4 Probing the Parity and Spin State

Classification into classes of superconductors with singlet and triplet pairing, respectively, needs information on the parity and spin state of the pairing state. These information can be accessed through measurements in a magnetic field due to the different response of the pairs with $S = 0$ and $S = 1$, respectively, on an applied magnetic field. In the following sections H_{c2} measurements, the nuclear magnetic resonance (NMR), and the muon spin rotation (μSR) are introduced as frequently used probes of the parity and spin state.

4.1 H_{c2} Measurements

Magnetic field can suppress superconductivity via two effects: orbital pair breaking of the superconducting pairs in the superconducting state and Pauli limiting due to the paramagnetism of the electron spins, which lowers the relative energy of the normal state. Keeping this in mind, measurements of the upper critical field H_{c2} can yield information on the parity of the superconducting state. A paramagnetic limitation of H_{c2} arises in even parity superconductors due to the drop of the Pauli susceptibility in the superconducting state χ_S which tends to zero as $T \to 0$. The limitation occurs at low temperatures when the increase in magnetic energy $\propto \mu_0^2 \mu_B^2 N_0 H^2$ becomes larger than the energy gain in the superconducting state $\propto N_0 \Delta_0^2/2$, where N_0 is the density of states per one spin projection. The superconducting state becomes unfavorable in a magnetic field higher than the so called *paramagnetic limit of superconductivity*[1] H_p given by

$$H_\mathrm{p} = \frac{\Delta_0}{\sqrt{2}\mu_0\mu_\mathrm{B}} \,, \tag{4.1}$$

and the singlet state of Cooper pairs is destroyed. For the importance of Pauli limiting the difference $\chi_N - \chi_S$ is decisive apart from the ratio χ_S/χ_N which is known for a given order parameter. χ_N is the susceptibility in the normal state. No Pauli limiting is expected in simple triplet states with equal spin pairing as $\chi_N = \chi_S$ in

[1] This limit is also known as the Clogston-Chandrasekhar paramagnetic limit named after Clogston and Chandrasekhar who first pointed out that a first-order transition to the normal state occurs at H_p due to the pair-breaking effect of an external field on the electronic spins [1, 2].

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these states. In heavy-fermion systems where the orbital limit is very large due to the large effective mass, paramagnetic limitation of H_{c2} can take place [3, 4]. Therefore, a simple H_{c2} measurement already might probe the spin state of the Cooper pairs.

So far, the considerations did only apply to isotropic systems without spin-orbit coupling. However, in systems with strong spin-orbit *coupling* the spin part of the order parameter cannot orientate itself freely with respect to the orbital part and χ_S can become smaller than χ_N for some orientations of the crystal relative to the magnetic field. Therefore, anisotropic Pauli limiting can occur even in a triplet superconductor. The analysis of H_{c2} curves is further complicated by impurity spin-orbit *scattering* which reduces the effect of paramagnetic limiting [5, 6, 7]. Spin-orbit scattering leads to a finite susceptibility in conventional superconductors, and thus increases the Clogston limit H_p. In conclusion, the occurrence respectively the absence of Pauli limiting in itself does not allow definite conclusions on the nature of the superconducting state.

4.2 Nuclear Magnetic Resonance and Knight Shift

The basic idea of nuclear magnetic resonance (NMR) is that radiofrequency signals can be used to measure resonant properties of nuclei in magnetic fields. In an external magnetic field the magnetic dipole moments of nuclei are partially aligned, and the magnetization can be changed by irradiating with a radiofrequency. The important concepts of nuclear magnetization and resonance absorption are widely discussed in a number of textbooks [8] and therefore, will not be repeated here. However, two items will be focused on in the following, namely the Knight shift $K = \Delta\omega/\omega$ which is the shift $\Delta\omega$ of the nuclear resonance at ω by *polarized conduction electrons* and the nuclear relaxation rate $1/T_1$ which accounts for the *spin-lattice relaxation* process in metals due to spin-flip scattering of conduction electrons by the nucleus.

