TOPICAL REVIEW

A review of two-band superconductivity: materials and effects on the thermodynamic and reversible mixed-state properties

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Received 18 December 2012
Published 11 February 2013
Online at stacks.iop.org/SUST/26/043001

Abstract
Two-band superconductivity has become an important topic over the past ten years. Extensive experimental and theoretical studies started with MgB$_2$ and are now focused on iron-based and other new superconductors. In this review, I describe how important thermodynamic, reversible mixed-state, and other superconducting properties are changed by two-band superconductivity and, for comparison, by other effects such as anisotropy in a single-band material or an energy-gap structure different from the conventional s-wave symmetry. The work consists of three main parts, in which I review (i) theoretical models and what they predict for experimentally accessible properties in the two-band and other scenarios, (ii) experimental methods applied for investigating superconducting properties and the results obtained in potential two-band materials, and (iii) materials, for which two- or multi-band superconductivity has been suggested. It is shown that two-band effects appear in most of the analyzed properties and that they can be quite significant but usually fade away as interband interactions increase. Anisotropy often leads to similar modifications in single-band superconductors, which is why the distinction of two-band and anisotropy effects is usually difficult, particularly when the temperature dependence of the quantities is examined. In contrast, the field-dependent effects are more often different and thus more often allow a reliable distinction between the models.

(Some figures may appear in colour only in the online journal)

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0953-2048/13/043001+36$33.00 © 2013 IOP Publishing Ltd Printed in the UK & the USA
1. Introduction

In this article, my guideline was to work out how two-band superconductivity shows up in experiments. To be more precise, my intention was to provide a literature overview on a multitude of effects by which conjectural two-band materials have been identified. Furthermore, it was also my intention to compare these effects with those expected from other models, such as the anisotropic single-band and the d-wave scenario and thus to find out which effects are unique to and hence unambiguously mark out two-band superconductivity.

Two-band superconductivity has been a prominent issue since the discovery of MgB$_2$ in 2001 [1], though it was sometimes considered for describing the unconventional behavior of materials before that. In MgB$_2$, numerous experiments revealed unconventional results such as a positive curvature of the upper critical field near the transition temperature, a shoulder in the specific heat at intermediate temperatures, and different anisotropies for different quantities. Those significant deviations from the expected (standard) single-band behavior initiated profound theoretical investigations of the two-band scenario. Accordingly, MgB$_2$ has formed today’s understanding of two-band superconductivity, and many effects have mainly been investigated for parameters close to those of MgB$_2$. Today the focus has shifted to the iron-based superconductors. Though there is little doubt that these materials are two-or even multi-band superconductors, their unconventional behavior is in part quite different from that of MgB$_2$, which may be due to quite different Fermi surfaces and gap structures. Theoretical work on the iron-based materials is as yet largely lacking but is anticipated to have further impact on our knowledge of multi-band effects. Beside these two major materials, other materials, some known much longer than our knowledge of multi-band effects. Beside these two major materials, other materials, some known much longer than MgB$_2$, have been found to resemble MgB$_2$ in some properties and have thus been supposed to be two-band materials.

Unconventional behavior does not necessarily mean two-band behavior but can also emerge from strong anisotropy in single-band materials, from gap symmetries different from s-wave, from a second superconducting phase, and from other effects. It is therefore a major task of this paper to point out that features originating from two-band effects are often similar to those from other effects, which often makes distinguishing the scenarios difficult. This holds, for instance, for quantities that mainly depend on the variation of the gap values or the Fermi velocities, as such a variation is available in both the anisotropic single-band and the two-band scenario. Nevertheless, differences are expected to show up in some properties, particularly when they are examined as a function of magnetic field, since in two-band materials superconductivity is often suppressed in one of the bands at sufficiently high magnetic fields.

Apart from the final summary in section 5, the review contains three main sections: section 2, where some theoretically predicted results calculated by applying different models are summarized; section 3, where two-band effects observed in some selected experiments are reviewed; and section 4, where most of the presumed two-band superconductors are listed.

2. Multi-band models

This section is devoted to the theoretical description of two-band superconductivity by applying Ginzburg–Landau theory, the separable model, BCS, and Eliashberg theory. We are mainly interested in the predictions of how experimentally accessible magnetic and thermodynamic superconducting properties are influenced by the presence of a second band. Properties of the anisotropic single-band and the d-wave model are partly discussed for comparison. The two-band model is assumed to consist of two basically independent Fermi bands, which differ in their properties. In particular, the coupling strength and thus the energy gaps should be distinctly different for the two bands. Moreover, different Fermi velocities, anisotropies, gap symmetries, impurity scattering rates, densities of states, etc are possible. The two bands are connected by interband coupling and impurity scattering. Because of the interaction, the system should have only one transition temperature ($T_c$), one upper critical field ($B_{c2}$), and other common properties. The formal extension to a multi-band model with more than two bands and connections between all of them is a straightforward process. In experiment, such conditions may be met by materials whose Fermi surface is crossed by two or more unconnected bands on which the energy gaps are distinctly different. In contrast, the anisotropic single-band model is assumed to consist of one band on which the energy gap and the Fermi velocity vary continuously between a maximum and a minimum value. This may fit materials in which the superconducting parts are connected.

2.1. Ginzburg–Landau theory

Let us start with the two-band Ginzburg–Landau model [2] which provides insight into superconducting parameters directly accessible to experiment. Deriving the free energy Ginzburg–Landau functional from a two-band BCS model, Zhitomirsky and Dao [3] found

\[ F_{GL} = \int d^3r \left( f_1 + f_2 + f_{12} + \frac{\vec{B}^2}{2\mu_0} \right) \]  \hspace{1cm} (1)
with

$$f_j = \alpha_j |\psi_j|^2 + \frac{1}{2} \beta_j |\psi_j|^4 + K_j \left( \nabla^2 + \frac{2\pi}{\Phi_0} \right) \psi_j$$

and

$$f_{12} = \sigma (\psi_1^* \psi_2 + \psi_2^* \psi_1)$$

with \( j = 1, 2 \) the index of the individual bands, \( \vec{B} \) the magnetic induction, and \( \vec{A} \) the corresponding vector potential; \( \mu_0 (= 4\pi \times 10^{-7} \text{ T m A}^{-1}) \) denotes the vacuum permeability and \( \Phi_0 (\approx 2.07 \times 10^{-15} \text{ V s}) \) the magnetic flux quantum. \( \psi_j \) is the order parameter of the superconducting state of each band. Finally, \( \alpha_j, \beta_j, \) and \( K_j \) are numerical coefficients expressed by BCS quantities. It was shown that \( \alpha_j \) deviates from the single-band definition by a constant that depends on the inter- and intraband coupling strengths (see also [4]). Possible dependences of the quantities on the spatial coordinates and temperature are omitted in the equations.

Expression (3) represents a Josephson-like interband interaction with coupling parameter \( \sigma \). This term ensures minimal coupling and is responsible for a common single transition temperature of the system, usually larger than the transition temperatures of both individual bands (i.e. the transition temperatures of the two bands when coupling is not present), and a single value of the critical fields. Several groups added additional coupling terms [5–7] or extended the Ginzburg–Landau functional [8, 9] to higher orders of \((1 - T/T_c)^2\) to extend the validity of the model to lower temperatures. In [10], the applicability of the two-band Ginzburg–Landau model with the minimal coupling term was studied by comparing the results with those from the Eilenberger equations. The authors found reliable agreement from the transition temperature to quite low temperatures, particularly in the case of weak interband coupling and/or when adjustable parameters (i.e. for \( \alpha_j, \beta_j, \) and \( K_j \)) are used instead of the microscopically derived values. The issue of the validity of the two-band Ginzburg–Landau theory for MgB\(_2\) was also addressed in [11], where an interval from about 30 K to \( T_c \) \((\sim 39 \text{ K})\) was derived.

If interband coupling is weak in comparison to the intraband properties, traces of the individual bands are likely to be observable in various thermodynamic or magnetic properties. In such a case, experiment may allow us to uncover two-band superconductivity. Different effects of two-band superconductivity on such experimentally accessible properties have been calculated within the Ginzburg–Landau model and were shown to resemble some of the unconventional experimental results. Note, however, that not only two-band superconductivity leads to unconventional behavior, as will be shown in section 2.2.

In [12], the two-band Ginzburg–Landau equations were expressed in terms of more conventional quantities such as the condensation energies of each band and the magnetic penetration depths. Fitting this model to the experimental data of MgB\(_2\) allowed the authors to determine various Ginzburg–Landau properties of the individual bands and of the total system. It was shown that the superconducting properties of the band with the smaller gap are suppressed by a rather low magnetic field, which is the reason for significant deviations of the in-field behavior of various properties from the single-band behavior. The field above which superconductivity is significantly suppressed in one of the bands is often assumed the upper critical field of this band, but, due to interband coupling, traces of superconductivity should be available in this band up to the global upper critical field. Further properties derived from Ginzburg–Landau theory are the upper and lower critical fields, the characteristic lengths, and the corresponding anisotropies as well as thermodynamic quantities [3, 5, 13, 14, 11, 15]. For example, it was demonstrated that a positive curvature of the upper critical field near the transition temperature may result from two-band superconductivity [3, 5, 13]. This would also result in a temperature-dependent anisotropy, which could be quite different from that of the magnetic penetration depth [5]. Furthermore, a second band was found to reduce the jump of the specific heat [5] at the transition temperature, and aspects of point-defect scattering were investigated [15].

In summary, the two-band Ginzburg–Landau theory is a typical example of a simple two-band model, namely the sum of two independent single-band and one or more coupling terms. The coupling term is responsible for a single common transition temperature, usually different from the two single-band values, and similar effects on other properties.

2.2. Separable model

In this section, I will discuss the separable model, which introduces anisotropy in a very simple way. Most interestingly, it helps to clarify whether modifications caused by a second band can be distinguished from those arising from anisotropy. We will see that two-band and anisotropy effects can be described by an equivalent set of equations within this model, which indicates that discriminating the two models by means of the temperature dependence of various experimental results may be difficult in most cases.

The separable model was originally introduced into BCS theory by Markovitz and Kadanoff [16], who defined the anisotropic pairing potential via

$$V_{\vec{k} \vec{k}'} = (1 + a_{\vec{k}}) V (1 + a_{\vec{k}'})$$

where \( V \) denotes the isotropic, i.e. averaged, value of the BCS coupling potential; \( \vec{k} \) and \( \vec{k}' \) are the momentum vectors of the electrons (or quasiparticles) before and after a scattering event, and \( a_{\vec{k}} \) specifies the anisotropy. We assume

$$\langle a_{\vec{k}} \rangle = 0$$

so that the Fermi surface average of this function vanishes. The concept was later adapted for Eliashberg theory [17] by defining the anisotropic Eliashberg spectral function—\( \alpha^2 F(\omega)\frac{\lambda(\omega)}{\lambda(\omega)} \)—in exactly the same way as the BCS potential, and hence the anisotropic electron–phonon interaction function is given by

$$\lambda(\omega) = (1 + a_{\vec{k}}) \lambda(\omega) (1 + a_{\vec{k}'})$$

with \( \lambda(\omega) \) the Fermi surface average of \( \chi_{\vec{k} \vec{k}'}(\omega) \). Setting \( \omega = 0 \) yields the coupling strength \( \lambda(0) = \lambda \).
Dividing the Fermi surface into two sheets, on which \( a_2 \) is constant, e.g. \( a_1 \) on sheet 1 and \( a_2 \) on sheet 2, with \( a_1 = -a_2 \) due to equation (5), leads to the simplest form of the model. Additionally, we can assume different electronic densities of states (DOS) with relative weights \( n_1 \) (\( n_1 + n_2 = 1 \)) on each sheet, and hence

\[
a_i = (-1)^{i+1} \sqrt{\langle a_k^2 \rangle n_j / n_i},
\]

where \( i, j = 1, 2 \) when \( a_2 \) is constant on the two sheets, and \( i, j = 1, 2 \) or \( 2, 1 \). The anisotropy is thus fully determined by a single parameter, namely \( \langle a_k^2 \rangle \).

The anisotropic electron–phonon coupling function can be described by a series of so-called Fermi surface harmonics [18]. Aborting this expansion after the first term, i.e. at zeroth order, leads to the separable model. Accordingly, the separable model may not provide a correct quantitative description, except for very small anisotropies, but it is plausible to assume that the most significant features of the system are reliably described.

Some properties, such as the upper critical field, additionally depend on the Fermi velocity and its anisotropy, which is taken into account by

\[
v_F, \bar{k} = (1 + b_2^2) v_F,
\]

where \( b_2 \), the anisotropy function, is defined in the same way as \( a_2 \), and \( v_F \) is the average of the Fermi velocity. To analyze different field orientations, the average and the corresponding anisotropy should be taken from the relevant plane, e.g. that perpendicular to the applied field in the case of calculating the upper critical field. Again, it is most simple to assume \( b_2 \) to be constant on the two sheets, \( b_1 \) and \( b_2 \), and to be defined in the same way as \( a_i \) in relation (7) by using a single anisotropy parameter \( b_2 \); but it should be noticed that the signs of \( a_i \) and \( b_i \) are opposite in most superconductors (i.e., a large Fermi velocity implies a small coupling strength at the same part of the Fermi surface and vice versa).

Now I come to the point that explains our interest in the separable model, namely its possible interpretation as a special case of the (isotropic) two-band model [19–22]. In the simple two-band model, the Fermi surface is divided into two spherical surfaces, usually having different radii. Each band is determined by an independent set of parameters, including a constant value of the coupling strength \( \lambda_i \) (\( i = 1, 2 \)) and of the Fermi velocity \( v_F, i \) (\( i = 1, 2 \)). Additionally, interband coupling parameters \( \lambda_{ij} \) (\( i \neq j \)) are to be defined. Accordingly, the same set of parameters as in the separable model of the anisotropic single-band superconductor is used, and the same set of equations has to be solved. If the two-band quantities are fixed by the relations introduced for the anisotropic single-band model, namely equations (6) and (8), both models will lead to the same results.

Note that the two-band model provides an additional parameter, the interband coupling strength, which is fixed in the single-band model by equation (6) but can be varied freely in the two-band model. Nevertheless, the separable model was found to match experimental data not only of anisotropic single-band but also of two-band superconductors quite well [25, 26, 24]. This was, for instance, demonstrated for the transition temperature and the thermodynamic critical field of the two-band superconductor MgB\(_2\) in [24]. Moreover, very good agreement was also achieved for the temperature dependence of the electronic specific heat, including the reproduction of the specific heat jump at the transition temperature, which is much smaller than anticipated from BCS theory, and the unconventional low-temperature behavior with its shoulder at about 7 K (see figure 1). Using the second anisotropy parameter \( \langle b_2^2 \rangle \) and Fermi velocities from the literature allowed the calculation of the upper critical fields for the two main crystallographic axes, resulting in the well-known upward curvature for one of the field directions and the corresponding temperature dependence of the anisotropy, in excellent agreement with experiment (see figure 2).

The separable model is of particular use for analyzing some basic effects of anisotropy [24, 26]. In the case of the two-band model the anisotropy refers to the difference of the two constant values on the two spherical Fermi bands, and in the case of the single-band model it refers to the variation within one band. Enhancing the anisotropy of the coupling function increases the transition temperature, for instance by a factor of roughly 2 in MgB\(_2\) [24]. As for the specific heat (see figure 1), the jump at the transition temperature decreases when the anisotropy grows, whereas it increases when the mean coupling strength grows. A larger anisotropy weakens the coupling strength on parts of the Fermi surface,
and at the same time increase the slope of the upper non-magnetic point impurities. In the anisotropic single-band function anisotropy grows.

velocity anisotropy grows, but is moderated as the coupling more prominent and extends to lower temperatures as the anisotropy perpendicular to the field is responsible for the dependence in a rather contrary way. The Fermi velocity enhance the upper critical field, but they affect its temperature dependence via the Fermi velocity anisotropies (solid lines [24]). For $H \parallel ab$, the upper line refers to an isotropic Fermi velocity and the lower line, which matches the experimental data, to an anisotropic one ($\langle b_i^2 \rangle = 0.4$). For $H \parallel c$ the line was calculated for almost isotropic behavior ($\langle b_i^2 \rangle = 0.03$). In the single-band case the anisotropy refers to different values in one band, and in the two-band case it refers to the different Fermi velocities of the two bands. For all lines, the relative density of states weights are $0.5$ and the coupling function anisotropy is given by $\langle a_i^2 \rangle = 0.3$ (see figure 1). The experimentally observed upward curvature at high temperatures for fields parallel to $ab$ emerges and becomes more prominent with increasing Fermi velocity anisotropy. As a result, the upper critical-field anisotropy, shown in the inset, becomes temperature dependent.

which makes the electronic specific heat grow faster with temperature at low temperatures, while a stronger mean coupling, which results in larger energy gaps, makes it grow more slowly. A shoulder or kink at low temperatures, which reflects the weak coupling parts, emerges only for a rather high anisotropy. The situation may be somewhat different in the two-band model due to the possibility of varying the interband coupling strength independently, and hence the shoulder may emerge at a smaller or larger anisotropy. Furthermore, anisotropy reduces the thermodynamic critical field and slightly changes its temperature dependence, which is nevertheless still close to the parabolic behavior. In contrast to the specific heat and the critical field, which are thermodynamic properties, the upper critical field (see figure 2) depends on the field orientation via the Fermi velocity anisotropy. Both the coupling and the velocity anisotropy enhance the upper critical field, but they affect its temperature dependence in a rather contrary way. The Fermi velocity anisotropy perpendicular to the field is responsible for the upward curvature at high temperatures. This effect becomes more prominent and extends to lower temperatures as the velocity anisotropy grows, but is moderated as the coupling function anisotropy grows.

I conclude this section by discussing the effects of non-magnetic point impurities. In the anisotropic single-band model, such impurities reduce the transition temperature and at the same time increase the slope of the upper critical field at the transition temperature (which will enhance the upper critical field at low temperatures if the suppression of the transition temperature is not too large). For the two-band model, we may define different impurity scattering rates for intraband and interband scattering. In the isotropic two-band model, intraband scattering increases the upper critical-field slope but does not affect the transition temperature, as known from the Anderson theorem; only interband impurity scattering reduces the transition temperature. Accordingly, the upper critical field should be modifiable almost independently from the transition temperature, which might explain the observation of quite different values of upper critical field in MgB$_2$ samples with equal transition temperature [27].

