



OPEN ACCESS

RECEIVED
9 April 2019REVISED
21 June 2019ACCEPTED FOR PUBLICATION
9 July 2019PUBLISHED
23 July 2019

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PAPER

Enhanced T_c and multiband superconductivity in the fully-gapped ReBe_{22} superconductorT Shang¹ , A Amon², D Kasinathan², W Xie³, M Bobnar², Y Chen³, A Wang³, M Shi⁴, M Medarde¹, H Q Yuan^{3,5}  and T Shiroka^{6,7} ¹ Laboratory for Multiscale Materials Experiments, Paul Scherrer Institut, Villigen CH-5232, Switzerland² Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, D-01187, Germany³ Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou, 310058, People's Republic of China⁴ Swiss Light Source, Paul Scherrer Institut, Villigen CH-5232, Switzerland⁵ Collaborative Innovation Center of Advanced Microstructures, Nanjing, 210093, People's Republic of China⁶ Laboratorium für Festkörperphysik, ETH Zürich, CH-8093 Zurich, Switzerland⁷ Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, SwitzerlandE-mail: tian.shang@psi.ch and tshiroka@phys.ethz.ch**Keywords:** superconductivity, multigap, intermetallics, μSR , time-reversal symmetry

Abstract

In search of the origin of superconductivity (SC) in diluted rhenium superconductors and their significantly enhanced T_c compared to pure Be (0.026 K), we investigated the intermetallic ReBe_{22} compound, mostly by means of muon-spin rotation/relaxation (μSR). At a macroscopic level, its bulk SC (with $T_c = 9.4$ K) was studied via electrical resistivity, magnetization, and heat-capacity measurements. The superfluid density, as determined from transverse-field μSR and electronic specific-heat measurements, suggest that ReBe_{22} is a fully-gapped superconductor with some multigap features. The larger gap value, $\Delta_0^l = 1.78 k_B T_c$, with a weight of almost 90%, is slightly higher than that expected from the BCS theory in the weak-coupling case. The multigap feature, rather unusual for an almost elemental superconductor, is further supported by the field-dependent specific-heat coefficient, the temperature dependence of the upper critical field, as well as by electronic band-structure calculations. The absence of spontaneous magnetic fields below T_c , as determined from zero-field μSR measurements, indicates a preserved time-reversal symmetry in the superconducting state of ReBe_{22} . In general, we find that a dramatic increase in the density of states at the Fermi level and an increase in the electron–phonon coupling strength, both contribute to the highly enhanced T_c value of ReBe_{22} .

1. Introduction

As one of the lightest elements, beryllium exhibits high-frequency lattice vibrations, a condition for achieving superconductivity (SC) with a sizeable critical temperature. Yet, paradoxically, its $T_c = 0.026$ K is so low [1], that its SC is often overlooked. Clearly, T_c is affected also by the electron–phonon coupling strength (typically large in elements with covalent-bonding tendencies) and the density of states (DOS) at the Fermi level $N(\epsilon_F)$ (rather low in pure Be). The latter depends on the details of crystal structure and on atomic volume, both effects being nicely illustrated by metal-hydride SCs under pressure (see, e.g. [2]). In this regard, recently researchers could demonstrate a purely phonon-mediated SC with T_c up to 250 K in actinium hydrides at 200 GPa [3]. The key insight of this work was the discovery of a link between chemical composition and SC. Namely, that SC is more likely to occur in materials containing metal atoms that are close to populating a new electronic subshell, such as the d_1 - (Sc, Y, La, and Ac) or p_0 (Be, Mg, and Ca) elements. In these cases, the electronic structure becomes highly sensitive to the positions of the neighboring atoms [4], resulting in stronger electron–phonon interactions and a higher $N(\epsilon_F)$. Based on this intuition, Be-rich alloys may achieve a T_c much higher than elementary beryllium, a prediction which turns out to be true for ReBe_{22} [5], whose $T_c \sim 9.6$ K is almost 400(!)

times higher than that of Be. This is a remarkable result, deserving more attention and a detailed investigation of the ReBe_{22} electronic properties.

ReBe_{22} represents also a very interesting case in an entirely different aspect. Recently, a number of studies have shown that Re-based superconductors exhibit unconventional superconducting behavior. For example, in non-centrosymmetric α -Mn-type $\text{Re}T$ alloys (T = transition metal), the time-reversal symmetry (TRS) is broken, and the upper critical field is close to the Pauli limit [6–8]. Surprisingly, our previous results show that, below T_c , even pure Re breaks TRS, thus behaving as an unconventional superconductor [8]. While binary Re-based superconductors have been investigated in both the full-(pure Re) and the intermediate Re limit ($\text{Re}T$), it is not clear if the unconventional behavior, in particular the TRS breaking, persists also in the dilute Re limit. With only 4% of Re content, ReBe_{22} is a good test case to verify such scenario.

In this paper, we report on an extensive study of the physical properties in the normal and superconducting state of ReBe_{22} , by means of electrical resistivity, magnetization, thermodynamic, and muon-spin relaxation (μSR) methods. In addition, we also present numerical density-functional-theory (DFT) band-structure calculations. ReBe_{22} exhibits a fully-gapped, spin-singlet superconducting state with preserved TRS. Despite the very small amount of Re, the ReBe_{22} alloy shows a remarkable increase in T_c compared to its elementary constituents, which we mostly attribute to the significant increase of DOS at the Fermi level.

2. Methods

Polycrystalline samples of ReBe_{22} were prepared by arc melting of elementary Be (Heraeus, 99.9%) and Re (Chempur, 99.97%) in an argon-filled glove box (MBraun, $p(\text{H}_2\text{O}/\text{O}_2) < 0.1$ ppm), dedicated to the handling of Be-containing samples [9]. To compensate for the evaporation losses and to avoid the formation of spurious Re–Be binary phases, a small excess of beryllium was used. Powder x-ray diffraction (XRD) measurements were performed on a Huber G670 image-plate Guinier camera (Ge-monochromator, $\text{Cu K}\alpha_1$ radiation). The lattice parameter of cubic ReBe_{22} was determined from a least-squares fit to the experimental peak positions. The sample purity was then checked by electron microscopy and energy-dispersive x-ray spectroscopy (EDX) on a JEOL JSM-6610 scanning electron microscope equipped with secondary electron-, electron backscatter-, and UltraDry EDS detectors (see figure A1 in the appendix). Besides traces of elemental Be, no chemical impurities or secondary phases could be detected.

The magnetic susceptibility, electrical resistivity, and specific-heat measurements were performed on a 7-T Quantum Design Magnetic Property Measurement System (MPMS-7) and on a 14-T Physical Property Measurement System (PPMS-14) equipped with a ^3He option. The μSR measurements were carried out at the GPS spectrometer of the Swiss muon source at Paul Scherrer Institut, Villigen, Switzerland [10]. The μSR data were analyzed by means of the `musrfit` software package [11].

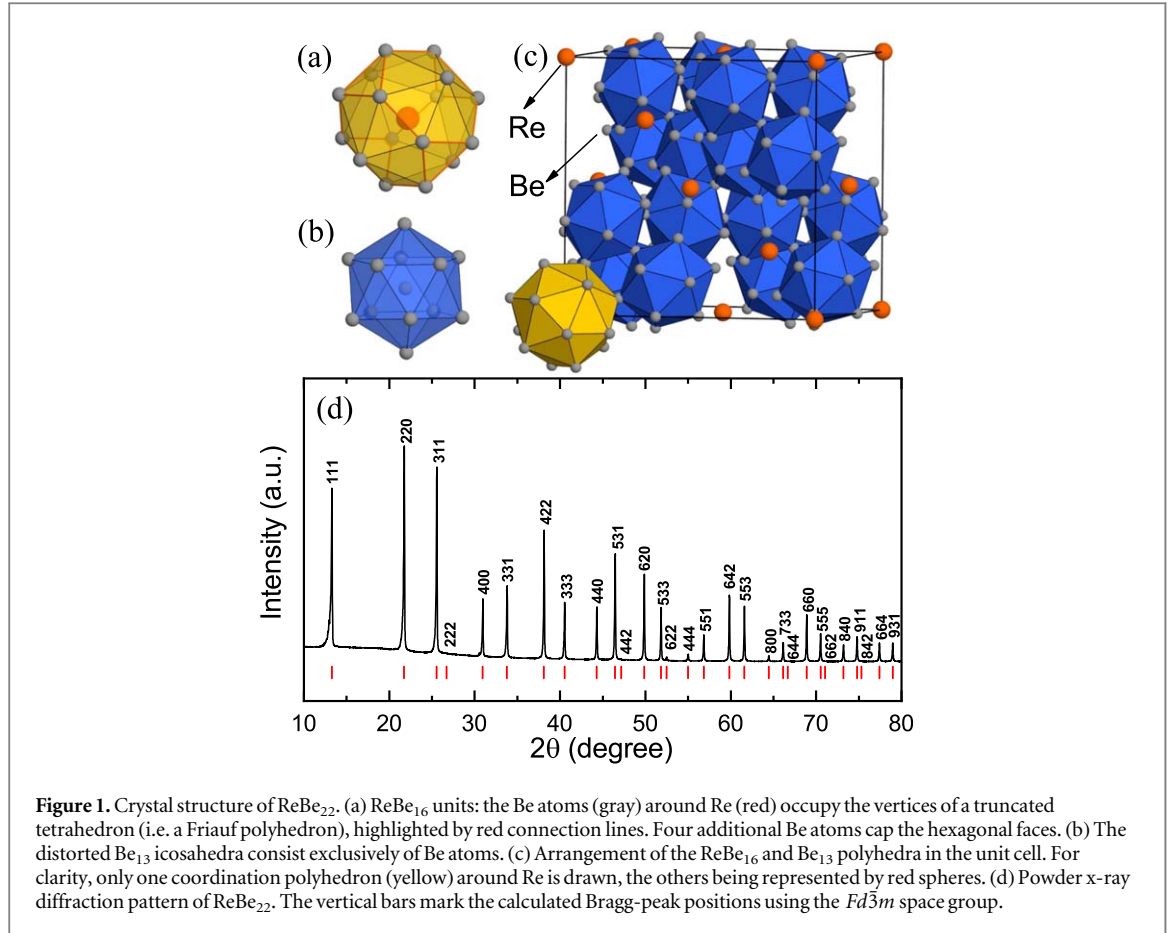
The band structure of ReBe_{22} was calculated by means of density-functional theory. Here we used the full-potential nonorthogonal local orbital code (FPLO) [12]. To calculate the nonmagnetic band structure we employed the local-density approximation parametrized by the exchange-correlation potential of Perdew and Wang [13]. The strong spin–orbit coupling of Re atoms was taken into account by performing full-relativistic calculations by solving the Dirac Hamiltonian with a generic potential.