The interaction responsible for both processes is the Fermi contact interaction given by

$$H_\mathrm{hf} = -\frac{2}{3}\mu_0\gamma_\mathrm{N}\gamma_\mathrm{e}|\phi(0)|^2(\boldsymbol{S}\cdot\boldsymbol{I}) \tag{4.2}$$

where $\mu_0 = 4\pi\cdot 10^{-7}$ Vs/Am is the vacuum permeability, γ_N and γ_e are the gyromagnetic ratio of the nucleus and electron, respectively, and $|\phi(0)|^2$ is the density of the electrons at the nucleus normalized to one electron per unit volume. The diagonal terms contribute to the Knight shift, but the nondiagonal part is responsible for the spin relaxation.

It follows that the Knight shift for s-electrons is given by

$$K = \frac{\Delta\omega}{\omega} = \frac{2}{3}\chi_\mathrm{Pauli}\frac{|\psi(0)|^2}{N} \tag{4.3}$$

which is equal (apart from a factor 2/3) to the Pauli susceptibility χ_Pauli multiplied by an amplification factor $|\psi(0)|^2/N$, which gives the ratio of the electron density at the nucleus to the average electron density.

For the relaxation rate $1/T_1$ one finds

$$1/T_1 = \frac{4\pi}{9}\mu_0^2\gamma_N^2\gamma_e^2\hbar^3|\phi(0)|^4 D(E_F)^2 k_B T \tag{4.4}$$

with $D(E_F)$ the density of states at the Fermi level and k_B the Boltzmann constant.

Both items are substantially influenced if a metal becomes superconducting. In an *s*-wave superconductor the spin susceptibility χ_{spin} drops to zero, while in equal-spin-pairing states the spin susceptibility is unchanged in all field directions as long as the order parameter $\boldsymbol{d}(\boldsymbol{k})$ is free to rotate[2]. This is the case if the energy of the spin-orbit coupling is weaker than that of the applied magnetic field. If the spin-orbit coupling is strong enough to lock the order parameter to the crystal lattice, only χ_{spin} perpendicular to $\boldsymbol{d}$ is unchanged, whereas χ_{spin} parallel to $\boldsymbol{d}$ approaches zero for $T \to 0$. Such a dependence of χ_{spin} on the direction and magnitude of the applied magnetic field was actually observed in the spin-triplet superconductors UPt_3 [12] and Sr_2RuO_4 [13] (see Sects. 9.1 and 10.1).

The relaxation process involves flipping of spins so that the relevant matrix element for nuclear-spin relaxation by interaction with quasiparticles have the case II coherence factors [14]. This corresponds to *constructive* interference in the relevant low-energy scattering process and causes the relaxation rate $1/T_1$ to *rise* above the normal value upon cooling through T_c before it exponentially drop-off to zero with the freeze-out of quasiparticles at lower temperatures. This phenomenon is called the Hebel-Slichter peak after Hebel and Slichter who first observed this peak in the nuclear relaxation rate of aluminum [15]. Its explanation was a great triumph for the BCS theory. For unconventional order parameters, case I and case II coherence factors are the same and do not lead to any enhancement[3] [17].

The temperature dependence of the relaxation rate also acts as a probe for the nodal structure of the superconductor. Even though the coherence peak might be suppressed, *s*-wave superconductivity is evidenced by an exponential decrease of $1/T_1$ below T_c. In contrast, the relaxation rate of unconventional superconductors exhibits a T^n power-law behaviour. For example, in the case of a line node $1/T_1 \sim T^3$ is observed. An overview over resonance experiments on heavy-fermion systems including heavy-fermion superconductors has been published by Kitaoka et al. [18].

[2] A constant Knight shift was also reported for the *s*-wave superconductor V [9]. The reason is that the orbital contribution to the Knight shift in V corresponding to the Van Vleck orbital susceptibility is the principal contribution, and this orbital shift is independent of the spin state of the conduction electrons. Other reasons for a constant spin susceptibility unrelated to pairing symmetry are strong spin-orbit coupling [10] or pecularities of the electronic structure [11].

[3] Although the existence of this peak is one of the crucial tests for BCS superconductivity, one should keep in mind that indeed, this peak might be absent in the classical superconductors Nb and V [16] and other strong-coupling superconductors.