In conclusion, though the separable model is a very simple model for the anisotropy, significant deviations from the isotropic (BCS) behavior can be described well, and the results often match the experimental data very well. This suggests that many of the unusual effects, found for instance in MgB$_2$, are rather general for strongly anisotropic superconductors, and do not rely heavily on the particular shape and properties of the Fermi surface but rather on the mean values of the anisotropies. Because the two-band and the anisotropic single-band model can be defined by the same set of parameters, anisotropy and two-band effects are expected to modify the temperature dependence of many superconducting properties in a similar way, making it difficult to distinguish between the models by experiment. As for the specific heat, increasing the anisotropy of the coupling function reduces its jump at the transition temperature, leads to a faster grow at low temperatures, and eventually generates a shoulder-like behavior at low temperatures. The curvature of the upper critical field becomes positive at high temperatures as a consequence of Fermi velocity anisotropy in this model.

2.3. BCS theory and quasi-classical equations

Two-band superconductivity was first formulated within BCS theory [28, 29] using the following Hamiltonian

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} + \hat{H}_{21}$$  \hspace{1cm} (9)

with

$$\hat{H}_i = \sum_{k, \sigma} \epsilon_{ki} \hat{c}^\dagger_{ki \sigma} \hat{c}_{ki \sigma} - V_i \sum_{k, \bar{k}} \hat{c}^\dagger_{ki \sigma} \hat{c}^\dagger_{k \bar{k} \bar{\sigma}} \hat{c}_{k \bar{k} \bar{\sigma}} \hat{c}_{ki \sigma}$$  \hspace{1cm} (10)

$$\hat{H}_{ij} = -V_{ij} \sum_{k, \bar{k}} \hat{c}^\dagger_{ki \sigma} \hat{c}^\dagger_{k \bar{k} \bar{\sigma}} \hat{c}_{k \bar{k} \bar{\sigma}} \hat{c}_{ki \sigma}.$$  \hspace{1cm} (11)

Here, $\epsilon_{ki}$ denotes the renormalized normal-state energy with respect to the chemical potential of a single particle with momentum vector $\bar{k}$ in band $i$ ($i = 1, 2$); $\hat{c}_{ki \sigma}$ and $\hat{c}^\dagger_{ki \sigma}$ are the corresponding creation and annihilation operators; $\sigma$ denotes the spin direction, which can be up ($\uparrow$) or down ($\downarrow$), and $V_i$ the effective coupling potential of the BCS theory. Definition (11), where $i, j = 1, 2$ or $i, j = 1, 2$ and $V_{12}$ and $V_{21}$ are the interband coupling potentials, introduces the interband effects.
Applying the standard techniques from single-band BCS theory allows one to evaluate various properties of the two-band system, such as the density of states, presented in figure 3, the temperature dependence of the energy gaps, and the transition temperature, which was shown to be higher than the values of each single band [30]. Fitting two-band BCS theory to experimental specific heat data worked well for MgB$_2$ [31, 3, 32, 33], revealing that the jump at the transition temperature is smaller than in the single-band case. Furthermore, the effects on the superfluid density and the magnetic penetration depth were reported to agree with the experimental data quite well [34, 35].

Aspects of anisotropy in single-band s-wave superconductors were construed in [36, 37] and compared with experimental data on MgB$_2$. It was shown that the anisotropy of the gap function results in a two-peak structure in the energy dependence of the tunneling conductance, similarly to that anticipated in a two-band system. Also thermodynamic properties, such as the specific heat and the critical magnetic field, could be brought into reliable agreement with experimental data on MgB$_2$. Consequently, the modifications due to anisotropy are again similar to those derived from two-band models.

More complex situations including finite magnetic fields and non-spherical Fermi surfaces can be studied by using the quasi-classical approximation of the Green’s function, i.e. by solving the corresponding Eilenberger [38] or—in the case of strong disorder (dirty limit)—the Usadel [39] equations. The Eilenberger equations are derived from Gorkov’s Green’s function approach to the BCS theory and simplify calculations at finite magnetic fields.

Several groups applied the approach to multi-band superconductivity. They showed that the thermodynamic properties [40–42] were modified in a similar way to that already mentioned for the previously discussed models. Interband scattering by non-magnetic impurities was found to reduce the transition temperature much faster when the interband coupling strength is repulsive [42] (i.e. $\lambda_{12} < 0$, implying that the gaps have opposite sign on the different sheets; the $s_\Delta$ scenario) than in the ordinary case ($\lambda_{12} > 0$).

The energy gap and the electronic density of states near or at the Fermi level can be calculated as a function of applied magnetic field and compared with experimental data from tunneling spectroscopy, which reveals the energy gap and the local density of states at a certain point of the sample surface, or with the Sommerfeld coefficient ($\gamma$), which is proportional to the volume average of the density of states and can be determined from specific heat measurements. Assuming the volume-averaged density of states to be proportional to the total volume of the normal-conducting vortex cores leads to a linear field dependence of the Sommerfeld coefficient in an isotropic s-wave superconductor, which is however changed to a concave function in real materials due to the field dependence of the coherence length and the overlap of vortex cores at high magnetic fields [43–45]. Above the upper critical field, the Sommerfeld coefficient matches the normal-conducting value, which is usually constant. Similarly, $\gamma \propto B^{\alpha\gamma}$ is expected for an isotropic d-wave material [46, 43].
fields (when dominated by the isotropic $\pi$-band) but strongly anisotropic at high fields (due to the anisotropic $\sigma$-band).

It was further reported that even when the density of states of the smaller gap band becomes saturated above a particular magnetic field the corresponding energy gap can be finite over the whole field range, i.e. both gaps close at the same field due to interband coupling [41, 47]. As for the energy dependence of the local density of states, it was indicated that the peak associated with the smaller gap may vanish at higher applied fields due to different band topologies [48]. Similar results were obtained for the dirty limit by solving the Usadel equations [49].

It is again interesting to compare the two-band results with anisotropic single-band results [47]. The exponent $\alpha$ in $\gamma(B) \propto B^\alpha$, which should be roughly one for isotropic superconductors, was shown to become smaller with increasing anisotropy. Hence the anisotropy effects are again similar to the two-band effects. Indeed, reliable agreement between the experimental data from the two-band superconductor NbSe$_2$ and calculated results from the anisotropic single-band model was demonstrated. Additional minor modifications are expected from impurity scattering [50].

In summary, the quasi-classical approximation makes calculations at finite magnetic fields possible. The field dependence of the Sommerfeld coefficient should be close to linear, though slightly curved, in the case of isotropic $s$-wave symmetry and close to a square root behavior in the case of $d$-wave symmetry. For a two-band superconductor in which one band is suppressed at relatively low magnetic fields, we expect a steep gradient at low fields and a flatter slope at high fields and the kink, indicating the upper critical field of the weaker band, to be smeared out by interband coupling. A similar behavior is expected in anisotropic single-band superconductors, where the isotropic linear dependence was demonstrated to become more concave with increasing anisotropy. Concerning the energy gaps, both should close at the same (upper critical) field even when the upper critical fields of the bands are different. The gap structure of the density of states near the Fermi energy may change considerably with magnetic field.

2.4. Eliashberg theory

Next, I will summarize results from the Migdal–Eliashberg theory, which takes strong coupling effects into account. Even if the mean coupling strength of a two-band superconductor is weak, one of the bands could be in the strong coupling regime, making strong coupling effects relevant. Some publications, which will be reviewed below, have provided a deep insight into the influence of the anisotropy, the interband coupling strengths, and the impurity scattering rates, etc on the thermodynamic and magnetic properties of two-band materials.

Results from the Eliashberg equations have often been found to agree with experimental data better than those from other models and even to describe the superconducting properties of many conventional (i.e. electron–phonon mediated) superconductors quantitatively precisely [51]. Basically, the Green’s function of the system has to be calculated by taking into account the self-energies related to the electron–phonon interaction, which is characterized by the Eliashberg spectral function $\alpha^2 F(\omega)_{kk'}$, the electron–electron Coulomb interaction, characterized by the Coulomb pseudopotential $\mu$$_{kk'}$, and the electron–impurity interaction, usually in the first Born approximation, specified by the mean scattering time $[52–54]$. The model allows us to determine all thermodynamic properties that can be derived from the free energy, and other properties, such as the transition temperature, the energy gap, the density of states, etc. Except for the upper critical fields, which additionally depend on the Fermi velocity $v_F$, magnetic field effects are usually inaccessible.

Two-band effects are naturally included when we solve the complete anisotropic form of the equations. To do so, the local values of the input parameters, at least of $\lambda$$_{kk'}$($\omega$), which can be determined from $\alpha^2 F(\omega)_{kk'}$, have to be known on the whole Fermi surface. To avoid that, the Fermi surface topology is often simplified. As already mentioned, the Fermi surface anisotropy may be approximated by the separable model or by the corresponding two-band model with two spherical bands, specified by two densities of states, four (frequency-dependent) coupling functions, four pseudopotentials, and the impurity scattering rates. Moreover, cylindrically, elliptically, and similarly shaped Fermi bands have been used.

Choi et al [55, 56] solved the fully anisotropic Eliashberg equations for the two-band superconducting material MgB$_2$. The $\hat{k}$, $k'$ and phonon energy $\omega$ dependence of $\alpha^2 F(\omega)_{kk'}$ was acquired from $ab$ initio methods, while the Coulomb pseudopotential $\mu$, supposed to have only minor influence on the superconducting properties and hence taken as isotropic, was chosen by adjusting the results to the correct value of the transition temperature. Using these parameters, they were able to calculate the energy-gap distribution, the specific heat, and the isotope effect in excellent quantitative agreement with experiment. It was concluded that the anisotropy and the two-band nature are responsible for the high transition temperature (which was approximately twice the value of the corresponding isotropic system) and that the low-energy excitations, which accompany the smaller values within the wide range of the energy-gap distribution, lead to the high-temperature shoulder of the specific heat.

Several other groups have investigated two-band properties—mainly of MgB$_2$—by Eliashberg theory but applied simpler models, such as mentioned above, for the anisotropy. Nevertheless, they were able to obtain similarly good agreement with experimental data as with the fully anisotropic theory. This again indicates that prominent two-band effects such as the low-temperature anomaly in the specific heat do not depend on details of the Eliashberg spectral function [57] but are common for anisotropic or two-band superconductors that have a wide distribution of energy-gap values. For instance, taking the same mean value of the coupling strength ($\lambda$) and the peak of the Eliashberg spectral function, simplified by an Einstein-like spectrum, at the same position as in the fully anisotropic model of Choi
et al [55, 56], allowed the excellent reproduction of various experimental results on MgB$_2$ by the separable model of the Eliashberg equations [24].

Diverse other effects of a second band have been investigated. For instance, the superfluid density (which is proportional to $1/\Lambda_x^2$, with $\Lambda_x$ the magnetic penetration depth for current flow in $x$ direction) of an isotropic s-wave superconductor is almost constant at low temperatures, but starts to decrease rapidly above a certain temperature. Similarly as for the specific heat, low-energy excitations, associated with the smaller gap values, reduce the threshold temperature and may significantly change the overall behavior from a concave towards a more linear or even convex behavior over a large temperature range [58, 60, 61], see figure 4. In the case of small interband effects, a kink indicating the weaker band may be observed at low temperatures. Strong impurity scattering in one band, particularly if the smaller gap band is in the dirty limit, can almost recover the conventional BCS behavior [60].

Calculations of the upper critical field reproduced the upward curvature found in many experiments. Applying the separable model [24] showed that the temperature at which the curvature of the upper critical field switches from negative to positive shifts to lower values when we increase the anisotropy of the Fermi velocity perpendicular to the applied field but to higher values when we increase the anisotropy of the coupling function. A two-band Eliashberg model based on MgB$_2$ with one spherical weak coupling ($\pi$) and one elliptical stronger coupling ($\sigma$) band was studied in [62]. The kink indicating the upper critical field of the $\pi$-band in the absence of interband interaction was demonstrated to be smeared out by quite small interband coupling parameters. The upward curvature of the upper critical field near the transition temperature was predicted to become more pronounced when the anisotropy of the Fermi velocities (here, the ratio of the values of the two bands) or the off-diagonal (interband) couplings increase (see figure 5). Similar effects were calculated for intraband impurity scattering. For instance, it was reported that $B_{c2}(T)$ may show an upward curvature in MgB$_2$ even for $H \parallel c$, for which the relevant Fermi velocities are quite similar and thus the upward curvature is usually not observed, if the $\sigma$-band is pushed into the dirty limit and the $\pi$-band remains clean. All these effects usually render the upper critical-field anisotropy temperature dependent.

Further systematic investigations on diverse properties such as the energy gaps, the specific heat, the superfluid density, and the thermodynamic critical-field deviation...
function, which measures how strongly the thermodynamic critical field deviates from a parabolic temperature behavior, were reported in \[58\]. Using parameters roughly based on the properties known for MgB\(_2\), the authors showed that not only anisotropy but also strong coupling could have a significant influence, so that BCS and Eliashberg results may diverge significantly in some cases. Furthermore, anisotropy and strong coupling were reported to lead to opposite corrections in most cases; for instance, strong coupling increases the specific heat jump at the transition temperature, whereas anisotropy associated with the ratio of the intraband coupling strengths, \(\lambda_{11}\) and \(\lambda_{22}\), decreases it; stronger interband coupling, however, increases the jump again. Moreover, studying the influence of the interband coupling strength and of the interband impurity scattering rate revealed that even a weak interband interaction significantly washes out the transition of the smaller gap band. The effects of interband impurity scattering are often similar to those of intraband coupling. Concerning the specific heat jump, a small impurity scattering rate may reduce the value when the transition temperature decreases strongly, but a high intraband impurity scattering rate should always increase the jump height (see also \[59\] for further impurity effects). Finally, interband coupling can induce superconductivity in a band with repulsive intraband coupling.

In conclusion, the Eliashberg equations give access to strong coupling effects and result in a quantitatively correct description of superconducting properties in many cases. Though any anisotropy can be implemented, simple Fermi surfaces with spherical or elliptical shapes have proved successful in describing diverse two-band effects. For instance, the superfluid density was found to drop faster at low temperatures and to change from a concave to a more linear or even convex temperature dependence with increasing intraband coupling anisotropy. The effects on the specific heat and the upper critical field correspond to those reported for the ‘separable model’ (section 2.2). In addition, stronger interband coupling enhances the specific heat jump and the kink representing the transition of the weaker band in the temperature dependence of diverse properties is washed out. Quite similar effects were predicted for interband impurity scattering.

### 3. Experiments

This section is considered the main part of this review. I will list and discuss several experimental techniques that have commonly been used for identifying two-band materials and will show the results. The selection of the methods is rather arbitrary, and omitted methods are not necessarily to be considered as less important. Except for the thermal conductivity and the energy gaps, I concentrate on thermal and mixed-state properties that are somehow linked to the reversible magnetic properties of the superconductor, namely the specific heat and the corresponding Sommerfeld coefficient, the superfluid density, the upper critical fields, the torque, the reversible magnetization, the anisotropy, and the field dependence of the characteristic lengths. For each subsection, I will give a brief introduction to the property and then review some results obtained on different samples, including not only two-band materials.

#### 3.1. Specific heat

Measurements of the specific heat in MgB\(_2\) have uncovered striking deviations from the so-called standard curve (i.e. that obtained from BCS theory), which were soon attributed to two-band superconductivity. Those remarkable features are the jump height at the transition, the unconventional low-temperature behavior and a kink or shoulder in between. Later, similar effects were found in other materials.

The difference in the specific heat of the normal conducting and the superconducting state follows from the difference in the free energy density \(\Delta F\) via \(\Delta C = -T\partial^2 \Delta F/\partial T^2\). The normal-conducting part \(C_n\) includes the electron \(C_{ne}\) and the phonon \(C_{np}\) contribution, of which the linear electron part,

\[
C_{ne} = \gamma_n T, \quad (12)
\]

with the Sommerfeld constant

\[
\gamma_n = \frac{2}{3}\pi^2 k_B^2 \zeta(1 + \lambda), \quad (13)
\]

dominates at low temperatures. In equation (13), \(k_B\) denotes the Boltzmann constant, \(\zeta\) the total electronic density of states at the Fermi energy, and \(\lambda\) the coupling strength. The phonon contribution is normally modeled by \(bT^3 + cT^5\), taken from the low-temperature limit of Debye’s theory, and is assumed to be equal in the normal-conducting and superconducting state; \(\Delta C\) is thus the difference in the electronic parts. At very low temperatures, the Schottky anomaly may become noticeable.

An easily accessible characteristic value of a superconducting material is the jump of \(\Delta C\) at the transition temperature normalized by its normal-conducting value \(\gamma_n T_c\), i.e.

\[
\frac{\Delta C(T_c)}{\gamma_n T_c} = k. \quad (14)
\]

Weak coupling BCS theory results in a material-independent universal value of \(k = 1.43\), which was indeed measured in aluminum, a material meeting the BCS preconditions fairly well due to its weak coupling strength (\(\lambda \approx 0.43\) in Al) and a near spherical Fermi surface. Both experiment and (Eliashberg) theory \[51\] demonstrated that this value should grow with the coupling strength—for instance, to about 2.8 in lead (\(\lambda \approx 1.55\)). Although the coupling strength of MgB\(_2\) is approximately 0.6, the jump magnitude was found to be much smaller than the weak coupling threshold, namely, as illustrated in figure 1, at about 1 ± 0.2 \[23, 63, 64\]. Similar results have been reported for some other materials. Theory was shown to predict that a second band should reduce that value as the disparity of the (two) intraband coupling strengths increases; the same should happen when the anisotropy of a single-band material increases \[58, 24\].