3. Results and discussion

3.1. Crystal structure

As shown in figure 1, the complex intermetallic compound ReBe_{22} adopts a cubic ZrZn_{22} -type structure with space group $Fd\bar{3}m$ (No. 227) and $Z = 8$ formula units per cell. The lattice parameter $a = 11.5574(4)$ Å, determined from the XRD pattern (see figure 1(d)), is consistent with the previously reported value [14]. No obvious impurity phases could be detected, indicating the high quality of the synthesized samples. The crystal structure can be visualized by means of two structural motifs. In the ReBe_{16} motif (see figure 1(a)), Re is coordinated by 12 Be atoms, lying 2.53 Å apart at the vertices of a truncated tetrahedron, also known as a Friauf polyhedron. Four additional Be atoms lie atop the hexagonal faces of the truncated tetrahedron at a distance of 2.50 Å from the center. A similar motif is also found in the NbBe_2 superconductor [15, 16]. As for the rest of Be atoms, these form distorted Be-centered Be_{13} icosahedra, with the short interatomic distances ranging from 2.05 to 2.29 Å (figure 1(b)). Such Be-icosahedra represent the structural building blocks of the complex $M\text{Be}_{13}$ (M = rare earths and actinides) phases with a NaZn_{13} -type structure [17].

As shown in figure 1(c), the ReBe_{16} and Be_{13} units are connected by sharing the polyhedra vertices. The arrangement of the two types of polyhedra within a unit cell can be described as hierarchically derived from the MgCu_2 -type structure, where the Mg positions are occupied by ReBe_{16} units and those of Cu by Be_{13} icosahedra [18]. Both motifs, the truncated tetrahedron and the icosahedron, are found in the close-packed Laves phase



structures. As a consequence of the high Be content, ReBe_{22} features structural motifs typically found in Be-rich intermetallic compounds, dominated by close-packing structures similar to that of hcp-Be [19, 20]. Since the ratio of metallic radii [$r_{\text{Re}}/r_{\text{Be}} = 1.223$] is close to the ideal value of 1.225, this facilitates the close-packing of unequal spheres in ReBe_{22} and the accommodation of Re in the structure [21, 22]. The high packing fraction in this deltahedral structure is an important factor for the stabilization of this unusual stoichiometry, also found in the isostructural MoBe_{22} and WBe_{22} compounds, both featuring similar ratios of radii [23].

3.2. Electrical resistivity

The temperature dependence of the electrical resistivity $\rho(T)$ of ReBe_{22} was measured in zero magnetic field from 300 down to 2 K. As shown in figure 2, the resistivity exhibits metallic features down to base temperature, dropping to zero at the superconducting transition at $T_c^{\text{zero}} = 9.42$ K (see inset). Between T_c and 300 K the electrical resistivity can be modeled by the Bloch–Grüneisen (BG) formula [24, 25]:

$$\rho(T) = \rho_0 + 4A \left(\frac{T}{\Theta_D^R} \right)^5 \int_0^{\frac{\Theta_D^R}{T}} \frac{z^2 dz}{(e^z - 1)(1 - e^{-z})}. \quad (1)$$

Here, the first term ρ_0 is the residual resistivity due to the scattering of conduction electrons on the static defects of the crystal lattice, while the second term describes the electron–phonon scattering, with Θ_D^R being the characteristic (Debye) temperature and A a coupling constant. The fit (black-line) in figure 2 results in $\rho_0 = 2.72(5) \mu\Omega \text{ cm}$, $A = 95(3) \mu\Omega \text{ cm}$, and $\Theta_D^R = 590(5)$ K. Such a large Θ_D^R value is consistent with the heat-capacity results (see below) and reflects the high frequency of phonons in ReBe_{22} . This is compatible with the high Debye temperature of elemental Be (~ 1031 K) [26], in turn reflecting the small mass of beryllium atoms. A relatively large residual resistivity ratio [$\text{RRR} = \rho(300 \text{ K})/\rho_0 \sim 16$] and a sharp superconducting transition ($\Delta T = 0.23$ K) both indicate a good sample quality.

3.3. Magnetization measurements

The bulk SC of ReBe_{22} can be probed by magnetization measurements. The temperature evolution of the magnetic susceptibility $\chi(T)$, measured at 1 mT using both field-cooled (FC) and zero-field-cooled (ZFC) protocols, is shown in figure 3(a). The splitting of the FC- and ZFC-susceptibilities is typical of granular superconductors, where the magnetic-field flux is trapped (in open holes) upon cooling the material in an

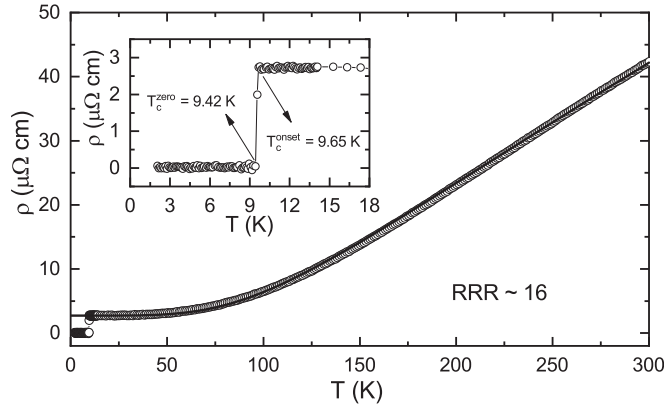


Figure 2. Temperature dependence of the electrical resistivity of ReBe₂₂. The solid line through the data is a fit to equation (1). The inset shows the data in the low-temperature region, highlighting the superconducting transition.

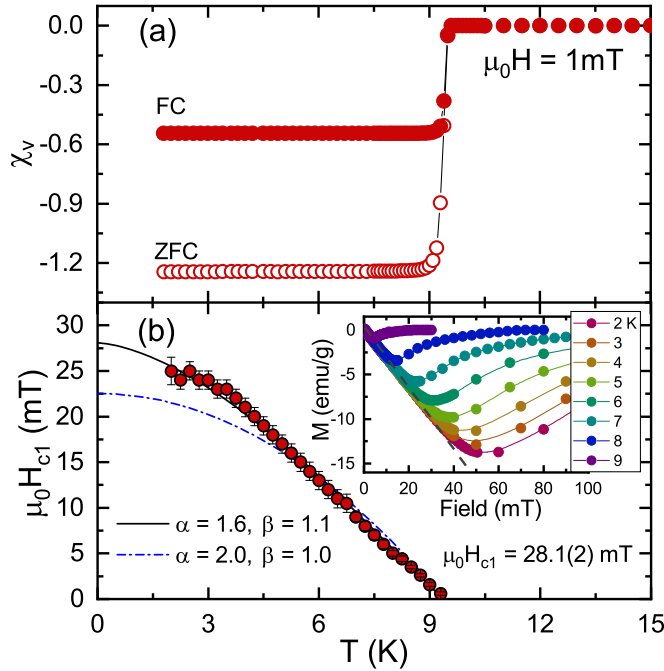
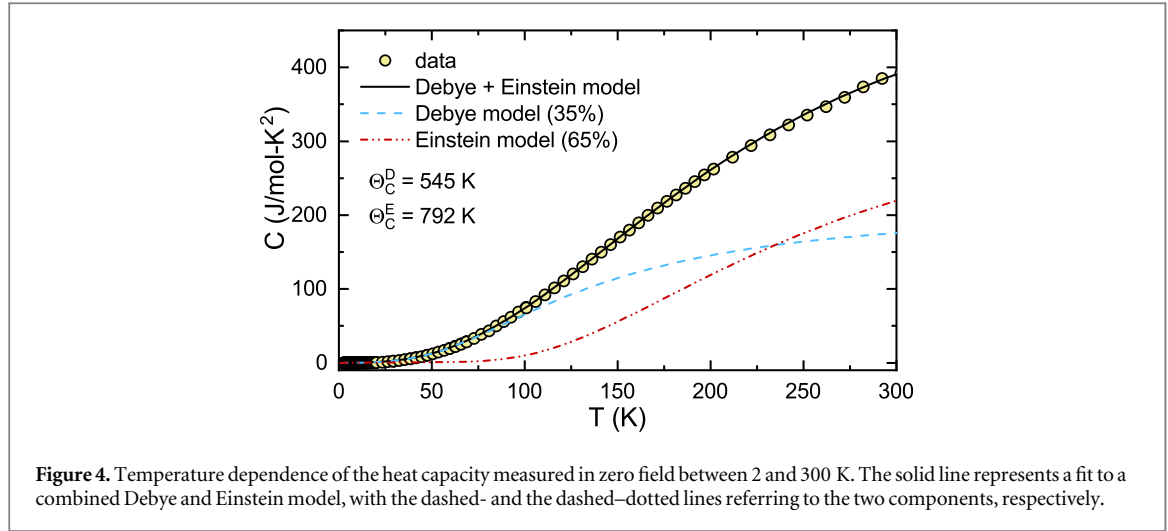


Figure 3. (a) Temperature dependence of the magnetic susceptibility of ReBe₂₂. Data were collected in a 1 mT applied field using both ZFC- and FC protocols. (b) Estimated lower critical field $\mu_0 H_{c1}$ as a function of temperature. Lines are fits to the phenomenological model $\mu_0 H_{c1}(T) = \mu_0 H_{c1}(0)[1 - (T/T_c)^\alpha]^\beta$. The inset shows the field-dependent magnetization $M(H)$ recorded at various temperatures up to T_c . For each temperature, the lower critical field $\mu_0 H_{c1}$ was determined as the value where $M(H)$ starts deviating from linearity (dashed line).

applied field [27]. The $\chi(T)$ curves show the onset of the superconducting transition at $T_c = 9.50$ K, in agreement with the values determined from electrical resistivity (figure 2) and heat capacity (see below).

