.

The spectral shape of these fluctuations is drawn in Fig. 3.10 for three different temperatures $T_1 > T_2 > T_3 > T^*$. The increase of spectral weight goes along with the decrease of the mass m(T) as shown in the inset. At the transition at T^* , the fluctuations vanish. In the case of thermal fluctuations, the mass obeys a power law of the form

$$m(T) = m_0 + a \cdot (T - T^*)^{2\nu}$$
(3.32)

where $T^* > 0$. For quantum fluctuations on the other hand, T^* becomes zero (*cf.* Sec. 2.2.3) and the relationship simplifies to $m(T) \propto T^{2\nu}$.



Figure 3.10: Spectral signature of AL-fluctuations for three different temperatures $T_1 > T_2 > T_3 > T^*$. The inset shows the corresponding mass m(T) which decreases towards the transition.

3.4. Response for interacting particles

Chapter 4

Experiment and samples

The following chapter outlines the optical setup and the preparation of the samples.

4.1 Scattering setup

The experimental setup used throughout this thesis is depicted in Fig. 4.1. The is positioned on the sample holder the position of which can be varied slightly along the *z*-axis of the laboratory frame. The surface of the sample is then moved into the confocal point of the scattering setup in Fig. 4.1. This setup is explained in the following:

The light source is a yellow solid state laser (Coherent, Genesis MX SLM) at $\lambda_{\text{exc}} = 575$ nm with a beam diameter of $\emptyset = 1$ mm and a divergence of $\Delta_{\text{div}} = 0.7$ mrad. The beam diameter is optimised and the divergence minimised, before entering the polarisation selection and being focussed onto the sample. This is done via a variety of optical elements. It is convenient to define an optical axis along the path of the laser beam as emitted from the laser head, preferably parallel to the optical table. The centre of each optical element is positioned along this optical axis. The lenses L1 and L2 expand the beam. The mirror M1 directs it through the lens L3 of the first pinhole system (PH1). The beam is focussed onto a pinhole S1. The focal point of lens L4 coincides with the focal point of L3 and thus the position of the pinhole. Only the parallel parts of the beam are focussed

onto this pinhole, while the divergent parts do not pass. Lens L4 parallelises the beam again. This process is repeated again at slit S2 ensuring a high beam quality.



Figure 4.1: Experimental setup in the Raman Lab I. The light sources are an ion and a solid state laser. The letters refer to the following optical elements: lenses L*i*, mirrors M*i*, slits S*i*, pinhole systems PH*i*, the prism monochromator PMC and objectives O*i*. The incident intensity is set with a $\lambda/2$ waveplate and the power meter PM, and the incident polarisation with a polariser P and a Soleil-Babinet compensator SBC. The scattered light is selected with a $\lambda/4$ waveplate and an analyser A. For details, see text. From Ref. [124].

Two quantities are set before the beam is focussed onto the sample: the polarisation configuration and the intensity. The Glan-Thompson polariser P selects a linear polarisation. The Soleil-Babinet compensator (SBC) creates a well defined polarisation state. An SBC can, in principle, create elliptic polarisation states. With this combination of P and SBC, it is possible to set any desired polarisation of the incident light inside the sample, and in particular circularly

and linearly polarised light. Then, the $\lambda/2$ is used to adjust the intensity measured at the power meter PM. Both, the SBC as well as the Glan-Thompson polariser, create interferences which are filtered with the second pinhole system (PH2). Lens L8 focusses the beam onto the sample. The objective O2 collects the scattered light. It passes the polarisation selection with the $\lambda/4$ waveplate and the analyser A before the $\lambda/2$ waveplate rotates the light into the preferential direction of the spectrometer. The spectrometer is a band-pass filter. The light exiting the spectrometer is parallelised at lens L9 and focussed onto a CCD chip with the objective O3. The shutter S is controlled by a measurement software developed at the WMI which determines the exposure time of the CCD.

4.2 Characterisation and preparation of the samples

The samples scrutinised in this thesis were superconducting single crystals of CaKFe₄As₄ and Co-doped BaFe₂As₂. The CaKFe₄As₄ sample was provided by the Canfield group at Ames Laboratory. The growth method is a high temperature solution growth out of FeAs flux [125], similar to the growth method of Ba(Fe_{1-x}Co_x)₂As₂ [19, 22, 126, 127]. The Ba(Fe_{1-x}Co_x)₂As₂ samples were provided by the Fisher group at Stanford University. The crystals grow such that the typical dimension of the single crystals are on the order $a \times b \times c = 5$ mm × 5mm × 1mm with the crystal axes a, b and c as defined in Fig. 2.1.

In the focus of this thesis stands the investigation of the superconducting phase. The knowledge of the transition temperature T_c is therefore mandatory. To serve this purpose, the transition temperatures of the samples were characterised by measuring the 3rd harmonic of the magnetic susceptibility χ_m as a function of temperature T. The experimental setup is described in detail in Ref. [107] and Ref. [128]. This method provides three advantages: for one, it is contactless. Two, it is more sensitive than, for instance, a regular susceptibility measurement, therefore enabling one to measure samples having a thickness in the mm range and smaller. Third, the method picks up on sample inhomogeneities.



Figure 4.2: Third harmonic of the susceptibility of CaKFe₄As₄ measured upon heating (red) and cooling (blue).

The method utilises the occurrence of Abrikosov vortices [129] in a type-II superconductor when emerged into an external magnetic field H_{ext} for which $H_{c1} < H_{\text{ext}} < H_{c2}$ (Shubnikov phase). For this phase, Bean predicted [130, 131] a constant critical current density j_c flowing in some depth δ which shields the interior of the superconductor. When H_{ext} is increased further, larger portions of the superconductor are penetrated by the vortices. Upon decreasing H_{ext} again, an inductive current opposite to j_c is created which traps a coercive magnetic field. This hysteretic behaviour leads to a sharp peak of the temperature dependence of $|\chi_{\text{m}}(3f)|^2$ for temperatures $T \leq T_{\text{c}}$.

This can be seen exemplarily for $CaKFe_4As_4$ in Fig. 4.2. The measurements were performed once upon heating (red) the sample and once upon cooling

(blue) the sample through the superconducting transition. Both show a welldefined peak. Extrapolating the high temperature side to zero, this gives $T_{\rm c}^{\rm heating} = 35.09$ K upon heating and $T_{\rm c}^{\rm cooling} = 35.33$ K upon cooling. The average is then $T_{\rm c} = 35.21$ K. The width of the transition is therefore $\Delta T_{\rm c} = 0.24$ K.



Figure 4.3: Third harmonic of the susceptibility of $Ba(Fe_{1-x}Co_x)_2As_2$ measured upon heating (red) and cooling (blue) with doping concentrations as indicated.

The small width as well as the shape of the signal indicate a homogeneous

sample.

The same measurements were performed for the $Ba(Fe_{1-x}Co_x)_2As_2$ compounds. The results are presented in Fig. 4.3, where (a1) and (a2) show the results of earlier studies [23,132]. The results of these measurements are summarised in Tab. 4.1.

Table 4.1: Summary with the superconducting transition temperature T_c , the magnetic transition T_{SDW} and the nematic or structural transition T_s .

Material	$T_{\rm c}$	$\Delta T_{\rm c}$	$T_{\rm SDW}$	T_{s}
CaKFe ₄ As ₄	35.21	0.24	-	-
$Ba(Fe_{0.949}Co_{0.051})_2As_2$	18.65	1.46	50.0	60.9
$Ba(Fe_{0.945}Co_{0.055})_2As_2$	21.57	0.14	-	50
$Ba(Fe_{0.94}Co_{0.06})_2As_2$	24.57	0.32	-	-
$Ba(Fe_{0.915}Co_{0.085})_2As_2$	20.5	0.23	-	-

After measuring T_c , the sample is glued onto a copper block using GE low temperature varnish. This is depicted in Fig. 4.4 (a), where the *c*-axis of the sample is parallel to the defined *c*-axis of the copper block c_{Cu} .

The copper block is inserted into the cylindrical sample holder in which it can be rotated around its a_{Cu} axis. In order to fully utilise the Raman selection rules presented in Sec. 3.3, the orientation of the crystal's main axes relative to the sample holder has to be set ex-situ. The *c*-axis has to point perpendicular to the front of the sample holder. This is ensured by using a polarisation microscope, where the copper block is rotated until the reflection from the sample becomes maximal.

The *a*-*b* plane is oriented using Laue diffraction with respect to the Laue coordinate system having axes x and y^1 . These axes coincide with the laboratory system of the scattering setup discussed below. For the orientation in the Laue experiment, the sample holder is placed in an adjustment tool so that it can be rotated clock or counter-clockwise. Iteratively, the Laue diffraction pattern is

¹Sometimes, cracks on the surface of the sample indicate the main axes of the crystal. This is visible under the polarisation microscope and can be used to set a starting point for the Laue diffraction experiment.



optimised so that the *a-b* axes are well defined in the *x-y* coordinate system.

Figure 4.4: Orientation of the sample. (a) The sample is glued onto a copper block where the axes a_{Cu} , b_{Cu} and c_{Cu} refer to the dimensions of the block as an aid for the explanation. (b) The copper block is inserted in an adjustment tool for the Laue diffraction. (c) The a-b plane is oriented iteratively by rotating the sample holder so that the main reflexes are well defined in the x-y coordinate system.

After preparing the orientation, the sample holder is mounted onto the coldfinger of the cryostat.

4.3 Checking the sample orientation and cleaving the surface

Before running the measurement schedule, the orientation of the sample is checked using Raman spectroscopy. For the 1144 as well as the 122 systems, this is can be done by probing the B_{1g} phonon at 210 cm⁻¹. If the crystal axes *a* and *b* are parallel to the laboratory frame with *x* and *y*, the phonon will not appear for the light polarisation configuration *xy*. In turn, the strong phonon line will be visible for x'y' polarisation.

If the surface of the sample shows poor quality, it can be cleaved using adhesive tape. Poor quality means here, that the laser spot on the surface of the sample is strongly visible. The pnictides usually exfoliate along (001).

Chapter 5

Subdominant *d*-wave interaction in CaKFe₄As₄

The dependence of the Raman response on the incoming and scattered light polarisations reveals the anisotropy of the energy gap and the existence of anisotropies of the pairing potential as discussed in Subsec. 3.4.1. This study is a litmus test for the universality of Cooper pairing in the BaFe₂As₂ compounds as anticipated from the band structure and earlier experiments in Ba_{1-x}K_xFe₂As₂ [24]. Part of the results were published in Ref. [45].

5.1 Overview: Raman spectra

Fig. 5.1 provides an overview over the Raman spectra of CaKFe₄As₄ above $T_c = 35.2 \text{ K}$ at T = 43 K (red), and below T_c at T = 11 K (blue). All spectra were measured within the frequency window $\Omega \in [10, 310] \text{ cm}^{-1}$.