At very low temperatures, BCS theory predicts

\[
C_{ne}(T) = AT^{-3/2}e^{-\Delta(0)/k_B T} \quad (15)
\]
for the electronic specific heat of a superconductor [65], with \( A \) a temperature-independent constant. Equation (15) is governed by the exponential function at low temperatures, which reflects the probability of destroying a Cooper pair by the thermal energy \( k_B T \). Accordingly, with increasing temperature the specific heat remains almost constant up to a threshold temperature, and then starts to grow rather quickly. The threshold value lies at about 0.177. As that ratio becomes smaller, \( C_{\text{se}} \) grows faster at low temperatures. In the case of different gap values, the threshold temperature is determined by the smaller gaps, and we thus expect similar low-temperature modifications for the anisotropic and the two-band scenario. The above is only valid for (fully gapped) s-wave superconductors, while in d-wave systems the gap nodes allow a significant occupation of the excitation spectrum at any finite temperature, which makes \( C_{\text{se}} \) increase strongly even at very low temperatures. More precisely, a quadratic (at zero magnetic field) or linear temperature dependence was predicted and confirmed by experiment [46, 66–68].

We conclude that the low-temperature behavior of the specific heat of two-band superconductors is dominated by the band with the smaller gap, while the high-temperature behavior is dominated by the band with the larger gap (see figure 6). In between, a crossover takes place which is smoothed by interband coupling and impurity scattering; nevertheless, a kink, a shoulder, or even a small peak may still be present, as for instance observed in MgB\(_2\) at about 7–8 K.

It is obvious that describing the total temperature dependence of those unconventional specific heat curves by conventional BCS theory would fail. A common approach to fitting the specific heat and other thermodynamic properties of superconductors is provided by the so-called \( \alpha \)-model [70], in which the temperature dependence of the energy gap, \( \Delta(T) \), follows BCS theory, but the absolute value at \( T = 0 \) K, i.e. \( \Delta(0) \) (or the ratio \( \Delta(0)/k_B T_c \)), is adjusted to fit experiment. We can often nicely describe two-band properties as the sum of two \( \alpha \)-model curves by adjusting the parameters \( \Delta_1(0) \) and \( \Delta_2(0) \) as well as the corresponding relative weights of the bands. Although that model is not at all a true two-band model, for interband interactions are ignored, it has been successfully used to describe the specific heat in many samples, such as that shown in figure 6. Moreover, using the parameters of MgB\(_2\), Dolgov et al [59] showed that the energy gaps resulting from this procedure were fairly close to the gaps obtained by Eliashberg calculations. Other results, such as the density of states ratio of the two bands, deviated more considerably from the Eliashberg results. In conclusion, the \( \alpha \)-model seems to be useful for roughly estimating the gap values of a two-band superconductor [71–74] but may fail in proving whether or not a material is two-band superconductor.

As already mentioned, MgB\(_2\) single crystals display all three characteristic features of a two-band (or strongly anisotropic single-band) specific heat curve, namely a rather fast increase at low temperatures, a small jump at the transition temperature, and a shoulder in between [71, 73]. The effect of disorder on MgB\(_2\) was studied by Putti et al [72]. As the amount of impurities introduced by neutron irradiation increased, the shoulder at intermediate temperatures was observed to fade away and the low-temperature specific heat grew more slowly, only the jump at the transition temperature was hardly affected. Eventually, the heavily irradiated samples even matched the single-band \( \alpha \)-model. These results confirm the theoretical prediction that impurity scattering masks two-band effects.

The temperature dependence of the specific heat in the ternary-iron silicide Lu\(_2\)Fe\(_3\)Si\(_5\) [69] was reported to be quite similar to that of MgB\(_2\) (see figure 6 for Lu\(_2\)Fe\(_3\)Si\(_5\) and compare with figure 1 for MgB\(_2\)). The measurements showed a specific heat jump of roughly 1.05 at the transition temperature, a very pronounced shoulder at about 0.2\( T_c \), and a fast, though still exponential rise of the curve at low temperatures.

Interband coupling and impurity scattering are supposed to suppress the shoulder at intermediate temperatures, and the absence of this anomaly does therefore not refute the two-band hypothesis. For instance, results on the two-band superconductor NbSe\(_2\) reported in [75] did not display a shoulder and, moreover, revealed a higher jump \( \Delta C(T_c)/\gamma_0 T_c = 2.12 \) than in BCS theory. Nevertheless, both the anisotropic gap and the two-band model agreed well with the specific heat data. Similar results were reported for NbS\(_2\) [74], though only the two-band fits revealed gap values in agreement with scanning tunneling data, while the single-band fits did not.

The majority of specific heat measurements on the new iron-based superconductors have been aimed at unraveling the properties of the order parameter [76–83]. Curves of slightly
overdoped BaFe$_{1−x}$Co$_x$$_2$As$_2$ (Ba122) were reported to grow exponentially at low temperature [76], indicating fully gapped bands, and to be nicely described by the two-band $\alpha$-model with different gaps, although the jump at the transition was found to be close to BCS theory and no significant shoulder was observed. A residual normal-state-like specific heat at 0 K was considered a possible indication of $s_\pm$ symmetry, i.e., of opposite phases in the order parameters of the two bands. Working on the same kind of materials, Gofryk et al [77] claimed that their optimally doped samples could be described well by fully gapped two-band models, while their overdoped and underdoped Ba122 samples should have nodes due to a power-law-like rise of the specific heat at low temperatures (see also [78]). The situation ought to be similarly complex in other iron-based materials. For instance, the specific heat of FeSe [79] nicely matched d-wave and diverse s-wave models. Only the low-temperature data showed that the two-band behavior with one isotropic and one extended s-wave order parameter agreed slightly better than the other expressions. However, it is not clear to what extent the $\alpha$-model is capable of covering the specifics of the different models in view of its ignoring interband effects. Two-band models were also adjusted to data of LiFeAs [80, 81], mainly to decide whether the gap has nodes on one of the bands or not.

Huang et al [84] analyzed the specific heat of a YNi$_2$B$_2$C single crystal. They reported best agreement for the two-band $\alpha$-model but still reliable matching with other models based on order parameters with nodes. In conclusion, the temperature dependence of the specific heat of suspected two-band superconductors often fits two-band and anisotropic single-band models equally well. In some cases, it is even difficult to distinguish between s-wave (when the gaps are very small on parts of the Fermi surface) and d-wave symmetry. In those problematic cases, a large number of low-temperature data may allow us to distinguish the fit quality of the different models, but the usefulness of the simplified models might be questionable, because interband interactions are usually ignored. It may be considered as support for the two-band scenario when the evaluated energy gaps match those determined by other methods, such as scanning tunneling spectroscopy.

### 3.2. Sommerfeld coefficient

The volume-averaged quasiparticle density of states (DOS) at the Fermi surface of a superconductor grows with magnetic field and can be acquired from the linear part of the specific heat at very low temperatures via the Sommerfeld constant or coefficient ($\gamma$), as defined in equation (13). The field dependence of the Sommerfeld coefficient, $\gamma(H)$, crucially depends on the Fermi surface and might help to distinguish different scenarios.

As the magnetic field increases, the number of vortices and the corresponding total volume of the normal-conducting vortex cores of the mixed-state grow and hence enhance the quasiparticle density of states. We expect the density of states of a standard s-wave single-band superconductor to be proportional to the number of vortices and thus to grow linearly with field. In two-band s-wave materials, the increase in the density of states should be linear at low fields but should become flatter at high fields, when superconductivity is suppressed and the density of states is thus saturated in one of the bands. In other words, two linear parts are anticipated, of which the low-field region should be steeper. The crossover indicates the upper critical field of the first band, while the saturation of $\gamma(H)$ at high fields marks the overall upper critical field. Finally, d-wave superconductors were predicted to show a $\sqrt{H}$ behavior [46], and thus the different models should be easily distinguishable.

As usual, reality is not that simple, because the field dependence of $\gamma(H)$ is influenced by further effects, such as the overlap of vortex cores, which becomes more prominent with smaller vortex–vortex distances, and the shrinkage of the vortex core size with increasing field [85]. These effects tend to reduce the slope of $\gamma(H)$, as confirmed by experiments on the rather isotropic conventional superconductor Nb [45], shown in figure 7, and by calculations already mentioned in section 2.3, which showed the linear dependence to change to a roughly $H^\alpha$ behavior, with $\alpha < 1$; an even stronger curvature was predicted for anisotropic materials. As the two-band curves are influenced by the same effects, and additionally by interband interactions, it again becomes difficult to distinguish anisotropic single-band behavior from two-band behavior, or either of them from d-wave behavior, as illustrated in figure 7.

The Sommerfeld coefficient is usually acquired from the low-temperature behavior of the specific heat in magnetic...
fields. Ignoring the superconducting electronic part at those low temperatures, we can acquire the Sommerfeld coefficient by extrapolating the same expression as used for the normal-conducting region in section 3.1 to 0 K. In some cases, the superconducting electronic part was taken into account by an exponential part corresponding to equation (15).

Several groups have determined $\gamma(H)$ of MgB$_2$ [23, 88, 86, 89]. In [63], the relationship $\gamma(H) \propto H^{0.23}$ was found. Having evaluated many data points, the authors of [88, 86] observed two rather linear regions separated by a significant drop of the slope at about 0.5 T, i.e. close to the lower upper critical field (see figure 7). Although Klein et al [89] also recorded a large number of data points, a similar kink did not appear in their data, instead the whole field dependence nicely matched a $\sqrt{H}$ behavior.

In NbSe$_2$ [75] and NbS$_2$ [74], both the anisotropic single-band and the two-band model were found to match $\gamma(H)$ reasonably well. In the case of NbSe$_2$, the two-band fits to $\gamma(H)$ and to the specific heat resulted in similar values for the gaps and the relative densities of states, while the anisotropic single-band fits did not, which might indicate that the single-band hypothesis is not appropriate for this material. Moreover, the experimental data indicated a possible kink in $\gamma(H)$, which could only be covered by the two-band scenario. For NbS$_2$ [74], a very high density of data points revealed a slight inconsistency with the anisotropic single-band fit at low fields, while the two-band model matched better.

Studying the Sommerfeld coefficient of iron-based Ba(Fe$_1-x$Co$_x$)$_2$As$_2$ superconductors, Goфryк et al [77] discovered concave curves close to the typical d-wave behavior for underdoped and overdoped samples, but an almost linear behavior, as anticipated for isotropic s-wave materials, for the optimally doped sample. The exact classification of the dependence, however, suffered from uncertainties in the upper critical fields, for these values are very high and normally not directly measurable. Data on the iron-based FeSe samples [79] revealed a rather strong increase of the Sommerfeld coefficient at very low fields and a much flatter, almost linear behavior at higher fields, hence indicating the two-band s-wave scenario.

In YNi$_2$B$_2$C, $\gamma(H) \propto H^{0.47}$, which is actually close to the d-wave prediction, was reported [84] and claimed to agree with a two-band model (as was found for the temperature dependence of the specific heat in this case). A field dependence of $\gamma(H) \propto H^{0.5}$ has been confirmed for several cuprate superconductors (figure 7) [90, 66, 91, 87, 68].

In conclusion, the field dependence of the Sommerfeld coefficient cannot clearly discriminate two-band from anisotropic single-band behavior. In some cases, the experimental data seem to reveal a kink in $\gamma(H)$ at a field much lower than the overall upper critical field, which would not be easy to explain within the single-band theory. Further indications may be gained by comparing the gaps and relative weights obtained from fits to $\gamma(H)$ with results from analyzing other properties, such as the specific heat.

3.3. Thermal conductivity

Thermal conductivity is governed by several mechanisms in a superconductor, which makes its interpretation often difficult. Nevertheless, at low temperatures its field dependence might be useful for identifying two-band superconductivity, as was demonstrated for MgB$_2$.

A temperature gradient in a material gives rise to heat flow, which is characterized by the thermal conductivity coefficient $\kappa$. In most cases, electrons ($\kappa_e$) and phonons ($\kappa_p$) contribute to the heat transport and thus

$$\kappa = \kappa_e + \kappa_p. \quad (16)$$

The equilibrium distribution is reached by scattering processes, such as electrons by impurities and phonons ($\kappa_e^{-1} = \kappa_{e,1}^{-1} + \kappa_{e,p}^{-1}$) and phonons by impurities and electrons ($\kappa_p^{-1} = \kappa_{p,1}^{-1} + \kappa_{e,p}^{-1}$). Each of these processes leads to different temperature dependences, such as $\kappa_{e,1} \propto T$ and $\kappa_{e,p} \propto T^{-2}$ at low temperatures, which may result in different and complicated conductivity curves. At very low temperatures, impurity or defect scattering often prevails. In normal-conducting metals the low-temperature thermal flow is usually dominated by electrons, though the situation may change in the superconducting state.

The quasiparticle number and consequently, as Cooper pairs do not contribute to the thermal flow, the electronic part of the thermal conductivity are reduced upon cooling in a superconductor. On the other hand, the smaller number of electrons reduces the number of scattering events by phonons and thus increases the corresponding phonon part $\kappa_{p,c}$. We see that superconductivity changes not only the electron but also the phonon contribution, which makes interpreting the thermal conductivity often more difficult than interpreting the specific heat.

The magnetic field dependence of the thermal conductivity may vary considerably from material to material. At low temperatures and as the magnetic field increases, we anticipate a drop of the conductivity immediately above the lower critical field, which is eventually superseded by an increase at higher fields and a constant behavior above the upper critical field. The drop follows from vortex formation above the lower critical field and the corresponding proliferation of phonon scattering events at the vortex core quasiparticles. The subsequent rise is carried by the delocalization of more and more vortex core quasiparticles, while quasiparticles bound in a vortex core do not participate in the thermal transport. The low-temperature thermal conductivity of a conventional s-wave material in the clean limit, such as Nb [92], is expected to increase roughly exponentially with field, i.e. it should slowly increase at low fields but rapidly increase just below the upper critical field, as a consequence of heavy vortex core overlapping, which is illustrated in figure 8. Increasing the impurity density should produce a larger slope at intermediate fields [93]. In the case of anisotropy, a steeper increase at low field, followed by a flatter part at intermediate fields, and again a steep slope below the upper critical field was reported [94]. This is basically similar to two-band effects. If the gap has nodes, a significant number of quasiparticles will be delocalized even at low temperatures, which will render the thermal conductivity more linear, or even concave, over the whole field range (e.g. [95, 96] and figure 8). The curves often become more complicated at higher temperatures.
Let us discuss the thermal conductivity of MgB$_2$ [97]. At low temperatures the curve was observed to drop rapidly at low fields and then to increase. This increasing part, shown in figure 8, was found to be independent of the field orientation below about 0.5 T and hence supposed to reflect the isotropic $\pi$-band with an upper critical field of roughly 0.5 T. At higher fields the conductivity became flatter at first, then steep again near the upper critical field, and almost constant in the normal-conducting state. The second part, i.e. that above 0.5 T, was found to be strongly anisotropic and hence assumed to reflect the conductivity of the anisotropic $\sigma$-band. Thermal conductivity was measured in other materials such as NbSe$_2$, FeSe, Lu$_2$ and Fe$_3$Si$_5$ [99, 98, 100] and similarities to the behavior of MgB$_2$ were considered to support the two-band scenario.

In conclusion, the effects of two-band superconductivity on the field dependence of the thermal conductivity appear significant if the bands have different upper critical fields. The expected curve is characterized by two steep slopes just below each of the upper critical fields and a flatter slope in between. Note, however, that a similar result was calculated for anisotropic single-band superconductors [94]. Finally, it should be borne in mind that the behavior may significantly depend on the dominant scattering process, and that less theoretical analysis than for some of the other properties presented in this paper is available.

3.4. Superfluid density and magnetic penetration depth

The temperature dependences of the superfluid density and the magnetic penetration depth are well known for standard s-wave and d-wave superconductors. In some materials, such as MgB$_2$, significant deviations from this standard behavior, for instance a faster drop of the superfluid density at low temperatures, were observed, which could be interpreted in terms of a two-band but, in many cases, also of an anisotropic single-band model.

The London penetration depth is defined by

$$\Lambda_L = \frac{m_s}{\mu_0 n_s q_s^2}$$  \hspace{1cm} (17)

with $m_s$ the mass, $n_s$ the density, and $q_s$ the charge of the superconducting charge carriers. It shows up in the second London equation via $\nabla^2 \Phi = -\Lambda_L \Phi$ and via $\nabla \times j = -\Lambda_L \nabla \Phi$, and thus determines the penetration of the magnetic induction ($B$) and of the electrical current density ($j$) at the surface of a superconductor in the Meissner state. The London equation refers to the local limit and is hence valid when the penetration depth is much larger than the coherence length. Corresponding relations are acquired from Ginzburg–Landau and BCS theory at low magnetic inductions.

It can be shown that

$$\frac{\Lambda^2_2(0)}{\Lambda^2_1(0)} = \frac{n_s(T)}{n_s(0)}$$ \hspace{1cm} (18)

i.e. the temperature dependences of the magnetic penetration depth and of the Cooper pair density are closely related. At low temperatures BCS predicts an exponential behavior [65], similarly as for the specific heat

$$\frac{n_s(T)}{n_s(0)} \simeq 1 - DT^{-0.5} e^{-\Delta(0)/k_B T}$$ \hspace{1cm} (19)

with $D$ a temperature-independent constant. Indicating the loss of superconducting particles by thermal excitations, the curve decreases continuously and reaches zero at the transition temperature. The weak coupling BCS behavior is universal for all materials (see dashed curve in figure 9). At low temperatures the superfluid density of fully gapped materials is governed by the exponential function and thus almost constant (and equal to 1) up to a particular temperature determined by $\Delta$. Strengthening the coupling usually enhances the energy gap and hence enlarges the range over which the superfluid density is nearly constant, while a smaller gap reduces this range and makes the superfluid density decrease with temperature more rapidly at low temperatures (see lines in figure 9, where the gap of the $n_s$ curve is smaller and that of the $n_s$ larger than the BCS value). When the energy-gap values diverge in a material, the lower values govern the low-temperature behavior, which is why the superfluid density drops faster than predicted by BCS theory, while the larger gaps govern the high-temperature behavior. If parts of the gap function are very small, the s-wave superconductor could even resemble d-wave behavior, for which we expect the superfluid density to decrease linearly at low temperatures.