The field-dependent magnetization $M(H)$, measured at various temperatures (up to T_c), was used to determine the lower critical field $\mu_0 H_{c1}$ of ReBe₂₂. As shown in the inset of figure 3(b), the $M(H)$ curves, recorded using a ZFC-protocol, exhibit the typical response expected for a type-II superconductor. The resulting $\mu_0 H_{c1}$ versus temperature data are summarized in figure 3(b) and the phenomenological model $\mu_0 H_{c1}(T) = \mu_0 H_{c1}(0)[1 - (T/T_c)^\alpha]^\beta$ was used to estimate $\mu_0 H_{c1}(0)$. With $\alpha = 1.6$ and $\beta = 1.1$, the curve shown by a solid line in figure 3(b) gives a lower critical field $\mu_0 H_{c1}(0) = 28.1(2)$ mT. At the same time, the general model, with $\alpha = 2$ and $\beta = 1$, shows a poor agreement with the experimental data. Since $\mu_0 H_{c1}$ is basically proportional to the inverse-square of the magnetic penetration depth (see section 3.5 and [28]), a complex T -dependence of $\mu_0 H_{c1}$ is indicative of multiband SC in ReBe₂₂.



3.4. Specific heat

The temperature dependence of the heat capacity $C(T)$ of ReBe_{22} was also measured in zero-field conditions from 300 K down to 2 K. Although a single Debye- or Einstein model cannot describe the data, as shown in figure 4, the normal-state $C(T)$ can be fitted by a combined Debye and Einstein model, with relative weights x and $(1 - x)$ [29]:

$$C(T) = \gamma_n T + nx C_D(T) + n(1 - x) C_E(T). \quad (2)$$

The number of atoms per ReBe_{22} formula-unit ($n = 23$) is considered in the above equation. The first term represents the electronic specific heat, which can be determined from the low- T heat-capacity data (see below). The second and the third terms represent the acoustic- and optical phonon-mode contributions, described by the Debye and Einstein model, respectively [29]:

$$C_D(T) = 9R \left(\frac{T}{\Theta_D^C} \right)^3 \int_0^{\frac{\Theta_D^C}{T}} \frac{z^4 e^z dz}{(e^z - 1)^2}, \quad (3)$$

$$C_E(T) = 3R \left(\frac{\Theta_E^C}{T} \right)^2 \frac{\exp(\Theta_E^C/T)}{[\exp(\Theta_E^C/T) - 1]^2}. \quad (4)$$

Here Θ_D^C and Θ_E^C are the Debye and Einstein temperatures, while $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the molar gas constant. The best fit curve (solid line in figure 4) is obtained for $\Theta_D^C = 545(5) \text{ K}$ and $\Theta_E^C = 792(5) \text{ K}$, with $x = 0.35(2)$. The resulting Debye temperature is comparable to that derived from electrical resistivity data (see figure 2).

The low- T specific-heat data were further analyzed, since they can offer valuable insight into the superconducting properties of ReBe_{22} through the evaluation of the quasiparticle DOS at the Fermi level. As shown in figure 5, the sharp specific-heat jump at T_c again indicates a bulk superconducting transition and a good sample quality. The electronic specific heat C_e/T was obtained by subtracting the phonon contribution from the experimental data. The DOS at the Fermi level $N(\epsilon_F)$ can be evaluated from the expression $N(\epsilon_F) = 3\gamma_n/(2\pi^2 k_B^2) = 3.25(3) \text{ states/eV-f.u.}$ (accounting for spin degeneracy) [30], where k_B is the Boltzmann constant and $\gamma_n = 15.3(2) \text{ mJ mol}^{-1} \text{ K}^{-2}$ is the electronic specific-heat coefficient. The electron–phonon coupling constant λ_{ep} , a measure of the attractive interaction between electrons due to phonons, was estimated from the Θ_D^C and T_c values by means of the semi-empirical McMillan formula [31]:

$$\lambda_{ep} = \frac{1.04 + \mu^* \ln(\Theta_D/1.45 T_c)}{(1 - 0.62 \mu^*) \ln(\Theta_D/1.45 T_c) - 1.04}. \quad (5)$$

The Coulomb pseudo-potential μ^* was fixed to 0.13, a typical value for metallic samples. From equation (5) we obtain $\lambda_{ep} = 0.64(1)$ for ReBe_{22} , almost *three times larger* than the reported value for elemental Be (0.21) [32]. By using this value, finally, the band-structure DOS $N_{\text{band}}(\epsilon_F)$ can be estimated from the relation $N_{\text{band}}(\epsilon_F) = N(\epsilon_F)/(1 + \lambda_{ep})$ [30], which gives $N_{\text{band}}(\epsilon_F) = 1.98(2) \text{ states/eV-f.u.}$

After subtracting the phonon contribution from the specific-heat data, the electronic specific heat divided by the electronic specific-heat coefficient, i.e. $C_e/\gamma_n T$, is obtained (main panel in figure 5). The temperature-dependent superconducting-phase contribution to the entropy was calculated by means of the BCS expression [33]:

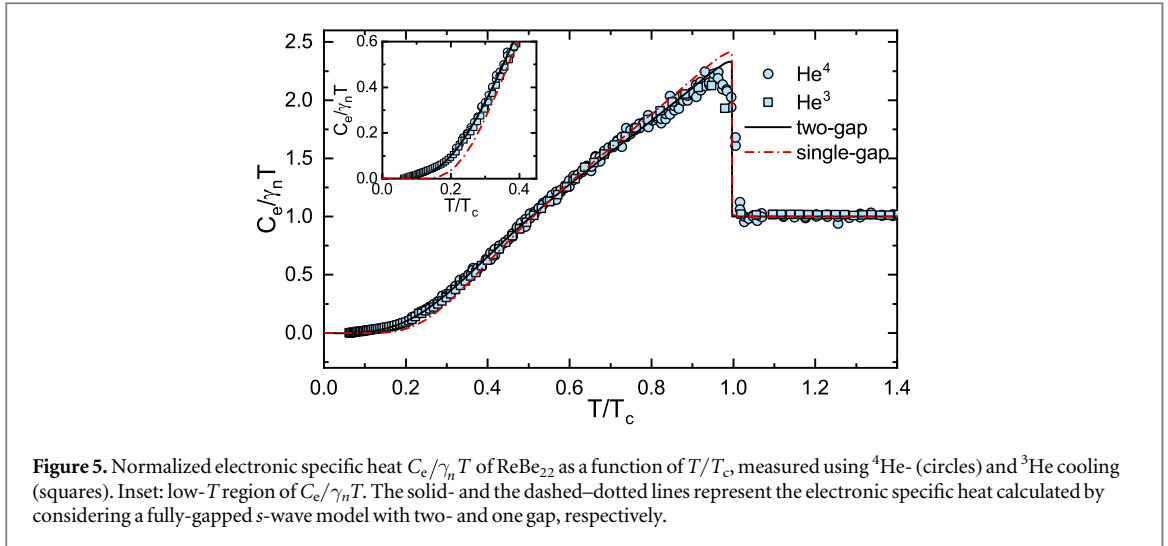


Figure 5. Normalized electronic specific heat $C_e/\gamma_n T$ of ReBe_{22} as a function of T/T_c , measured using ^4He - (circles) and ^3He cooling (squares). Inset: low- T region of $C_e/\gamma_n T$. The solid- and the dashed-dotted lines represent the electronic specific heat calculated by considering a fully-gapped s -wave model with two- and one gap, respectively.

$$S(T) = -\frac{6\gamma_n}{\pi^2 k_B} \int_0^\infty [f \ln f + (1-f) \ln(1-f)] d\epsilon, \quad (6)$$

where $f = (1 + e^{E/k_B T})^{-1}$ is the Fermi function and $E(\epsilon) = \sqrt{\epsilon^2 + \Delta^2(T)}$ is the excitation energy of quasiparticles, with ϵ the electron energies measured relative to the chemical potential (Fermi energy) [33, 37]. Here $\Delta(T) = \Delta_0 \tanh\{1.82[1.018(T_c/T - 1)]^{0.51}\}$ [38], with Δ_0 the gap value at zero temperature. The temperature-dependent electronic specific heat in the superconducting state can be calculated from $C_e = T \frac{dS}{dT}$. The dashed-dotted line in figure 5 represents a fit with an s -wave model with a single gap $\Delta_0 = 1.40(1)$ meV. While this reproduces well the experimental data in the $0.4 < T/T_c < 0.8$ range, out of it the single-gap model clearly deviates from the data (see lower inset). On the contrary, the two-gap model exhibits a better agreement, both at low temperatures as well as near T_c . The solid line in figure 5 is a fit to the two-gap s -wave model, known also as α model [39]:

$$C_e(T)/T = w C_e^\Delta(T)/T + (1-w) C_e^L(T)/T. \quad (7)$$

Here each term represents a single-gap specific-heat contribution, with Δ^s the small- and Δ^L the large gap, and w the relative weight. The two-gap model gives $w = 0.13$, $\Delta_0^s = 0.68(1)$ meV and $\Delta_0^L = 1.43(1)$ meV, with both superconducting gap values being consistent with the μSR results (see figure 9). In addition, the larger gap is comparable to the weak-coupling BCS value (1.4 meV), indicating weakly-coupled superconducting pairs in ReBe_{22} . The specific-heat discontinuity at T_c , i.e. $\Delta C/\gamma_n T_c = 1.24$, is smaller than the BCS value of 1.43. There are two possibilities for such a reduced specific-heat discontinuity, despite a good sample quality and full superconducting volume fraction: (i) gap anisotropy, including a nodal gap, as observed in some heavy-fermion superconductors or in Sr_2RuO_4 [40, 41], or (ii) multiband SC, as e.g. in MgB_2 or LaNiGa_2 [36, 42]. Due to a highly-symmetric crystal structure and to a lack of gap nodes (see below), only the second scenario is applicable to the ReBe_{22} case.