4.3 Muon Spin Rotation

The muon spin rotation (μSR) technique is a local-probe hyperfine method like nuclear magnetic resonance discussed above. Together with neutron scattering and NMR, it is one of the very few microscopic methods investigating the bulk of the material, as the muons penetrate tenth of a millimetre into the sample. In recent years, μSR has become a primary method for the study of type-II superconductors, because muons are an ideal tool to investigate weak-magnetism phenomena in zero external field, and can be utilized to search for the occurrence of spontaneous magnetism below T_c, which would signal a possible breakdown of the time-reversal symmetry invariance. Moreover, μSR transverse-field measurements below T_c can furnish valuable information on the possible anisotropies of the temperature dependence of the London penetration depth, which could indicate a crystal symmetry breaking. Due to the local character of the μ^+ probe and its uniform implantation in a sample, μSR has been utilized to check whether the coexistence of magnetism and superconductivity in the heavy-fermion superconductors appears on a microscopic scale. In the following a brief introduction to the μSR technique is given, for more details the reader is referred to textbooks or specialized reviews (see e. g. [8, 19, 20] and refs. therein). Here, only μ^+ spin rotation is considered since positive muons are used much more extensively than negative muons in solid state physics research.

Muons belong to the lepton family and are produced via pion decay within the pion mean lifetime of $\tau = 26\,\text{ns}$. The muon is implanted in the solid sample and decays within $2.2\,\mu\text{s}$ according to $\mu^+ \longrightarrow e^+ + \nu_e + \bar{\nu_\mu}$, where e^+ is a positron and ν_e and $\bar{\nu_\mu}$ are neutrinos. Two important properties make the muons suitable as a solid state probe: 1. muons produced in the above way are 100% spin-polarized in the pion rest frame and 2. the muon decay is anisotropic, i. e. the positrons are emitted preferentially in the direction of the muon spin. Hence, by measuring the positron distribution, it is possible to determine the original μ^+ spin direction. Polarized muons are implanted into a sample where the polarization is affected by the local magnetic field until they decay. Because of its positive charge, the muon localizes at an interstitial site. If the implanted μ^+ is subject to magnetic interactions it precesses about the local magnetic field $\boldsymbol{B}(\boldsymbol{r})$ with a Larmor frequency

$$\omega_\mu = \gamma_\mu B(\boldsymbol{r}) \,, \tag{4.5}$$

where $\gamma_\mu/2\pi = 135.5342\,\text{MHz/T}$ is the muon gyromagnetic ratio. Consequently the polarization $\boldsymbol{P}_\mu$ becomes time dependent with $\boldsymbol{P}_\mu(t) = G(t)P_\mu(0)$, where $G(t)$ reflects the normalized μ^+-spin autocorrelation function which depends on the average value, distribution, and time evolution of the internal fields and therefore contains all physics of the magnetic interactions of the μ^+ inside the sample. The envelope of $G(t)$ is called the μ^+ depolarization function and a fast Fourier transformation yields the μSR spectrum whose line shape and position can be further analyzed.

Two techniques are important for the investigation of superconductors: the zero-field (ZF) μSR technique and the transverse-field (TF) μSR technique. The zero-field (ZF) μSR technique monitors the time evolution of the muon ensemble under

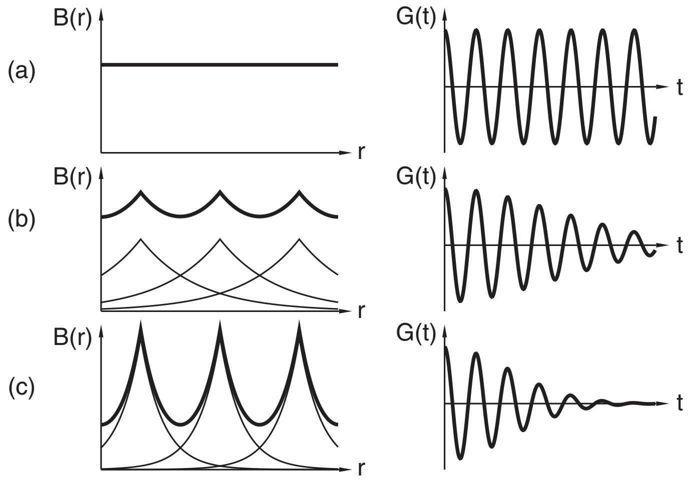

Fig. 4.1. The field distribution inside a superconductor as a function of position and the corresponding muon-spin relaxation function in the normal state (**a**), the superconducting state (**b**), and in the superconducting state with a shorter penetration depth (**c**) (from [20])