Without interband interactions the superfluid density is just the sum of the contributions from the two bands, with the smaller gap band dominating the low-temperature region and the larger gap band dominating the high-temperature region. The crossover at intermediate temperature is marked by a kink. As interband coupling and impurity scattering are turned on and then increased, the kink is smoothed and
Figure 9. The superfluid density of MgB$_2$ (symbols [103]) compared with theoretical models (left panel) and of YBa$_2$Cu$_3$O$_{7-\delta}$ [104] (right panel) as a function of reduced temperature. In the left panel, the experimental data were acquired by evaluating reversible magnetization curves. The solid lines represent the two-band $\alpha$-model, from which the lower (thin) line refers to $\Delta_1 = 2$ meV ($n_x$), the upper (thin) line to $\Delta_2 = 6.5$ meV ($n_y$), and the (bold) line in the middle to the two-band result $\Delta_\alpha = 0.43n_x + 0.57n_y$. The selected energy gaps and relative weights are reliable values for MgB$_2$. Finally, the dashed line displays the BCS behavior. Note that at high fields the $\sigma$-band properties dominate and the single-band behavior is expected, which is indeed confirmed by the closeness of the high-field data (full circles) to the single-band $n_{BCS}$ and $n_e$ curves in the figure, while at low fields both bands influence the properties and the experimental data (open symbols) are thus better described by the two-band $\alpha$-model. In the right panel, the data were acquired from muon-spin rotation measurements at an applied field of 0.1 T. The low-temperature behavior does not reflect the expectation of a d-wave superconductor; instead, the significant rise below a reduced temperature of about 0.1 was interpreted as evidence for an additional s-wave band in [104], but assumed to be induced by vortex pinning effects in [105].

Much experimental data is available for iron-based superconductors [108–114]. Though varying from material to material and depending on doping, the superfluid density seems to resemble the known two-band trends, i.e. it decreases rapidly at low temperatures and becomes almost linear, or even convex, at elevated temperatures, so that a conventional BCS fit does not match but a two-band fit does.

Different energy gap values, from which the smaller ones dominate the low-temperature behavior and the larger ones dominate the high-temperature behavior, are also found in an anisotropic single-band superconductor. Accordingly, the resulting curve could easily resemble two-band behavior. Though it seems difficult to imitate the extreme two-band case, in which the contributions of the two gaps can still be distinguished (i.e. when interband effects are very weak), most experimentally observed curves showing almost linear or slightly convex behavior over large parts of the temperature range fit the anisotropic single-band model well, as was demonstrated for MgB$_2$ [36].

In conclusion, in the case of different energy gap values at the Fermi surface, the low-temperature superfluid density behavior is governed by the smaller gaps and the high-temperature behavior by the larger gaps. Accordingly, the superfluid density of both anisotropic and two-band s-wave materials, having a small and a large gap, decreases more rapidly than expected from BCS theory at low temperatures and may become more linear, or even convex, at elevated temperatures. Consequently, distinguishing anisotropy from two-band effects is again difficult.

3.5. Upper critical field

The upper critical field ($B_c2$) was one of the first properties of MgB$_2$ for which unconventional behavior was discerned, namely by a pronounced upward (positive) curvature of its temperature dependence near the transition temperature [115–117]. Since then, the effect has been discovered in many materials and often considered as a confirmation of two-band superconductivity. I shall point out, however, that the same effect occurs in anisotropic single-band and even in d-wave superconductors.

The upper critical field can be easily determined in most superconductors, for it marks the continuous phase transition from the superconducting to the normal-conducting state, observable, for instance, by a jump in the electric resistivity or the specific heat, or by a kink in the reversible magnetization. Calculating the upper critical field within Eliashberg theory allows one to take into account different coupling strengths, impurity scattering rates, order parameter symmetries, and arbitrary Fermi surfaces, including multi-bands.

The weak coupling BCS limit leads to the well-known WHH (Werthamer, Helfand, and Hohenberg [118, 119]) behavior, predicting that the slope of $B_c2(T)$ is constant near the transition temperature and becomes gradually less negative upon cooling. Universal behavior is reached by defining a reduced upper critical field

$$b_{c2}(t) = \frac{B_{c2}(t)}{B_{c2}(t = 1)}$$

(20)
with \( t = T/T_c \). Ignoring Pauli spin paramagnetism, WHH found \( b_{2z}(0) = 0.727 \), which has been well confirmed, not only for almost isotropic conventional superconductors but also for many strongly anisotropic or two-band materials along their uniaxial crystallographic axis (if available). For instance, \( b_{2z}(0) \) equal to 0.75 was reported for MgB_2 in fields perpendicular to the boron planes \[115\]. Those results are confirmed by Eliashberg theory, which shows \( b_{2z}(0) \) to grow only slightly with coupling strength \[51\], e.g. to about 0.76 for \( \lambda = 1.55 \) (which corresponds to lead). Moreover, \( b_{2z}(0) = 0.69 \), acquired in the dirty limit of the weak coupling case, suggests that impurity scattering effects are small.

Early measurements of the upper critical field in MgB_2 revealed a remarkable deviation from the WHH behavior, namely a pronounced upward curvature near the transition temperature in fields parallel to the boron planes (\( ab \)-direction) but a conventional behavior along the uniaxial axis (\( c \)-axis), making the anisotropy \( \Gamma = B_{c2}/B_{c} \) decrease with temperature \[115–117\], as shown in figure 2. These peculiarities have also been reported for other materials, such as Nb \[120, 25\], V \[120\], NbSe_2 \[121–123\] (figure 10), borocarbides and nitrides \[124, 22, 26\], heavy fermion systems \[125\], iron-based \[126–130\] (figure 10), and cuprate \[131, 132\] superconductors, and have often been considered as an indication or a confirmation of two-band superconductivity. The effect may change from sample to sample and is sometimes quite small.

The upward curvature of the upper critical field of two-band superconductors has also been confirmed by theory. Within Eliashberg theory, this curvature was shown to appear when the Fermi velocities of the two bands are different and to become more pronounced when the ratio of the velocities increases \[62\]. This would explain why the feature is observed for \( H \parallel ab \) but not for \( H \parallel c \) in MgB_2, for the mean Fermi velocities perpendicular to the applied field are quite different in the case of \( H \parallel ab \) (\( v_F,\sigma < v_F,\pi \)) but similar for \( H \parallel c \) \[133\]. Accordingly, two-band superconductors do not necessarily display this feature for any field direction. The curvature is affected by the coupling and the impurity scattering parameters in different manners. For instance, it was claimed that different intraband scattering rates could produce the upward curvature even if the Fermi velocities are similar \[62\]. A small positive \( B_{c2}(T) \) curvature for the field along the uniaxial axis was indeed found after heavy neutron irradiation in a MgB_2 single crystal \[134\], but ascribed to inhomogeneities in the transition temperature caused by the defect distribution.

In samples with uniaxial symmetry, the positive curvature usually occurs for measurements in fields perpendicular to this axis, which is mostly also the direction of the maximal upper critical-field values. A different behavior, namely an upward curvature for a field orientation not showing the highest upper critical-field values, was observed in some iron-based superconductors, such as the 1111 and 122 compounds (see section 4.3) \[126–130\]. Also in contrast to MgB_2, the corresponding anisotropy was found to increase with temperature, which might be an effect of Pauli paramagnetic pair breaking, occurring at low temperatures in high magnetic fields and flattening the upper critical-field behavior (see figure 10).

It should be mentioned that an upward curvature of the upper critical field and hence a temperature-dependent anisotropy have long been known for anisotropic s-wave superconductors. The theory based on the Eliashberg model was elaborated in \[21, 136\]. The effect was even observed in niobium and shown to match theory well \[25\]. Similar results have been reported for other materials. In many cases, the simple separable model, introduced in section 2.2, was found to fit the experiments quite well. Because this model formally agrees with a spherical two-band model, similar effects in both scenarios are anticipated. Indeed, the anisotropic single-band theory was shown to reproduce the upper critical field of MgB_2 \[24\] (see figure 2) and other potential two-band materials \[26\] nicely. The upward curvature of \( B_{c2}(T) \) in single-band superconductors was also derived from the Eilenberger equations \[137\]. In principle, theory shows the upper critical field to be governed by an integral over the Fermi surface which includes the Fermi velocities perpendicular to the field orientation. Thus, details of the anisotropy do not show up in the upper critical field and hence quite different Fermi surfaces with a similar mean anisotropy may lead to a similar \( B_{c2}(T) \) behavior.
The upward curvature was also predicted for d-wave symmetry [138], and was recently confirmed by measurements of a temperature-dependent anisotropy in SmBa$_2$Cu$_3$O$_y$ [131] and YBa$_2$Cu$_3$O$_y$ [132].

Differences between the single-band and two-band model might become visible when introducing impurities. In the single-band scenario, scattering by non-magnetic point defects smears out the anisotropy of the Fermi surface and thus reduces the transition temperature until saturation is reached. At the same time, $B_{c2}(T)$ becomes steeper near the transition temperature, which may lead to an increase in $B_{c2}(0)$. In the case of the two-band scenario, the different channels for impurity scattering affect the upper critical field and the transition temperature in different ways [62, 139]. For instance, if the bands are spherical, intraband impurity scattering increases the upper critical field, but does not change the transition temperature (as known from the Anderson theorem), while interband scattering modifies both quantities. Consequently, in contrast to anisotropic single-band materials, the two-band scenario would allow us to increase the upper critical field without lowering the transition temperature if we succeeded in changing impurity scattering only for a selected channel.

To conclude, identifying two-band materials from measurements of the upper critical field appears hardly feasible, for the characteristic upward curvature of the upper critical field near the transition temperature and the corresponding temperature dependence of the anisotropy may also emerge in anisotropic single-band and d-wave superconductors.

3.6. Torque

The anisotropies of the magnetic penetration depth and of the coherence length have often been claimed to be different in two-band superconductors, which can be verified by studying the angular dependence of the magnetic torque. We will see that the experiments have not confirmed this statement thus far. Moreover, torque experiments are an efficient tool for acquiring several superconducting properties from a single measurement.

The single-band Ginzburg–Landau model for uniaxial superconductors needs but one anisotropy parameter $\Gamma = \sqrt{m_e/m_{ab}}$, where $m_e$ and $m_{ab}$ are the effective masses of the principal crystallographic axes. The same quantities determine the ratio of the penetration depths ($\Lambda$) and of the upper critical fields ($B_{c2}$), i.e.,

$$\Gamma = \frac{B_{c2}^e}{B_{c2}^a} = \Lambda_e/\Lambda_{ab}. \quad (21)$$

Here, uniaxial anisotropy, with $e$ the uniaxial direction and $ab$ perpendicular to it, is assumed. In equation (21), the indices of the lengths indicate the flow direction (e.g. of the currents) and the superscripts the field orientation. The anisotropy of the coherence length is usually supposed to match that of the upper critical field: $\Gamma = \xi_e/\xi_a$.

The magnetic torque is defined by $\tau = \vec{m} \times \vec{B}$, with $\vec{m}$ the magnetic moment of a sample with volume $V$. The reversible torque of a superconductor can be derived within London theory [140, 141]. If we assume the magnetic induction to be equal to the applied field (which usually holds well for not too low fields), we obtain

$$\tau(\vartheta) = -\frac{VH_0\Phi_0}{16\pi \Lambda_{ab}^2} (1 - \Gamma^{-2}) \sin 2\vartheta \frac{\ln \left( \frac{\eta \xi_e}{\epsilon \mu_0 H_a} \right)}{\epsilon} \quad (22)$$

with

$$\epsilon = \epsilon(\vartheta, \Gamma) = \sqrt{1 - 2\sin^2 \vartheta + \cos^2 \vartheta}. \quad (23)$$

Here, $\vartheta$ denotes the angle between the field orientation and the $c$-axis of the sample, $H_a$ the applied magnetic field, and $\eta \sim 1$ is a parameter that depends on the vortex configuration. Usually, different background signal terms are to be added.

Equation (22) can be adjusted to experimental data by varying the parameters $\Lambda_{ab}, B_{c2}^e$, and $\Gamma$ freely. The magnetic penetration depth is simply a proportionality factor, the upper critical field is highly sensitive to the curvature of the torque, and the anisotropy is mainly determined by the slope near the $ab$ direction. Thus there is a good chance of determining each variable quite independently from the others. Nevertheless, reducing the number of fit parameters by taking results from other experiments, such as the upper critical field from SQUID measurements, should improve the quality of the fit procedure. Usually, the reversible torque has to be acquired from the irreversible branches, obtained by measuring at opposite rotation directions. Evaluation errors, in particular those for the anisotropy, will become substantial with increasing hysteresis width between the irreversible branches.

Quite early, very pure single crystals of MgB$_2$, whose magnetic properties were almost fully reversible and which were thus excellently suited for torque experiments, were made available [142]. Describing the torque data by equation (22) was shown to work well, as illustrated in figure 11, and to reveal parameters in good agreement with results from other experiments, for instance with the upper critical field and its anisotropy determined from SQUID magnetometry [143].

As already mentioned, the anisotropies of the upper critical field

$$\Gamma_H = \frac{B_{c2}^h}{B_{c2}^e} \quad (24)$$

and of the magnetic penetration depth

$$\Gamma_\Lambda = \frac{\Lambda_e}{\Lambda_{ab}} \quad (25)$$

were proposed to be unequal, i.e. $\Gamma_H \neq \Gamma_\Lambda$, in two-band superconductors. Equation (22) holds only when both anisotropies are equal; for $\Gamma_H \neq \Gamma_\Lambda$, Kogan [144] derived:

$$\tau(\vartheta) = -\frac{VH_0\Phi_0}{16\pi \Lambda_{ab}^2} (1 - \Gamma^{-2}) \sin 2\vartheta \frac{\ln \left( \frac{\eta \xi_e}{\epsilon \mu_0 H_a} \right)}{\epsilon} \times \ln \left( \frac{\eta \xi_e}{\epsilon \mu_0 H_a} \right) + 1 + \frac{1 - \Gamma_H}{\Gamma_\Lambda} \epsilon \Lambda \left( \frac{1 - \Gamma_H^2}{\Gamma_\Lambda^2} \epsilon H \right) \right]. \quad (26)$$

with $\epsilon \Lambda = \epsilon(\vartheta, \Gamma_\Lambda)$ and $\epsilon H = \epsilon(\vartheta, \Gamma H)$ (see equation (23)).
Torque measurements were also carried out on iron-based superconductors and analyzed via equations (22) and (26), but the results suffer from large hysteresis widths between the two irreversible branches. In [147], XFeAsO$_{0.8}$F$_{0.2}$ (X = Nd or Sm) single crystals with transition temperatures between 44 and 48 K were analyzed at a field of 1.4 T and at temperatures from about 20 to 44 K. Employing expression (22) led to excellent agreement with experiment, and the anisotropy was found to decrease from about 15–20 at 20 K to 7 near the transition temperature. Since the results were in striking contrast to resistivity measurements, from which $\Gamma_H \simeq 5$ at 34 K was obtained [127], equation (26), with $\Gamma_H$ fixed by the resistivity data, was applied. Again, good agreement with experiment was reached and $\Gamma_A$ found to be equal to $\Gamma$ from the single-band evaluation (22), i.e. 15–20 at 20 K to 7 near the transition. This demonstrates that $\Gamma_H$ has virtually no effect on the quality of the fit and that the relation between the anisotropies could thus not be determined in this case. Note that $\Gamma_H$ from the resistivity measurement referred to much higher fields than the results from the torque experiments. Further experiments on iron-based materials have been carried out [148, 149] and could be described well by the single-band expression (22). Applying the method to LaFeAsO$_{0.9}$F$_{0.1}$ ($T_c \sim 15$ K) revealed a temperature-dependent and field-dependent anisotropy [148].

In conclusion, the magnetic torque is not able to reveal two-band behavior of a superconductor directly, for the data are usually described well by the conventional expression valid for single-band materials. The temperature and, in particular, the field dependence of the evaluated properties, such as the anisotropy and the magnetic penetration depth, may, however, help to identify a two-band material, as we will see later.

3.7. Reversible magnetization

The reversible magnetization, $M_r$, of a superconductor is another property that may be sensitive to two-band effects. Indeed, its field dependence should allow us to discriminate the two-band from the anisotropic single-band scenario. Unfortunately, acquiring samples in which the reversible magnetization can be determined often proves difficult due to the interfering effects caused by flux-line pinning.

Measurements of the magnetic moment are routinely performed in SQUIDs and vibrating sample magnetometers. Direct access to the reversible part is often blocked by the irreversible properties, accompanying the flux-line pinning and showing up in a hysteresis of the magnetization loop. The volume-averaged reversible magnetization can then be calculated via

$$M_r(H) = \frac{m(H_+)}{2V} + \frac{m(H_-)}{2V}$$  (27)

Figure 11. The torque as a function of angle. The upper panels show experimental data of MgB$_2$ [103] compared with theory. The open circles display the reversible torque obtained from the irreversible branches, indicated by dashed lines, as discussed in the text. At 2 T (upper panel) the reversible and irreversible curves coincide. The solid lines show the single-band fits according to equation (22). Notice that the data at 2 T, displayed in the upper panel, refers to the high-field single-band regime, while the data at 0.3 T, displayed in the middle panel, refers to the low-field two-band regime of MgB$_2$; yet, both curves excellently match the single-band model, in which the anisotropies of the penetration depth and the coherence length are assumed to be equal. The bottom panel illustrates the effect of diverging anisotropies according to equation (26) at a field of 0.3 T. The upper critical-field (or coherence length) anisotropy is held constant at 4.5, while the penetration depth anisotropy changes from 4.5 (solid line) to 2.7 (dashed line) to 1.1 (dashed–dotted), which modifies the curves in a profound way. All data refer to MgB$_2$ at 5 K and a $B_{oc}$ of 2.8 T.
with \( m \) the measured magnetic moment, \( V \) the sample volume, and \( H \) the applied field \( H \). For the increasing \((H_+)\) and for the decreasing \((H_-)\) sweep branch, \( H_+ \) and \( H_- \) should roughly refer to the same magnetic induction \( B \) in equation \((27)\). When the irreversible contributions are significantly larger than the reversible part, the result of the above equation will usually become highly unreliable. The hysteresis width can, however, be reduced by employing the so-called vortex shaking technique [150, 151].

For some materials, such as MgB\(_2\), NbSe\(_2\), V\(_3\)Si, Nb, pure single crystals are available, in which the hysteresis is small or completely absent over a large field and temperature range. If additionally the upper critical field of that material is not too high, the reversible magnetization can be determined over a large part of the superconducting phase diagram. Calculating \( B = \mu_0(H - DM_r + M_r) \), where \( D \) is the demagnetization factor of the sample, gives \( M_r(B) \), i.e. the reversible magnetization as a function of the magnetic induction, which we can compare with theory.