Three polarisation configurations were used as indicated by the pictograms, projecting the symmetries as described in Sec. 3.3.



Figure 5.1: Raman response in CaKFe₄As₄ for symmetries and polarisations as indicated. The raw data for $T \ll T_c$ and $T > T_c$ are shown in blue and red, respectively. The difference spectra are presented in orange. Phonon modes are present in the A_{1g} and B_{2g} spectra. (a) In A_{1g}, the pair-breaking features set in at $\Omega_0^{(A1g)} = 120 \pm 2 \text{ cm}^{-1}$ and extend to $\Omega_m \approx 230 \text{ cm}^{-1}$. The gap energies $2\Delta_i$ for the four bands *i* observed by angle-resolved photo emission spectroscopy (ARPES) [30] are reproduced as horizontal bars. (b) The B_{1g} pair-breaking features set in at $\Omega_0^{(B1g)} = 116 \pm 5 \text{ cm}^{-1}$. (c) The B_{2g} pair-breaking response lies above $2\Delta_\beta$. The intersection of the normal and superconducting spectra is close to $\Omega_0^{(B2g)} = 130 \pm 5 \text{ cm}^{-1}$. From Ref. [45].

Six and four phonon modes can be observed in *RR* and x'y' polarisation, respectively which will be discussed in appendix A.3.

In the normal state spectrum in xy polarisation [Fig. 5.1 (b)] no phonon leakage can be detected. Moreover, the response is flat which indicates an absence of impurity scattering inferring a high quality of the crystal. In orange, the difference spectra

$$\Delta R \chi''(\Omega) = R \chi''(T = 11 \,\mathrm{K}, \Omega) - R \chi''(T = 43 \,\mathrm{K}, \Omega), \tag{5.1}$$

are shown where temperature independent features are subtracted out. The remaining signal stems for the most part from the superconducting response, as described in Subsec. 3.4.1, and illustrates the redistribution of spectral weight in the superconducting state.

In (a), the horizontal bars indicate the gap energies derived from the ARPES measurements by Mou *et al.* [30] (*cf.* Sec. 3.4.1). The magnitude of the superconducting gap derived from the Raman spectra is by and large consistent with the ARPES results. Additionally, the analysis of the temperature dependence below will reveal the subtle hints of a subdominant interband interaction similar to the results in $Ba_{1-x}K_xFe_2As_2$ [24].

5.2 Temperature dependence below *T*_c

Fig. 5.2 comprises the inelastic light scattering data $R\chi''(\Omega, T)$ at temperatures as indicated on the left. On the right, the difference spectra $\Delta R\chi''(\Omega, T)$ as defined in Eqn. 5.1 are shown.



Figure 5.2: A_{1g} response of CaKFe₄As₄ for 43 K and temperatures below T_c as indicated. The raw response is shown on the left, the difference spectra on the right. From Ref. [45].

At 11 K, the difference between the normal state and the superconducting spectrum is most pronounced: as the superconducting gap opens up, the spectral weight below a threshold of $\Omega_0 = 120 \text{ cm}^{-1}$ is suppressed. The intensity above the threshold increases due to the breaking of Cooper pairs superposed with a second process in which fermions are lifted above the energy gap, creating a particle-hole excitation. These are called Bogoliubov quasiparticle (BQ) excitations [133]. The gap opening in the difference spectra is characterised by $\Delta R \chi''(\Omega, T) < 0$, and pair-breaking and BQ excitations set in where $\Delta R \chi''(\Omega, T)$ changes sign. The increase in intensity for $\Omega \rightarrow 0$ results from diffuse elastic scattering from the sample's surface due to the adsorption of gas molecules. The broad feature of the A_{1g} response collapses as temperature is increased towards the superconducting transition and vanishes almost entirely at 30 K.



Figure 5.3: B_{2g} response of CaKFe₄As₄ for 43 K and temperatures below T_c as indicated. The raw response is shown on the left, the difference spectra on the right. From Ref. [45].

The B_{2g} response is weaker and less pronounced than the A_{1g} response as can be seen in Fig. 5.3. Nonetheless, the intersect between the normal and superconducting spectra lies at $\Omega_0 = 130 \text{ cm}^{-1}$, similar to the A_{1g} spectra. The pair-breaking feature extends to $\Omega_m = 250 \text{ cm}^{-1}$ and reaches its maximum at approximately 215 cm⁻¹ which coincides with the energy of the Fe phonon. Already at 20 K, the spectral redistribution is weak.



Figure 5.4: B_{1g} response of CaKFe₄As₄ for 43 K and temperatures below T_c as indicated. The raw response is shown on the left, the difference spectra on the right. Close to 50 cm^{-1} there is a weak maximum in the superconducting state observable in the raw data and the difference spectra in the temperature range 11-20 K. The superconducting and normal state spectra merge with increasing temperature. From Ref. [45].

In contrast, the superconducting features in B_{1g} symmetry survive up to 31 K as can be seen in Fig. 5.4. At 11 K, the cross-over energy $\Omega_0 = 116 \text{ cm}^{-1}$ is similar to the other symmetries. However, a weak hump at 50 cm⁻¹ is visible up to at least 17 K. The pronounced maximum at 135 cm⁻¹ at 11 K decreases in intensity and visibly shifts to lower energies as temperature is increased towards 31 K. On the high-energy side there is a second structure at 165 cm⁻¹.

5.3 Pair breaking and collective modes

To summarise the results above: firstly, the superconducting features in all symmetries emerge at essentially the same energies in the interval $[\Omega_0, \Omega_m]$. Secondly, the redistribution of spectral weight in the range $\Omega_0 < \Omega < \Omega_m$ varies substantially and is entirely different from the typical shape discussed in Subsec. 3.4.1 for all symmetries. It is therefore attempted in this section to discuss this variation in the different symmetries and the subtle deviations of the gap energies from the ARPES results.

We start with the B_{2g} response which shows the highest pair-breaking energy at $2\Delta_{max} \approx 215 \text{ cm}^{-1}$: This pair-breaking energy corresponds to $\Delta_{max} = 13.3 \text{ meV}$ which is slightly larger than the largest average gaps derived from the ARPES data *et al.* [30] (see Tab. 2.1) on the β and δ bands with $\Delta_{\beta,\delta} = 12 \text{ meV}$. The position of the B_{2g} maximum is consistent with the weak hump in A_{1g} at 215 cm⁻¹. Therefore, the ARPES data underestimate the gap energies of the largest gaps found in the Raman experiment which was already observed in $Ba_{1-x}K_xFe_2As_2$ [27,28], but is overall consistent with view on the experimental error depicted in Fig. 5.1 (a) and reported in Ref. [30].

The lowest gap on the γ band with $\Delta_{\gamma} = 8$ meV coincides with the cross-over energy in the A_{1g} symmetry. Therefore, the peak structure at 11 K in the difference spectra positioned at roughly 140 cm⁻¹ is again larger than the smallest gap energy found by ARPES. A signal from the γ band is entirely missing in B_{2g} symmetry. There is no clear signal in A_{1g} and B_{2g} symmetry of the gap on the α band with $\Delta_{\alpha} = 10.5$ meV. Consequently, the maximal gap energies found in the Raman signal are similar to optimally doped Ba_{1-x}K_xFe₂As₂ at approximately 9 k_BT_c [28]. The signal in A_{1g} symmetry is by and large compatible with the selection rules shown in Fig. 3.3. From these, it is clear, that similar contributions from all bands should be expected to the spectral weight in A_{1g} symmetry. This holds true, as shown in Fig. 5.1, since the superconducting plateau in A_{1g} symmetry covers the entire energy range.

The B_{2g} spectra partially challenge that view, as the B_{2g} spectra should show contributions from the hole and electron bands with a similar spectral weight. However, only the largest gap is weakly visible. Additionally, the signal from the γ band is entirely missing what cannot be explained by the selection rules. Although the peak hight varies as $|\Delta|^2$ [see Ref. [94] and Eqn. 3.22], remnants of the γ band should be visible in B_{2g} symmetry. To fully explain the observed response, a phenomenological treatment as outlined in Ref. [28] is needed, including an explicit calculation of the response according to Eqn. 3.22 which, however, is beyond the scope of this work. While the A_{1g} and B_{2g} spectra reproduce the single particle gap energies, the B_{1g} spectra cannot be explained on the basis of pair breaking alone. Firstly, in B_{1g} symmetry, one should capture the full response from the gaps on the δ bands and only a marginal response from the hole bands at the Γ point, if any according to the selection rules in Fig. 3.3. However, the peak energy at 134 cm⁻¹ is well below the maximum gap energies in A_{1g} and B_{2g} symmetries and below the gap energy of the δ band [Fig. 5.1 (c)]. As the intensities from the hole bands are to be expected marginal in comparison to that of the δ bands, a scenario in which the maximum stems from the γ band can be discarded.

Alternatively, the B_{1g} signal may be considered to not originate solely from the superconducting gaps, but from final state interactions resulting in a strong peak maximum well below $2\Delta_{\delta}$ as discussed for $Ba_{1-x}K_xFe_2As_2$ in earlier work [24, 27, 28]. Fig. 5.5 directly compares the difference spectra of the Raman response in B_{1g} symmetry of CaKFe₄As₄ and Ba_{0.65}K_{0.35}Fe₂As₂. Additionally, $2\Delta_{\delta}$ highlighted by an orange arrow is depicted in Fig. 5.5 (e).

The temperature dependence of the difference spectra in CaKFe₄As₄ clearly indicates a shoulder on the high-energy side. The comparison with the data on $Ba_{0.65}K_{0.35}Fe_2As_2$ immediately highlights the similarity of the spectral shapes. On the basis of this comparison, the maximum at 134 cm⁻¹ in B_{1g} symmetry



Figure 5.5: Difference spectra of the B_{1g} Raman response. (a)-(e) Difference spectra of CaKFe₄As₄. The main peak exhibits a double structure (orange and blue arrows). A second hump is visible from 25 K down to 13 K (green asterisk). (f) Difference spectrum of Ba_{0.65}K_{0.35}As₂Fe₂ [24] with two BS modes at 3.1 (green arrow) and 5.2 k_BT_c (orange arrow) and the remainder of the pair breaking peak at $6.2 k_BT_c$ (blue arrow). Figure taken from Ref. [45].

is identified as a collective mode, as described in Sec. 3.4.1, resulting from a subdominant *d*-wave interaction. This subdominant interaction drains spectral weight from the pair-breaking peak [28, 42, 104] into a δ -like excitation below the gap edge. Theoretically, this was predicted by Scalapino and Devereaux [42] and experimentally verified in Ba_{1-x}K_xFe₂As₂ [24].