The multiband SC of ReBe_{22} can be inferred also from the field dependence of the electronic specific heat coefficient γ_H . As shown in figure 6(a), at a given applied field, γ_H is obtained as the linear extrapolation of C/T versus T^2 (in the superconducting phase) to zero temperature. The dependence of the normalized γ_H/γ_n versus the reduced magnetic field $H/H_{c2}(0)$ is shown in figure 6(b) (here γ_n is the zero-field normal-phase value). Note that, the field dependence of γ_H/γ_n at 2 K exhibits similar features to that evaluated at zero temperature. Due to the multiband effects, it is difficult to describe the field dependence of γ_H in ReBe_{22} with a simple formula. As can be seen in figure 6(b), $\gamma_H(H)$ clearly deviates from the linear field dependence (dashed-dotted line) expected for single-gap BCS superconductors [43], or from the square-root dependence \sqrt{H} (solid line) expected for nodal superconductors [44, 45]. In fact, ReBe_{22} exhibits similar features to other multiband superconductors, as e.g. LaNiC_2 [34], FeSe [35], and MgB_2 [36] (the latter being a prototypical two-gap superconductor), although the slopes of $\gamma_H(H)$ close to $H = 0$ are different.

3.5. Upper critical field

The upper critical field $\mu_0 H_{c2}$ of ReBe_{22} was determined via temperature-dependent resistivity $\rho(T, H)$ and specific heat $C(T, H)/T$ measurements at various applied magnetic fields, as well as from the field-dependent magnetization $M(H, T)$ at various temperatures. The derived $\mu_0 H_{c2}$ values as a function of the reduced temperature $T_c/T_c(0)$ are summarized in figure 7(a). Upon applying a magnetic field, the superconducting transition in both $\rho(T)$ and specific heat $C(T)/T$ data shifts towards lower temperatures (see figures 7(b) and (c)). In the $M(H, T)$ case, the diamagnetic signal disappears once the applied magnetic field exceeds the upper critical

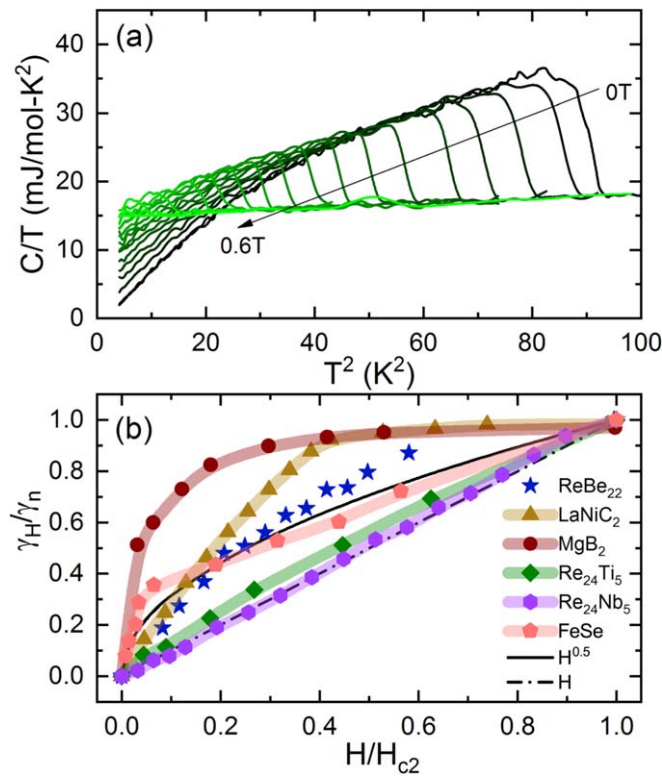


Figure 6. (a) Specific heat of ReBe_{22} as a function of T^2 , measured under increasing magnetic fields (up to 0.6 T). (b) Normalized specific-heat coefficient γ_H/γ_n versus the reduced magnetic field value $H/H_{c2}(0)$. γ_H is estimated by extrapolating the data in (a) to zero temperature. The dashed-dotted line indicates a linear dependence as predicted for an s -wave gap structure, the solid line represents the dependence expected for an anisotropic gap or a gap with nodes, e.g. d -wave. The data for the reported samples were adopted from the [7, 8, 34–36].

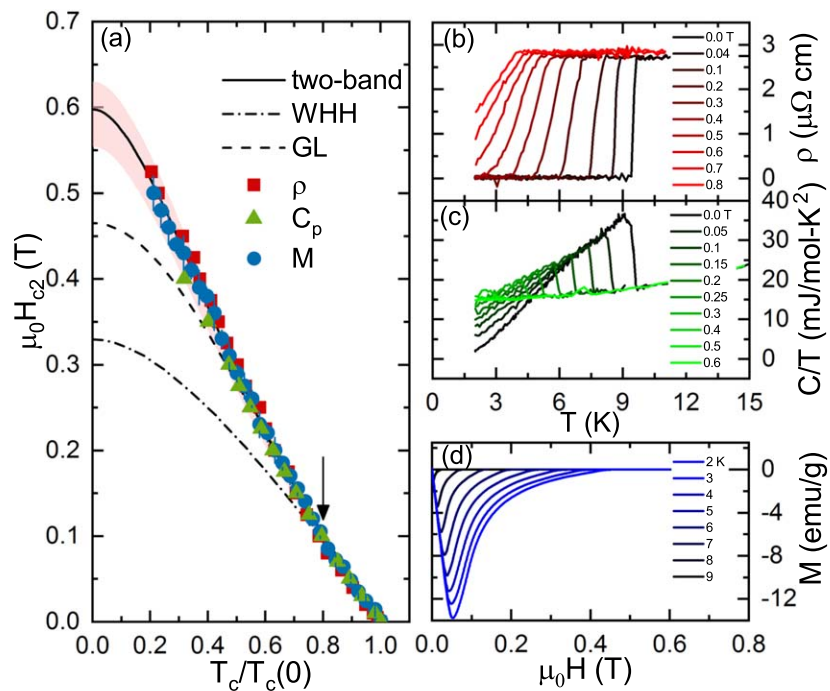
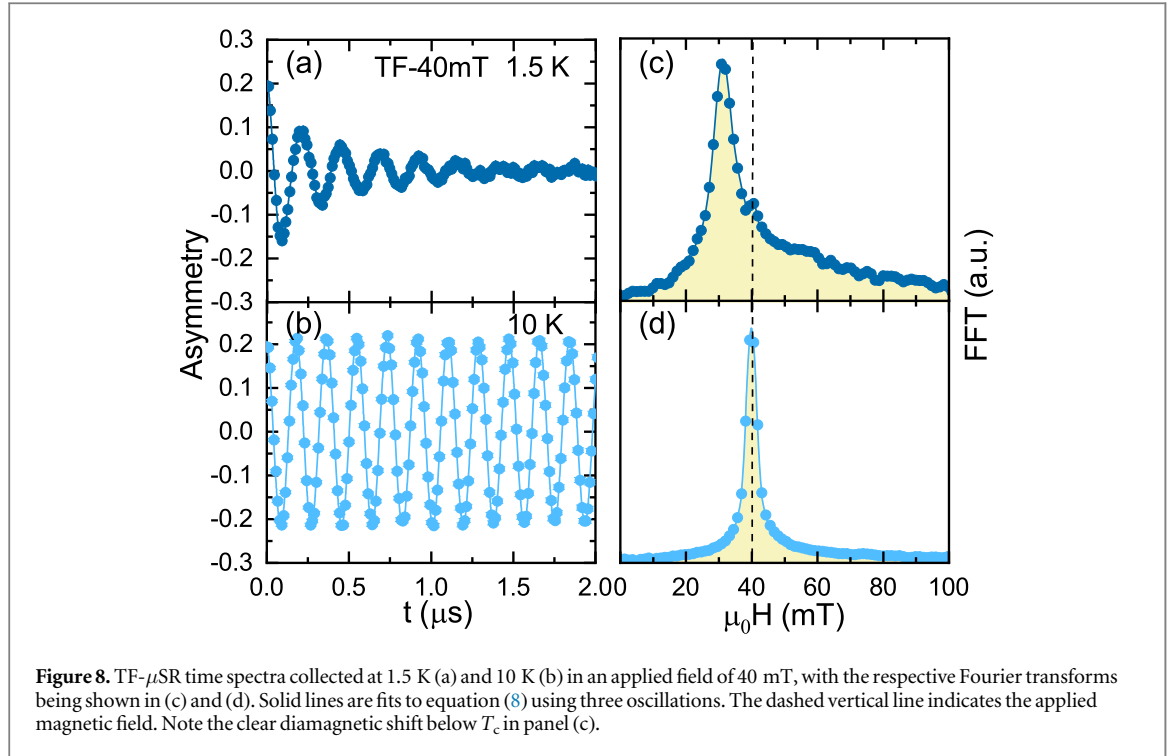


Figure 7. (a) Upper critical field $\mu_0 H_{c2}$ versus reduced transition temperature $T_c/T_c(0)$ for ReBe_{22} . The T_c values were determined from temperature-dependent electrical resistivity $\rho(T, H)$ (b) and specific-heat $C(T, H)/T$ data (c) at various applied fields, and from field-dependent magnetization $M(H, T)$ (d) at different temperatures. For the $\rho(T, H)$ measurements, T_c was defined as the onset of zero resistivity. Three different models, including two-band (solid line), WHH (dashed-dotted line), and GL model (dashed line), are shown in (a). In case of the WHH model, the spin-orbit scattering was neglected. The shadowed region indicates the upper and lower H_{c2} limits, as determined using the two-band model.