The theoretical \( M_r(B) \) curve can be taken from any model; for instance, Ginzburg–Landau theory appears quite convenient—not only because simple interpolation formulas, provided by Brandt [152, 153], are available. The Ginzburg–Landau model depends on two parameters, namely on the upper critical field, at which \( M_r(B) \) vanishes, and on the Ginzburg–Landau parameter \( \kappa \). Both quantities can be acquired by fitting theory to the experimental \( M_r(B) \) data. In Ginzburg–Landau theory, anisotropy is specified by the appropriate effective masses at the Fermi surface (see equation \( 2 \)), but it was shown that the anisotropic model can be mapped onto the isotropic single-band model, when the magnetic field points along a principal axis of the sample [154, 155]. Thus, in contrast to two-band effects, anisotropy should not significantly affect the shape of \( M_r(B) \).

Figure 12 presents reversible magnetization curves of NbSe\(_2\) and MgB\(_2\) as a function of field [103]. The dashed lines display the best single-band Ginzburg–Landau fits when the upper critical field is fixed by the field where the experimental data become zero. The striking differences between theory and experiment provide evidence for a non-single-band behavior in these materials.

Ginzburg–Landau theory is known to hold strictly only sufficiently close to the transition temperature and the upper critical field. As the temperature decreases, larger deviations between the Ginzburg–Landau and the experimental behavior are likely, although we do not expect considerable qualitative effects if we adjust the parameters of the model in a convenient way. This was verified for V\(_3\)Si (right inset of figure 12), for which reliable agreement was not only found at high temperatures \((T/T_c \approx 0.8)\), but also at relatively low temperatures \((T/T_c \approx 0.3-0.4)\) [156], and for Nb. Good matching was also reported for the anisotropic superconductors YBa\(_2\)Cu\(_3\)O\(_8\), Nd\(_{1.85}\)Ce\(_{0.15}\)CuO\(_4\), and YBa\(_2\)CuO\(_{7-\delta}\) [157–159]. It should be noted, however, that for all those samples two-band superconductivity has been suspected in some publications. Nevertheless, I point out that for MgB\(_2\) and NbSe\(_2\) the disagreement between experiment and single-band theory is not essentially changed at higher temperatures.

![Figure 12](image_url)

Figure 12. The reversible magnetization of several single-crystal samples as a function of magnetic induction (open circles) compared with single-band Ginzburg Landau theory (lines) [123, 103]. The two main panels show results on NbSe\(_2\) for fields parallel \((c, \text{ left panel})\) and perpendicular \((ab, \text{ right panel})\) to the uniaxial axis at a temperature of 4.2 K \((T/T_c \approx 0.6)\). The left inset displays data of MgB\(_2\) for \( H || c \) at 5 K \((T/T_c \approx 0.13)\) and the right inset displays data of V\(_3\)Si at 13.5 K \((T/T_c \approx 0.8, \text{ upper curve})\) and 7 K \((T/T_c \approx 0.4)\). The dashed lines indicate fits to the whole experimental field range, while the solid lines refer either to the low-field or high-field regime alone. We find qualitative disagreement between single-band Ginzburg Landau theory and NbSe\(_2\) or MgB\(_2\) and that two different theoretical curves, one for the low-field and one for the high-field regime, can cover most of the experimental data. The deviation from single-band theory does not essentially change at other temperatures in these materials. In contrast, reliable agreement between single-band theory and reversible magnetization over the whole field range is observed in V\(_3\)Si at high temperatures and, though slightly worse, at low temperatures [156].

To evaluate two-band properties, we can analyze the experimental data by applying two independent single-band fits, one for the low-field and one for the high-field regime, as illustrated in figure 12. It should be kept in mind that this procedure does not yield a two-band model, for interband effects are not taken into account, but rather resembles the \( \alpha \)-model used for fitting the specific heat (see section 3.1) and other properties. The point is that in two-band superconductors, such as MgB\(_2\) and NbSe\(_2\), the properties of one of the bands are apparently suppressed above a particular magnetic field, associated with the upper critical field of that band, and thus a nearly single-band behavior, matching the single-band Ginzburg–Landau model, appears at high fields, while both bands significantly contribute to the superconducting state at low fields. The high-field fit reveals \( \kappa \), \( B_{c2} \), and, by applying the well-known Ginzburg–Landau relations [160], further critical fields and lengths as well as the anisotropy of the band with the higher upper critical field. Even at low fields, a single-band model was found to describe MgB\(_2\) and NbSe\(_2\) well, but the corresponding fit leads to effective quantities representing both bands, though the properties of the second band might dominate in this field region in the cases of MgB\(_2\) and NbSe\(_2\). Note that, although the global upper critical fields are quite different for the \( c \) and the \( ab \) directions in these materials, the upper critical fields from the low-field fits are almost equal, as shown in figures 10.
and 13. This reflects the shape of the two bands, of which one is strongly anisotropic and the second almost isotropic.

The procedure not only probes two-band superconductivity, but can also reveal the field dependence of several quantities. A more elaborate model of the two-band Ginzburg–Landau magnetization curve, including interband effects, was applied in [12], and led to more detailed results of the temperature and field dependence of several superconducting properties (e.g. top right panel of figure 13).

The above method was successfully applied to MgB$_2$ and NbSe$_2$ [103, 123]. Unfortunately, iron-based superconductors usually have a large hysteresis, so that the reversible part has not been reliably determined so far, which is similar to the situation in many cuprates. Moreover, the upper critical fields of these materials are often much larger than the maximum field provided by the experimental equipment.

To conclude, comparing the measured field dependence of the reversible magnetization with the theoretical single-band behavior appears to be a useful tool for probing two-band superconductivity. This holds at least when the superconducting properties of one of the bands are significantly suppressed at higher magnetic fields and, as a consequence, a single-band fit of $M_r(B)$ does not match over the whole field range. Using the Ginzburg–Landau model seems sensible, though some uncertainties remain due to the restrictions of the model. The single-band fits allow us to extract the field and temperature dependence of several superconducting properties.

3.8. Anisotropy and field dependence of the characteristic lengths

Peculiarities in the anisotropy have frequently been considered a strong confirmation of two-band superconductivity. Indeed, while a temperature dependence of the anisotropy is rather common, a strong field dependence is difficult to explain by non-two-band effects. Those field dependences are mirrored by different anisotropies of, for instance, the magnetic penetration depth and the upper critical field when these properties are measured at different fields.

Anisotropy shows up in many superconducting properties, such as the magnetic penetration depth ($\Gamma_\lambda$), the coherence length ($\Gamma_\xi$), the Ginzburg–Landau parameter ($\Gamma_\kappa$), the upper critical field ($\Gamma_{Bc2} = \Gamma_H$) and the lower critical field ($\Gamma_{Bc1}$), when different crystal directions are probed. In the following, I will concentrate on uniaxial anisotropy, since most samples discussed in this text have uniaxial or near-uniaxial symmetry. In simple single-band materials, all anisotropies are equal, in accordance with Ginzburg–Landau theory, i.e. $\Gamma_\lambda = \Gamma_\xi = \Gamma_\kappa = \Gamma_{Bc2} = \sqrt{m_e/m_{ab}}$.

In the case of two- or multi-band superconductivity, a more complicated situation arises, as different bands may have different Fermi surface shapes. In fact, when people determined the anisotropy of MgB$_2$ they reported quite different results for different quantities and techniques. Basically, the anisotropy of the upper critical field was found to be large (~5) at low temperature and to decrease upon warming, while that of the penetration depth was small at low temperature (~1) and increased on warming, such that roughly the same value was reached at the transition temperature [161, 102]. This could be explained by theory. Within the Elienberger model, the ratio of the penetration depths at 0 K [162] was found to depend only on the ratio of the Fermi velocities, which gives roughly unity in MgB$_2$, while the larger values at higher temperature were explained by the additional influence of the gap anisotropy. Concerning the anisotropy of the upper critical field [137], the same expression as for the penetration depths was derived at the transition temperature, which explains the experimentally observed merging of the two anisotropies at this point, while a rather large anisotropy, corresponding to the shape of the band dominating at high fields, was theoretically derived and experimentally acquired at low temperatures.

It should be noted that in the above experiments and theoretical calculations, the anisotropies of the upper critical field
fields and penetration depths refer to different magnetic fields, namely to low or zero fields in the case of the penetration depth but to high fields in the case of the upper critical field. Some methods allow us to determine the penetration depth and thus $\Gamma_A$ at different magnetic fields. A simple method providing two values, one for the high-field and one for the low-field region, is fitting two single-band curves to the reversible magnetization (as presented in section 3.7), which was reported to yield rather small values—$\Lambda_{ab} \approx 50$ nm and $\Lambda_c \approx 60$ nm—in low magnetic fields, and larger values—$\Lambda_{ab} \approx 80$ nm and $\Lambda_c \approx 360$ nm in high fields for MgB$_2$ [103]; accordingly, also this anisotropy increased from about 1 to 4.5 with increasing field at 0 K. A more elaborate evaluation of the reversible magnetization within two-band Ginzburg–Landau theory [12, 27] revealed a smoother behavior of the quantities over the whole field range and basically confirmed the above-mentioned trend. A quite different technique, neutron scattering by flux lines of MgB$_2$ [145], suggested 30–60% larger penetration depths, but the same trend for the field dependence of its anisotropy.

Because talking about the field dependence of the upper critical-field anisotropy does not make sense, we will turn to the closely related coherence length. The coherence lengths, acquired from the reversible magnetization of MgB$_2$ [103], were reported to be about 10.7 and 2.3 nm at high fields and 17.4 and 34 nm at low fields, which gives an anisotropy comparable to that of the penetration depth in the same field regime. Again, similar but more reliable results were obtained from the two-band Ginzburg–Landau model [12, 27]. Klein et al [89] determined the field dependence of the coherence length from the Sommerfeld coefficient by assuming $\gamma(B)$ to be proportional to the core size ($\sim \xi(B)^2$) and to the number of vortices ($\sim N \propto B$), i.e. $\xi^2(B) \propto \gamma(B)/B$; their experimental finding that $\gamma(B)$ of MgB$_2$ roughly behaves like $\sqrt{B}$ resulted in $\xi(B) \propto B^{-0.25}$. A strong field dependence of the coherence length was also suggested from scanning tunneling spectroscopy measurements of the vortex core, indicating that the low-field coherence length might be much larger (factor $\sim 5$) than that expected from Ginzburg–Landau theory at the upper critical field [165] ($B_{c2} = \Phi_0/2\pi\xi^2$). In NbSe$_2$, muon-spin rotation measurements [166] showed the coherence length to decrease strongly with increasing field at low fields and to become almost constant above a certain field, associated with the upper critical field of the first band, which confirmed the results from the reversible magnetization in this material [123]. The same held for the magnetic penetration depth.

It should be noted that a field-dependent coherence length is not a specific property of multi-band materials, but shows up even in s-wave single-band materials as a roughly $1/\sqrt{B}$ behavior [43, 85], which is a consequence of vortex overlapping and the corresponding delocalization of core quasiparticles [167, 168]. The field dependence turned out to be particularly large in clean samples and at low temperatures, and might even become comparable to the effect in MgB$_2$ or NbSe$_2$ for $H \parallel c$, where $\xi(0)/\xi(B_{c2}) \sim 2$, but for $H \parallel ab$, these ratios may be larger in the two-band materials. Furthermore, an abrupt change, as seen in NbSe$_2$ [166] due to the suppression of one of the bands, is not expected in conventional materials.

We see that the anisotropies of the coherence length and of the magnetic penetration depth display similar behavior in several two-band superconductors, such as MgB$_2$ and NbSe$_2$. They are not only temperature dependent but also significantly field dependent, as can be seen in figure 13. For instance, the anisotropies of MgB$_2$ and NbSe$_2$ are small at low fields, increase strongly with field, and are rather constant at high fields. Obviously that reflects the dominant influence of the more isotropic band at low fields and of the more anisotropic band at high fields. The correspondence of the coherence length and the penetration depth anisotropy at all fields and temperatures cannot unambiguously be proved experimentally, but has not been refuted by the known experiments thus far. At least, the anisotropies were shown not to differ significantly, as was also confirmed by the torque results of section 3.6. Moreover, the anisotropy of the lower critical field of MgB$_2$ [169], which naturally corresponds to the low-field regime, was found to be in reasonable agreement with the low-field $\Gamma_A$. Also, the anisotropy of the Sommerfeld coefficient, acquired from specific heat measurements at different magnetic fields, agreed with the other anisotropies [86, 88]. Finally, direct tunneling spectroscopy measurements indicated a small vortex lattice anisotropy, i.e. an almost undistorted hexagonal lattice, and rather circular vortex cores at low fields perpendicular to $c$ [170].

The low-field penetration depth and the high-field upper critical-field anisotropies are significantly different in the iron-based superconductors as well, though their functionalities are contrary to MgB$_2$ and NbSe$_2$, as illustrated in figure 13. The question of different anisotropies at the same field and temperature has not been addressed thus far. Torque data could be described well by the single-band model with equal anisotropies and at the same time by a model including different anisotropies [147].

In conclusion, considering a significant number of experiments on MgB$_2$ and similar materials leads us to the suggestion that the anisotropies of the superconducting properties, in particular of the penetration depth and the coherence length, are equal or almost equal in these two-band samples. These anisotropies change with temperature and magnetic field. The field dependence of the characteristic lengths and of their anisotropies reflects the properties and anisotropies of the different bands. The situation is currently unsettled in the iron-based materials.

3.9. Superconducting energy gap

The most direct evidence for two-band superconductivity should be gained from a measurement of the energy-gap structure on the Fermi surface, which appears to be a straightforward task. However, things are again not that simple, as we will see in the following. For instance, not all energy gaps necessarily show up in tunneling or point-contact spectroscopy measurements; moreover, anisotropy would also lead to varying gap values. Finally,
angle-resolved photoemission spectroscopy, which allows a direct assignment of gaps to certain bands, does not work for all materials.

Studying two-band materials with distinct gaps reveals two independent gaps with BCS-like temperature behavior and two different transitions when interband coupling is ignored. According to calculations [58], slightly turning on interband coupling hardly changes the larger gap, while the lower gap curve should become flat near its single-band transition, so that it eventually vanishes at the same temperature as the larger gap, as indicated in figure 5. As interband coupling grows, the lower gap becomes larger and smoother but still deviates from a BCS-like shape, particularly at high temperature. The larger gap is less affected, though some deviations from BCS behavior are to be expected. The ratio of the gaps is reduced. Almost the same effects were predicted from increasing the interband impurity scattering rate. Notice that both parameters also affect the transition temperature.

Scanning tunneling spectroscopy (STS) provides a direct way of measuring the superconducting gap structure. In principle, a metallic tip is brought very close (≈1 nm) to the superconducting surface, so that charge carriers can tunnel between them when a bias voltage \( V \) is applied. At \( T = 0 \) K tunneling is only possible for \( |V| > |\Delta|/e_0 \), with \( e_0 \) the positive elementary charge, and the gap magnitude, \( |\Delta| \), thus becomes apparent when we record the tunneling current as a function of voltage (e.g. [171]). The expression (e.g. [172])

\[
d\frac{I}{dV} \propto \rho_s(E_F + e_0 V) \tag{28}
\]

provides an approximate relation between the tunneling current \( I \) and the local quasiparticle density of states of a superconductor \( \rho_s \), where \( E_F \) is the Fermi energy, which will be set to zero from now on; the density of states of the tip is assumed constant near the Fermi level. The density of states of a conventional s-wave superconductor, acquired from tunneling spectroscopy, may be described by [173]

\[
\rho_s(E, \gamma) = \text{Re} \frac{|E| + i\gamma}{ \sqrt{(|E| + i\gamma)^2 - \Delta^2}} \tag{29}
\]

Setting \( \gamma = 0 \) gives the standard BCS behavior of a superconductor. The parameter \( \gamma \)—usually denoted by \( \Gamma \) in the literature—takes the broadening of the curve features into account, which is mainly a consequence of impurity scattering.

The spectra of two-band superconductors have usually been modeled by \( \rho_s = n_1 \rho_1 + n_2 \rho_2 \), with \( \rho_i \) the densities of the different bands and \( n_i \) their relative contributions to the tunneling current \( (n_1 + n_2 = 1) \). Dependent on the five parameters \( \Delta_1, \Delta_2, \gamma_1, \gamma_2, \) and \( n_1 \), the density of states may show two peaks on each side of the Fermi level or one peak and one shoulder at the positions of the gap energies, as illustrated in figure 3. Unfortunately, similar structures can be acquired from anisotropic single-band materials (e.g. [36]), while d-wave materials are indicated by a V-shaped density of states around the Fermi level.

Tunneling spectroscopy of MgB\(_2\) revealed only one gap for currents parallel to the uniaxial c-axis [165]. This result was actually expected, for the contribution of the \( \sigma \)-band to the conductivity was estimated to be not more than about 1% of that of the \( \pi \)-band. [175] (see also figure 3). For currents perpendicular to \( c \), the ratio of \( n_{\sigma} \) to \( n_{\pi} \) is about 1:2, and thus a double-peak structure could be detected [170]. In NbSe\(_2\) and NbSn\(_2\), experiments revealed one peak and one shoulder at a lower energy value for the tunneling current parallel to \( c \) [176, 177].

In many materials, surfaces appropriate for tunneling spectroscopy are difficult to prepare. Point-contact spectroscopy often places fewer demands on the sample preparation; for a detailed review of point-contact spectroscopy see [178]. In principle, a metallic tip is brought into contact with a superconducting surface. To obtain reliable spectroscopy results, the size of the contact should be smaller than the mean free scattering length of an electron. Usually, an additional barrier, whose height is characterized by the dimensionless parameter \( Z \), emerges between the metal and the superconductor. For \( Z = 0 \) a direct contact between the metal and the superconductor is established. When we apply a voltage \( V \) smaller than the gap, i.e. \( e_0 |V| < |\Delta| \), only Andreev reflection takes place, which doubles the electrical conductance at the interface (with respect to a metal–normal-conducting interface); if the voltage becomes larger (\( e_0 |V| > |\Delta| \)), electrons may also directly propagate from the normal-conducting to the superconducting part and the conductance drops. Usually, a finite barrier is present (\( Z > 0 \)), at which electrons can be simply reflected, which leads to a peak at the position of the gap and a reduction of the conductance at lower values of \( |V| \); eventually, at about \( Z > 10 \), the behavior matches that of tunneling spectroscopy (equation (29)). A theoretical description of the conductance curves is given by the so-called BTK model [179].