Although the overall spectral shape in CaKFe₄As₄ is very similar to that of $Ba_{0.65}K_{0.35}Fe_2As_2$, one caveat has to be discussed: in $Ba_{1-x}K_xFe_2As_2$, not one but two subleading channels were found indicated by the green arrow in Fig. 5.5 (f). The faint peak at roughly 50 cm⁻¹ in CaKFe₄As₄ may be a second collective excitation. The weakness of this peak could be explained, if CaKFe₄As₄ was on the brink of a *d*-wave instability. This scenario, although not entirely conclusively demonstrated experimentally, is the most plausible explanation of the peak at 50 cm⁻¹. The nesting conditions between the electron pockets in CaKFe₄As₄ [see Fig. 2.7 and Ref. [30]] may in fact further enhance the sub-leading channel. The weakness of this mode, however, makes a clear identification difficult. In order to substantiate this claim, a similar analysis as in $Ba_{1-x}K_xFe_2As_2$ [24] has to be conducted.

In summary, the gap energy found in the B_{2g} symmetry at 215 cm⁻¹ is in the same range as the gaps derived from the ARPES measurements for the β and δ bands. The superconducting and normal state spectra merge at $\Omega_m = 230 \text{ cm}^{-1}$ in all symmetries. The feature at 215 cm⁻¹ is visible in A_{1g} symmetry as well. Additionally, the pair-breaking feature is plateau-like and sets in at $\Omega_0^{(A1g)} = 120 \text{ cm}^{-1}$. The plateau covers by and large the entire range of gap energies derived from ARPES [30]. Although the response of individual bands could not be resolved, the results in A_{1g} symmetry are consistent with the ARPES results [30].

The B_{1g} response shows a maximum at an energy lower than that in A_{1g} and B_{2g} symmetry. The sharp maximum at 134 cm⁻¹ is interpreted as a collective excitation similar to that in $Ba_{0.65}K_{0.35}Fe_2As_2$. This collective mode is a manifestation of a subdominant *d*-wave interaction resulting from a strong interaction between the electron bands. This mode drains most of the spectral weight from the pair-breaking peak leaving behind only a shoulder at 165 cm⁻¹. Whether or not the weak structure at 50 cm⁻¹ is another BS mode with even stronger

coupling cannot be decided with certainty on the basis of the current results. If this interpretation could be supported further, CaKFe₄As₄ would be closer to a *d*-wave instability than Ba_{1-x}K_xFe₂As₂. The smaller T_c of CaKFe₄As₄ argues in this direction since a strong *d*-wave pairing channel frustrates the *s*-wave ground state and reduces T_c .

5.3. Pair breaking and collective modes

Chapter 6

Quantum criticality in Ba(Fe_{1-x}Co_x)₂As₂

In the previous chapter fluctuations were identified as potential players in the context of superconductivity. In addition, the QCP at the critical doping x_c may contribute by enhancing T_c . Therefore the study of fluctuations around x_c is a natural continuation of the of the work on Cooper pairing in the preceding chapter. In the discussion two methods for analysing the the low energy part of the spectra will be explored. Parts of this chapter have been published in Ref. [134].

6.1 Spectra

In Fig. 6.1 the Raman susceptibility on underdoped Ba $(Fe_{1-x}Co_x)_2As_2$ is depicted as a function of the Raman shift Ω and temperature *T* in the range from *T* = 333 K to *T* = 26 K > T_c = 21.6 K. The absorbed laser power was set at 2 mW.

In Fig. 6.1 (a), the spectra in *RR* polarisation project out $A_{1g} + A_{2g}$ symmetry. Superimposed on the particle-hole continuum are three modes, which harden as temperature is decreased. These three modes can be identified as two E_g modes at 125 cm⁻¹ and 260 cm⁻¹ and one A_{1g} mode at 185 cm⁻¹ [135]. The E_g modes are visible due to a finite projection of the polarisation of the incident light on the *c*-axis [107]. The initial slope as well as the overall intensity at low frequencies below $\Omega_m = 600 \text{ cm}^{-1}$ increases upon decreasing the temperature. Above approximately Ω_m the spectra merge.



Figure 6.1: Raman response in Ba(Fe_{0.945}Co_{0.055})₂As₂ at temperatures as indicated. (a) In *RR* polarisation two E_g phonon modes at 125 cm⁻¹ and 270 cm⁻¹ and the A_{1g} mode at 185 cm⁻¹ are present. The electronic continuum shows a weak temperature dependence at low energies and is constant for energies above 600 cm⁻¹. (b) For *xy* polarisation, no phonon modes are observed. The spectral weight at low frequencies increases strongly as temperature decreases down to 53 K. Below 53 K the intensity decreases in the range below 250 cm⁻¹.

Fig. 6.1 (b) displays data from measurements with xy polarisation which projects out the B_{1g} + A_{2g} in the 1-Fe unit cell as discussed in Sec. 3.3. Upon cooling from 333 K to 53 K the spectral weight increases in the range up to $\approx 600 \text{ cm}^{-1}$ and a broad peak forms which shifts continuously to lower energies upon cooling. This peak sharpens and reaches its maximum intensity at $T \sim 53 \text{ K}$ below which the spectral weight decreases again. Above 600 cm⁻¹ the spectra are temperature independent.



Figure 6.2: Raman response in Ba(Fe_{0.94}Co_{0.06})₂As₂ at temperatures as indicated. (a) Phonon modes are present in *RR* polarisation with two E_g modes at 125 cm⁻¹ and 270 cm⁻¹ and the A_{1g} mode at 185 cm⁻¹. The electronic continuum shows a weak temperature dependence at low energies and is independent of temperatures above 600 cm⁻¹. Superconducting features for $T < T_c$ with a maximum at 95 cm⁻¹ can be observed. (b) For *x y* polarisation an increase of spectral weight is observed as temperature decreases down to 38 K below which the intensity remains constant. Superconducting features are observed for the lowest temperature measured with a maximum at 105 cm⁻¹. The strong peak for 10 K results from superconductivity. The spectra are independent of temperature above 600 cm⁻¹.

The *RR* response for Ba(Fe_{0.94}Co_{0.06})₂As₂ in Fig. 6.2 (a) shows in total three phonon modes: the two E_g phonon modes at 125 cm⁻¹ and 260 cm⁻¹ and the A_{1g} phonon mode at 185 cm⁻¹. The low frequency part increases upon cooling for $T > T_c = 24.6$ K. Below T_c at 10 K, a feature is observed at 100 cm⁻¹. This stems from pair-breaking as described in Subsec. 3.4.1. The high frequency part of the spectrum starts to merge at $\Omega_m \approx 600$ cm⁻¹.

In Fig. 6.2 (b), xy spectra are depicted with the projected symmetries being $B_{1g} + A_{2g}$. At low frequencies, the spectral weight increases as temperature is decreased down to 43 K. For temperatures $T_c < T < 43$ K, the spectra remain

constant. Below the critical temperature T_c , a peak at 100 cm⁻¹ is visible which results from pair-breaking features. The spectra converge above $\Omega_m \approx 600$ cm⁻¹.

Fig. 6.3 presents the data of the overdoped sample $Ba(Fe_{0.915}Co_{0.085})_2As_2$. The *RR* polarisation is depicted in Fig. 6.3 (a). The three phonon modes of A_{1g} , and E_g symmetry are visible at the respective energies. The low frequency part varies with temperature as for $Ba(Fe_{0.945}Co_{0.055})_2As_2$ and $Ba(Fe_{0.94}Co_{0.06})_2As_2$ and the spectra converge at high frequencies. Qualitatively different is the B_{1g} response in panel (b) to those of $Ba(Fe_{0.945}Co_{0.055})_2As_2$ and $Ba(Fe_{0.94}Co_{0.06})_2As_2$. The low frequency response is less temperature dependent than the B_{1g} data of the underand optimally doped samples. It increases monotonically towards T_c , similar to the low frequency behaviour of the A_{1g} signal depicted panel (a).



Figure 6.3: Raman response of Ba(Fe_{0.915}Co_{0.085})₂As₂ at temperatures as indicated. (a) In *RR* polarisation two E_g phonon modes at 125 cm^{-1} and 270 cm^{-1} and the A_{1g} mode at 185 cm^{-1} are observed. The electronic continuum shows a weak temperature dependence above T_c . The superconducting spectrum exhibits a maximum at 95 cm⁻¹. (b) For *xy* polarisation, no phonon modes are observed. The low frequency part increases towards $T > T_c$. The signal stemming from superconductivity exhibits a maximum at 85 K.
6.2 Analysis

Summarising the results above: The temperature dependence of the electronic continuum in A_{1g} symmetry does not vary with doping. The A_{1g} and E_g phonons harden and sharpen with decreasing temperature for all doping concentrations. The low frequency spectral weight increases as temperature is decreased.

The low-frequency behaviour of the particle-hole continuum in B_{1g} symmetry changes from x = 0.055 to x = 0.060 and finally to x = 0.085 qualitatively and quantitatively. The increase is strongest in $Ba(Fe_{0.945}Co_{0.055})_2As_2$, where the spectral weight piles up towards 53 K. Then, the intensity decreases monotonically towards the superconducting transition. In $Ba(Fe_{0.94}Co_{0.06})_2As_2$, the spectral weight increases down to 43 K as well. The intensity over the entire frequency range stays constant down to the superconducting transition at T_c . Only in $Ba(Fe_{0.915}Co_{0.085})_2As_2$, the dichotomy between the A_{1g} and B_{1g} is absent, and the temperature dependence of the continua in both symmetries are similar.

The dichotomy between A_{1g} and B_{1g} channels has been studied in a previous work [44] for doping concentrations x = 0, x = 0.025 and x = 0.051. There, the low frequency pile-up of spectral weight in B_{1g} symmetry was identified as a result of spin-fluctuations driving the nematic transition in underdoped $Ba(Fe_{1-x}Co_x)_2As_2$. Due to the similarities of the $Ba(Fe_{0.945}Co_{0.055})_2As_2$ and $Ba(Fe_{0.94}Co_{0.06})_2As_2$ samples with this earlier study, the current data will now be treated in the same fashion as in Ref. [44] and Ref. [97].

6.2.1 Relaxation rate analysis

In a first step, the bare fluctuation response shall be separated from the electronic continuum. For this it is assumed, that the B_{1g} Raman response is the sum of two independent contributions,

$$\chi_{B_{1g}}^{\prime\prime}(\Omega,T) = \chi_{p-h\ cont}^{\prime\prime}(\Omega,T) + \chi_{fluct}^{\prime\prime}(\Omega,T)$$
(6.1)

i.e. of the particle-hole continuum and the superimposed fluctuation response. Our task is therefore to identify the contribution from the particle-hole excitations which can then be subtracted from the full response. The following recipe will be followed:

- 1. Extract the dynamic Raman relaxation rate $\Gamma(\Omega, T)$ from the experimental data in A_{1g} and B_{1g} symmetry.
- 2. Calculate the static relaxation rates $\Gamma^0_{A_{1g}}(T)$ and $\Gamma^0_{B_{1g}}(T)$.
- 3. Model the B_{1g} particle-hole continuum such that the average of the A_{1g} and B_{1g} relaxation rates track the in-plane resistivity.
- 4. Subtract the particle-hole continuum from the full response.