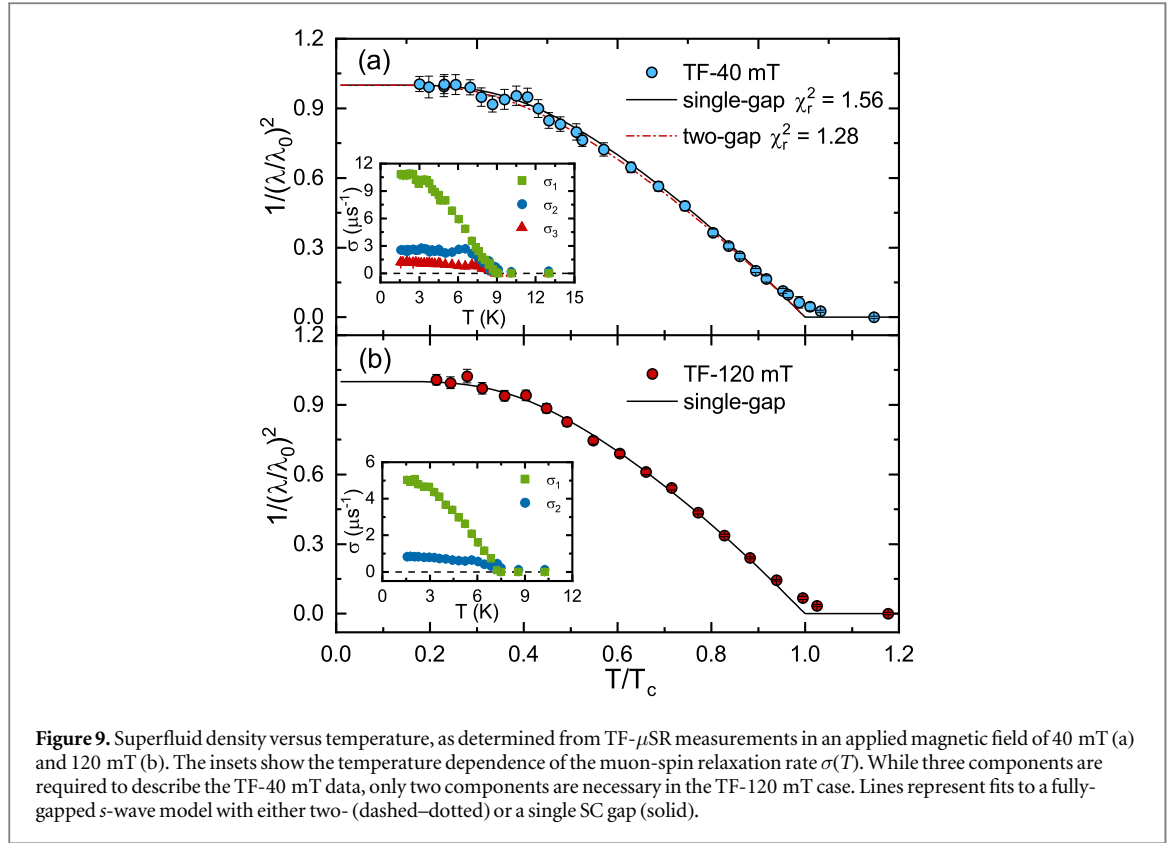
field (figure 7(d)). The $\mu_0 H_{c2}$ values determined using different techniques are highly consistent. The temperature dependence of $\mu_0 H_{c2}(T)$ was analyzed by means of three different models, i.e. a Ginzburg–Landau (GL) [46], a Werthamer–Helfand–Hohenberg (WHH) [47], and a two-band (TB) [48] model. As can be seen in figure 7(a), at low fields, both GL and WHH models reproduce very well the experimental data. However, at higher magnetic fields, both models deviate significantly from the experimental data, providing underestimated $\mu_0 H_{c2}(0)$ values.

A positive curvature of $\mu_0 H_{c2}(T)$ near T_c is considered a typical feature of multiband superconductors, as e.g. MgB_2 [49, 50]. It reflects the gradual suppression of the small superconducting gap with increasing magnetic field, as evidenced also by the specific-heat data shown in figure 6. The arrow in figure 7(a) identifies the small kink in $\mu_0 H_{c2}(T)$ close to 0.1 T, here considered to coincide with the field value which suppresses the small superconducting gap. Also γ_H changes its slope near this critical field (corresponding to $H/H_{c2} = 0.17$ in figure 6(b)). The remarkable agreement of the TB model with the experimental data across the full temperature range is clearly seen in figure 7(a), from which we find $\mu_0 H_{c2}^{\text{TB}}(0) = 0.60(3)$ T.

The superconducting coherence length ξ can be calculated from $\xi = \sqrt{\Phi_0/2\pi H_{c2}}$, where $\Phi_0 = 2.07 \times 10^{-3}$ T μm^2 is the quantum of magnetic flux. With a bulk $\mu_0 H_{c2}(0) = 0.60(3)$ T, the calculated $\xi(0)$ is 23(1) nm. The lower critical field $\mu_0 H_{c1}$ is related to the magnetic penetration depth λ and the coherence length ξ via $\mu_0 H_{c1} = (\Phi_0/4\pi\lambda^2)[\ln(\kappa) + 0.5]$, where $\kappa = \lambda/\xi$ is the GL parameter [28]. By using $\mu_0 H_{c1} = 28.1$ mT and $\mu_0 H_{c2} = 0.60(3)$ T, the resulting magnetic penetration depth $\lambda_{\text{GL}} = 109(1)$ nm, is comparable to 87(1) nm (40 mT) and 104(1) nm (120 mT), the experimental values evaluated from TF- μ SR data (see section 3.6). A GL parameter $\kappa \sim 4.7(3)$, much larger than the threshold value of $1/\sqrt{2}$, clearly indicates that ReBe_{22} is a type-II superconductor.

3.6. Transverse-field μ SR

μ SR measurements in an applied transverse field (TF) were carried out to investigate the superconducting properties of ReBe_{22} at a microscopic level. Preliminary field-dependent μ SR depolarization-rate measurements at 1.5 K were carried out to determine the optimal field value for the temperature-dependent study (see figure A2 in Appendix). To track the additional field-distribution broadening due to the flux-line-lattice (FLL) in the mixed superconducting state, the magnetic field was applied in the normal state, prior to cooling the sample below T_c . After the field-cooling protocol, which ensures an almost ideal FLL even in case of pinning effects, the TF- μ SR measurements were performed at various temperatures upon warming. Figures 8(a) and (b) show two representative TF- μ SR time spectra collected in the superconducting (1.5 K) and the normal state (10 K) in an applied field of 40 mT at the GPS spectrometer. The enhanced depolarization rate below T_c reflects the inhomogeneous field distribution due to the FLL, causing an additional distribution broadening in the mixed state (see figure 8(c)). The μ SR spectra can be modeled by the following expression:



$$A_{\text{TF}}(t) = \sum_{i=1}^n A_i \cos(\gamma_\mu B_i t + \phi) e^{-\sigma_i^2 t^2/2} + A_{\text{bg}} \cos(\gamma_\mu B_{\text{bg}} t + \phi). \quad (8)$$

Here A_i and A_{bg} represent the initial muon-spin asymmetries for muons implanted in the sample and sample holder, respectively, with the latter not undergoing any depolarization. B_i and B_{bg} are the local fields sensed by implanted muons in the sample and sample holder, $\gamma_\mu = 2\pi \times 135.53 \text{ MHz T}^{-1}$ is the muon gyromagnetic ratio, ϕ is a shared initial phase, and σ_i is a Gaussian relaxation rate of the i th component. The number of required components is material dependent, generally in the $1 \leq n \leq 5$ range. For superconductors with a large κ ($\gg 1$), the magnetic penetration depth is much larger than the coherence length. Hence, the field profiles of each fluxon overlap strongly, implying a narrow field distribution. Consequently, a single-oscillating component is sufficient to describe $A(t)$, as e.g. in ReT [7, 8] or $\text{Mo}_3\text{Rh}_2\text{N}$ [51]. In case of a small κ ($\gtrsim 1/\sqrt{2}$), as e.g. in ReBe_{22} , the magnetic penetration depth is comparable to the coherence length. The rather small λ implies fast-decaying fluxon field profiles and a broad field distribution, in turn requiring multiple oscillations to describe $A(t)$ [52]. The fast-Fourier-transform (FFT) spectra of the TF- μ SR datasets at 1.5 and 10 K are shown in figures 8(c) and (d). The solid lines represent fits to equation (8) using three oscillations (i.e. $n = 3$) in the superconducting state and one oscillation in the normal state. The TF- μ SR spectra collected at 120 mT require only two oscillations (i.e. $n = 2$), indicating a narrower field distribution compared to the 40 mT case. The derived Gaussian relaxation rates as a function of temperature are summarized in the insets of figure 9.

Above T_c , the relaxation rate is small and temperature-independent, but below T_c it starts to increase due to the onset of the FLL and the increase in superfluid density. In case of multi-component oscillations, the first-term in equation (8) describes the field distribution as the sum of n Gaussian relaxations [52]:

$$P(B) = \gamma_\mu \sum_{i=1}^n \frac{A_i}{\sigma_i} \exp \left[-\frac{\gamma_\mu^2 (B - B_i)^2}{2\sigma_i^2} \right]. \quad (9)$$

Then, the first- and the second moment of the field distribution can be calculated by:

$$\langle B \rangle = \sum_{i=1}^n \frac{A_i B_i}{A_{\text{tot}}}, \quad \text{and} \quad (10)$$

$$\langle B^2 \rangle = \frac{\sigma_{\text{eff}}^2}{\gamma_\mu^2} = \sum_{i=1}^n \frac{A_i}{A_{\text{tot}}} \left[\frac{\sigma_i^2}{\gamma_\mu^2} - (B_i - \langle B \rangle)^2 \right], \quad (11)$$

where $A_{\text{tot}} = \sum_{i=1}^n A_i$. The superconducting Gaussian relaxation rate related to the FLL (σ_{FLL}) can be extracted by subtracting the nuclear contribution according to $\sigma_{\text{FLL}} = \sqrt{\sigma_{\text{eff}}^2 - \sigma_n^2}$, where σ_n is the nuclear relaxation rate. The superconducting gap value and its symmetry can be investigated by measuring the temperature-dependent $\sigma_{\text{FLL}}(T)$, which is directly related to the magnetic penetration depth and thus the superfluid density ($\sigma_{\text{FLL}} \propto 1/\lambda^2$).