A second band was shown to entail an additional peak or shoulder in the density of states, as recently reviewed in [180]. Similar to the tunneling results, the conductance can be described by the sum of two weighted BTK single-band curves. Though this model includes seven independent fit parameters, \( \Delta_1, \Delta_2, \gamma_1, \gamma_2, Z_1, Z_2, \) and \( n_1 \), the values obtained for the two gaps are often reliable. Again, single-band anisotropy provides similar modifications [180].

Several point-contact spectroscopy investigations have been carried out on MgB\(_2\). Applying the two-band fits led to good matching with the experimental data and revealed gaps in good agreement with results from other methods. Also the weights, \( n_{\sigma} \) and \( n_{\pi} \), were found in fair agreement with the theoretical prediction [175], namely, for instance, \( n_{\sigma} \) very small and the corresponding gap thus hardly detectable for the \( c \) direction. Applying a magnetic field of 1 T or more suppressed the \( \pi \)-gap and revealed the larger \( \sigma \)-gap [174].

Point-contact and tunneling spectroscopy experiments on the iron-based materials often suffer from difficulties in surface preparation. Nevertheless, two peaks or a peak and a shoulder in the density of states have been observed by both methods [8, 181–183] (see also figure 14).
Angle-resolved photoemission spectroscopy (ARPES) should provide the most direct way of detecting superconducting gaps on different Fermi surface sheets [184]. In principle, the kinetic energy and the momentum vector (i.e. the angular dependence) of electrons, which are activated by photons of known energy and thus emitted from the sample by the photoelectric effect, are determined. As a result, the Fermi surface and, if present, the corresponding gap amplitude can be acquired. It should be noted that only surface states can be probed by this method, and that the surface preparation and a high stability are thus critical. Moreover, the energy resolution may be an issue in some cases. Nevertheless, results that might be representative for the superconducting bulk state were obtained in many samples and compared with numerical calculations of the Fermi surface.

ARPES on NbSe$_2$ [185] revealed three Fermi surface sheets, from which two exhibited a superconducting gap at 5.3 K. In MgB$_2$, the $\sigma$-band and $\pi$-band gaps were determined [186] in good agreement with results from other methods. Finally, several ARPES studies, showing up to five gaps on five different Fermi surface sheets, have been performed on the iron-based materials [187–189].

To conclude, finding two peaks or a peak and a shoulder in tunneling or point-contact spectroscopy measurements provides confirmation of a two-band system, though the anisotropic single-band scenario cannot be completely excluded. On the other hand, the absence of such structures does not definitively disprove two-band superconductivity. Cogent evidence for the two- or multi-band scenario should be gained from angle-resolved photoemission spectroscopy by directly observing superconducting gaps on different bands.

4. Materials

In this section, I will describe several materials for which attributes of two- or multi-band superconductivity have been reported. I will mainly take those into account that have been investigated since the discovery of MgB$_2$, as this was the origin of a broader comprehension of the phenomenon, while earlier reports on two-band effects in materials, such as Nb [190, 191], Ta [190], V [190, 192], Nb-doped SrTiO$_3$ [193], Mo$_{60}$Te$_{40}$ [194], etc, are not further discussed here. In the following, the more prominent materials, namely MgB$_2$, NbSe$_2$ (with NbS$_2$), iron-based superconductors, cuprates, and borocarbides, will be introduced in some detail. Then several other potential two-band superconductors are presented more briefly. The list is not exhaustive, but I hope that not too many important materials have been missed. In some of these materials, multi-band superconductivity is quite well established, in others the situation has yet to be clarified by further experiments, and in some the reports are rather questionable. I will mainly report on experimental data suggesting support or confirmation of the two-band state, and I will not point out possible different interpretations, for instance in terms of anisotropic single-band behavior, in each case.

4.1. MgB$_2$

Since the discovery of its superconductivity in 2001 [1], MgB$_2$ has become one of the most intensively studied superconducting materials, not only because of its potential for applications, but also because it was the first material in which two-band effects were established. Today, it can be considered as the prototype of a two-band superconductor, with which other two-band candidates are compared, and to which most theoretical calculations refer.

MgB$_2$ has a hexagonal crystal structure, built up by a hexagonal magnesium cell and a ring of six boron atoms in the interior. The lattice parameters are approximately 0.31 and 0.35 nm. The Fermi surface of MgB$_2$ has been calculated by several groups and found to be not very complicated, though quite anisotropic [195, 55]. Four bands crossing the Fermi surface were identified, two $\sigma$-bands that have a cylindrical shape and are strongly anisotropic, and two $\pi$-bands that are rather isotropic. The $\sigma$-bands are usually treated as one ($\sigma$) band, and likewise the $\pi$-bands, making a two-band description feasible. The energy gap has s-wave symmetry and opens on all bands; the corresponding absolute values are around 7 meV in the $\sigma$-band and 2 meV in the $\pi$-band. Two-band effects are experimentally observable because both bands have similar densities of states and thus contribute to
superconductivity significantly, but at the same time diverge considerably in their properties.

A multitude of experiments and in particular their quantitative agreement with theoretical results established that electron–phonon interactions drive superconductivity in MgB$_2$. For instance, measurements of the transition temperature showed the isotope effect, namely $T_c \propto M^{-\alpha}$, where $M$ is the mass of the element, with exponents $\alpha \simeq 0.26$–0.30 for boron [196, 197] and $\alpha \simeq 0.02$ for magnesium [196], which could be well reproduced by Eliashberg theory [55]. Thus, apart from the two-band effects, MgB$_2$ is classified as a conventional superconductor.

The two-band nature of MgB$_2$ was suggested quite early and confirmed by many experiments, yet most of them can also be interpreted by other models, as discussed in the previous sections. Some of these experiments have been described above (see, for instance, figures 1, 2, 7–9, 11–14) and shall not be discussed again here; more can be found in review papers, such as Refs. [27, 198], and references therein. Unambiguous evidence that energy gaps exist on two different bands was given by ARPES experiments [186, 199], showing $\Delta \simeq 5.5$–7 on the $\sigma$-band and about 2 meV on the $\pi$-band at low temperatures.

Interesting effects are revealed when MgB$_2$ is probed in different magnetic fields. Due to interband interactions, both bands have the same upper critical fields, but as the field increases the relative contribution of the $\pi$-band to the overall superconducting quantities apparently diminishes, so that eventually the $\sigma$-band dominates. The field above which the $\pi$-band becomes negligible, which is around 1 T at low temperatures, is usually denoted as the second upper critical field of this band (yet, due to interband coupling, traces of superconductivity are still expected at higher fields). The suppression of the $\pi$-band makes the field dependence of diverse properties different from that of an anisotropic single-band material. For instance, the anisotropic single-band model was shown to fail in describing the reversible magnetization of MgB$_2$ over the whole field range from 0 T to $B_{c2}$ [103]. Instead, a single-band fit worked well only for fields above the $\pi$-band upper critical field, thus indicating a near single-band ($\sigma$) behavior at high fields, in agreement with the above-mentioned suppression of the $\pi$-band. The corresponding $\sigma$-band properties were reported to be about 3 T for the upper critical field, 0.07 T for the lower critical field, and 0.3 T for the thermodynamic critical field, as well as 77 nm for the magnetic penetration depth and 11 nm for the coherence length for fields parallel to $c$ at 0 K. The low-field region could be described by a different single-band fit, but the corresponding results include both $\pi$-band and $\sigma$-band contributions and are thus effective parameters only, though more indicative of the $\pi$-band. For fields parallel to $c$ and low temperatures, an upper critical field of about 1 T, a lower critical field of 0.11 T, a magnetic penetration depth of about 51 nm and a coherence length of 17 nm were determined for this region. Those absolute values are in good agreement with a more sophisticated two-band evaluation of the reversible magnetization that gives a smooth field dependence of the properties [12, 27]. To conclude, most quantities depend on the magnetic field in a different way from that expected according to single-band theory.

Like the characteristic fields and lengths, also the corresponding anisotropies change with magnetic field. At the upper critical field, the anisotropy is mainly determined by the $\sigma$-band and is thus about 4.5. As the field decreases, the anisotropy remains almost constant at first, then, starting at about the upper critical field of the $\pi$-band, continuously reduces to approximately 1 at 0 T due to the emerging influence of the $\pi$-band. Close to the transition temperature, the field dependence of the anisotropy becomes considerably weaker. As regards the temperature dependence, the high-field anisotropy is about 4.5 over a large range and slightly decreases close to the transition temperature, while at low fields the quantity is about 1 over a large range and slightly increases close to the transition temperature, as shown in figure 13. The experimental differences between the anisotropies of different quantities, such as between the coherence length and the penetration depth, at the same field and the same temperature were found to be small, and are usually within the expected experimental uncertainties [143, 103, 27]. Assuming the anisotropy of all relevant quantities to be equal in MgB$_2$, we can nicely explain most of the diverging reports on this property in the literature by considering the field dependence of the anisotropy.

### 4.2. NbSe$_2$ and NbS$_2$

NbSe$_2$ is one of the most interesting and most studied superconductors. Although its properties have been analyzed for many years, its two-band character was realized only recently in the wake of MgB$_2$. Today, there is little doubt that NbSe$_2$ is a multi-band superconductor. The two-band effects that show up in this material are quite similar to those of MgB$_2$.

NbSe$_2$ has a layered structure with a hexagonal unit cell. The layers consist of two parallel Se planes and a Nb plane in between. Along the uniaxial $c$-axis, these layers are only weakly bound by van der Waals forces. The transition temperature of NbSe$_2$ is about 7.2 K and its upper critical field is about 4 T in the $c$ direction and 12 T in the $ab$ (perpendicular to $c$) direction [122], giving an anisotropy of 3. Accordingly, most parts of the superconducting phase diagram are available for experiments. Moreover, large pure single crystals, whose superconducting magnetic properties are reversible over most of the phase diagram, can be grown.

Thanks to the properties mentioned above, NbSe$_2$ is well suited for a wide range of investigations. In particular, its layered structure makes preparing an atomically flat surface by cleaving a crystal along the $ab$ planes easy, and, in contrast to most other materials, this surface is very stable even in air. Therefore, NbSe$_2$ was the first material to which scanning tunneling microscopy was successfully applied for imaging vortex cores [200] and distributions [201] (at arbitrary magnetic fields), and it is still widely used for such investigations. Below about 33 K we can study the charge density wave state [202] and at even lower temperatures its possible competition with the superconducting gap [203].
The existence of high-quality single crystals, showing almost no vortex pinning effects, allows us to investigate the reversible magnetic properties and, by introducing small defects suitable for vortex pinning, the second magnetization peak [205] (fishtail).

Following the discovery of MgB$_2$, new experiments were carried out on NbSe$_2$ and interpreted in terms of a two-band scenario, although most could be described as well by the anisotropic single-band model. Some of these experiments have been presented in the previous sections and partly illustrated in figures 10, 12, and 13. The Fermi surface of NbSe$_2$ was found to consist of three bands: two rather anisotropic (Nb 4d derived) bands and a more three-dimensional (Se 4p) band [206]. ARPES [185] revealed gaps of about 0.9–1.0 meV at 5.3 K on the two cylindrical bands, while no gap was detected on the Se-band. Later, a gap variation from 0.3 to 1.2 meV was measured, though again on the two Nb bands [203], which was in better agreement with tunneling spectroscopy showing a gap range from about 0.4 to 1.4 meV close to 0 K [207, 176]. Two-band fits resulted in gaps of 0.73 and 1.26 meV from the specific heat [75] with comparable values from penetration depth measurements [106].

Recently, it was shown that the field dependence of the reversible magnetization of a NbSe$_2$ single crystal [123] cannot be properly described by a single-band model but by a simplified two-band model. Separating the reversible magnetization into a high-field and a low-field region allowed the assessment of some two-band properties by fitting single-band Ginzburg–Landau theory to both regions separately, in the same way as done for MgB$_2$. As in MgB$_2$, single-band behavior was found in the high-field region and two-band behavior in the low-field region. The field below which the effects of the second band emerge is usually declared as the upper critical field of this band and was found at about 2 T for both field orientations at 0 K, as shown in figure 10. It was concluded that at least two bands contribute to the superconducting state of NbSe$_2$, one is rather isotropic and suppressed above roughly 2 T (at 0 K), and the second is strongly anisotropic ($\Gamma \simeq 3$). It appears natural to identify the isotropic part with the more three-dimensional Se 4p band, but it should be recalled that ARPES did not indicate a gap on this band (at 5.3 K), hence this point remains to be clarified. As in MgB$_2$, the anisotropy of NbSe$_2$ was reported to change strongly with applied field, namely from a large value of about 3 at high fields to almost isotropic behavior at low fields, and also to depend only slightly on the temperature. No significant differences in the anisotropy of the characteristic lengths were detected when acquired at the same field and temperature (see figure 13).

NbS$_2$ belongs to the same family, NbX$_2$, with X a chalcogen element, as NbSe$_2$ and exhibits similar behavior. Its transition temperature is slightly lower, about 6 K, while the upper critical-field anisotropy rises to about 7–8 [208, 74]. Tunneling spectroscopy revealed one peak at about 1 meV and one shoulder at about 0.5 meV in the density of states [177]; similar gap values resulted from a two-band fit to specific heat data [74] and to the superfluid density [209]. Although these results do not prove NbS$_2$ to be a two-band superconductor, its close relation to NbSe$_2$ makes it probable.

### 4.3. Iron-based superconductors

Though the first of the new iron-based superconductors was discovered in 2006 (LaOFeP [210]; $T_c \sim 4$ K), the current boom in these materials broke out only after a much higher transition temperature, namely 26 K [211], was reported for LaO$_{1-x}$F$_x$FeAs. Since then, many materials with similar iron structures, reaching transition temperatures of up to 56 K, have been discovered. The main components of this kind of superconductor are the parallel FeX layers, with X a pnictogen (usually P or As) or, less frequently, a chalcogen (Se, Te, and S) atom. The pure layers form the so-called ‘11’ family, with transition temperatures of up to 14 K (FeTe$_{1−x}$Se$_x$). Putting an additional layer between the FeX blocks yields further families. The most investigated are ‘122’ materials with alkaline-earth metals, such as Ba, Sr, and Ca, in between (e.g. BaFe$_2$As$_2$), ‘111’ with alkali metals (e.g. LiFeAs), and ‘1111’ with LnO layers, where Ln is a metal of the lanthanide series (La, Ce, Sm, Nd, etc). e.g. LaFeAsO. Almost all elements can be partly replaced by different dopants, which may have a significant effect on the superconducting properties. The highest transition temperatures of about 56 K were observed in the ‘1111’ family. The unit cells are usually orthorhombic, though the in-plane anisotropy of the lattice parameters is almost negligible. For recent reviews see [212–214].

Many properties of the iron-based superconductors resemble those of the cuprates. For instance, antiferromagnetism appears in both materials in the strongly underdoped regime but is successively suppressed by doping. Eventually, antiferromagnetism vanishes and superconductivity, with a dome-like shaped transition temperature as a function of doping, appears. In both types of material the superconducting pairing mechanism has yet to be found, though electron–phonon coupling is excluded by most researchers, while spin fluctuations are a good candidate. Contrary to the cuprates, the iron-based materials are metallic in the underdoped regime. Moreover, the order parameters of the materials are apparently different, namely d-wave symmetry in the cuprates, but most likely s-wave in most iron-based materials.

Though many aspects of the iron-based superconductors are not settled, there is little doubt that they are multi-band materials. It was theoretically and experimentally shown that most materials have two anisotropic electron Fermi sheet pockets around the ‘M’ symmetry point of the Brillouin zone and at least two anisotropic hole pockets around the ‘I’ point; additional hole pockets around ‘I’ that may be more isotropic have occasionally been reported. The superconducting order parameter is commonly believed to have s-wave symmetry and to appear on the hole and the electron Fermi surface sheets, and is supposed to change its sign, in other words the phases might differ by an angle $\pi$ on different sheets, which defines the so-called $\delta_{\pi}$ scenario. The question of whether the electron band-gap has (accidental) nodes or not...
has been discussed more controversially. Both viewpoints have been supported by a couple of experiments. At present, there are indications that different scenarios may prevail in different samples. In particular, it was reported [77] that optimally doped Ba211 samples might have a fully gapped order parameter, while underdoping and overdoping might induce nodes. A review of the gap symmetry and structure was recently presented [215].

Results of a large number of experiments have been published on the multi-band nature of the iron-based superconductors. Of particular interest are angle-resolved photoemission spectroscopy (ARPES) measurements, as such experiments are capable of revealing the energy gap at different positions of the Fermi surface (restricted to the sample surface, however). Results on different samples suggest gaps on several Fermi sheets with different values. For instance, in Ba0.5K0.4Fe2As2, gaps of about 12 meV were assigned to the anisotropic hole and the electron sheet, and a smaller 6 meV gap to a larger hole sheet also surrounding the Γ point [187]. A more recent study on LiFeAs revealed (nodeless) gaps on all four Fermi sheets, with larger gap values of around 4–5 meV on one of the two hole-like and one of the two electron-like sheets and smaller values of around 2.5–2.8 meV on the remaining sheets [188]. Gaps on five sheets were identified in BaFe2(As0.7P0.3)2 [189].

For a review, see [216]. The results indicate up to five superconducting bands in the iron-based materials, but since the gap magnitudes seem to cluster around two different values, one larger and one smaller than the BCS gap, a two-band description might be sufficient for describing most properties.

Further experimental results have partly been mentioned in the previous sections. For instance, specific heat measurements have been carried out on different samples. In contrast to the isotropic single-band model, the two-band model usually worked well, though a shoulder at intermediate temperatures, like that in MgB2, was observed only in some iron-based samples. The two-band evaluations typically resulted in gaps in the ratio of two to one, gap larger and one gap smaller than the BCS prediction. The corresponding weights of the density of states were about 0.3–0.7 to 0.5–0.5 (or even 0.1–0.9 in one case) [76–83]. Probing the superfluid density by two-band fits resulted in similar gap ratios [108–114]; see [217] for a review. As in MgB2, the anisotropy of the penetration depths was found to be temperature dependent, but contrary to MgB2 decreasing upon warming [218, 219, 147, 149].