Starting with the first point, the dynamic relaxation rate may be determined by [136]

$$\Gamma(\Omega, T) = R \cdot \frac{\bar{\chi}''(\Omega, T)}{[\bar{\chi}''(\Omega, T)]^2 + [\Omega K(\Omega, T)]}$$
(6.2)

in which $\bar{\chi}''(\Omega, T) = \chi''(\Omega, T)/\Omega$ and *R* is a scaling factor which is fixed by a sum rule [136]. Additionally

$$K(\Omega, T) = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\Omega' \bar{\chi}''(\Omega', T)}{\Omega'^2 - \Omega^2} \, \mathrm{d}\Omega'$$
(6.3)

is the Kramers-Kronig transform of $\bar{\chi}''(\Omega, T)$. Since the spectra do not converge sufficiently fast, the upper limit of the integral needs to be finite and is typically set at the band width. Fig. 6.4 (a) and (b) depict the dynamic relaxation rates $\Gamma(\Omega, T)$ as a function of temperature extracted via this method from the data shown in Fig. 6.1. The A_{1g} relaxation rates in panel (a) show a vanishing slope at low frequencies, deviating only at low temperatures. The overall spectral shape changes slightly over the entire temperature range by an offset proportional to the temperature. In contrast, the B_{1g} spectra in panel (b) show a stark temperature dependence at low frequencies, where the slope vanishes at high temperatures, but becomes finite for decreasing temperature. At high frequencies, both A_{1g} and B_{1g} relaxation rates depend on the temperature linearly. Therefore, the dichotomy between the A_{1g} and B_{1g} Raman spectra observed at low frequencies extends to the dynamic relaxation rates.



Figure 6.4: Relaxation rate analysis of $Ba(Fe_{0.945}Co_{0.055})_2As_2$. (a) Dynamic relaxation rate extracted from the A_{1g} data. (b) Dynamic relaxation rate of the B_{1g} data. The black curves show the fits as described by Eqn. 6.5. (c) Static relaxation rate as a function of temperature from the A_{1g} (red diamonds) and B_{1g} (black squares) data. The dark red curve is the resistivity $\rho(T)$ taken from Ref. [22].

In order to systematically extract the $\Omega \rightarrow 0$ frequency response, the parallel resistor model is used [137–139]

$$\frac{1}{\Gamma(\Omega,T)} = \frac{1}{\Gamma^0(\Omega,T)} + \frac{1}{\Gamma^{\max}(T)}.$$
(6.4)

Here, two contributions to the dynamical relaxation rate $\Gamma(\Omega, T)$ are introduced, where $\Gamma^0(\Omega, T) = \alpha(T) + \beta(T)\Omega^2$ describes the low frequency part and $\Gamma^{\max}(T)$ the high frequency part. Inverting Eqn. 6.4 yields

$$\Gamma^{\text{fit}}(\Omega, T) = \frac{(\alpha(T) + \beta(T)\Omega^2) \cdot \Gamma^{\max}(T)}{\alpha(T) + \beta(T)\Omega^2 + \Gamma^{\max}(T)}$$
(6.5)

in which $\alpha(T)$, $\beta(T)$ and $\Gamma^{\max}(T)$ are the fit parameters. The static relaxation rate at $\Omega = 0$ is then given by

$$\Gamma^{0}(T) = \frac{\alpha(T) \cdot \Gamma^{\max}(T)}{\alpha(T) + \Gamma^{\max}(T)}.$$
(6.6)

The result is depicted in Fig. 6.4 (c) as a function of temperature. The red diamonds show the rates $\Gamma^0(T)$ extracted from the A_{1g} data and the black squares those from the B_{1g} data. The dark red curve describes the resistivity $\rho(T)$ as measured by Chu *et al.* [22]. In a Drude model, this resistivity is connected to the static relaxation rate via [136]

$$\Gamma^0(T) = 1.08 \cdot \rho(T) \cdot \omega_{\rm pl}^2 \tag{6.7}$$

with the plasma frequency ω_{pl} . Above 200 K, both the A_{1g} and B_{1g} relaxation rates track $\rho(T)$. Below a temperature $T_f \sim 150$ K, $\Gamma^0_{B_{1g}}(T)$ deviates from $\rho(T)$ and $\Gamma^0_{A_{1g}}(T)$. The B_{1g} data decrease, develop a minimum around 50 K and increase only slightly upon moving towards the superconducting transition.

The same analysis was performed for the data of Ba(Fe_{0.94}Co_{0.06})₂As₂ and Ba(Fe_{0.915}Co_{0.085})₂As₂ (see appendix B.1). The results are collected in Fig. 6.5. $\Gamma_{B_{1g}}^{0}(T)$ starts deviating from the temperature dependence expected from the resistivity at $T_{f} \sim 120$ K developing a minimum at 50 K and saturating towards T_{c} [Fig. 6.5 (b)]. For Ba(Fe_{0.915}Co_{0.085})₂As₂ [Fig. 6.5 (c)], $\Gamma_{A_{1g}}^{0}(T)$ and $\Gamma_{B_{1g}}^{0}(T)$ both decrease similarly as $\rho(T)$ towards T_{c} , and no deviation can be detected for the B_{1g} channel.



Figure 6.5: Overview of the static relaxation rates for various doping levels and in symmetries as indicated as a function of temperature. The plasma frequencies ω_{Pl} are in the expected range [140–142].

With this in mind, we start to model the particle-hole continuum given by the phenomenological function

$$\chi_{B_{1g}}^{\prime\prime}(\Omega) = a \tanh\left[\frac{\Omega}{c}\right] + b\Omega$$
 (6.8)

which for large Ω becomes $a + b\Omega$. The fit parameters vary with temperature as $a = a1 + a2 \cdot T$ and $b = b1 + b2 \cdot T$ and $c = c1 + c2 \cdot T$. Fitting a high-temperature spectrum first to set the initial parameters, these were then optimised as follows: the static relaxation rate of the analytic approximation to the p-h continuum

[Eqn. 6.8] was calculated and set so that $(\Gamma^0_{A_{1g}}(T) + \Gamma^0_{B_{1g}}(T))/2 \approx \rho(T)$.

The last step is the subtraction of the particle-hole continuum from the full response. Exemplarily, two spectra are depicted showing $Ba(Fe_{0.945}Co_{0.055})_2As_2$ and $Ba(Fe_{0.94}Co_{0.06})_2As_2$ in Fig. 6.6 (a) to (d).



Figure 6.6: Subtraction of the particle-hole continuum from the full response for 73 K and 53 K for $Ba(Fe_{0.945}Co_{0.055})_2As_2$ and $Ba(Fe_{0.94}Co_{0.06})_2As_2$, respectively. In (a) and (c) the grey area represents the analytic approximation to the particle-hole continuum given by Eqn. 6.8. The subtraction yields the fluctuation response depicted in (b) and (d).

For the spectrum of underdoped Ba(Fe_{0.945}Co_{0.055})₂As₂ [Fig. 6.6 (a)], the particle-hole continuum described by the grey area deviates from the experimental data in the low frequency regime and merges for energies above $\Omega_{\rm m} \approx 500 \text{ cm}^{-1}$. The subtraction yields the response of $R\Delta\chi''(\Omega)$ in Fig. 6.6 (b) in which $\Delta\chi''(\Omega \rightarrow 0) = 0$ and a sharp maximum is visible at 25 cm⁻¹. Above this energy, the intensity decreases and converges to zero above $\Omega_{\rm m}$.

The spectra of optimally doped $Ba(Fe_{0.94}Co_{0.06})_2As_2$ is in agreement with the particle-hole continuum for a larger range, starting at 100 cm⁻¹. At low

frequencies, the response increases sharply towards $\Omega \rightarrow 0$. This is qualitatively different to Ba(Fe_{0.945}Co_{0.055})₂As₂. After being separated from the p-h continuum the low-energy response will be analysed further.

6.2.2 Aslamazov-Larkin fluctuations

The spectral shape of $\Delta \chi''(\Omega)$ for Ba(Fe_{0.945}Co_{0.055})₂As₂ is analysed using the analytic expression of Eqn. 3.29 [Sec. 3.4.2]. The procedure to fit the data with this function is followed as described by Caprara *et al.* [43]: first, the spectral shape for the data at one temperature is reproduced by adjusting the mass m(T), the vertex strength Λ_0^2 and the cut-off frequency Ω_0 , where this cut-off is given by a typical phonon frequency [43]. The remaining spectra are then fitted by varying only the mass and keeping Λ_0^2 and Ω_0 fixed.

Fig. 6.7 (a) and (b) shows the experimental spectra along with the analytic functions in which Ω_0 was set at 350 cm⁻¹ consistent with earlier studies [23, 44, 132]. One can distinguish two regimes: (i) the intensity of the fluctuation response increases steadily upon cooling for temperatures above 53 K [Fig. 6.7 (a)]. The response develops from a broad hump at 153 K into a well defined peak which exhibits a maximum at 53 K at an energy of 25 cm⁻¹. (ii) The second regime for temperatures below 53 K shows, that the intensity decreases again [Fig. 6.7 (b)]. However, the peak does not vanish and maintains approximately one half of its spectral weight down to 26 K.

The spectra at temperatures $T \ge 53$ K were fitted by varying the mass m(T). For the temperature range $T \le 48$ K, the spectral shape could not be reproduced any more by only varying the mass m(T). The scaling factor Λ had to be varied in order to match the spectral shape.

Since the function in Eqn. 3.29 is defined down to $\Omega = 0$ the initial slope can be readily extracted as

$$\tau_{\rm AL} \equiv \lim_{\Omega \to 0} \frac{\partial \Delta \chi_{\rm AL}''(\Omega, T)}{\partial \Omega}$$
(6.9)

As can be seen in panel (d), τ_{AL} becomes maximal for 53 K and decreases below 48 K but does not vanish down to 26 K.



Figure 6.7: Analysis of the fluctuation response in Ba(Fe_{0.945}Co_{0.055})₂As₂. (a) The fluctuation response above T_s increases from a broad hump at 154 K into a well defined peak at 53 K, where the intensity become maximal. (b) Below T_s , the peak loses intensity, but does not vanish. The straight lines indicate the analytic spectral functions derived from the Aslamazov-Larkin diagrams. (c) The mass *m* and the scaling factor Λ_0^2 corresponding to the AL-functions. (d) The initial slope for $\Omega \rightarrow 0$ which develops a maximum at 53 K. The dashed line indicates the structural transition temperature T_s .