Since the upper critical field of ReBe_{22} is relatively small (600 mT) compared to the applied fields used in the TF- μSR study (40 and 120 mT), the effects of the overlapping vortex cores with increasing field ought to be considered when extracting the magnetic penetration depth λ from σ_{FLL} . For ReBe_{22} , λ was calculated by means of [28, 53]:

$$\sigma_{\text{FLL}} = 0.172 \frac{\gamma_\mu \Phi_0}{2\pi} (1 - h) [1 + 1.21(1 - \sqrt{h})^3] \lambda^{-2}, \quad (12)$$

where $h = H_{\text{appl}}/H_{c2}$, with H_{appl} the applied magnetic field. The above expression is valid for type-II superconductors with $\kappa \geq 5$ in the $0.25/\kappa^{1.3} \lesssim h \leq 1$ field range. With $\kappa \sim 4.7$ and $h = 0.067$ (TF-50 mT) and 0.2 (TF-120 mT), ReBe_{22} fulfills the above condition. Note that, in the above expression, only the absolute value of the penetration depth, but not its temperature dependence is related to the h value. By using equation (12), we calculate the inverse-square of the magnetic penetration depth, which is proportional to the superfluid density, i.e. $\lambda^{-2}(T) \propto \rho_{\text{sc}}(T)$. As can be seen in figure 9, below $T_c/3$, $\rho_{\text{sc}}(T)$ is practically independent of temperature, in agreement with the specific-heat results shown in figure 6, once more indicating a nodeless SC in ReBe_{22} . $\rho_{\text{sc}}(T)$ was further analyzed by means of a two-gap s -wave model, previously applied to the well-established two-gap superconductor MgB_2 [38, 54]. In general, the superfluid density can be described by:

$$\rho_{\text{sc}}(T) = w\rho_{\text{sc}}^{\Delta^s}(T) + (1 - w)\rho_{\text{sc}}^{\Delta^l}(T). \quad (13)$$

As in the specific-heat case, $\rho_{\text{sc}}^{\Delta^s}$ and $\rho_{\text{sc}}^{\Delta^l}$ are the superfluid densities related to the small (Δ^s) and large (Δ^l) gaps, and w is a relative weight. For each gap, $\rho_{\text{sc}}(T)$ is given by:

$$\rho_{\text{sc}}(T) = 1 + 2 \int_{\Delta(T)}^{\infty} \frac{E}{\sqrt{E^2 - \Delta^2(T)}} \frac{\partial f}{\partial E} dE, \quad (14)$$

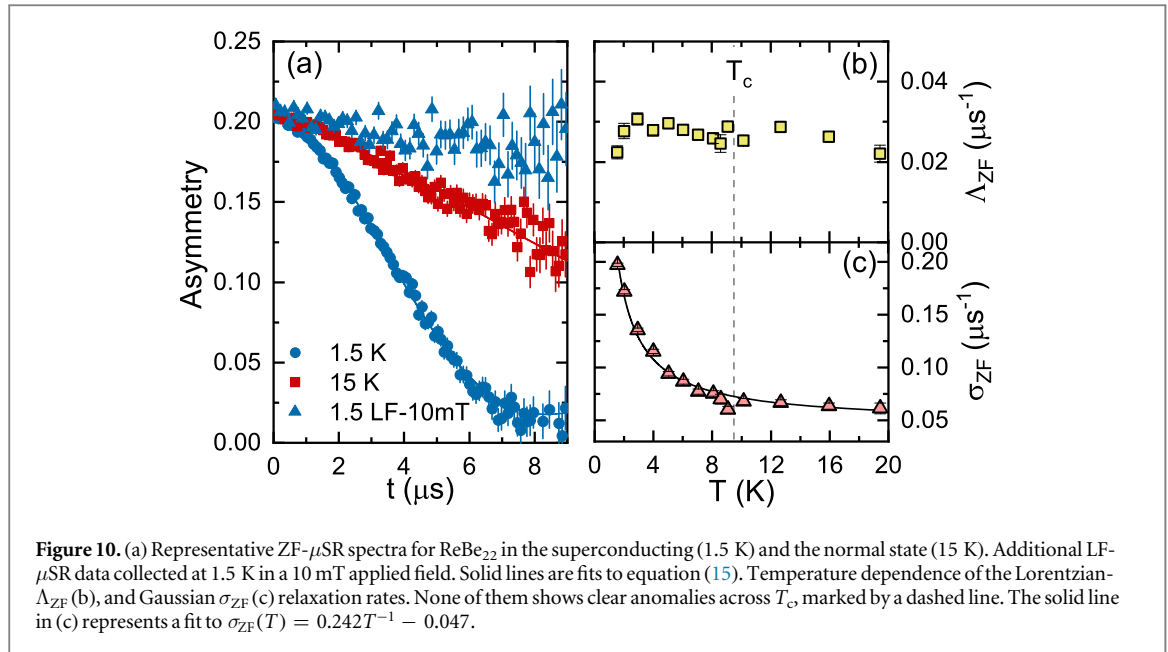
where f and Δ are the Fermi- and the gap function, respectively, as in section 3.4. Here, the gap value at zero temperature Δ_0 is the only adjustable parameter. As can be seen in figure 9(a), for TF-40 mT, the temperature-independent behavior of $\lambda^{-2}(T)$ is consistent with an s -wave model with either a single- (solid line) or two gaps (dashed-dotted line). The single-gap model, however, shows a less good agreement with the measured $\lambda^{-2}(T)$, as confirmed by the larger χ_r^2 value (goodness of fit) compared to the two-gap model. Such conclusion is also supported by the low- T specific-heat data shown in figures 5 and 6(b) and the upper critical field in figure 7. For the two-gap model, the zero-temperature magnetic penetration depth is $\lambda_0 = 87(1)$ nm and the estimated gap values are $\Delta_0^s = 0.83(1)$ meV and $\Delta_0^l = 1.35(1)$ meV, with a weight $w = 0.1$. The latter are consistent with the gap values obtained from specific-heat data. For the single-gap model, the estimated gap value is $\Delta_0 = 1.33$ meV, with the same λ_0 as in the two-gap case. In the TF- μSR with $\mu_0 H_{\text{appl}} = 120$ mT (see figure 9(b)), the applied field suppresses the smaller gap (see details in figures 6(b) and 7). Hence the $\lambda^{-2}(T)$ dependence is consistent with a single-gap s -wave model, leading to $\lambda_0 = 104(1)$ nm and $\Delta_0 = 1.10(1)$ meV.

3.7. Zero-field μSR

To search for a possible weak magnetism or TRS breaking in the superconducting state of ReBe_{22} , ZF- μSR measurements were performed in the 1.5–20 K temperature range. Normally, in the absence of external fields, there is no change in the ZF muon-spin relaxation rate across T_c . However, in case of a broken TRS, the onset of tiny spontaneous currents gives rise to associated (weak) magnetic fields, causing an increase in the muon-spin relaxation rate in the superconducting state. Representative ZF- μSR spectra for ReBe_{22} collected above (15 K) and below (1.5 K) T_c are shown in figure 10. No oscillations could be observed, implying a lack of magnetic order in ReBe_{22} . In such case, in absence of applied fields, the relaxation is mainly determined by the randomly oriented nuclear moments. Consequently, the ZF- μSR spectra of ReBe_{22} can be modeled by means of a combined Lorentzian and Gaussian Kubo–Toyabe relaxation function [55, 56]:

$$A_{\text{ZF}} = A_s \left[\frac{1}{3} + \frac{2}{3} (1 - \sigma_{\text{ZF}}^2 t^2 - \Lambda_{\text{ZF}} t) e^{\left(-\frac{\sigma_{\text{ZF}}^2 t^2}{2} - \Lambda_{\text{ZF}} t \right)} \right] + A_{\text{bg}}. \quad (15)$$

Here A_s and A_{bg} are the same as in the TF- μSR case in equation (8). In polycrystalline samples, the 1/3-nonrelaxing and 2/3-relaxing components of the asymmetry correspond to the powder average of the local internal fields with respect to the initial muon-spin orientation. The resulting fit parameters versus temperature,