The upper critical fields of many iron-based materials were reported to match those of the cuprates in absolute values (~100 T) for \( H \parallel c \), yet their shapes and anisotropies may be quite different. In most materials, an upward curvature of the upper critical field emerges for magnetic fields perpendicular to a uniaxial or near-uniaxial crystal axis, but in the iron-based materials, this feature was observed for fields parallel to this axis and, contrary to other materials, to appear over the whole or a large part of the temperature range in some samples (e.g. ‘1111’ and ‘122’) [126–130, 149, 220, 163, 135] (see figure 10). For fields parallel to the iron layers (\( H \parallel ab \)), higher upper critical fields, displaying no or only a slight upward curvature near the transition temperature, were measured. At low temperatures, the upper critical fields of many iron-based samples rise beyond the Pauli paramagnetic limit, which is about 1.84 \( T_c \) in units of tesla in the BCS limit, and the curves thus become noticeably flatter. The corresponding Zeeman energy is rather isotropic, which could partly explain why the upper critical-field anisotropy of iron-based superconductors was found to rise with increasing temperature [127, 129, 130, 149, 163, 221, 222, 135], which is contrary to the behavior of most other known two-band superconductors, as illustrated in figure 13, and to anisotropic single-band superconductors. The maximum anisotropy near the transition temperature was reported as between about 2 and 7. For a review of the upper critical fields in the iron-based materials, see [223].

As for the anisotropy of the iron-based superconductors, we can summarize that the low-field penetration depth anisotropy was reported to decrease while the upper critical-field anisotropy increased upon warming [147, 149] towards a common value at the transition temperature (≈2–7). This resembles the behavior of MgB2 when the upper critical field and the penetration depth anisotropy behaviors are swapped, as depicted in figure 13. The temperature dependence of the penetration depth anisotropy is usually assumed to be a consequence of the multi-band character, while that of the upper critical field might be a consequence of the Pauli paramagnetism limit, but microscopic confirmations and detailed multi-band model calculations have yet to be provided for this material. In MgB2, the differences seem to disappear when the anisotropies, e.g. of the penetration depth and the coherence length, are determined at the same field and temperature. This issue has not been addressed in the iron-based samples thus far, though torque measurements [147, 224, 148, 225] did not indicate an unconventional behavior (e.g. additional nodes in the reversible torque vs. angle curve) as may be the case for different anisotropies.

Tunneling spectroscopy has been carried out on several samples, though uncertainties due to sample surface quality issues are to be expected. Moreover, it was predicted that tunneling mainly probes the bands around the ʻΓ’ point, whereas the electron pockets around ‘M’ provide only negligible contributions to the tunneling current [226], which might explain the single-band behavior found in many tunneling spectroscopy studies. Nevertheless, two gaps were resolved in [182] Ba(Fe1–xCosx)2As2 and [227, 8] Ba0.6K0.4Fe2As2, in both cases with a gap ratio of about 1:2. For a review, see [181].

Point-contact spectroscopy on iron-based samples also struggles with several problems that led to different results and quite different interpretations of the gap structure [180], however, clear two-band spectra with either two peaks or a peak and a shoulder were found and fitted using the two-band models [228–231]. A review was recently given in [183].

4.4. Cuprates

The cuprate superconductors, discovered in 1986 by Bednorz and Müller [232], reach the highest known transition
temperatures. Though still among the most intensively studied materials, they are far from being fully understood.

In the following, I will point out some salient points of the cuprates, though for details the reader is referred to one of the numerous books or reviews on this subject (e.g. [233–236]). The superconducting cuprates have a layered structure with a strongly anisotropic orthorhombic or tetragonal unit cell. The copper–oxygen (CuO$_2$) planes are common to all varieties and are the places where superconductivity is induced. They are sandwiched between other non-metallic layers supplying charge carriers. Among the most prominent representatives are YBa$_2$Cu$_3$O$_{7-\delta}$ and Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4-\delta}$, having transition temperatures of up to 92 K and of up to 110 K, respectively; the highest known transition temperature of 135 K is reached in HgBa$_2$Ca$_2$Cu$_3$O$_8$. In the undoped state (e.g. YBa$_2$Cu$_3$O$_6$) the materials are antiferromagnetic Mott insulators. Adding dopants (e.g. oxygen atoms) gradually reduces their Neel temperature to zero and eventually induces the superconducting state, displaying a dome-like shape in the transition temperature versus doping diagram. Optimal doping refers to the maximum transition temperature. The cuprates are classified as extreme type II superconductors, for their Ginzburg–Landau parameter is often in the range of 100, they are classified as extreme type II superconductors, for their Ginzburg–Landau parameter is often in the range of 100, they reduce their Neel temperature to zero and eventually induces the superconducting state, displaying a dome-like shape in the transition temperature versus doping diagram. Optimal doping refers to the maximum transition temperature. The cuprates are classified as extreme type II superconductors, for their Ginzburg–Landau parameter is often in the range of 100, they have the highest known transition temperatures thus far, and their anisotropy reaches values from about 5 to more than 100. Many questions concerning these materials are still not resolved, including that on the mechanism responsible for Cooper pairing. The most frequently mentioned candidate is coupling by antiferromagnetic spin fluctuations, which should lead to d-wave symmetry of the order parameter.

There is wide consensus that d-wave symmetry predominates in the cuprates [237], yet not all experiments are in full agreement with this assumption. For instance, Khasanov et al. [107] determined the in-plane magnetic penetration depth of La$_{1.85}$Sr$_{0.17}$CuO$_4$ by muon-spin rotation and found the temperature dependence of the superfluid density to rise abruptly below about 10 K at low magnetic fields, which was no longer observed at higher fields ($>$0.64 T). This anomaly was assumed to indicate a second band. Fitting the curves with the two-band $\alpha$-model revealed gap values of 8.2 meV for the dominant d-wave band and 1.6 meV for the second band, for which s-wave character was supposed. Similar results were reported for YBa$_2$Cu$_3$O$_{7-\delta}$, presented in figure 9, and YBa$_2$Cu$_4$O$_8$ [104, 238]. Conclusions on a possible s-wave admixture to the d-wave symmetry were also drawn from other techniques [239–242]; a second d-wave component was considered in [243]. A temperature-dependent anisotropy, resembling that of MgB$_2$, was detected in Sm- and Y-based cuprates [131, 132], which, however, is not exclusively explicable by two-band effects, as mentioned in section 3.5. Application of ARPES in samples such as YBa$_2$Cu$_3$O$_8$ suffers from sample surface preparation difficulties. Nevertheless, deviations from a pure d-wave symmetry were suggested, and a $d + is$ symmetry was proposed [244].

Not all unexpected results in the cuprates have been interpreted in terms of a second band. For instance, Wojek et al. [105] reproduced the low-temperature low-field anomaly of the superfluid density in La$_{1.83}$Sr$_{0.17}$CuO$_4$, but attributed it to vortex pinning effects, and were thus able to describe the whole temperature dependence with a single d-wave gap band. Clearly, many experiments have pointed to a single d-wave band [237], yet it was suggested that the suppression of the contribution of the second band may be a consequence of surface-sensitive measurements [245].

To conclude, most experiments on superconducting cuprates are explained well by a single d-wave band. Nevertheless, the discrepancies found in some experiments, which were partly supposed to indicate a second band, should be clarified.

4.5. Borocarbides

Borocarbides were discovered in 1994 [246, 247]. They have transition temperatures of more than 20 K and exhibit unconventional properties. Most investigated are the rare-earth nickel borocarbides RNi$_2$B$_2$C, with R = Y, Lu, Tm, Er, etc. They have a strongly anisotropic tetragonal unit cell with lattice parameters of about 0.35 nm in the $a$ direction and 1 nm in the $c$ direction and consist of alternate stacks of Ni$_2$B$_2$ and RC layers. Several properties make the borocarbides interesting objects for investigation, such as the competition and partial coexistence of superconducting and magnetic ordering. The borocarbides were originally thought to be conventional phonon-mediated s-wave superconductors. Later, a strong anisotropy of the superconducting gap, which is not mirrored by the rather isotropic normal-conducting electronic properties, was noticed, and nodes in the gap were indicated by several experiments. This led to the suggestion that $s + g$ wave symmetry [248], which means a gap with point nodes, exists in these materials. Alternatively, experiments have also been described by a two-band model. For reviews see [249–251]. In the following I will concentrate on the non-magnetic borocarbides, such as YNi$_2$B$_2$C and LuNi$_2$B$_2$C. They have transition temperatures of about 15–16 K and Ginzburg–Landau parameters of 10–20, and their upper critical fields may slightly surpass 10 T. The electron–phonon coupling strength was shown to be close to 1.

The Fermi surface of the borocarbides was experimentally and numerically determined by several groups [252–259] and found to be multi-sheeted. ARPES of RNi$_2$B$_2$C showed that a superconducting gap opens on at least two Fermi sheets [256], making multi-band superconductivity possible. The two-band model for describing borocarbides was first reported by Shulga et al. [22] even before the advent of MgB$_2$. They reported a pronounced upward curvature in the upper critical field of YNi$_2$B$_2$C and LuNi$_2$B$_2$C, which they could bring into agreement with the two-band Eliashberg theory. Later, a similarly good agreement was achieved by applying the single-band separable model [26]. Four different scenarios (line nodes, point nodes, $s + g$, and the two-band model) were adjusted to specific heat data of YNi$_2$B$_2$C in [84], of which the two-band model worked best, while the $s + g$ was rather ruled out by the authors. The resulting gap energies were about 2.7 and 1.2 meV. Additionally, they found the Sommerfeld coefficient to increase with magnetic field $H$ as $H^{0.47}$, which is actually close to the d-wave forecast, though
likewise explicable by the two-band model. Multi-band superconductivity was also suspected from point-contact spectroscopy measurements [260], which revealed gap values of approximately 2.3 and 1.5 meV in the same material. Finally, the field dependences of the two gaps were studied by point-contact spectroscopy [261]. The larger gap was reported to vanish at the upper critical field while the smaller one vanished at a much lower field, which was considered as evidence for the two-band scenario. Other experiments such as point-contact spectroscopy presented in [262] did not reveal any signs of a second band. Two gaps were also claimed to exist in the magnetic borocarbide TmNi$_2$B$_2$C as a result of analyzing point-contact spectroscopy curves [263].

To conclude, the borocarbides are serious candidates for two-band superconductivity, as seen from their multi-sheeted Fermi surface and several experiments such as upper critical field, specific heat, and point-contact spectroscopy measurements. For an unambiguous decision more experimental and theoretical studies are necessary.

4.6. Further potential multi-band superconductors

After presenting the most prominent potential two-band superconductors, I will attach shorter descriptions of further materials in which possible two-band effects were suspected. The status of verification differs from material to material, but to unambiguously clarify whether or not multi-band superconductivity occurs calls for further experiments in most cases.

$\text{Nb}_3\text{Sn}$. $\text{Nb}_3\text{Sn}$ has been one of the best-known superconducting materials for many years. After niobium–titanium, it is the most important commercial superconductor, mainly used for high-field magnets. Its transition temperature is about 18 K, and upper critical fields of up to 30 T can be reached; see [264] for a recent review. A specific heat anomaly at low temperatures has long been known and led to early speculations about a two-band scenario in this material [265]. This was supported by the recent finding of a shoulder in the specific heat of a polycrystalline sample at about 0.25 $T_c$ [266]. Applying the two-band $\alpha$-model revealed two gaps with 0.6 and 3.7 meV and corresponding band weights of 7.5:92.5. The anomaly vanished at magnetic fields above about 5 T. Several other explanations for the shoulder, including the possible existence of a different superconducting phase, were rejected. Point-contact spectroscopy on samples from the same source confirmed the specific heat results on the gaps [267]. In contrast, later specific heat measurements on several $\text{Nb}_3\text{Sn}$ single crystals showed no trace of the low-temperature anomaly, and the authors [268] thus concluded that $\text{Nb}_3\text{Sn}$ was a single-band material.

$\text{V}_3\text{Si}$. Several authors have quoted $\text{V}_3\text{Si}$ as an example of two-band superconductivity and several authors have quoted $\text{V}_3\text{Si}$ as an example of single-band superconductivity. The typical transition temperature of this material is about 17 K and the low-temperature upper critical field is roughly 20 T. In [269], the microwave response of $\text{V}_3\text{Si}$ single crystals was shown to deviate significantly from BCS behavior. The corresponding temperature dependence of the superfluid density was fitted by applying a two-band model with two gaps of about 2.5 and 1.3 meV; the interband coupling was claimed to be very weak in this material. These results were confirmed in [42]. A two-band state was also proposed from infrared spectroscopy data of oriented films [270]; in the same work, the Fermi surface was calculated and shown to be crossed by four bands.

Other studies led to contrary conclusions. For instance, the field dependence of the reversible magnetization was shown to match the predicted single-band behavior reliably well over the whole field range [123], as shown in figure 12, which is in stark contrast to the two-band materials $\text{NbSe}_2$ and $\text{MgB}_2$ [103]. This was confirmed by thermal conductivity and specific heat experiments, in which $\text{V}_3\text{Si}$ displayed the expected single-band field dependence [99]. In [271], the magnetic field effects on the vortex core size and on the magnetic penetration depth, measured via muon-spin rotation, could be explained within the single-band picture (see also [168] for a comparison with two-band materials). In [266], the temperature dependence of the specific heat of polycrystalline and single-crystal $\text{V}_3\text{Si}$ was determined (to compare with $\text{Nb}_3\text{Sn}$) and no low-temperature anomaly was reported. Such a low-temperature anomaly is not an inevitable consequence of two-band superconductivity, as mentioned in section 4.5, but rather expected when interband coupling is weak, as was claimed in this material [269, 42]. To conclude, even for such a long-known superconductor as $\text{V}_3\text{Si}$, further experiments are necessary to clarify the possible two-band state.

CeCoIn$_5$. The heavy fermion superconductor CeCoIn$_5$ has a transition temperature of 2.3 K and displays d-wave gap symmetry [272]. Point-contact spectroscopy revealed a multiple-structured curve [273], interpreted as a reflection of two superconducting d-wave gaps of about 0.95 and 2.4 meV. This interpretation was questioned [274, 275], and it was shown that the Andreev reflection data may also be described within a single-band model [276]. Thermal conductivity measurements seemed to support the two-band scenario [277], though with much smaller gaps than claimed in [273]. A two-band scenario was also proposed from the temperature and field dependence of the anisotropy determined by torque measurement [278], though the effects were not very significant. Finally, band structure calculations revealed a multi-sheeted Fermi surface [279].

$\text{PrX}_5\text{Sb}_{12}$ (X = Os, Ru), $\text{LaRu}_4\text{As}_{12}$, and $\text{LaOs}_4\text{Sb}_{12}$. For $\text{PrOs}_4\text{Sb}_{12}$ ($T_c \approx 1.85$ K; $B_{c2}(0 \text{ K}) \approx 2.2$ T) two-band superconductivity was assumed due to the unconventional field dependence of the thermal conductivity [280]. The low-temperature thermal conductivity was reported to increase strongly at very low fields, less steeply at intermediate fields, and again strongly near the upper critical field, which is similar to the results on $\text{MgB}_2$, while in conventional single-band materials a more gradual increase is expected. As in $\text{MgB}_2$, a band with a smaller upper critical field ($<0.07B_{c2}$) was held responsible for the steep rise at low fields and a second band with a higher upper critical field
for the rise at high fields. In [281], two s-wave gaps with a ratio of about 3 were proposed, while in [282] only one of the bands was assumed to be fully gapped and the other one to have nodes. Two bands with s-wave symmetry were also reported for PrRu$_4$Sb$_{12}$, based again on thermal conductivity measurements [282]. LaRu$_4$As$_{12}$ has a transition temperature of about 10 K and an upper critical field of 12 T. Observations of an upward curvature in the upper critical field, a non-BCS specific heat temperature dependence, though without a shoulder at intermediate temperatures, and a non-linear field dependence of the Sommerfeld coefficient led to the suggestion of a two-band scenario [283, 284]. In LaOs$_4$Sb$_{12}$ ($T_c \simeq 0.74$ K), such a suggestion came from a convex temperature dependence of the superfluid density [285].

$Ba_2Si_{36}$. $Ba_2Si_{36}$ has a transition temperature of about 8 K, an upper critical field of roughly 5 T at 0 K, and might be mediated by electron–phonon coupling. The gap function appears to have s-wave symmetry, and the Fermi band was found to be crossed by several bands [286]. Specific heat curves were published in [287] and claimed to be best described by a two-band model with one small gap of about 0.35 meV, which contributes only 10% to the data, and one dominating second gap, which is about four times larger. A possible two-band state, though with a smaller gap ratio of about 1.4, was also deduced from tunneling spectroscopy results [288].

$Na_{0.3}CoO_2\cdot 1.3H_2O$. Samples of $Na_{0.3}CoO_2\cdot 1.3H_2O$ have a maximum transition temperature of about 4.5 K, but were shown to change their superconducting properties with time when kept at room temperature. Specific heat measurements revealed a resemblance to MgB$_2$ and were therefore analyzed by applying the two-band s-wave $\alpha$-model [289]. Two different samples were investigated, in which the gap ratio, obtained from a two-band fit, changed from about 3 in the first sample to 2 in the second sample, and the corresponding density of states ratio changed from about 1 to 4. The upper critical fields of the first sample were roughly estimated to be about 2 T for the first band and 8–9 T for the second band.

$OsB_2$. The layered boride material OsB$_2$ becomes superconducting below about 2.1 K. Its upper critical field is roughly 20 mT and its Ginzburg–Landau parameter is rather small though still in the type II regime. A two-band state was concluded [290] from measurements of the superfluid density, which could not be described well by a single-band s-wave model but by a two-band model with two s-wave gaps, of which one was larger and one smaller than the BCS value, with a ratio of about 0.66. The assumption was supported by the specific heat jump at the transition temperature, which was found to be smaller than expected from BCS theory (as is also the case for MgB$_2$), namely $\Delta C(T_c)/(\gamma_0T_c) \simeq 1.3$.