For Ba(Fe_{0.94}Co_{0.06})₂As₂, the situation is different. Fig. 6.8 (a) and (b) show the fluctuation contribution. In contrast to the data for Ba(Fe_{0.945}Co_{0.055})₂As₂, the hump at high temperatures is not as broad. Upon cooling, the peak sharpens down to 53 K. Below 53 K, the decrease on the high energy side is temperature dependent in that the fall off becomes even steeper. The red lines are the fits by Eqn. 3.29 with the corresponding masses as shown in panel (c). The cutoff had to be set to $\Omega_0 = 85$ cm⁻¹ for all temperatures in order to sufficiently reproduce the spectra. In contrast to the results of Ba(Fe_{0.945}Co_{0.055})₂As₂, the mass decreases down to the lowest temperature measured without any saturation and extrapolates linearly to $T_s = 0$. The relaxation time τ_{AL} increases monotonically



towards T_c . Below T_c the analysis cannot be continued because of the opening of the superconducting gap.

Figure 6.8: Analysis of the fluctuation response in Ba(Fe_{0.94}Co_{0.06})₂As₂. (a) The fluctuations become first visible at 113 K and develop into a sharp peak upon cooling towards 53 K which rapidly falls off as frequency is increased. (b) Below 53 K, the spectra show a weak temperature dependence where the cut-off becomes slightly sharper. The red lines represent fits using Eqn. 3.29. (c) The mass m(T) decreases monotonically and can be extrapolated to zero for low temperatures (red line). (d) The relaxation time τ increases monotonically towards low temperatures.

6.2.3 Imaginary-time dynamics

From the real frequency dynamics, it is possible to extract the imaginary time dynamics, as will be outlined in this section.

Quantities involving the imaginary time are usually not scrutinised in experimental studies. In contrast, theoreticians deploy the transformation $t \rightarrow -it = \tau$ regularly [143, 144] in quantum field theoretical calculations. A pedagogical introduction is given in Ref. [145]. There the substitution $\tau = -it$ in the timedependent Schrödinger equation makes it possible to directly simulate the ground state of the system. Thus, simulations are simplified by the introduction of τ . A problem occurs, when one tries to infer real-time dynamics from the results on the imaginary time axis in order to compare simulations with experiments. This problem is sometimes circumvented by using an analytic continuation, as mentioned in Sec. 3.2 for the derivation of the Raman response.

Lederer *et al.* [134] showed, that one can calculate the imaginary time ordered correlation function $\tilde{\Lambda}(\tau)$ via

$$\tilde{\Lambda}(\tau) = \frac{1}{2\pi} \int d\Omega \, \chi''(\Omega, T) \, \frac{\exp\left[\left(\tau - \beta/2\right)\Omega\right]}{\sinh\left[\beta\Omega/2\right]}.$$
(6.10)

from the imaginary part of an experimentally derived response function $\chi''(\Omega, T)$ as, for instance, measured by Raman spectroscopy. Here, $\beta = 1/k_B T$ is the inverse temperature and τ is the imaginary time. τ is proportional to the inverse temperature β and runs in the interval $(0, \beta)$. Example transforms are depicted in Fig. 6.9 (b) where data was published in Ref. [44, 97]. In panel (a) the B_{1g} Raman response of undoped BaFe₂As₂ is given for temperatures as indicated. At 325 K, the spectrum is dominated by particle-hole excitations. In the vicinity of the structural phase transition at T_s , the low-frequency pile up is maximal and collapses below T_s forming a gap associated with the SDW phase. The full transformation according to Eqn. 6.10 in Fig. 6.9 (b) is depicted as a function of the dimensionless quantity $r = \tau/\beta$.

The possibility to calculate this quantity provides us with an additional tool to investigate the low frequency Raman response dominated by fluctuations. This is because for the longest imaginary time $\tau \sim \beta/2$ given by the Matsubara condition for Fermions, $\omega_n = \pi (2n + 1)/\beta$, Eqn. 6.10 reduces to

$$\tilde{\Lambda}(\beta/2,T) = \frac{1}{2\pi} \int d\Omega \, \frac{\chi''(\Omega,T)}{\sinh[\beta\Omega/2]}.$$
(6.11)

The important point is the factor $1/\sinh[\beta\Omega/2]$ which is depicted in Fig. 6.9 (a) as dashed lines for the indicated temperatures. It resembles a temperature dependent cut-off which collects the spectral contribution for energies of the

order of the temperature, $\Omega \sim T$, thereby cutting off the high frequency part of the spectrum.



Figure 6.9: Example transformations from real to imaginary frequencies. (a) Raman response of BaFe₂As₂ in B_{1g} symmetry. At T = 325 K, the continuum is flat. The pile up of spectral weight at low frequencies for T = 136 K > T_s above the nematic transition collapses below T_s , forming the SDW gap. The otherwise forbidden A_{1g} mode is visible in B_{1g} due to the presumably magnetic ordering breaking the Z2 symmetry. From [44]. The dashed lines indicate the cut-off functions for the corresponding temperatures. (b) Imaginary time ordered correlation function $\tilde{\Lambda}(r, T)$ from the experimental Raman data where $r = \tau/\beta$ is a dimensionless quantity. At $\tau = \beta/2$ or r = 1/2, this correlation function encapsulates the Raman response for frequencies $\Omega \sim T$.

The quantity $\beta \tilde{\Lambda}(\beta/2, T)$ has an upper boundary in the static susceptibility $\chi'(0, T)$ as derived from the Kramers-Kronig transformation of $\chi''(\Omega, T)$ via

$$\chi'^{0}(T) \equiv \chi'(0,T) = \frac{1}{\pi} \int d\Omega \, \frac{\chi''(\Omega,T)}{\Omega}.$$
(6.12)

The static susceptibility is related to the nematic susceptibility [121]. The relation between $\tilde{\Lambda}^{\beta/2}(T)$ and $\chi'^0(T)$ is easy to see if one considers the series expansion $\sinh[\beta\Omega/2] \approx \beta\Omega/2 + ...$ and therefore

$$\tilde{\Lambda}^{\beta/2}(T) \equiv \beta \tilde{\Lambda}(\beta/2, T) \le \frac{1}{\pi} \int d\Omega \, \frac{\chi''(\Omega, T)}{\Omega} = \chi'(0, T). \tag{6.13}$$

As a second remark, it is noted that the exact calculation of the static susceptibility from the KK transformation is only possible if $\chi''(\Omega)$ converges as $\Omega^{-\epsilon}$ with $\epsilon > 0$ or faster for high frequencies. Otherwise, the integration gives a logarithmically growing contribution to the integral in lowest order, as $\int 1/\Omega$ does not converge. In this case, one needs to introduce an upper cut-off which is not easily justified. In contrast, $1/\sinh[\beta\Omega/2]$ of $\tilde{\Lambda}^{\beta/2}(T)$ converges to zero exponentially fast for high frequencies. Therefore no cut-off is needed. To compare these methods, we apply both transformations to data of underdoped Ba(Fe_{1-x}Co_x)₂As₂ previously under investigation [44].

The transformations calculated from the Raman spectra with Eqn. 6.11 are depicted in Fig. 6.10. $\tilde{\Lambda}^{\beta/2}(T)$ and $\chi'^0(T)$ show a similar high-temperature behaviour in A_{1g} and B_{1g} symmetry for all doping concentrations. $\tilde{\Lambda}^{\beta/2}_{B_{1g}}(T)$ and $\chi'^0_{B_{1g}}(T)$ deviate from the A_{1g} signals at approximately T_f . Upon cooling towards the nematic transition T_s , the A_{1g} signal stays constant whereas both $\chi'^0_{B_{1g}}(T)$ and $\tilde{\Lambda}^{\beta/2}_{B_{1g}}(T)$ develop a maximum at T_s for all doping concentrations. A discontinuity at the magnetic transition temperature T_{SDW} can be observed as well for $\tilde{\Lambda}^{\beta/2}(T)$, albeit it is weak for x = 0.051. $\tilde{\Lambda}^{\beta/2}_{A_{1g}}(T)$ vanishes for $T \to 0$, whereas $\chi'^0_{A_{1g}}(T)$ stays roughly constant over the entire temperature range.



Figure 6.10: Comparison between $\tilde{\Lambda}^{\beta/2}(T)$ (left) and $\chi'(0, T)$ (right) of Ba(Fe_{1-x}Co_x)₂As₂ for doping concentrations as indicated with the structural transition temperature T_s and the magnetic transition temperature T_{SDW} . The black squares represent the results in A_{1g} symmetry and the red diamonds those in B_{1g} symmetry.

The $\tilde{\Lambda}_{A_{1g}}^{\beta/2}(T)$ and $\tilde{\Lambda}_{B_{1g}}^{\beta/2}(T)$ both vanish for $T \to 0$, whereas $\chi'^0_{A_{1g}}(T)$ and $\chi'^0_{B_{1g}}(T)$ remain finite even for low temperatures.

The same analysis is used for the doping concentrations x = 0.055, x = 0.060 and x = 0.085. The results are shown in Fig. 6.11. For x = 0.055 [Fig. 6.10 (a1) and (a2)], the B_{1g} signal deviates from the A_{1g} signal at around 153 K for both methods. The signals in B_{1g} symmetry becomes maximal at 53 K what is consistent with a nematic transition temperature $T_s = (50 \pm 2)$ K.



Figure 6.11: Comparison between $\beta \Lambda(\beta/2, T)$ (left) and $\chi'(0, T)$ (right) of Ba(Fe_{1-x}Co_x)₂As₂ for doping concentrations as indicated with the structural transition temperature T_s and the magnetic transition temperature T_{SDW} . The black squares represent the results in A_{1g} symmetry and the red diamonds those in B_{1g} symmetry.

At optimal doping [panels (b1) and (b2)], the B_{1g} and A_{1g} signals start to deviate from $T_{\rm f} = 113$ K downwards. $\tilde{\Lambda}^{\beta/2}_{A_{1g}}(T)$ goes to zero and $\chi'^0_{A_{1g}}(T)$ increases over the entire temperature range. $\tilde{\Lambda}^{\beta/2}_{B_{1g}}(T)$ increases towards 50 K and decreases for decreasing temperature, but does not match $\tilde{\Lambda}^{\beta/2}_{A_{1g}}(T)$ even at the lowest temperatures. $\chi'^0_{B_{1g}}(T)$ increases down to 50 K where it saturates.

For the results on the overdoped side, no significant difference between the

 A_{1g} and B_{1g} signals can be observed. $\tilde{\Lambda}_{A_{1g}}^{\beta/2}(T)$ and $\tilde{\Lambda}_{B_{1g}}^{\beta/2}(T)$ approach zero for low temperature. $\chi'^0_{A_{1g}}(T)$ and $\chi'^0_{B_{1g}}(T)$ increase towards zero temperature.

6.3 Discussion

The analysis above shows that the temperature dependence of the Raman data in B_{1g} symmetry can be explained in terms of a fluctuation response sitting on top of a particle-hole continuum. To discuss the possible origins of this fluctuation response further, the qualitative change from $Ba(Fe_{0.945}Co_{0.055})_2As_2$ to $Ba(Fe_{0.94}Co_{0.06})_2As_2$ is outlined in the following.