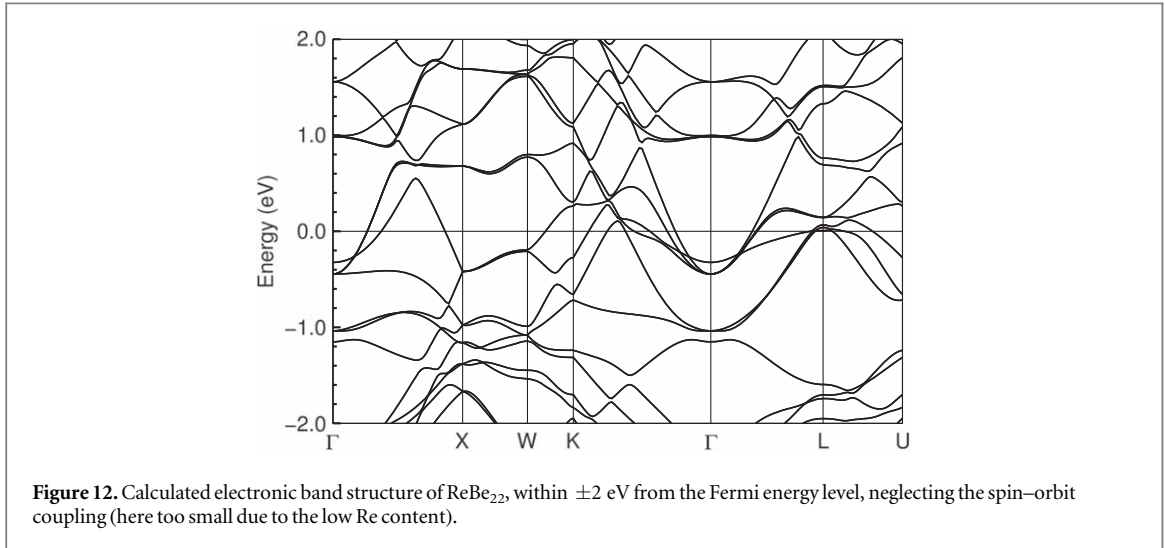
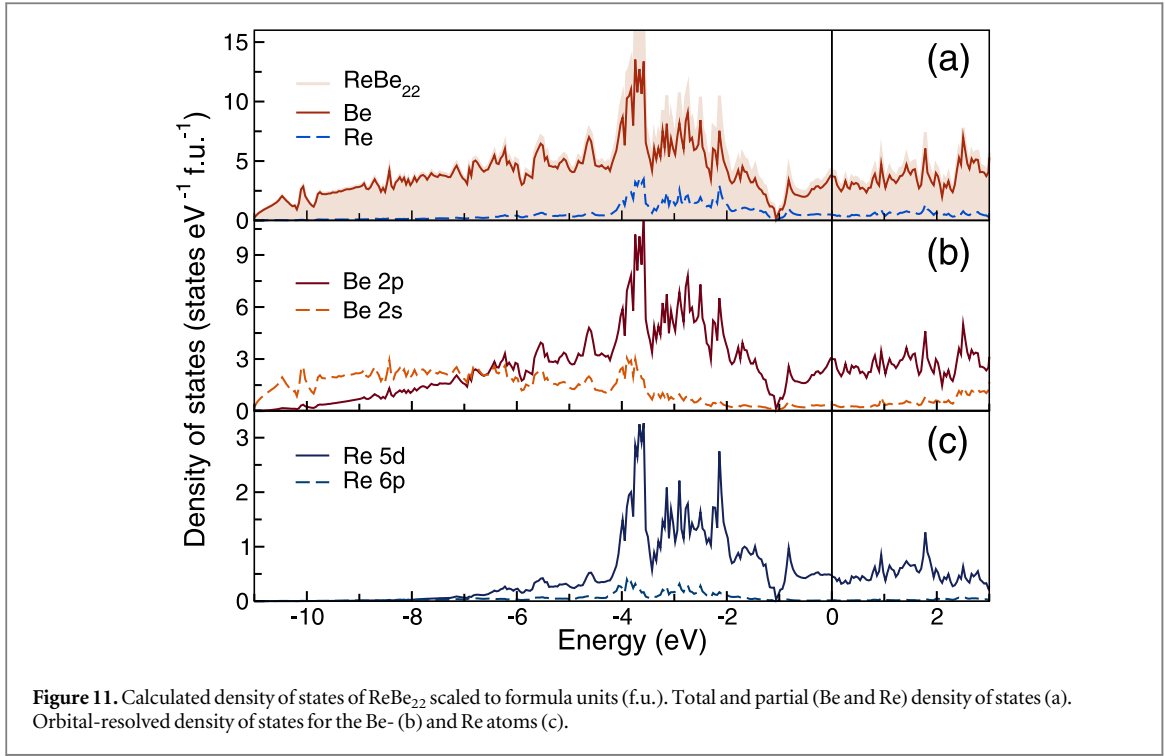
including the Lorentzian- Λ_{ZF} and Gaussian relaxation rates σ_{ZF} , are shown in figures 10(b) and (c). Here A_3 was fixed to its average value of 0.205, however, the same features are also found in fits with released A_3 .

The large relaxation rates reflect the significant nuclear magnetic moments present in ReBe₂₂. A similarly fast Gaussian relaxation was also found in other Re-based alloys [7, 8]. This is in contrast to superconductors containing nuclei with small magnetic moments, as e.g. Mo₃Rh₂N [51], which exhibit a negligibly small relaxation. Despite the clear difference in the ZF- μ SR spectra recorded in the normal and superconducting states (figure 10(a)), neither $\Lambda_{ZF}(T)$ nor $\sigma_{ZF}(T)$ show distinct changes across T_c . The enhanced σ_{ZF} below 6 K in figure 10(c) might be caused by tiny amounts of magnetic impurities, below the XRD and EDX detection threshold. This is also indicated by the Curie-Weiss-like behavior of $\sigma_{ZF}(T)$ in figure 10(c), i.e. $\sigma_{ZF} = 0.242T^{-1} - 0.047$, whose positive curvature is opposite to the negative one, common in case of TRS breaking [7, 8]. To further distinguish the intrinsic versus extrinsic effects in $\sigma_{ZF}(T)$, samples synthesized using even higher purity chemicals are desirable. We also performed auxiliary longitudinal field (LF) μ SR measurements at 1.5 K. As shown in figure 10(a), a field of 10 mT is already sufficient to lock the muon spins and to completely decouple them from the weak magnetic fields, confirming the sparse presence of magnetic impurities. In conclusion, the ZF- μ SR results indicate a preserved TRS in the superconducting state of ReBe₂₂.

3.8. Electronic band structure

To shed more light on the underlying electronic properties of ReBe₂₂, we performed electronic band-structure calculations based on DFT, including spin-orbit coupling. Figure 11 shows the total-, atomic-, and orbital-projected DOS, disclosing the metallic nature of the system through its nonzero DOS at the Fermi level. The main contributions to the latter arise from the Re-*d* and Be-*p* orbitals. While the Be-Be bonding is comprised primarily of 2*s* orbitals, the Re-Be hybridization consists of Re-5*d* and Be-2*p* states. Notwithstanding a 4% Re-to-Be ratio in a ReBe₂₂ formula unit, Re atoms are over-represented with an almost 3 times larger weight of 12% in the DOS at the Fermi level. Our calculations estimate a total DOS at the Fermi level of $N(\epsilon_F) = 4$ states/eV-f.u., comparable to the 3.25 states/eV-f.u. extracted from specific-heat data. Both values are significantly larger (~ 50 times) than that estimated for elemental Be [57] and, consequently, may justify the huge increase in T_c with respect to Be (from 0.026 to 9.4 K). Interestingly, a similar T_c value has been observed also when Be is deposited as a quenched condensed film [58]. Also in this case, the surge in T_c was shown to originate from the increase of DOS at E_F in the structurally disordered condensate [57].

The ReBe₂₂ band structure shown in figure 12 reveals multiple dispersive bands crossing the Fermi energy. In particular, the electron pockets centered around the Γ point are much larger than the hole pockets centered around the *L* point. This circumstance is typical of multigap/multiband superconductors, as clearly reflected also in our experimental results. Finally, the band splitting due to the spin-orbit coupling of Re is barely visible here due to the low Re/Be ratio.



3.9. Discussion

The different families of superconductors can be classified according to the ratio of the superconducting transition temperature T_c to the effective Fermi temperature T_F , in a so-called Uemura plot [63]. As can be seen in figure 13, several types of unconventional superconductors, including heavy-fermion, organic, high- T_c iron pnictides, and cuprates, all lie in a $1/100 < T_c/T_F < 1/10$ range, here indicated by the shadowed region. Conversely, conventional BCS superconductors exhibit $T_c/T_F < 1/1000$, here exemplified by the elemental Sn, Al, and Zn. Three typical examples of multiband superconductors, LaNiC₂, ThFeAsN, and MgB₂, are also shown in figure 13. According to the superconducting parameters obtained from our measurements (here summarized in table 1), the calculated T_c/T_F value for ReBe₂₂ is $9.5/20700 \sim 4.6 \times 10^{-4}$ (diamond in figure 13). Although it cannot be classified as an unconventional superconductor, ReBe₂₂ is far away also from the region of conventional superconductors and shows practically the same ratio as the multiband superconductor LaNiC₂ (both lying in the same dashed-dotted line). Compared to pure Be ($T_c/T_F = 0.026/1.64 \times 10^5 = 1.58 \times 10^{-7}$) [1, 30], the T_c/T_F value of ReBe₂₂ is enhanced due to the presence of diluted Re, the latter being characterized by a lower Fermi temperature and, hence, by a larger T_c/T_F ratio (see Re in figure 13). Such conclusion is further supported by our electronic band-structure calculations, which show that, although Re contributes only 4% to the atomic ratio, with its 12% weight, it is over-represented in the DOS at the Fermi level.

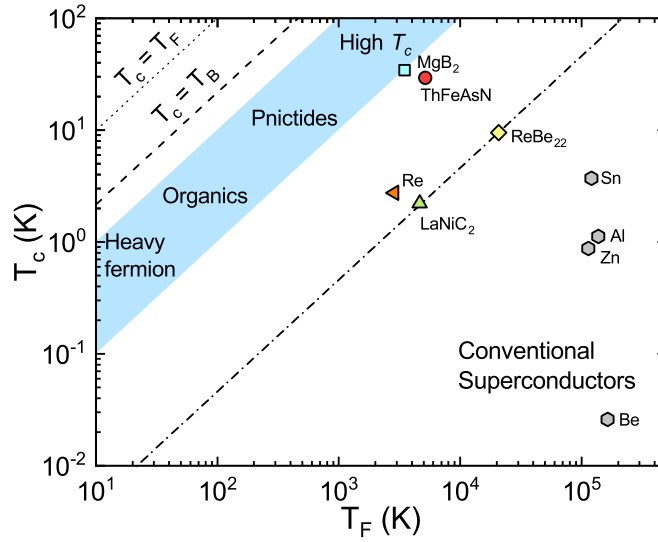


Figure 13. Uemura plot of the superconducting transition temperature T_c against the effective Fermi temperature T_F for different kinds of superconductors. The shaded region, with $1/100 < T_c/T_F < 1/10$, indicates the band of unconventional superconductors, such as heavy fermions, organic, fullerenes, pnictides, cuprates, etc. The dotted and dashed lines correspond to $T_c = T_F$ and $T_c = T_B$ (T_B is the Bose–Einstein condensation temperature), while the dashed–dotted line indicates $T_c/T_F = 4.6 \times 10^{-4}$ for ReBe_{22} . The data of the reference samples were adopted from [8, 59–63].