$XMgO_S8$ ($X = Sn, Pb$). The superconducting Chevrel phases are known for their rather high transition temperatures, of up to 15 K, and very high upper critical fields, about 40 T in SnMgO$_8$S$_8$ and 80–90 T in PbMgO$_8$S$_8$. In a recent paper, Petrovic et al [291] reported possible two-band effects in these materials from tunneling spectroscopy and specific heat measurements. The density of states, obtained from tunneling spectroscopy, partly showed a shoulder in addition to the main coherence peak. A simple fit model led to energy gaps of about 2.95 and 1.05 meV with relative densities of states of 0.62 and 0.38 for SnMo$_6$S$_8$ and about 3.1 and 1.4 meV with relative densities of states of 0.66–0.9 and 0.34–0.1 for PbMo$_6$S$_8$. Analyzing specific heat measurements, which probe the bulk state, using the two-band $\alpha$-model confirmed the gap values but resulted in somewhat different weights, namely about 0.96:0.04 in SnMo$_6$S$_8$ and 0.9:0.1 in PbMo$_6$S$_8$. Based on a small kink in the field dependence of the Sommerfeld coefficient, the authors estimated the smaller band upper critical fields to be about 2.8 and 4.3 T in the two samples.

$ZrB_{12}$. $ZrB_{12}$ becomes superconducting below about 6 K. It has a rather low Ginzburg–Landau parameter (even a change from type I to type II behavior with decreasing temperature was assumed [292]), upper critical fields of roughly 100 mT, and electron–phonon coupling seems to be responsible for Cooper pairing. Two-band effects were suggested from an unconventional temperature dependence of the superfluid density and of the upper critical field in a single crystal [293].

A two-band fit of the superfluid density, showing a shoulder similar to MgB$_2$ at about 4 K, led to gap values of 2.1 and 0.73 meV. The upper critical field was found to increase almost linearly, even close to 0 K, which was explained by the dirty-limit two-band model, as discussed in [294]. The conclusions were backed by showing the Fermi surface to consist of several distinct sheets [295]. In [296], the anomaly at about 4–5 K, observed in this case in the specific heat, was supposed to be caused by a possible structural phase transition similar to that in LuB$_{12}$. Other experimental data, namely from tunneling [297], point-contact spectroscopy [298], and specific heat measurements [299] also pointed to single-band s-wave superconductivity in this material.

$X_2C_3$ ($X = La, Y$). The sesquicarbides La$_2$C$_3$ and Y$_2$C$_3$ reach transition temperatures of up to 18 K and upper critical fields of some 10 T. Recent nuclear-magnetic-resonance measurements [300] suggested that Y$_2$C$_3$ was a noncentrosymmetric, yet spin-singlet and s-wave multi-band superconductor. The temperature dependence of the nuclear spin–lattice relaxation rate showed an atypical kink at about 5 K, which was taken as a sign of two-band effects. Fitting these data with an $\alpha$-model-like curve revealed two gaps with sizes of 3.4 and 1.4 meV and relative weights of 0.75:0.25. Confirmation came from muon-spin relaxation measurements in Y$_2$C$_3$ and La$_2$C$_3$ [301]. In La$_2$C$_3$ polycrystals, the temperature dependence of the superfluid density showed an abrupt kink or shoulder, indicating two gaps of 2.7 and 0.6 meV and relative weights of 0.38:0.62. In Y$_2$C$_3$, the two-band effects were less obvious, but still a single-band BCS fit did not work well. The two-band fit resulted in slightly larger gaps than in La$_2$C$_3$, but in smaller gaps than those from the nuclear-magnetic-resonance method, namely 3.1 and 0.7 meV and weights of 0.86:0.14. For both materials s-wave symmetry was assumed, and different interband coupling strengths were held responsible for part of the differences. On the other hand, based on tunneling spectroscopy results,
the authors of [302] rejected multi-band superconductivity in \(Y_2C_3\) and ascribed its seeming appearance in diverse experiments to local phase differences and inhomogeneities in the investigated samples.

\[X_2Fe_2Si_5\ (X = Lu, Sr).\] Lu\(_2Fe_2Si_5\) is a member of the ternary-iron silicide superconductors \(X_2Fe_2Si_5\) \((X = Lu, Y, Sc, Tm, Er)\). They have some interesting and peculiar properties, some of which were assumed to originate from \(Y\), \(Sc\), \(Tm\), \(Er\). They have some interesting and peculiar properties, some of which were assumed to originate from two-band effects as early as 1983 [303]. Lu\(_2Fe_2Si_5\) has a transition temperature of about 6 K and upper critical fields in the range of 10 T, with a moderate anisotropy of roughly 2. Band structure calculations showed the Fermi surface to be crossed by three bands having different anisotropies [69]. As in MgB\(_2\), the specific heat of single crystals [69, 304] displayed a distinct shoulder at about 0.2T\(_c\), and the normalized jump \(\Delta C(T_c)/(\gamma_0 T_c)\) = 1.1 was found to be smaller than the BCS value of 1.43, as presented in figure 6. Two-band superconductivity was thus proposed and proved by the \(\alpha\)-model fit, resulting in two s-wave gaps with the ratio of 1:4 but almost equal Sommerfeld constants. Penetration depth measurements [305, 304] confirmed two, though slightly smaller, gaps. The field dependence of the thermal conductivity [100] indicated two bands with upper critical fields of approximately 6.4 and 0.26 T. This was confirmed by measurements of the Sommerfeld coefficient, revealing an almost isotropic upper critical field of approximately 0.33 T on the smaller gap band and a more anisotropic behavior (~2) on the larger gap band. Sr\(_2Fe_2Si_5\) has a slightly smaller transition temperature of about 5 K and smaller upper critical fields, though with a similar anisotropy. The temperature dependence of the specific heat was reported to have a shoulder as well; the corresponding two-band fit led to a gap ratio of about 2 and to relative weights of the two bands of 0.36:0.64 [306]. The specific heat jump at the transition temperature was observed to be only about half of the BCS height.

\(MgCNi_3\). The cubic antiperovskite compound \(MgCNi_3\) is usually described as a fully gapped, rather strong coupling phonon-mediated superconductor with a transition temperature of 7 K and an upper critical field on the order of 10 T. Although specific heat and upper critical-field data of a polycrystal could be reasonably well described by a single-band model, the authors of [307] suggested a two-band model, which they claimed would be necessary to explain literature data of the Hall conductivity and thermopower and reports of different gap values on the Fermi surface. Data on single crystals, including the specific heat, point-contact spectroscopy, and the penetration depth [308, 309], did not indicate multi-band effects.

\(Sr_2RuO_4\), \(Sr_2RuO_4\) is certainly one of the most unconventional superconducting materials. Its tetragonal crystal structure is highly anisotropic and similar to that of the cuprates. The transition temperature is not more than about 1.5 K; the upper critical field is strongly anisotropic (~20) and reaches a maximum of roughly 1.5 T [310]. Experiments indicated triplet pairing and broken time-reversal symmetry, suggesting a chiral p-wave order. Moreover, topological superconductivity and Majorana fermions have been studied in this material. For details, I refer to recent review papers [311, 312] and references therein. To make things even more complicated, multi-band effects were suggested in order to resolve some of the discrepancies between theory and experiment. The cylindrical-like Fermi surface is crossed by three bands [313], named \(\alpha\), \(\beta\), and \(\gamma\), of which the \(\gamma\)-band, carrying about 60% of the density of states, has usually been assumed to dominate the superconducting properties. Measurements of the specific heat showed that the jump at the transition temperature is much smaller than the BCS prediction and that a significant kink in the field dependence at about 0.15 T [314, 315] appears, which was assumed to mark the low-field influence and upper critical fields of the \(\alpha\) and the \(\beta\) band. While the \(\gamma\)-band was assumed to be fully gapped, nodes were supposed for the gaps of the other bands. Other studies rejected the two-band scenario for \(Sr_2RuO_4\). For instance, the anomalous field dependence of the specific heat was attributed to strong Pauli paramagnetic effects, which was confirmed by calculations within the Eilenberger model [316]. Tunneling spectroscopy [317] uncovered just one (fully open) gap with a size of about 0.3 meV, which is close to the predicted BCS value.

\(URu_2Si_2\). \(URu_2Si_2\) is a heavy fermion compound that becomes superconducting below about 1.5 K and has an anisotropic upper critical field between approximately 3 and 12 T. The material has attracted interest due to its phase transition to a still unknown ordered state, called a hidden order state, at about 17 K; for a review see [318]. In [319], the field dependence of the thermal conductivity was regarded as a confirmation of two-band superconductivity. The authors observed a steep increase below about 0.4 T for different field orientations, as expected from an isotropic band with a low upper critical field, and a flatter, more anisotropic behavior at higher fields, assumed to mirror the second anisotropic band. Both bands were supposed to have nodes. In [320], parts of the lower critical field could be described by a two-band model. Some of the unconventional properties of the thermal conductivity were found to be reflected in the field dependence of the Sommerfeld coefficient, namely the rather isotropic behavior below about 0.5 T and the strongly anisotropic behavior above [321]. These authors, however, held nodes in the gap and the influence of the Pauli paramagnetism at higher fields responsible for the effects. Low-temperature tunneling spectroscopy detected just one gap of about 0.2 meV with nodes [322].

\(UPt_3\). The heavy fermion compound \(UPt_3\) becomes anti-ferromagnetic below about 5 K and superconducting below 0.5 K and has an upper critical field of roughly 2–3 T at 0 K. Its field versus temperature diagram decomposes into three regions of different superconducting phases with different order parameter symmetries, of which two exist at zero field. Multi-band superconductivity was suggested in view of the several bands that cross the Fermi surface [323]. Confirmation by the methods presented in this paper is difficult since the expected effects seem to be covered by other unconventional properties of this compound. For
instance, specific heat measurements [324] showed two distinct transitions at different temperatures, indicating the different phases, and a considerable upturn below about 0.1 K. For reviews see [325, 326].

UCoGe. UCoGe orders ferromagnetically below approximately 2.5 K and condenses into the superconducting state at approximately 0.6 K. The upper critical field is strongly anisotropic and reaches fields of up to 30 T. Possible two-band effects were indicated by an upward curvature of the upper critical field near the transition temperature [327], but alternative explanations related to the interplay with the ferromagnetic phase were also provided [328].

5. Summary

Many superconducting properties and potential two-band effects as well as several two-band candidate materials have been reviewed. The two-band effects were compared with those expected from anisotropy in the single-band model and, in some cases, with those from different energy-gap structures. Basically, the temperature dependence of many properties was found to be similar in the two-band and in the anisotropic single-band model, making a distinction between the two scenarios difficult in these cases. On the other hand, the field dependences may be quite different in the two models, because in two-band materials, such as MgB$_2$ and NbSe$_2$, superconductivity is apparently suppressed in one of the bands at sufficiently high fields, making the field-dependent behavior of some properties a better candidate for successfully discriminating the two-band from other scenarios.

In section 2, the theoretical results predicted by the two-band and by other models within Ginzburg–Landau theory, the separable model, BCS, the quasi-classical model, and Eliashberg theory have been reviewed. The main results are:

- Many experimentally observed two-band effects can be reproduced well by the theoretical models, even when we assume simple spherical Fermi surfaces. This indicates that the basic properties of two-band superconductors do not strongly rely on the details but rather on the averaged values of the anisotropy and the coupling strength.
- Ignoring coupling between the two bands, which are assumed to have distinctly different energy-gap magnitudes and may differ also in other properties, leads to two transitions in the temperature dependence of diverse properties, such as the specific heat, superfluid density, etc. As interband coupling or interband impurity scattering is enhanced, the low-temperature transition, usually associated with the band with the smaller gap, is washed out and eventually fades away, making the curves similar to single-band behavior. Any small interband interaction leads to a common transition temperature and upper critical field of both bands, though the superconductivity of one band may be strongly suppressed above a certain magnetic field, which is then usually denoted the upper critical field of that band.
- Increasing the gap ratio or the coupling strength often has opposite effects. For instance, the specific heat jump becomes lower as the gap ratio increases, but it becomes higher as the coupling or interband interaction increases. Similarly, the low-temperature specific heat and the superfluid density change more rapidly with temperature as the gap ratio increases but more slowly as coupling increases.
- The upward curvature of the upper critical field is sensitive to several properties but basically appears and becomes more prominent as the Fermi velocity ratio becomes larger.
- The separable model can be interpreted as an anisotropic single-band as well as a two-band model with two spherical Fermi surfaces. Anisotropy effects in a single-band material and two-band effects would thus lead to the same unconventional behavior in this model, making a distinction between the two scenarios by comparing the temperature dependence of experimental data with theoretical models often problematic.

In section 3, several experimental techniques were briefly described and some results obtained for possible two-band and other materials reviewed. Two-band effects, in most cases investigated in MgB$_2$, have been found to result in the following modifications:

- The specific heat increases more rapidly upon warming at low temperatures, and its jump height at the transition temperature is reduced. A kink may show up at elevated temperatures if not suppressed by large interband coupling or impurity scattering. Basically, the same effects are predicted for the anisotropic single-band model.
- As the applied magnetic field increases, the Sommerfeld coefficient was found to grow rapidly at low fields and, when superconductivity is suppressed in one of the bands, to grow at a lower rate at high fields. Experiments indicate that distinguishing this behavior from that in non-two-band materials might prove difficult.
- The field dependence of the low-temperature thermal conductivity was reported to be rather flat at intermediate fields, and steep at low and high fields, which again is similarly predicted for anisotropy effects.
- As the temperature increases, the superfluid density decreases faster at low temperatures and may become linear, or even convex, at intermediate temperatures. The same holds for the anisotropic single-band model.
- The curvature of the upper critical field may become positive near the transition temperature, as is also well known for non-two-band materials having a non-spherical Fermi surface. In some iron-based superconductors, the upward curvature stretches over the whole temperature range.
- The angular dependence of the magnetic torque usually fits the conventional single-band model quite well, assuming the same anisotropy for the coherence length and the magnetic penetration depth, even in two-band samples.
In contrast to the anisotropic single-band model, the reversible magnetization of two-band superconductors cannot be described well by the single-band Ginzburg–Landau theory over the whole field range. Instead, two fits, one for the low-field and one for the high-field regime, are needed, which reflects the different upper critical fields of the two bands.

The anisotropy may change significantly with magnetic field. In \( \text{MgB}_2 \) and \( \text{NbSe}_2 \), the anisotropy is high at high magnetic fields and low at low magnetic fields, explained by a strongly anisotropic band dominating at high fields and an almost isotropic band dominating at low fields in these materials. The high-field anisotropy decreases, while the low-field anisotropy increases upon warming, so that both seem to merge at the transition temperature. No significant differences of the anisotropies of different properties have been observed when the results refer to the same field and temperature. The situation appears different in the iron-based superconductors, where the high-field upper critical-field anisotropy was found to be small and that of the low-field magnetic penetration depth was rather large.

Measurements of the superconducting gaps by tunneling or point-contact spectroscopy may reveal a single peak, two peaks, or a peak and a shoulder in the energy dependence of the electrical conductance. Anisotropy in single-band materials may lead to similar structures. A clear proof of that can be provided by angle-resolved photoemission spectroscopy.

In section 4, I have listed several potential two-band materials, of which the more prominent ones were described in more detail.

\( \text{MgB}_2 \), being unquestionably a two-band superconductor, consists of a quite isotropic band having a rather small s-wave energy gap and a quite anisotropic band having a large s-wave energy gap. In the isotropic band, superconductivity is obviously suppressed at sufficiently high fields. Possible two-band effects have also been found in \( \text{NbSe}_2 \).

\( \text{NbSe}_2 \) has unconventional properties that are often amazingly similar to those of \( \text{MgB}_2 \). As in \( \text{MgB}_2 \) the experiments indicate an isotropic band with a small gap and an anisotropic band with a large gap as well as suppression of superconductivity in the isotropic band at high fields. Possible two-band effects have also been found in \( \text{NbS}_2 \).

Concerning the iron-based superconductors, the whole family is widely accepted to show two- or multi-band superconductivity, though many of their properties deviate significantly from those of \( \text{MgB}_2 \). The Fermi surface is crossed by several bands on which a superconducting gap opens. These gaps might have s-wave symmetry, though different signs on different bands, and nodes may exist in some cases.

The cuprates are actually known for their d-wave character, but some experiments could not be explained within this model. For instance, a significant boost of the superfluid density at low temperatures measured by muon-spin rotation was regarded as evidence for a second band by one group of authors, but as an effect coming just from vortex pinning by another group.

The borocarbides were analyzed within different models. A possible two-band scenario has been confirmed by many experimental and theoretical results showing similar properties to those in \( \text{MgB}_2 \), though a clear distinction from all other models is currently not fully accepted.

Many other materials have been considered as two-band superconductors on the basis of various experiments. In some of these materials, the results strongly point to the two-band scenario, while in others the data are not convincing, but in most cases a clear interpretation demands more experiments. The materials listed in this paper are \( \text{Nb}_x \text{Sn}, \text{V}_x \text{Si}, \text{CeCoIn}_5, \text{Pr}_x \text{Xb}_12 \) (\( X = \text{Os}, \text{Ru} \)), \( \text{LaRu}_4 \text{As}_12, \text{LaOs}_5 \text{Sb}_12, \text{Ba}_x \text{Si}_{16} \), \( \text{Na}_x \text{CoO}_2 \cdot x \text{H}_2 \text{O}, \text{OsB}_2, \text{XMn}_5 \text{S}_8 \) (\( X = \text{Sn}, \text{Pb} \)), \( \text{ZrB}_2, \text{X}_2 \text{C}_3 \) (\( X = \text{La}, \text{Y} \)), \( \text{X}_2 \text{Fe}_5 \text{Si}_5 \) (\( X = \text{Lu}, \text{Sr} \)), \( \text{MgCuI}_3, \text{Sr}_2 \text{RuO}_4, \text{URu}_2 \text{Si}_2, \text{UPt}_3, \) and \( \text{UCoGe} \).

Acknowledgments

I would like to thank Professor H W Weber, M Eisterer and F Sauerzopf for their support and numerous discussions, and the first two for proofreading the manuscript. This work was supported by the Austrian Science Fund under Contract Nos 21194 and 23996.

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