For Ba(Fe_{0.945}Co_{0.055})₂As₂, the results for $T > T_s$ are qualitatively similar to those shown in Ref. [44]. The relaxation rate analysis [Fig. 6.4] clearly shows the dichotomy between A_{1g} and B_{1g} symmetry setting in at the fluctuation temperature $T_f = (153 \pm 20)$ K. While $\Gamma^0_{A_{1g}}(T)$ resembles the in-plane resistivity down to T_s , $\Gamma^0_{B_{1g}}(T)$ deviates for $T < T_f$ and develops a minimum at 53 K.

For Ba(Fe_{0.94}Co_{0.06})₂As₂, the deviation between the A_{1g} and B_{1g} relaxation rates sets in at $T_f = (133 \pm 20)$ K. However, here the relaxation rate does not develop a distinct minimum. Instead, it decreases further towards T_c . This first difference hints towards the absence of a nematic phase transition above T_c .

The second difference is revealed by the subtraction of the particle-hole continuum. The spectral shape $R\Delta\chi''(\Omega, T)$ of Ba(Fe_{0.945}Co_{0.055})₂As₂ has a maximum at 100 cm⁻¹ for 153 K which hardens down to $\Omega \sim 25$ cm⁻¹ above the nematic phase transition. The data can be fitted with the analytic function derived from AL-fluctuation-like diagrams using the same cut-off $\Omega_0 = 350$ cm⁻¹ as for the underdoped compounds [97]. In contrast, the fluctuation response of Ba(Fe_{0.94}Co_{0.06})₂As₂ is more narrow, even at high temperatures. The visible peak maximum moves from 50 cm⁻¹ at 113 K down to 10 cm⁻¹ at 53 K. From the data, one cannot say, if it moves even further down in energy, as the experimental limitation is reached at 5-10 cm⁻¹. Nonetheless, the procedure with the AL-description works for a smaller cut-off of $\Omega_0 = 85$ cm⁻¹ for all temperatures. The peak maximum lies at most at (10 ± 5) cm⁻¹ which is a factor of 2 lower than for Ba(Fe_{0.945}Co_{0.055})₂As₂.

The analysis indicates that Ba(Fe_{0.945}Co_{0.055})₂As₂ undergoes a nematic phase transition around $T_s \sim 50$ K. The general behaviour is consistent with previous studies and we therefore adopt the spin-fluctuation picture for Ba(Fe_{0.945}Co_{0.055})₂As₂. For optimal doping in Ba(Fe_{0.94}Co_{0.06})₂As₂, no other phase transition can be observed above T_c . In the following, it is argued, that the fluctuations are associated with a quantum critical point (QCP). In order to pin down the quantum critical point, we start with the temperature dependence of the mass m(T, x) used in the AL-fits. We deploy [62]

$$m(T, x) = m_0(x) + a(T - T_s)^{2\nu(x)}$$
(6.14)

in which $m_0(x)$ is the residual mass at the nematic phase transition and $\nu(x)$ the critical exponent. In the case of a nematic quantum critical point, one should be able to find that the transition temperature at the critical doping x_c approaches zero $T_s \rightarrow 0$ and that the mass therefore scales with $m(T, x_c) \propto T^{2\nu}$ [62].



Figure 6.12: (a) Temperature dependent mass m(T, x) for doping concentrations as indicated. The red curves represent fits with Eqn. 6.14. The results of x = 0, x = 0.025, x = 0.051 were taken from Ref. [62]. (b) The residual mass $m_0(x)$ derived from the fit decreases with increased doping. The critical exponent v(x) increases from v(0) = 0.75 to almost unity at $v(x_c = 0.060) = 0.98$ for optimally doped Ba(Fe_{0.94}Co_{0.06})₂As₂.

The fits with Eqn. 6.14 are depicted in Fig. 6.12 (a) as red lines with the nematic transition temperature of $Ba(Fe_{0.94}Co_{0.06})_2As_2$ at $T_s = 0$. Both, the

results of Ba(Fe_{0.945}Co_{0.055})₂As₂ and Ba(Fe_{0.94}Co_{0.06})₂As₂ are reproduced well. The doping dependence of the residual mass $m_0(x)$ and the critical exponent v(x) are depicted in Fig. 6.12 (b). $m_0(x)$ decreases monotonically as a function of doping x, whereas the critical exponent v(x) increases and almost reaches unity at x_c . Additionally, the initial slope $\tau_{AL}(T, x)$ is depicted in Fig. 6.13. The initial slope increases as a function of doping suggesting, that the magnitude of fluctuations increases.



Figure 6.13: Initial slope $\tau(x)$ from the AL-fits which increases as a function of doping and is largest for the optimally doped Ba(Fe_{0.94}Co_{0.06})₂As₂.

The last two arguments for the quantum critical fluctuations originate from the imaginary time formalism. A QMC simulation of $\tilde{\Lambda}(\beta/2)$ for a nematic quantum critical point by Sam Lederer [146] suggests, that $\tilde{\Lambda}(\beta/2)$ diverges with $T \to 0$. However, pinning down this divergence in the experiment proofs to be challenging, as the numerical cut-off of $\tilde{\Lambda}(\beta/2)$ requires knowledge of the response below the experimental cut-off at $\Omega \approx 10 \text{ cm}^{-1}$. This prevents a clear divergence of $\tilde{\Lambda}_{B_{1g}}^{\beta/2}(T)$ for $T \to 0$ at optimal doping x_c and results in a hump for $T > T_c$. In the absence of any other phase transition apart from superconductivity in Ba(Fe_{0.94}Co_{0.06})₂As₂, this is associated with the fluctuations from a zero temperature phase transition.

Furthermore, a more qualitative argument enables us to make a suggestion about the spectral shape of the Raman response. Close to a QCP, the bosonic correlator reads [134]

$$\tilde{\Lambda}(\tau) = A \left[\frac{1}{\left| \tau \right|^{\nu}} + \frac{1}{\left| \beta - \tau \right|^{\nu}} \right]$$
(6.15)

where *A* is a constant, τ the imaginary time and β the inverse temperature. From this, one derives the expression for the imaginary part of the response function $\chi''(\Omega)$,

$$\chi''(\Omega) = \frac{A}{T^{1-\nu}} F(\beta \Omega)$$
(6.16)

where $F(\beta \Omega)$ is the scaling function:

$$F(\beta\Omega) = \frac{\pi\beta\Omega}{\Gamma(\nu)} \left| \frac{1}{\beta\Omega} \right|^{2-\nu} \left[1 - \exp\left[-\left| \beta\Omega \right| \right] \right]$$
(6.17)

with the Gamma function $\Gamma(\nu)$. From the mass we derive the critical exponent $\nu \approx 1$. For energies $T \ll \Omega \ll \Omega_c$ where Ω_c is an ultraviolet cut-off, Eqn. 6.16 yields a power-law behaviour,

$$\chi''(\Omega) \sim \frac{\Omega}{|\Omega|^{2-\nu}}.$$
(6.18)

For $\nu \sim 1$, $\chi''(\Omega)$ is a constant which describes the raw data for temperatures T < 53 K. To conclude, the fluctuation response in Ba(Fe_{0.945}Co_{0.055})₂As₂ fits in with previous results. The signal stems most likely from spin-fluctuations. The fluctuation response in Ba(Fe_{0.94}Co_{0.06})₂As₂ is best explained with the occurrence of quantum critical fluctuations. As the nematic transition temperature at optimal doping can be estimated to approach zero from the doping dependence of the mass [see Fig. 6.12], the corresponding QCP can be classified as a nematic quantum critical point. To illustrate the interplay of fluctuations and superconductivity, consider the phase diagram of Ba(Fe_{1-x}Co_x)₂As₂ in Fig. 6.14.



Figure 6.14: Phase diagram of Ba(Fe_{1-x}Co_x)₂As₂. The grey area is the region of the spindensity-wave, the magenta stripe corresponds to the nematic phase and the transparent blue area to superconductivity. The colour gradient indicates the fluctuations and relates to the magnitude of $\tau_{AL}(x)$ [black diamonds from Fig. 6.13 (b)] which increases towards optimal doping at the putative QCP (blue dot) and decreases on the overdoped side. The data for $x \le 0.051$ were published in Ref. [44].

The area coloured in shades of red indicates the value of $\tau_{AL}(x)$ which was extrapolated from the data in Fig. 6.13, and particularly in the region beneath the superconducting dome. The data were extrapolated on the overdoped side where T_c decreases by considering, that the fluctuations vanish in Ba(Fe_{0.915}Co_{0.085})₂As₂. The strength of fluctuations increases towards and is largest at optimal doping where T_c is largest. This concomitant doping dependence of T_c and $\tau_{AL}(x)$ may indicate, that critical fluctuations play a role in the formation of Cooper pairs in superconducting Ba(Fe_{1-x}Co_x)₂As₂.

6.3. Discussion

Chapter 7

Summary

Cooper pairing in unconventional superconductors remains one of the major challenges in condensed matter physics. The relevant interactions are much harder to pin down than in conventional systems. It is the purpose of this thesis to access the related interactions by Raman spectroscopy. For the analysis of the low-energy spectra a novel method is developed, applied and tested. Critical fluctuations of spin or charge are studied and identified in Ba(Fe_{1-x}Co_x)₂As₂ and may contribute to the pairing, at least close to optimal doping. The spectra of CaKFe₄As₄ suggest the existence of a similar hierarchy of pairing channels as in Ba_{1-x}K_xFe₂As₂.

In stoichiometric CaKFe₄As₄, the electronic continuum was studied above and below the superconducting transition temperature T_c in three polarisation configurations projecting A_{1g}, B_{1g} and B_{2g} symmetries with individual sensitivities in momentum space. Below T_c , a redistribution of spectral weight from below to above the gap energy was observed in all three symmetries. The spectral shapes vary across the symmetries. The weakest redistribution was found in B_{2g} symmetry having the intensity maximum at an energy close to the largest superconducting gaps derived from angle-resolve photoemission spectroscopy (ARPES). The superconducting feature in the A_{1g} signal is broad and shows contributions from all bands in agreement with the Raman selection rules. In contrast, a well-defined peak appears in B_{1g} symmetry at 134 cm⁻¹. This energy is substantially lower than expected from the results in A_{1g} and B_{2g} symmetry. On the high-energy side of the B_{1g} peak there is a hump at an energy roughly corresponding to the energy gap on the electron pockets. In analogy to $Ba_{0.65}K_{0.35}Fe_2As_2$ the maximum at 134 cm⁻¹ was interpreted in terms of a Bardasis-Schrieffer (BS) exciton resulting from a competing sub-leading $d_{x^2-y^2}$ wave interaction. The weak hump at 50 cm⁻¹ well below the peak maximum was tentatively assigned to a second BS mode. The low absolute energy and small spectral weight suggest a substantially higher binding energy indicating, that CaKFe₄As₄ may even be closer to a *d*-wave instability than $Ba_{0.65}K_{0.35}Fe_2As_2$.