Table 1. Normal-state and superconducting properties of ReBe_{22} , as determined from electrical resistivity, magnetic susceptibility, specific-heat, and μSR measurements. The London penetration depth λ_L , the effective mass m^* , bare band-structure effective mass m_{band}^* , carrier density n_s , BCS coherence length ξ_0 , electronic mean-free path l_e , Fermi velocity v_F , and effective Fermi temperature T_F were estimated following the equations (40)–(50) in [62].

Property	Value	Property	Value
T_c^ρ	9.42(2) K	$\mu_0 H_{c2}$	0.60(3) T
ρ_0	2.72(5) $\mu\Omega \text{ cm}$	$\xi(0)$	23(1) nm
Θ_D^R	590(5) K	$T_c^{\mu\text{SR}}(40 \text{ mT})$	8.8(1) K
T_c^X	9.50(1) K	$w^{\mu\text{SR}}$	0.10
$\mu_0 H_{c1}$	28.1(2) mT	$\Delta_0^s(\mu\text{SR})$	0.83(1) meV
$\mu_0 H_{c1}^{\mu\text{SR}}$	24.9(5) mT	$\Delta_0^l(\mu\text{SR})$	1.35(1) meV
T_c^C	9.36(2) K	$\lambda_0(40 \text{ mT})$	87(1) nm
γ_n	15.3(2) $\text{mJ mol}^{-1} \text{ K}^{-2}$	$\lambda_0(120 \text{ mT})$	104(1) nm
Θ_D^C	545(5) K	λ_L	64(1) nm
Θ_E^C	792(5) K	κ	4.7(3)
λ_{ep}	0.64(1)	m^*	3.0(1) m_e
$N(\epsilon_F)$	3.25(3) eV-f.u.	m_{band}^*	1.9(1) m_e
$N_{\text{band}}(\epsilon_F)$	1.98(1) eV-f.u.	ξ_0	53(1) nm
$N(\epsilon_F)^{\text{DFT}}$	4 eV-f.u.	l_e	62(1) nm
w^C	0.13	n_s	$2.06(5) \times 10^{28} \text{ m}^{-3}$
$\Delta_0^s(C)$	0.68(1) meV	v_F	$3.29(7) \times 10^5 \text{ ms}^{-1}$
$\Delta_0^l(C)$	1.43(1) meV	T_F	$2.07(5) \times 10^4 \text{ K}$
$\Delta C/\gamma_n T_c$	1.24(2)		

4. Conclusion

To summarize, we investigated the physical properties of the ReBe_{22} superconductor by means of electrical resistivity, magnetization, heat capacity, and μSR measurements, as well as by electronic band-structure calculations. We find that ReBe_{22} is a type-II superconductor ($\kappa \sim 4.7$), with a bulk $T_c \sim 9.4$ K and critical fields $\mu_0 H_{c1} = 28.1$ mT and $\mu_0 H_{c2} = 0.6$ T. The temperature dependence of the zero-field electronic specific heat and superfluid density reveal a nodeless SC, well described by an isotropic s -wave model, which is more consistent with a multigap- rather than a single-gap SC. The multigap features are further supported by the

field-dependent electronic specific-heat coefficient, the upper critical field, and the calculated electronic band structure. The lack of spontaneous magnetic fields below T_c indicates that, unlike in the Re-rich cases, in a Re-diluted superconductor such as ReBe_{22} , TRS is preserved. Compared to pure Be, the observed 400-fold increase in T_c is shown to be due to the concomitant increase of both the electron–phonon coupling strength and of the DOS at the Fermi level. Future high-pressure studies of ReBe_{22} should reveal the evolution of its superconducting properties upon decreasing the lattice parameter.

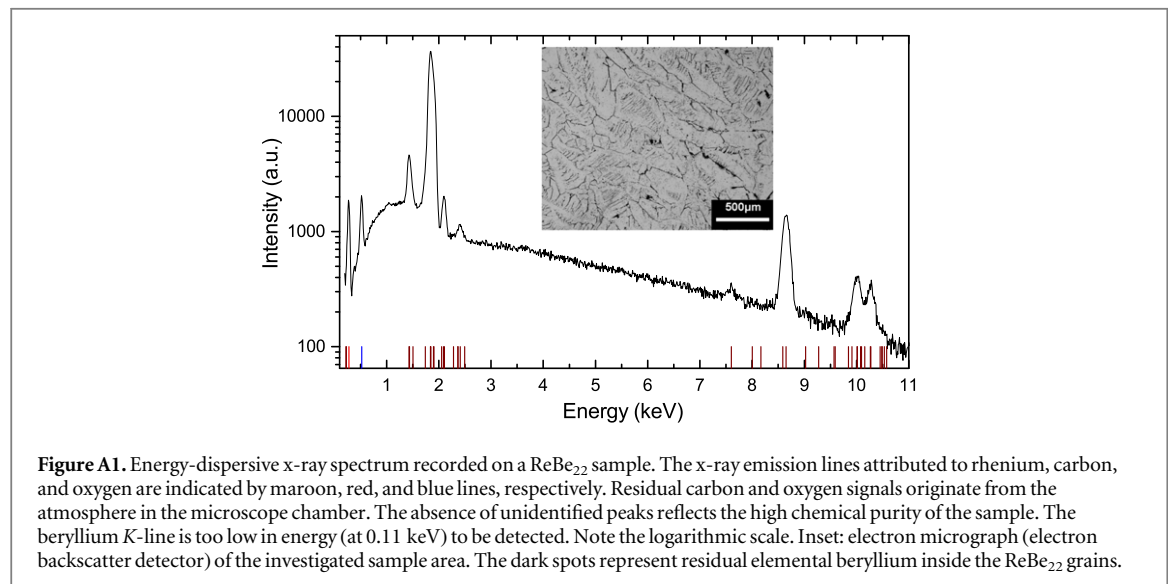
Acknowledgments

The authors thank J A T Verezhak for fruitful discussions and the $S\mu S$ beamline scientists for the assistance. The DFT calculations were performed at the IFW-ITF cluster with the assistance of U Nitzsche. This work was supported by the National Key R&D Program of China (Grants No. 2016YFA0300202 and No. 2017YFA0303100), National Natural Science Foundation of China (Grants No. 11874320 and No. U1632275), and the Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung, SNF (Grants No. 200021-169455 and No. 206021-139082).

Appendix. EDX and field-dependent muon-spin relaxation

A typical energy-dispersive x-ray spectrum of ReBe_{22} and the respective electron micrograph are shown in figure A1. The high chemical purity of the sample is reflected in the lack of unknown peaks.

Figure A2(a) shows the time-domain TF- μ SR spectra of ReBe_{22} , collected in two applied fields, 40 and 400 mT. The solid lines represent fits using the same model as that described in equation (8). The resulting superconducting Gaussian relaxation rate $\sigma_{\text{FLL}}(H)$ is summarized in figure A2(b). Above the lower critical field $\mu_0 H_{c1}$ (28.1 mT), the Gaussian relaxation rate decreases continuously. By considering the decrease of the inter vortex distance with the field and the vortex-core effects, a field of 40 mT was chosen for the temperature-dependent TF- μ SR studies. For a comparison, the TF- μ SR relaxation was also measured in a field of 120 mT, here expected to suppress the small superconducting gap.



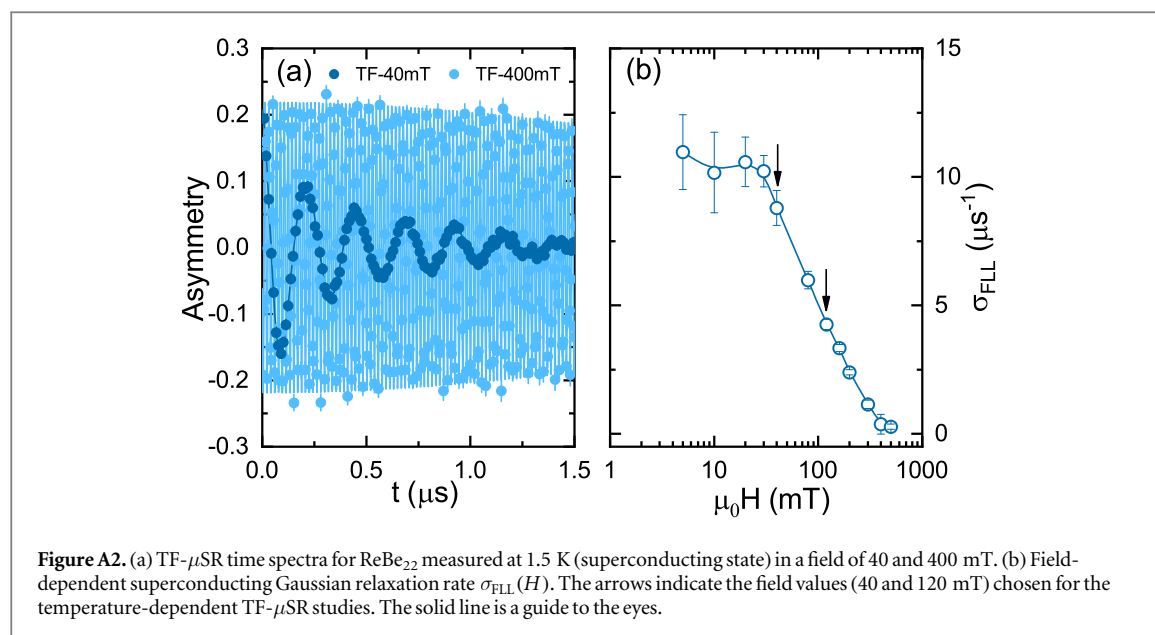


Figure A2. (a) TF- μ SR time spectra for ReBe₂₂ measured at 1.5 K (superconducting state) in a field of 40 and 400 mT. (b) Field-dependent superconducting Gaussian relaxation rate $\sigma_{\text{FLL}}(H)$. The arrows indicate the field values (40 and 120 mT) chosen for the temperature-dependent TF- μ SR studies. The solid line is a guide to the eyes.

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