the action of internal magnetic fields in *zero* external fields. The very large magnetic moment of the muon makes μSR sensitive to extremely small internal magnetic fields down to the order of 0.1 G. The zero-field technique has been widely utilized to measure the spontaneous μ^+ Larmor frequencies in magnetically ordered phases, providing valuable information about the values of the static moment and the magnetic structures. In superconductors with time-reversal symmetry-breaking ordered state an internal field occurs which leads to an additional μ^+ depolarization due to electronic magnetic moments. A broadening of the μSR line in zero field can further be caused by a static distribution of internal fields or by fluctuations arising from fluctuating magnetic moments. For the latter process the depolarization rate $\sigma_1 = 1/T_1$ describes the spin-lattice relaxation ($1/T_1$ process).

The transverse-field (TF) μSR technique gives access to the μ^+ Knight shift. The μ^+ Knight shift originates from the magnetic-field-induced polarization of the conduction electrons. Local electronic moments can also contribute to the frequency shift by producing an effective dipolar field and an additional hyperfine contact field at the muon site. In the heavy-fermion compounds the μ^+ Knight shift corresponds to contributions to $\boldsymbol{B}_{\mathrm{int}}$ both from the polarization of conduction electrons and localized f moments induced by $\boldsymbol{H}_{\mathrm{ext}}$. For this technique, an external field $\boldsymbol{H}_{\mathrm{ext}}$ is applied perpendicular to the initial polarization $\boldsymbol{P}_\mu(0)$. $\boldsymbol{P}_\mu(t)$ precesses around the total field $\boldsymbol{B}_\mu$ at the μ^+ site. From the oscillatory component of $G(t)$ (see Fig. 4.1) the total field $\boldsymbol{B}_\mu$ can be extracted. After correction for the contribution of demagnetization and Lorentz field one obtains the μ^+ Knight shift

$$K_\mu = \frac{|\boldsymbol{B}_{\mathrm{int}}| - |\boldsymbol{H}_{\mathrm{ext}}|}{|\boldsymbol{H}_{\mathrm{ext}}|} , \tag{4.6}$$

where $\boldsymbol{B}_{\mathrm{int}}$ are the internal fields induced by $\boldsymbol{H}_{\mathrm{ext}}$.

If an inhomogeneous field distribution is present, the muons located at different sites will feel slightly different fields which will result in a loss of polarization by dephasing the muon ensemble and consequently to a line broadening in the μSR spectrum. A further origin of line broadening is the so-called $1/T_2$ process which arises from the dephasing of the μ^+ spins with depolarization rate $\sigma_2 = 1/T_2$.

For transverse-field μSR studies in type-II superconductors two effects play a role: 1. the presence of the flux-line lattice causes an additional field distribution, and 2. below T_c the μ^+ Knight shift changes due to the formation of the Cooper pairs. For $H_{\text{ext}} \gg H_{c1}$ where H_{c1} is the lower critical field, a type-II superconductor is in the mixed state, where both superconducting and normal regions (vortex cores) coexist. The muons implanted close to the vortex core experience a larger magnetic field than those implanted in the superconducting regions between vortices. The frequency shift is expected to be different in the superconducting and in the normal regions, and consequently there is a spread in precession frequency. Therefore, the measured field distribution is a convolution of the distribution due to the Knight shift and the flux-line lattice [21].

The line broadening due to the presence of the flux-line lattice is traditionally assumed to be Gaussian. The muon depolarization rate then is given by $\sigma \propto 1/\lambda^2 \propto n_s$, where λ is the magnetic penetration depth and n_s the superfluid density. Therefore, such studies yield information on the absolute value of λ, its anisotropy, and the temperature dependence $\lambda(T)$ which gives information about the gap nodes (see Sect. 3.2). However, as pointed out by Sonier et al. in a recent review [22], a simple Gaussian fit of the line shape is sometimes not sufficient and even yields false conclusions (see below in Sect. 7 and [22]).

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