The symmetries of the ground state and of the sub-leading channels argue for unconventional pairing in the pnictides but do not specify any origin of the respective instabilities. As fluctuations indicate an enhanced susceptibility and have been identified to boost T_c , the temperature and symmetry dependence of the fluctuations was studied in Ba $(Fe_{1-x}Co_x)_2As_2$. In three superconducting samples having x = 0.055, 0.060 and 0.085 the response was measured in detail below 500 cm⁻¹. The low-frequency part in A_{1g} spectra increases monotonically with decreasing temperature as expected from the resistivity. In contrast, the B_{1g} signals of Ba(Fe_{0.945}Co_{0.055})₂As₂ and Ba(Fe_{0.94}Co_{0.06})₂As₂ change drastically below the onset temperature of fluctuations $T_{\rm f}$. In Ba(Fe_{0.915}Co_{0.085})₂As₂, the temperature dependence of the B_{1g} and A_{1g} signal are similar, and the low-energy parts track the resistivity. This indicates that the fluctuations are superimposed on the particle-hole continuum and vanish in the range $0.060 < x \le 0.085$. The bare fluctuation response can be isolated and reproduced using a model function on the basis of Aslamazov-Larkin (AL) diagrams. The temperature dependence of the model function facilitates the derivation of the nematic transition temperature in Ba(Fe_{0.945}Co_{0.055})₂As₂ to be $T_s = (50 \pm 2)$ K.

The low-frequency spectra are further analysed by deriving the response for imaginary times from the real frequency Raman data. The method is applied in the doping range $0 \le x \le 0.085$ and revealed signatures of fluctuations for $x \le 0.060$ but not for Ba(Fe_{0.915}Co_{0.085})₂As₂. For x = 0.06 the nematic transition temperature is determined to approach zero arguing for the existence of a nematic QCP in Ba(Fe_{1-x}Co_x)₂As₂. The fluctuation strength as well as T_c enhancement towards optimal doping and decrease for x > 0.06 indicate a possible contribution of critical fluctuations to the Cooper pairing in Ba(Fe_{1-x}Co_x)₂As₂.

Appendix A

Phonons in CaKFe₄As₄

This appendix completes the analysis of the CaKFe₄As₄ Raman data. First, the possible eigenvectors are presented in comparison to those in BaFe₂As₂ [135]. Then, the phonon lines are identified in the Raman spectra. The temperature dependences of the phonons in A_{1g} symmetry are analysed by extracting the peak energy $\Omega_c(T)$ and the linewidth $\Gamma(T)$.

At least two phonon modes observed in A_{1g} symmetry show signs of a finite electron-phonon coupling (EPC). The total EPC constant λ of the Raman-active phonons in CaKFe₄As₄ was estimated.

A.1 Number of phonons and eigenvectors

The primitive unit cell of CaKFe₄As₄ is twice as large as that of BaFe₂As₂. This, in turn doubles the number of Raman-active phonons in CaKFe₄As₄. This can be well understood with the following argument: the base vectors which project the unit cell onto themselves are (a/2, b/2, c/2) and (a, b, c) in BaFe₂As₂ and CaKFe₄As₄, respectively. In-phase vibrational modes occur, if, and only if, the atoms of these unit cells are projected onto themselves. In the case of the CaKFe₄As₄, this disentangles the As(1) and As(2) as well as the Fe planes giving rise to two additional A_{1g} and two additional E_g modes.

Using the Bilbao server [147] one can extract the number of Raman-active phonons from the Wyckoff positions of the atoms. The results are collected in

Tab. A.1 and Tab. A.2 for BaFe₂As₂ and CaKFe₄As₄, respectively.

Wyckoff position	atom	A _{1g}	A _{2g}	B _{1g}	B _{2g}	Eg
2a	Ва	-	-	-	-	-
4d	Fe	-	-	1	-	1
4e	As	1	-	-	-	1

Table A.1: Raman-active phonons in BaFe₂As₂. Wyckoff positions taken from [4].

Table A.2: Raman-active phonons in CaKFe₄As₄. Adapted from Ref. [47]. Wyckoff positions from Ref. [30].

Wyckoff position	atom	A _{1g}	A _{2g}	B _{1g}	B _{2g}	Eg
1a	Ca	-	-	-	-	-
1d	K	-	-	-	-	-
4i	Fe	1	-	1	-	2
2g	As(1)	1	-	-	-	1
2h	As(2)	1	-	-	-	1

Fig. A.1 shows the B_{1g} phonon which stems from the displacement of the out-of-phase vibrations of the Fe atoms in each layer. The B_{1g} phonon branch does not change from I4/mmm to P4/mmm.

Fig. A.2 shows the displacement of the As atoms changing from $BaFe_2As_2$ in (a) to $CaKFe_4As_4$ in (b)-(d). While $BaFe_2As_2$ allows only for the eigenvectors as indicated, $CaKFe_4As_4$ frees up the As(1) layers to move either in-phase or out-of-phase with the As(2) layers. We will denote the former as $A_{1g}^{(As(1))}$ and the latter as $A_{1g}^{(As(2))}$ mode.

Additionally, the Fe atoms of each layer may vibrate in-phase giving rise to the third mode denoted as $A_{1g}^{(Fe)}$. Fig. A.3 shows the displacement of the Fe and As layers which result in phonons of E_g symmetry. There are two E_g phonons in BaFe₂As₂. The same argument as above (CaKFe₄As₄ unit cell is twice as large as the BaFe₂As₂ unit cell) applies, which results in the four E_g modes in CaKFe₄As₄.



Figure A.1: B_{1g} phonon branch for CaKFe₄As₄ and BaFe₂As₂. The Fe atoms vibrate out-of-phase.



A_{1g} lattice vibrations from *I4/mmm* to *P4/mmm*

Figure A.2: Raman active A_{1g} modes in $BaFe_2As_2$ and $CaKFe_4As_4$ vibrating along the c-axis. The black arrows indicate the atom displacement. (a) The vibrations of A_{1g} symmetry in $BaFe_2As_2$ split up into (b) in-phase vibrational modes of As(1) and As(2) atoms and (c) out-of-phase As(1) and As(2) vibrations. (d) An additional A_{1g} mode resulting from the Fe displacement.



Figure A.3: Raman-active E_g modes in $BaFe_2As_2$ and $CaKFe_4As_4$. Fe and As atoms are displaced as indicated by the black arrows in the *a-b*-plane.



Figure A.4: Raman-active phonons in CaKFe₄As₄ at 43 K. (a) The blue and magenta arrows indicate the six *RR* phonon lines in A_{1g} and E_g symmetry, respectively. (b) In x'y' polarisation, the upward red arrow shows the B_{1g} phonon. The red line corresponds to a two-peak Voigt fit. The black curve in the inset is a one-peak Voigt of the B_{1g} phonon line. The crystallographic unit cell is depicted along with the polarisation configurations for *RR* and x'y' in the upper and lower panel, respectively. Taken from Ref. [45].

A.2 Raman active modes

The Raman-active phonon lines in $CaKFe_4As_4$ are displayed in Fig. A.4, exemplary for 43 K. Their resonance frequencies were extracted with least-square fits and are summarised in Table A.3. In Fig. A.4 (a) six phonon modes can be seen with *RR* polarisation. Three of these six phonon lines occur only for *RR* polarisation and are therefore ascribed A_{1g} symmetry. The in-phase *c*-axis vibrational modes corresponding to the As(1) and As(2) planes (*cf.* Subsec. A.1) are located at 67.6 cm⁻¹ and 187.9 cm⁻¹. The third mode is located at 288 cm⁻¹ and results from the in-phase vibration of the Fe atoms along the *c*-axis.

pol	unit	E _g ⁽¹⁾	$A_{1g}^{(As(1))}$	E _g ⁽²⁾	$A_{1g}^{(As(2))}$	B _{1g} ^(Fe)	E _g ⁽³⁾	A ^(Fe) _{1g}
RR	cm^{-1}	40.4	67.6	120.9	187.9		231.9	287.5
	meV	5.0	8.4	15.0	23.3	26.7	28.8	35.6
x'y'	cm^{-1}	40.5		120.9		215.2	231.1	

Table A.3: Phonon frequencies in CaKFe₄As₄ at 43 K as derived from the fit functions.

For x'y' polarisation (Fig. A.4 (b)) we find the strongest phonon line at 215 cm⁻¹. This corresponds to the out-of-phase vibration of the Fe atoms along the *c*-axis. In the crystallographic 2-Fe unit cell this is B_{1g} symmetry. Three modes are visible for both *RR* and x'y' polarisations. As both polarisations yield a finite projection onto the *z*-axis, these lines are assigned E_g symmetry. The E_g phonons result from Fe and As atoms moving parallel to the FeAs planes. The E_g mode at 232 cm⁻¹ does not show up as a clear peak in x'y' polarisation due to its proximity to the B_{1g} phonon. However, an analysis with a two-peak Voigt function in Fig. A.4 (b) in red is more convincing than a one-peak Voigt function in the inset (black).

The fourth E_g phonon was not observed, either because of too low intensity or because it occurs at higher energies than the ones observed.

The temperature dependence of the peak energy and the line width were extracted for the *RR* data with the Voigt fit which results from the convolution of a Gaussian with Lorentzian function:

$$y(\Omega) = y_0 + m \cdot \Omega + A \frac{2\ln 2}{\pi^{3/2}} \frac{\Gamma_L}{\Gamma_G^2} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{\left(\sqrt{\ln 2\frac{\Gamma_L}{\Gamma_G}}\right)^2 + \left(\sqrt{4\ln 2\frac{\Omega-\Omega_c}{\Gamma_G}} - t\right)^2} dt \quad (A.1)$$

The electronic background is approximated with the linear term $y_0 + m \cdot \Omega$. Γ_L is the width of the Lorentzian and Γ_G the width of the Gaussian function. Γ_G is

determined by the resolution of the spectrometer. For $\lambda_{\text{exc}} = 575 \text{ cm}^{-1}$, this is $\Gamma_G = 4.85 \text{ cm}^{-1}$. The Full-Width-Half-Maximum (FWHM) is defined as

$$FWHM = 0.5346\Gamma_L + \sqrt{0.2166\,\Gamma_L^2 + \Gamma_G^2} \tag{A.2}$$

The $A_{1g}^{(As(1))}$ and $A_{1g}^{(As(2))}$ modes were better fitted with a convolution of a Gaussian with a Fano function. These are discussed in the next section.

The result for the $E_g^{(1)}$, $E_g^{(2)}$, $E_g^{(3)}$ and $A_{1g}^{(Fe)}$ modes are depicted in Figs. A.5-A.8. Overall, the peak energy Ω_c increases upon cooling. The linewidth Γ_L decreases for all modes except for the $E_g^{(3)}$ mode. Here, the resolution may have played a role



Figure A.5: Analysis of the $E_g^{(1)}$ mode. (a) Spectra in *RR* polarisation for temperatures as indicated. The black lines show the Voigt fit. (b) The resonance frequency Ω_c as a function of temperature shows the hardening of the lattice as one tunes to lower temperatures. (c) The Lorentzian line-width Γ_L decreases for decreasing temperature. The resolution was at the limit of the spectrometer. (d) The Full-Width-Half-Maximum of the Voigt shows, that the width of the spectra is dominated by the resolution of the spectrometer due to the small intrinsic linewidth of the phonon.



Figure A.6: Analysis of the $E_g^{(2)}$ mode. (a) Spectra in *RR* polarisation for temperatures as indicated. The black lines show the Voigt fit. (b) The resonance frequency as a function of temperature shows the hardening of the lattice as one tunes to lower temperatures. (c) The Lorentzian line-width Γ_L decreases for decreasing temperature. (d) The Full-Width-Half-Maximum of the Voigt fit.



Figure A.7: Analysis of the $E_g^{(3)}$ mode. (a) Spectra in *RR* polarisation for temperatures as indicated. The black lines show the Voigt fit. (b) The resonance frequency as a function of temperature shows the hardening of the lattice as one tunes to lower temperatures. (c) The Lorentzian line-width Γ_L decreases for decreasing temperature. (d) The Full-Width-Half-Maximum of the Voigt fit.



Figure A.8: Analysis of the $A_{1g}^{(Fe)}$ mode. (a) Spectra in *RR* polarisation for temperatures as indicated. The black lines show the Voigt fit. (b) The resonance frequency as a function of temperature shows the hardening of the lattice as one tunes to lower temperatures. (c) The Lorentzian line-width Γ_L decreases for decreasing temperature. The resolution was at the limit of the spectrometer. (d) The Full-Width-Half-Maximum of the Voigt.

A.3 Electron-phonon coupling

Separated from the discussion in chapter 5 is the analysis of the phonon modes and the electron-phonon coupling (EPC) here. This is initially owed to the marginal effect which one expects from the EPC on superconductivity in the pnictides. Nonetheless, as the 1144 compounds, although being very similar to the BaFe₂As₂ systems, are relatively new, it is worthwhile to check if the paradigm of a very weak EPC holds for CaKFe₄As₄ as well.

A.3.1 Analysis

The two A_{1g} modes which provide hints for an EPC are the $A_{1g}^{(As(1))}$ and $A_{1g}^{(As(2))}$ mode. The $A_{1g}^{(As(1))}$ mode exhibits an asymmetry for all temperatures (Fig. A.9 (a)). The intrinsic lineshape corresponds to a Fano resonance [148]. In a slighty modified form, this is given by [149]

$$F(\Omega') = \left| \frac{A}{q^2 - 1} \right| \frac{2}{\Gamma_L \pi} \left[\frac{(q + \Omega')^2}{1 + {\Omega'}^2} - 1 \right]$$
(A.3)

with the area *A*, the asymmetry parameter *q*, the Lorentzian width Γ_L and $\Omega' = 2(\Omega - \Omega_c)/\Gamma_L$, modulo a linear background.



Figure A.9: Analysis of the $A_{1g}^{(As(1))}$ mode. (a) Spectra in *RR* polarisation for temperatures as indicated. The black lines show the fit function in which a Fano is convoluted with a Gaussian. The following values were extracted from the fit function: (b) The resonance frequency as a function of temperature shows the hardening of the lattice as one tunes to lower temperatures. (c) The asymmetry factor *q* decreases as the temperature decreases. (d) The Lorentzian line-width Γ_L decreases for decreasing temperature. The red curve corresponds to the temperature dependence from anharmonic decay.

From the temperature dependence of Γ_L , one can extract the dimensionless phonon-phonon coupling λ_{ph-ph} via [150, 151]:

$$\Gamma(T) = \Gamma_{0,L} \left[1 + \frac{2\lambda_{\rm ph-ph}}{\exp\left[\frac{\hbar\Omega_0}{2k_{\rm B}T}\right]} \right]$$
(A.4)
Here $\Gamma_{0,L}$ is the zero temperature linewidth and Ω_0 the zero temperature frequency. From Fig. A.9, we estimate $\Gamma_{0,L} = 0.51 \text{ cm}^{-1}$ and $\Omega_0 = 67.9 \text{ cm}^{-1}$. Leaving the phonon-phonon coupling as the only free parameter, the fit of the linewidth delivers $\lambda_{ph-ph} = 0.11$. The fact that the $A_{1g}^{(As(1))}$ mode exhibits a Fano lineshape is indicative of a coupling to the electronic continuum. Therefore, one may estimate the electron-phonon coupling from the phonon-phonon coupling via $\lambda_{el-ph}^2 \propto \lambda_{ph-ph}$ [152]. One then finds $\lambda_{el-ph} \sim 0.32$. The coupling of the $A_{1g}^{(As(2))}$ mode to the continuum manifests as a Fano lineshape

as well. Additionally, this mode does not narrow as temperature decreases, but broadens, specifically for $T < T_c$. We use this to get a figure on the contribution λ_i to the total electron-phonon coupling with [153, 154]

$$\lambda_i = \frac{d_i}{\pi N(E_F)} \frac{\Delta \Gamma_{0,i}}{\Omega_{0,i}^2}$$
(A.5)

where $\Delta\Gamma_{0,i}$ is the linewidth broadening [150, 155, 156] and $N(E_F)$ the density of states at the Fermi energy E_F per spin. d_i is the mode degeneracy. For A_{1g} symmetry, this is equal to unity. For a rough estimate of $\Delta\Gamma_L$, the linewidth of the $A_{1g}^{(As(2))}$ mode is compared with the A_{1g} mode of undoped BaFe₂As₂. This is done by extracting the phonon-phonon coupling λ_{ph-ph} for the A_{1g} phonon of the BaFe₂As₂. This is used to estimate the $\Gamma_{0,L}$ value of the $A_{1g}^{(As(2))}$ mode in CaKFe₄As₄ in the absence of broadening. This value is $\Gamma_{0,L}^{anharm} = 5.03 \text{ cm}^{-1}$. The extrapolation of the data, on the other hand, gives us $\Gamma_{0,L}^{extra} = 12.41 \text{ cm}^{-1}$ and the difference therefore is $\Delta\Gamma_0 = 7.4 \text{ cm}^{-1}$. The contribution of the $A_{1g}^{(As(2))}$ mode to the electron-phonon coupling is then $\lambda_i = 0.12$ which gives us a total $\lambda = 0.45$.



Figure A.10: Analysis of the $A_{1g}^{(As(2))}$ mode. (a) Spectra in *RR* polarisation for temperatures as indicated. The black lines show the fit function in which a Fano is convoluted with a Gaussian. The following values were extracted from the fit function: (b) The resonance frequency as a function of temperature shows the hardening of the lattice as one tunes to lower temperatures. (c) The asymmetry factor *q* decreases as the temperature decreases. (d) The Lorentzian line-width Γ_L stays constant in the range $T > T_c$ and increases for $T < T_c$. The red curve corresponds to the temperature dependence from anharmonic decay in which the phonon-phonon interaction was derived from undoped BaFe₂As₂ for comparative reasons and to extract the linewidth broadening.

To estimate T_c , we plug this value into the modified McMillan formula [157, 158]

$$T_{\rm c} = \frac{\Omega_{\rm log}}{1.2 \, k_{\rm B}} \exp\left[-\frac{1.04 \, (1+\lambda))}{\lambda - \mu^* \, (1+0.62\lambda)}\right] \tag{A.6}$$

in which μ^* is the pseudo potential and Ω_{\log} is the logarithmic average over all

phonon frequencies contributing to the electron-phonon coupling. It should be clarified, that Eqn. A.6 is a crude approximation, since the value for the pseudopotential μ^* is not easy to come by. If the Coulomb repulsion is uniform in the FeSC, the pseudopential ranges from 0.15 to 0.2 [26]. On the other hand, if the unrenormalised Coulomb interaction is different for interband and intraband interactions, it may be reduced and therefore μ may be reduced [26]. In the absence of additional data on the pseudopotential, μ was considered to be in the range from 0.1 [153] to 0.2. With the above λ , the order of the critical temperature from EPC is $T_c \sim 0.05 - 1.3$ K. Even in the extreme case of $\mu^* = 0$, the transition temperature would reach $T_c \sim 4.8$ K.

A.3.2 Conclusion

As expected, the EPC derived from the Raman-active phonons cannot explain the T_c in CaKFe₄As₄. However, this does not mean, that the role of phonons in the superconducting pairing can be entirely ruled out. This becomes clear by considering the case of FeSe thin films on SrTiO₃ in which T_c is enhanced by at least a factor of 8. Here, the enhancement of T_c in the thin film may be caused due to coupling to the oxygen phonons of the substrate [159].

This mechanism may extend to bulk systems as well. A recent study on the cuprate superconductor Bi-2122 [160] showed an enhancement effect of the electron-electron interaction and the electron-phonon coupling which may increase T_c in these materials. While the analysis above is far from claiming a similar effect in CaKFe₄As₄, it may be fruitful to scrutinise the EPC of the Raman-active phonons in future studies. The elusiveness of explanations of high temperature superconductors may result from a too simplified picture which might have to be replaced by a more complex approach of intertwining coupling mechanisms, ranging from EPC to spin fluctuations and quantum critical phenomena.

A.3. Electron-phonon coupling

Appendix **B**

$Ba(Fe_{1-x}Co_x)_2As_2$

B.1 Relaxation rates for x = 0.06 and x = 0.085

The dynamic relaxation rates of $Ba(Fe_{0.94}Co_{0.06})_2As_2$ and $Ba(Fe_{0.915}Co_{0.085})_2As_2$ are shown in Fig. B.1 and Fig. B.2. From these, the static relaxation rates depicted in 6.5 (b) and (c) were derived. The calculation of the relaxation rates is described in Sec. 6.2.1. The straight lines in the respective figures correspond to the fit of the data with the parallel resistor model of Eqn. 6.5.



Figure B.1: Relaxation rate analysis of Ba(Fe_{0.94}Co_{0.06})₂As₂. (a) Dynamic relaxation rate of the data in A_{1g} symmetry. (b) Dynamic relaxation rate of the data in B_{1g} symmetry. The straight lines are the fits from the parallel resistor model. (c) The static relaxation rates derived from the PRM as a function of temperature in B_{1g} as black diamonds and A_{1g} with red diamonds along with the resistivity $\rho(T)$ from Ref. [22].



Figure B.2: Relaxation rate analysis of Ba(Fe_{0.915}Co_{0.085})₂As₂. (a) Dynamic relaxation rate of the data in A_{1g} symmetry. (b) Dynamic relaxation rate of the data in B_{1g} symmetry. The straight lines are the fits from the parallel resistor model. (c) The static relaxation rates derived from the PRM as a function of temperature in B_{1g} as black diamonds and A_{1g} with red diamonds along with the resistivity $\rho(T)$ from Ref. [22].

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